



Methanation of CO₂ over Nickel and Molybdenum Bi-metallic Catalyst System Supported on Activated Carbon

Submitted in fulfillment of the academic requirements for the degree of **Doctor of Engineering** in the **Department of Chemical Engineering** under the **Green Engineering Research Group**, Faculty of Engineering, and the Built Environment at the Durban University of Technology

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PREFACE

This doctoral research was conducted in collaboration with the Green Engineering Research Group within the Department of Chemical Engineering at Durban University of Technology (DUT), South Africa. The study focused on developing a novel nickel (Ni) and molybdenum (Mo) bimetallic catalyst system supported on activated carbon (AC) for CO₂ methanation. Prof. Sammy Lewis Kiambi served as the lead supervisor, with co-supervisors Prof. Yusuf Isa Makarfi, Dr. Thembisile Patience Mahlangu, and Dr. Peterson Thokozani Ngema, who provided invaluable guidance throughout the research. Nickel nitrate (Ni(NO₃)₂·6H₂O) and ammonium heptamolybdate ((NH₄)₆Mo₇O₂₄·4H₂O) were used as precursors in synthesizing the catalyst system. The study utilized a packed bed reactor to evaluate the catalyst's effectiveness, resulting in the development of a promising new catalyst for CO₂ methanation. The thesis is organized into seven chapters, incorporating both published and unpublished research findings.

DECLARATION

I, **Stephen Okiemute Akpasi**, the undersigned candidate, declares that

- i. The research reported in this thesis, except where otherwise indicated, is my original work.
- ii. This thesis has not been submitted for any degree or examination at any other university.
- iii. This thesis does not contain other persons' data, pictures, graphs, or other information unless specifically acknowledged as being sourced from other persons.
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Date

DEDICATION

I dedicate this work to my family, whose love, support, and encouragement have been my constant strength throughout this journey. To my mentors and friends, thank you for your guidance and belief in me. And to the next generation, may you always chase your dreams with passion and perseverance.

“Never give up on your dream... because you never know what the Lord can bless you with.”

Kelly Rowland

“The future belongs to the competent. Get good, get better, be the best!”

Brian Tracy

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Starting a PhD journey comes with only one certainty: the starting date. The research, results, and timeline are often unpredictable, but that's what makes the journey exciting and full of wonder. I would like to dedicate this section to everyone who made these 3 years + Δt (where Δt is some well-deserved extra time) a memorable experience.

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SUMMARY

The escalating environmental impact of CO₂ emissions has driven the demand for innovative solutions to capture and convert CO₂ into useful energy forms, with CO₂ methanation standing out as a viable approach for generating methane (CH₄) as a clean fuel. This research focuses on developing and evaluating bimetallic Ni–Mo catalysts supported on activated carbon (AC) for CO₂ methanation, exploring the effects of Mo concentration and synthesis techniques on catalytic performance. The catalysts, synthesized with a Ni base of 13 wt.% and Mo as a promoter (5–11 wt.%), were prepared using three distinct methods: incipient wetness impregnation (IWI), sol-gel (SG), and mechanical mixing (MM). These methods provided a range of catalyst properties, allowing for a thorough investigation of how synthesis conditions influence activity, stability, and CO₂-to-CH₄ conversion efficiency.

Advanced characterization techniques, including X-ray diffraction (XRD), scanning electron microscopy (SEM), Brunauer-Emmett-Teller (BET) surface area analysis, and X-ray photoelectron spectroscopy (XPS), were employed to reveal the structural, morphological, and electronic properties of the catalysts. The introduction of Mo significantly modified the Ni/AC catalyst, enhancing pore size, and active site dispersion. Results indicated that optimal Mo concentration, specifically 7 wt.%, improved Ni dispersion and electron transfer properties, reducing the catalyst's activation energy for CO₂ methanation to 54.6 kJ/mol, compared to 115 kJ/mol for undoped Ni/AC. This facilitated superior catalytic activity, with Ni-7%Mo/AC achieving a high CO₂ conversion rate of 92% and CH₄ selectivity of 80% at a moderate reaction temperature of 250 °C.

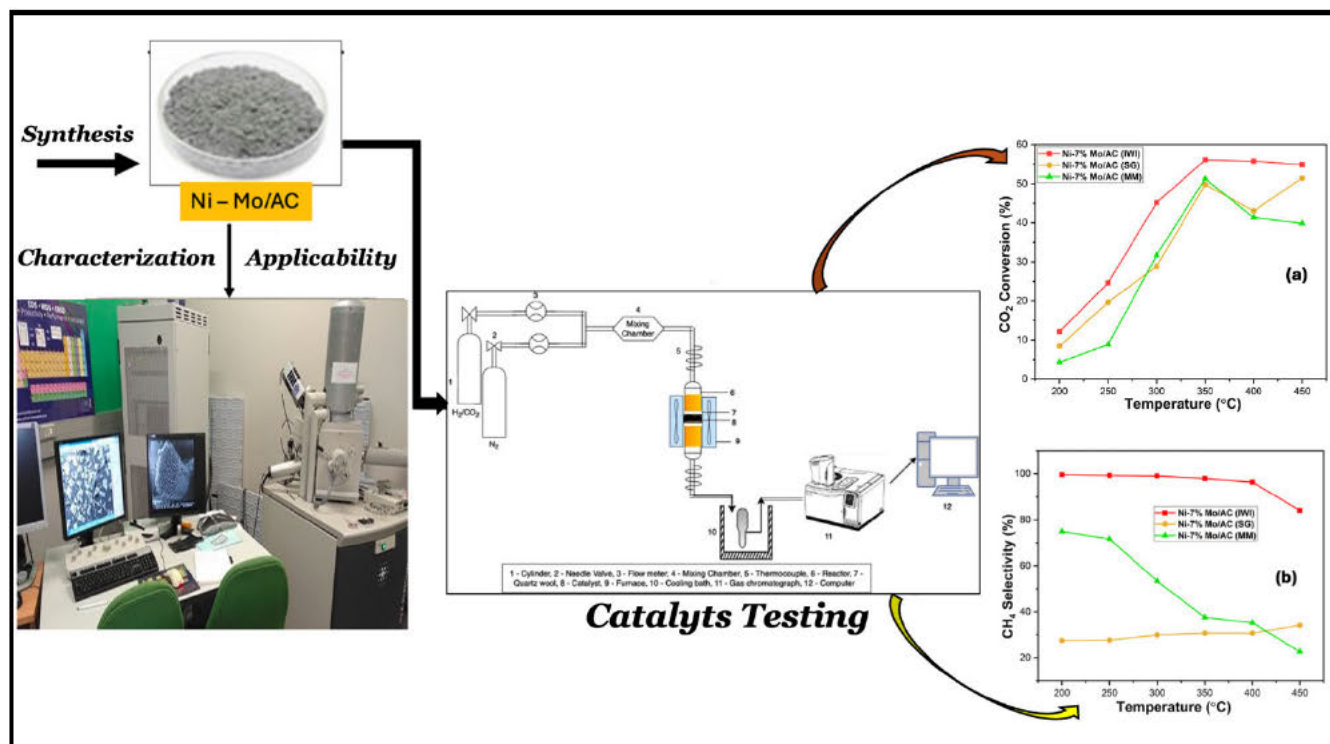
Among the preparation techniques, the incipient wetness impregnation (IWI) method yielded the most promising results, with the Ni-7%Mo/AC catalyst synthesized via IWI showing the highest CO₂ conversion (56%) and (>95%) CH₄ selectivity at 350 °C. This enhanced performance is attributed to improved metal dispersion, stronger metal-support interactions, and structural stability, resulting from the IWI method. The sol-gel and mechanical mixing methods, while effective, demonstrated lower CO₂ conversion rates of 51.4% and 51.2%, respectively, under similar conditions. These variations highlight the critical role of synthesis techniques in optimizing catalyst performance for CO₂ methanation.

To complement the experimental findings, an informetric analysis was conducted on global research trends in molybdenum-enhanced Ni-based catalysts for CO₂ methanation. This analysis utilized VOSviewer and RStudio to identify publication trends, collaboration networks, and research focus areas across highly cited studies from 1994 to 2023. The results highlighted an increasing interest in Mo-doped Ni catalysts, particularly for their ability to enhance CO₂ methanation activity, stability, and resistance to deactivation through sintering and coking. The bibliometric insights highlighted the relevance of Mo in creating efficient, long-lasting catalysts and identified key contributors and leading publications in the field.

A review of AC-based materials further illustrated their potential for sustainable CO₂ methanation applications, emphasizing AC's large surface area, porosity, and cost-effectiveness as a catalyst support. The role of AC in enhancing catalyst stability and facilitating CO₂ adsorption positions it as an ideal material for carbon capture and utilization (CCU) technologies. Despite these advantages, challenges remain in optimizing the catalyst formulation for industrial-scale applications, particularly in maintaining stability and minimizing energy requirements.

Conclusively, this study demonstrates that Ni-7%Mo/AC, synthesized via incipient wetness impregnation, is an optimal catalyst for CO₂ methanation, achieving high efficiency in converting CO₂ to CH₄. These findings not only advance the understanding of CO₂ methanation over Ni-Mo catalysts but also establish a foundation for scaling up this process to support global sustainability goals.

GRAPHICAL ABSTRACT



RESEARCH OUTPUTS AND KNOWLEDGE DISSIMILATION

This thesis is based on the author's published papers and unpublished works under consideration for publication (Journal, Conference papers and Book chapters). The author was the corresponding author in all the papers, while the co-authors assisted in writing by making valuable comments and corrections.

I. LIST OF PUBLICATIONS

Out of the published journal articles listed, Papers (1-5) as referred to were linked to the objectives of this study as supporting information to compile the chapters of the thesis.

Publications from this work

1. **Akpasi, S. O.** and Isa, Y. M. 2022. Review of carbon capture and methane production from carbon dioxide. *Atmosphere*, 13 (12): 1958. <https://www.mdpi.com/2073-4433/13/12/1958>.
2. **Akpasi, S. O.**, Isa, Y. M., Mahlangu, T. P. and Kiambi, S. L. 2024. Effects of molybdenum addition to activated carbon supported Ni-based catalysts for CO₂ methanation. *Greenhouse Gases: Science and Technology*, 14 (1): 152-167. <https://scijournals.onlinelibrary.wiley.com/doi/full/10.1002/ghg.2257>.
3. **Akpasi, S. O.**, Isa, Y. M., Mahlangu, T. P., Ngema, P. T. and Kiambi, S. L. 2024. Evaluating the potential of Ni-7%Mo/AC catalysts prepared by different strategies for CO₂ methanation. *Topics in Catalysis: Springer Nature. Under Review*.
4. **Akpasi, S. O.**, Isa, Y. M., Monama, T. P., Kiambi, S. L. and Ngema, P. T. 2024. CO₂ methanation: a bibliometric analysis and review of activated carbon-based materials (2014–24). *Clean Energy*, 8 (6): 148-174. <https://doi.org/10.1093/ce/zkae082>.
5. **Akpasi, S. O.**, Isa, Y. M., Mahlangu, T. P., Kiambi, S. L. and Ngema, P. T. 2025. Molybdenum-promoted nickel catalysts for CO₂ methanation: a critical review and informetric perspective. *Discover Chemical Engineering*, 5 (1): 1-29. <https://doi.org/10.1007/s43938-025-00076-x>.
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7. Anekwe, I. M. S., **Akpasi, S. O.**, Enemuo, E. M., Ashiegbu, D., Mustapha, S. I. and Isa, Y. M. 2024. Innovations in catalytic understanding: A journey through advanced characterization. *Materials Today Catalysis*, 7: 100061. <https://doi.org/10.1016/j.mtcata.2024.100061>.
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and its Role in a Sustainable Energy Future. *Clean Energy*: zkae112. <https://academic.oup.com/ce/advance-article/doi/10.1093/ce/zkae112/7942071>.

Book Chapters

9. Anekwe, I. M., **Akpasi, S. O.**, Mkhize, M. M., Zhou, H., Moyo, R. T. and Gaza, L. 2024. Renewable energy investments in South Africa: Potentials and challenges for a sustainable transition-a review. *Science Progress*, 107 (2): 00368504241237347. <https://journals.sagepub.com/doi/full/10.1177/00368504241237347>.
10. **Akpasi, S. O.**, Anekwe, I. M. S., Adedeji, J. and Kiambi, S. L. 2022. Biochar development as a catalyst and its application. In: *Biochar-Productive Technologies, Properties and Applications*. IntechOpen. <https://www.intechopen.com/chapters/82348>.
11. Anekwe, I. M. S., Tetteh, E. K., **Akpasi, S. O.** and Isa, Y. M. 2024b. Current Advances and Potentials of Nanotechnology for Biofuel Production. *Sustainable Engineering: Concepts and Practices*: 379-394. https://link.springer.com/chapter/10.1007/978-3-031-47215-2_22.
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13. Anekwe, I. M. S., Tetteh, E. K., **Akpasi, S.O.**, Atuman, S. J., Armah, E. K. and Isa, Y. M. 2023. Carbon dioxide capture and sequestration technologies—current perspective, challenges and prospects. *Green Sustainable Process for Chemical and Environmental Engineering and Science*: 481-516. <https://www.sciencedirect.com/science/article/abs/pii/B9780323994293000345>.

II. CONFERENCES/PRESENTATION

The author was the main presenter at both the local and international conferences.

14. **Akpasi, S. O.**, Isa, Y. M., Mahlangu, T. P. and Kiambi, S. L. 2024. “Effects of molybdenum addition to activated carbon supported Ni-based catalysts for CO₂ methanation”, *Presented at the 2nd Sustainable Bioenergy and Processes Conference (SBP 2022)*. 12-14th December 2022. Cape Town International Convention Centre (CTICC 2), Cape town, South Africa. <https://onlinelibrary.wiley.com/action/doSearch?ContribRaw=Akpasi%2C+Stephen+Okiemute>.
15. **Akpasi, S. O.**, Isa, Y. M., Mahlangu, T. P. and Kiambi, S. L. 2024. “Evaluating the Potential of Ni-7%Mo/AC Catalysts Prepared by Different Synthesis Method for CO₂ Methanation”, *Presented at the Chem4Energy Annual Conference Materials and Processes for a Sustainable Energy Future*. 20 – 24th March 2024. 26° South Hotel, Muldersdrift, South Africa.

16. **Akpasi, S. O.**, Isa, Y. M., Mahlangu, T. P. and Kiambi, S. L. 2024. “CO₂ methanation over Ni-7%Mo/AC catalyst”, *Presented at the 2024 AIChE Annual Meeting*. October 27 – 31, 2024. San Diego Convention Centre, Hilton San Diego Bayfront, California, USA. <https://aiche.confex.com/aiche/2024/meetingapp.cgi/Paper/700979>.

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LIST OF ACRONYMS

AC	Activated Carbon
ACFs	Activated Carbon Fibers
ACNPs	Activated Carbon Nanoparticles
AEL	Alkaline Electrolysis
ASU	Air Separation Unit
BSE	Backscattered Electron
CA	Citric Acid
CAPEX	Capital Expenditures
CAS	Chinese Academy of Sciences
CCS	Carbon Capture and Sequestration
CLC	Chemical Looping Combustion
CMSMS	Carbon Molecular Sieve Membranes
CNF	Carbon Nanofibers
CNT	Carbon Nanotubes
CSCM	Capture, Sequestration, and Conversion to Methane
CTLs	Coal-to-Liquids
DAC	Direct Air Capture
DEA	Diethanolamine
DFT	Density Functional Theory
DMC	Dimethyl Carbonate
DRIFT	Diffuse Reflection Infrared Spectroscopy
EoS	Equations of State
EPRI	Electric Power Research Institute
ESA	Electric Swing Adsorption
FE-SEM	Field emission scanning electron microscopy
FT	Fischer Tropsch

FTIR	Fourier Transform Infrared Spectrometer
GHGs	Green House Gases
GHSV	Gas Hourly Space Velocity
GTL	Gas to liquid
HCL	Hydrochloric Acid
IEA	International Energy Agency
IGCC	Integrated Gasification Combined Cycle
ILs	Ionic liquids
IRP	Integrated Resource Plan
IWI	Incipient Wetness Impregnation
KPIS	Key Performance Indicators
LAU	Lebanese American University
LCA	Life Cycle Assessments
L-H	Langmuir-Hinshelwood
LHHW	Langmuir- Hinshelwood-Hougen-Watson
LPG	Liquefied Petroleum Gas
MASI	Most Abundant Surface Intermediates
MDEAV	Methyl-di-ethanolamine
MEA	Monoethanolamine
MM	Mechanical Mixing
MMMs	Mixed Matrix Membranes
MOF	Metal Organic Framework
MOPs	Microporous Organic Polymers
NASA	National Aeronautics and Space Administration
NPs	Nanoparticles
OECD	Organisation for Economic Cooperation and Development
ONCS	Ordered Nanoporous Carbons

OPEX	Operational Expenditure Costs
PEM	Proton exchange membrane
PFR	Plug Flow Reactor
PSA	Pressure Swing Adsorption
PV	Photovoltaics
PVSA	Pressure vacuum swing adsorption
PW	Dodecatungstophosphoric Acid
RDI	Research, Development and Innovation
RDSS	Rate-Determining Surface Species
SAFT	Statistical Associating Fluid Theory
SASOL	South African Coal and Oil Company
SDG	Sustainable Development Goals
SEM	Scanning Electron Microscopy
SEM/EDS	Scanning electron microscopy/energy-dispersive X-ray spectrometry
SG	Sol Gel
SMSI	Strong-Metal Support Interactions
SNG	Synthetic Natural Gas
TCD	Thermal Conductivity Detector
TEM	Transmission Electron Microscopy
TOC	Total Organic Carbon
TOS	Time on Stream
TRL	Technological Readiness Level
TSA	Temperature Swing Adsorption
UCAS	University of Chinese Academy of Sciences
VP SA	Vacuum Pressure Swing Adsorption
VSA	Vacuum Swing Adsorption
WGSR	Water Gas Shift Reaction
WoS	Web of Science

XAS	X-ray absorption spectroscopy
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction analysis

CHAPTER 1: INTRODUCTION

1.1 Background

Global temperatures and climate have changed in a significant way over the past century due to increased atmospheric carbon dioxide (CO₂) levels. The quick increase in atmospheric CO₂ concentrations from 315 parts per million in 1960 to concentrations above 400 parts per million in recent years is depicted in Figure 1.1. This increase is attributed to the world's growing energy demand, which is met by the exploitation and combustion of fossil fuel reserves. The unabating rise in atmospheric CO₂ is likely causing the polar ice sheets to melt, more deserts, and rising sea levels (McCarthy 2001). If no action is taken, the global average temperature is expected to exceed the currently accepted threshold of 2 °C due to the continued burning of fossil fuels (McGlade and Ekins 2015).

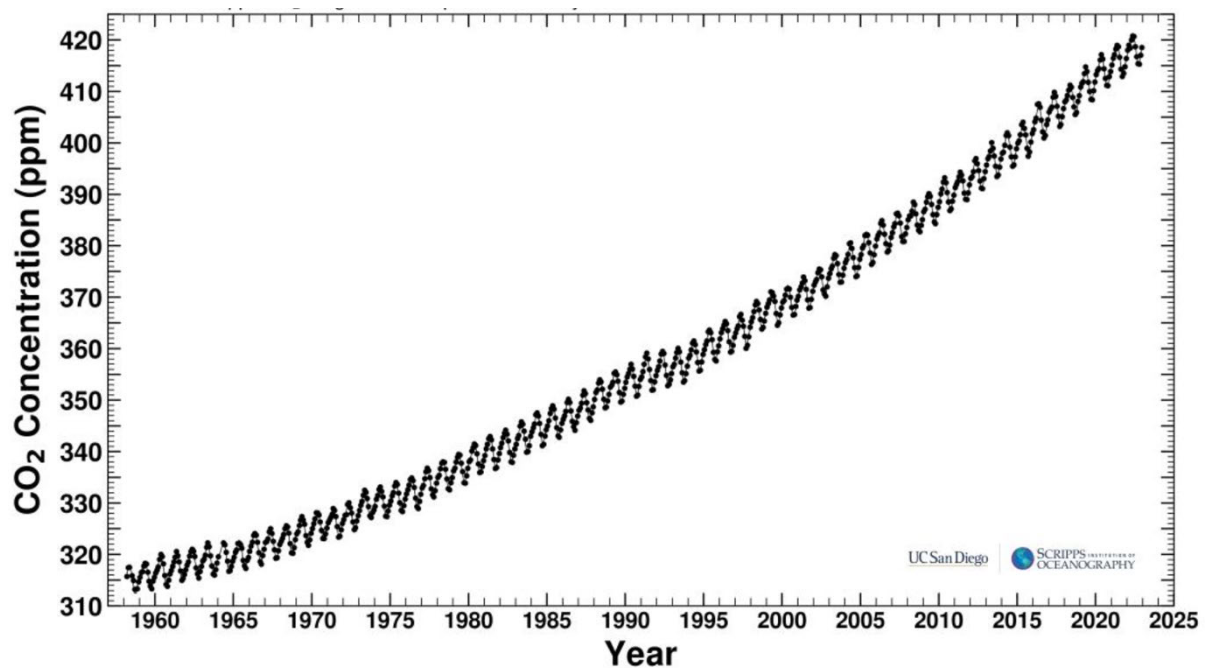


Figure 1-1. Atmospheric CO₂ concentrations worldwide 1960 – 2025.
Adapted from (Keeling *et al.* 2005).

It is anticipated that by 2040, low-carbon technologies, comprising natural gas and renewable energy sources, will fulfil over 80% of the predicted increase in worldwide energy demand (IEA 2022). Recently, the most difficult and important global challenges have been those related to energy and the environment. In 2018, global energy consumption increased by 2.3 %, according to the Global Energy Statistical (Yearbook 2019) (Figure 1.2). This is the first time this growth has occurred since 2010 (Yearbook 2019). All types of fuels saw an increase

in demand, with renewables (71 Mtoe, 18% of the increase worldwide) and gas (168 Mtoe, 43% of the increase worldwide) showing the strongest growth. In the Organisation for Economic Cooperation and Development (OECD) countries, energy consumption has risen by 82% and gas demand by 70%.

Energy demand increased by 308 Mtoe in non-OECD nations; gas demand increased by 98 Mtoe, coal demand by 85 Mtoe, and oil demand by 47 Mtoe. However, the largest increase in CO₂ emissions in seven years is attributable to energy consumption, which rose by 2% (British Petroleum 2019).

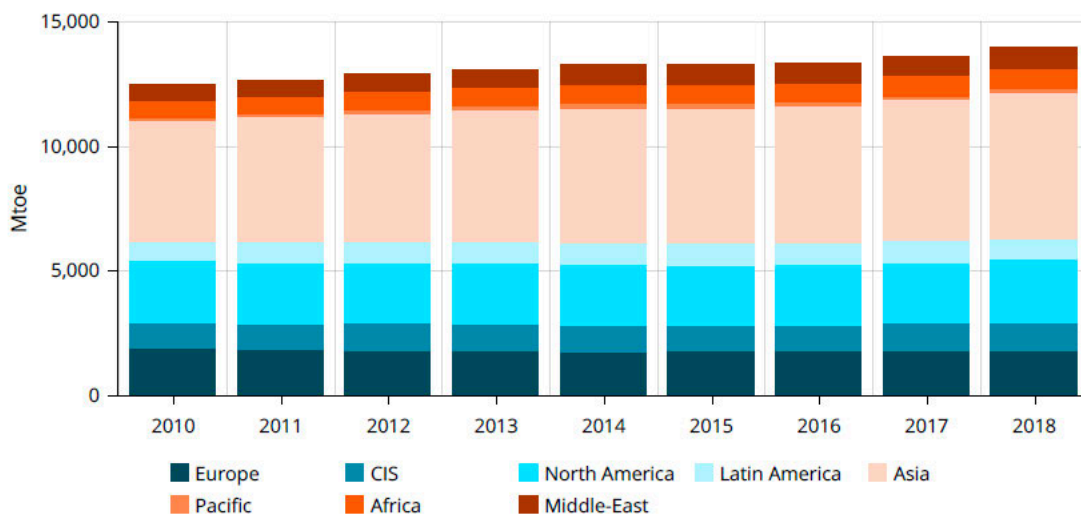
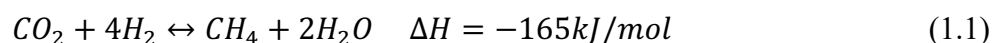


Figure 1-2. Global energy consumption [Mtoe], 2010 – 2018.
(Yearbook 2019).

Instead of releasing the carbon stored in fossil fuels as CO₂ into the atmosphere, synthetic fuel production processes, such as Fischer–Tropsch (FT) synthesis capture and convert this carbon into valuable liquid fuels, effectively reducing net greenhouse gas emissions. Currently, the FT method catalyzes the formation of higher hydrocarbons from syngas (a mixture of CO and H₂) generated during the gasification of coal or biomass into liquid fuels. In addition, natural gas can be produced via catalytic methanation of mixtures containing H₂ and CO₂ (or CO) using a nickel catalyst, with biomass feedstock reducing the net carbon input to atmospheric CO₂.



Building on this concept, the focus shifts to the CO₂ methanation process for producing synthetic natural gas, as shown in Equation (1.1). This reaction which was discovered by Sabatier (1902), enables the conversion of CO₂ to lucrative synthetic natural gas. The

expansion of research and development efforts pertaining to carbon capture and sequestration (CCS) technology has been prompted by the recent surge in political and social concern surrounding the mitigation of CO₂ atmospheric levels. With their application most practical for large emitters, including power plants, these technologies have the potential to restrict the discharge of CO₂ into the environment. Carbon capture and storage involves pumping CO₂ into exhausted oil reserves or storing it in geological formations. This could lessen the demand for additional exploitation of fossil fuels because it could also be used as a feedstock to produce synthetic fuels and value-added chemicals like methanol (CH₃OH), dimethyl ether (C₂H₆O), synthetic natural gas (SNG), and liquid fuels produced via the FT process.

According to the International Energy Agency (2014), fossil fuels accounted for 82% of the world's total primary energy supply in 2015, with natural gas accounting for 22% of the total. In 2018, 65% of South Africa's primary energy came from coal, 11% from renewables and 18% from crude oil. In the same time frame, natural gas contributed 3% and nuclear energy 2% of the total primary supply (Figure 1.3) (Energy 2018).

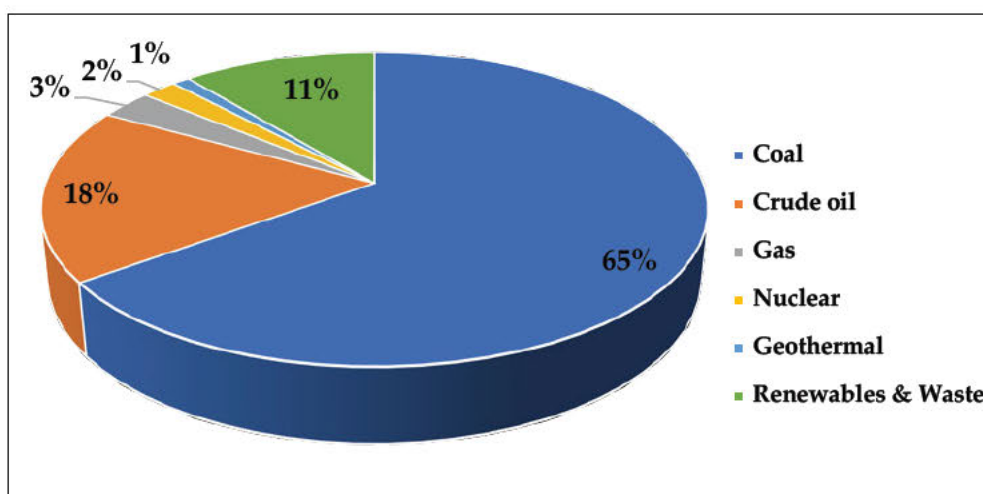


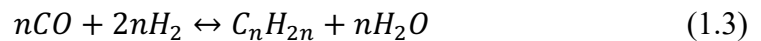
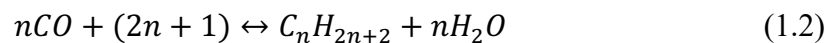
Figure 1-3. South Africa total primary energy supply (Energy 2018).

Commercial BioSNG plants have been built as a result of recent investments, including the GoGreenGas project in the United Kingdom (Materazzi and Taylor 2019) and the GoBiGas project in Sweden (Larsson, Hedenskog and Thunman 2015). These plants use CO₂ methanation to produce SNG from waste and biomass. Another recognized and proposed approach is the large-scale conversion of CO₂ into methane instead of CO. In this way, electricity generation from renewable sources could be balanced out, with methane synthesis acting as a chemical energy store in times of high demand (Schaaf *et al.* 2014b). The demand

for new infrastructure could be diminished by using SNG production to take advantage of natural gas distribution and storage facilities already in place. With the help of the hydrogen created by electrolysis during SNG generation, it is also possible to store renewable energy for up to a decade with an efficiency of 64% (Schaaf *et al.* 2014b).

There are many new applications for SNG. For example, to use SNG in its natural gas/gasoline dual-fuel vehicles, Audi AG has built a factory to produce it. Drivers of Audi vehicles can obtain carbon-neutral gas from the company's power-to-gas (PtG) plant in Lower Saxony, Germany. Hydrogen is extracted from water using predominantly renewable electrical sources, whereas CO₂ is produced by the combustion of plant waste and straw (Hay *et al.* 2013).

CO₂ methanation is currently being used on the International Space Station to recover oxygen from CO₂ and convert it into water, which is of crucial importance for applications in space research (Junaedi *et al.* 2011). According to reports (Holladay *et al.* 2007), the conversion of CO₂ from the Martian atmosphere and water from the surface ice is crucial for the production of fuel for human colonization of Mars (Holladay *et al.* 2007).



The FT process provides a method for synthesizing liquid fuels, which are essential for many modern modes of transportation. Equations (1.2) and (1.3) illustrate the mechanism, which is a stepwise polymerization reaction between hydrogen and carbon monoxide that can produce a wide range of hydrocarbon chain lengths. Industry interest in the FT process has changed with the price of oil since its discovery in the early 1920s. In Germany, between 1926 and 1945, its initial development and final commercialization occurred (Schulz 1999). Shortly after World War II ended, fixed-bed, fluidized-bed, slurry reactors and circulating-bed were developed out of concerns over a scarcity of liquid fuel (Schulz 1999). Meanwhile, global interest in the FT method has declined significantly due to the discovery of large oil deposits, which led to cheap and abundant petroleum. The one exception is South Africa, where trade embargoes and the advent of apartheid prompted the South African Coal and Oil Company (SASOL) to commercialize the FT method for operating coal-to-liquids (CTLs) reactors using the country's vast coal reserves.

SASOL is currently involved in the industrial development of FT slurry reactor technology and has made a significant contribution to researching and improving the FT process (Brübach, Wolf and Pfeifer 2025). The FT process has attracted considerable interest due to current economic and environmental concerns. Numerous GTL (gas to liquid) and CTL plants are largely utilized to manufacture transportation fuels. With a commercial interest in producing jet fuel from biomass, such as Velocys BTL, biomass gasification permits the production of liquid fuel with a reduced carbon footprint via the FT process (Michaga *et al.* 2021). In 2012, British Airways backed a proposal for a biomass-to-jet-fuel plant in the United Kingdom, but due to a fall in crude oil prices, the project was recently abandoned (Neslen 2016).

Numerous hydrocarbons (C_1 – C_{100+}) can be produced by the FT process, and the specific composition of these hydrocarbons depends strongly on the operating conditions. Mass transfer limitations often hinder the reaction in industrial reactors, causing the large catalyst particles to fill with liquid hydrocarbon products. Reactors are usually operated to promote the formation of waxy and heavy hydrocarbons because this reduces methane and light gas emissions. The heavier products are then broken down and converted into hydrocarbons suitable for fuels.

1.2 Limitations to Fossil Fuels

Fossil fuels have two significant disadvantages. First, fossil fuels are running out. These fuels represent the aggregate of millions of years consumed in a few decades by societies that rely heavily on them.

Second, fossil fuels emit emissions, particularly CO_2 and other greenhouse gases. Over the past decades, CO_2 levels in the atmosphere have risen to 406 ppm (Egiyi and Ofoegbu 2020). This intensifies floods, droughts, the greenhouse effect, and global warming. In addition, as the permafrost melts, there is more soil with organic material accessible to be decomposed by microbes. This permits extra CO_2 emissions, which exacerbates the warming effect. Under the Paris Agreement, 196 parties promised to achieve Net-Zero Emissions by 2050. In conclusion, it is undesirable for fossil fuels to become the primary energy source by the year 2019.

1.3 Limitations to Renewable Energy

Renewable energy has been underutilized in the economy until the last several decades, even though it is superior to fossil fuels in that it does not produce emissions and replenishes itself continuously. This is due to a mismatch between supply and demand for energy. The industrial demand is relatively constant throughout the day, whereas the home demand swings significantly between day and night. As illustrated in Figure 1.4, the energy supply has a bigger influence due to the intermittent nature of renewables such as solar and wind (Kariuki 2018).

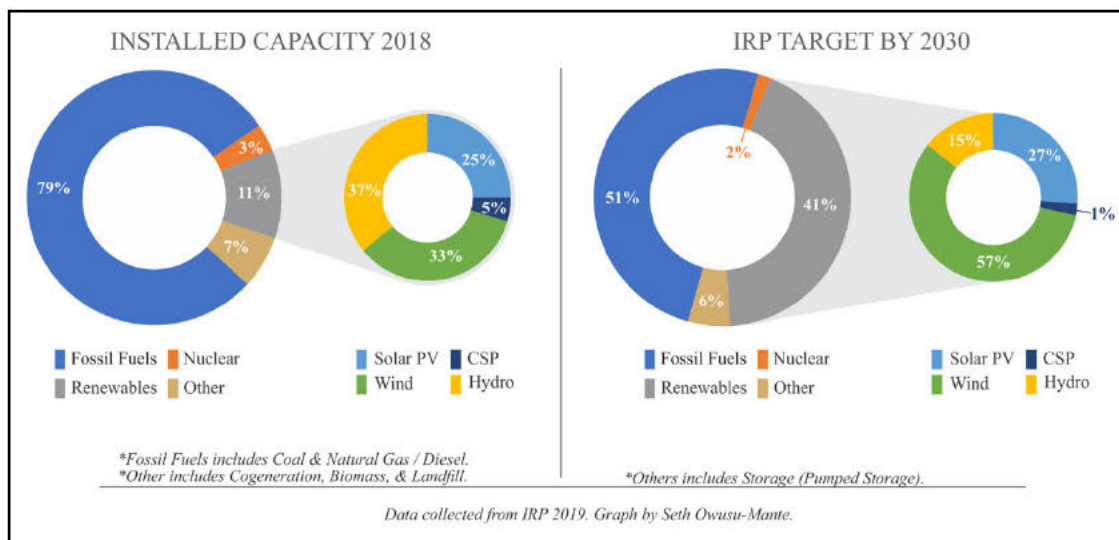


Figure 1-4. South Africa's 2018 IRP renewable energy targets (Electricity 2013).

Renewable energy seems promising due to the short replenishment *'period and no pollution advances the greenhouse effect.'*

Comparing the constraints of renewable and fossil fuels, the heavily dependent fossil fuels should be replaced with renewable energy sources that are sustainable. This creates a technological difficulty, that of bridging the dynamic imbalance between energy supply and demand, notably the intermittent nature of renewable energy.

1.4 Problem Statement

Since the Industrial Revolution, fossil fuels have been indispensable to our everyday lives. The consumption of fossil fuels has increased dramatically. Due to human activity-generated exhaust emissions, the CO₂ and other greenhouse gases concentration in the atmosphere has reached a new high. This phenomenon will lead to global warming as the atmosphere absorbs more heat energy from the earth's surface instead of being radiated into space. We cannot give

an effective solution to the problem at this time, but we can lessen the greenhouse effect by reducing emissions of greenhouse gases.

Reducing greenhouse gas emissions is becoming an essential objective for all nations and regions. South Africa has fulfilled its goal of reducing total per capita greenhouse gas emissions by 11,8 % from 2014 to 2019 (Balsalobre-Lorente *et al.* 2022). South Africa's next goal is to reduce emissions by 22–34 % below 1990 levels, or roughly 366–444 MtCO_{2e}. This goal was accomplished by implementing a carbon price, the National Climate Change Adaptation Strategy, South Africa's Low Emissions Development Strategy, a Presidential Climate Commission, and the Just Transition Framework. There is still much work to be done to close a portion of this gap.

Although converting CO₂ into synthetic fuels and chemicals does not entirely eliminate emissions, it harnesses the full value of CO₂ by integrating it into the existing energy system, thereby achieving a significant reduction in net emissions. There is currently an increasing interest in CO₂ methanation, also referred to as the Sabatier reaction. In addition to using CO₂ that would otherwise be emitted (or stored), converting CO₂ to CH₄ creates valuable fuels that can be easily injected into the existing energy system. Within the two chemical bonds, the energy of renewable power can be stored as chemical energy. CO₂ usage via PtG can remedy the worsening global warming problem brought on by greenhouse gas emissions.

The hydrogen required for CO₂ methanation can be produced through water electrolysis. However, a crucial factor in CO₂ conversion is ensuring that the energy or hydrogen used in the process comes from sources with minimal carbon footprints. If the hydrogen used for water electrolysis is sourced from a power station that relies on fossil fuels, the carbon footprint of the methanation process will remain positive, and converting CO₂ into CH₄ will not effectively reduce overall emissions.

1.5 Rationale/Motivation for this Study: Alignment to Sustainable Development Goals (SDGs)

The study on CO₂ methanation aligns closely with several SDGs, particularly SDG 7, SDG 11, and SDG 13, as discussed.

The study investigates the catalytic conversion of CO₂ into CH₄ (CO₂ methanation), which is integral to achieving multiple SDGs, particularly SDG 7, which aims to ensure access to clean, affordable, reliable, and sustainable energy. By converting CO₂ into methane, the study promotes the development of renewable methane that can be used as a cleaner alternative to conventional fossil fuels. This aligns with the goal of fostering energy systems that reduce dependence on non-renewable energy sources and enhance energy efficiency. At the same time, CO₂ methanation directly supports SDG 13 by providing a method to recycle CO₂, a major greenhouse gas, into a useful energy carrier. This process helps mitigate climate change by reducing the amount of CO₂ released into the atmosphere, thereby contributing to the global efforts to curb greenhouse gas emissions (GHGs) and their associated impacts. The conversion of CO₂ into renewable methane can aid in achieving SDG 11 by improving waste management and reducing environmental degradation. As this technology can utilize CO₂ captured from various sources, it supports the efficient management of industrial emissions and contributes to more sustainable urban environments. The process also has the potential to integrate with existing infrastructure, promoting cleaner and more sustainable energy systems within communities.

Summary of Rationale:

- Advancement in the development of sustainable energy solutions by converting CO₂ into renewable methane, supporting SDG 7.
- Contribute to immediate action on climate change and reduce greenhouse gas emissions by converting CO₂ to methane, aligning with SDG 13.
- Promote waste management and environmental sustainability by utilizing CO₂ methanation, thereby supporting SDG 11.
- Provide a renewable fuel option to enhance the efficiency of energy systems and decrease reliance on fossil fuels.
- Support the use of regional resources and promote a transition towards more sustainable and resilient energy systems by producing renewable methane.

In conclusion, the study on CO₂ methanation holds significant potential for contributing to sustainable development by offering innovative solutions to energy and climate challenges. It aligns with the goals of enhancing clean energy access, reducing greenhouse gas emissions, and improving environmental management.

1.6 Research Aim and Objectives

Recent reliance on fossil fuels and domestic energy security have exacerbated environmental issues. These issues directly threaten the Sustainable Development Goals (SDGs) of the United Nations (UN, 2015), particularly those linked with climate action (SDG 13), excellent health and well-being (SDG 3), and clean and affordable energy (SDG 7). In light of this, transitioning South Africa's energy sector into a circular economy asset will require the development of clean, inexpensive energy solutions with long-term advantages. The research intended to synthesize a novel catalyst system combining nickel (Ni) and molybdenum (Mo) for CO₂ methanation, with the added benefit of lowering anthropogenic gas (CO₂) emissions. In addition, bi-metallic catalysts were developed to facilitate the optimization of CO₂ conversion and enhance catalytic activity, selectivity, and stability at lower temperatures for enhanced methane (CH₄) output and quality. To achieve the aim of this study, the research was carried out in accordance with the following specific objectives:

- i. To investigate the effect of Ni and Mo metal loading in the catalyst system on CO₂ methanation.
- ii. To evaluate optimal Mo concentrations for maximizing CO₂ conversion and CH₄ selectivity in Ni–Mo/AC catalysts.
- iii. To synthesize catalyst systems using incipient wetness impregnation (IWI), sol-gel (SG), and mechanical mixing (MM) and study how the catalyst preparation method affects the catalyst activity.
- iv. To investigate the advancements in AC-based materials for CO₂ methanation (2014–2024) and their sustainable energy potential.
- v. To conduct an informetric analysis on the role of Mo in enhancing Ni-based catalysts for CO₂ methanation.

While the micropores of activated carbons (ACs) with well-developed micropores (pore size < 2 nm) are highly advantageous for the adsorption and mass transfer of small molecules like H₂, CH₄, and CO₂. Hence, their narrow size can limit the mass transfer of large molecules by restricting their access to catalytic sites, impeding their diffusion, and potentially causing blockages. Therefore, the novelty of this study was to synthesize a newly developed bimetallic Ni/Mo catalyst supported on AC as an alternative to the conventional Ni/Al₂O₃ catalyst with potential for recoverability and by developing an optimized CO₂ methanation reaction reactor

for CH₄ production. Additionally, this research is expected to lead to the development of a strategically designed CO₂ methanation reactor that will enhance CH₄ production and contribute to a more sustainable energy system in South Africa.

1.7 Thesis Framework and Layout

This thesis consists of 7 chapters, as shown in Figure 1.6, with a clear framework linking the study objectives to the papers (1-5) in each chapter. Each chapter begins with a brief remark (abstract) that gives the reader an overview of the content and its relevance to the thesis. The chapters are structured as follows:

Chapter 1: *Introduction:* This introduction chapter provides a comprehensive overview, background, problem statement and conceptualization of the research. It justifies the need for alternative (renewable) energy sources due to the environmental impact of fossil fuels and the need to develop a tunable mesoporous catalyst for the conversion of CO₂ to CH₄.

Chapter 2: *Review of Carbon Capture and Methane Production from Carbon Dioxide (Paper 1):* This chapter provides a comprehensive literature review of a sustainable approach that combines CCS with CH₄ production from CO₂. It discusses the practicality of CCS technology in generating renewable energy, reducing CO₂ emissions, and enhancing energy security. The study recommends converting CO₂ into CH₄ as a highly promising and feasible approach due to CH₄'s significant benefits in reducing pollution and promoting sustainability. The literature review chapter has been published and linked to all the objectives. Specifically, paper 1 presents a comprehensive overview of advancements in carbon capture, utilization, and emissions mitigation, including technical, economic, and environmental aspects, with a focus on trends and global warming potentials. The study also provides recent advances that have been made towards reducing the impacts of CH₄ emissions.

Chapter 3: *Effects of molybdenum addition to activated carbon supported Ni-based catalysts for CO₂ methanation (Paper 2):* This chapter discusses the effects of Mo on the properties and catalytic performance of AC supported Ni-based catalysts for CO₂ methanation. This chapter is linked to the objective I - II.

Chapter 4: *Evaluating the potential of Ni-7%Mo/AC catalysts prepared by different strategies for CO₂ methanation (Paper 3):* This chapter provides insight into the influence of different synthesis methods of Ni-7%Mo/AC catalysts on catalysts performance for CO₂ methanation.

The chapter explores the synthesis of Ni-Mo/AC catalysts using IWI, MM, and SG methods and provides a detailed characterization of the catalysts produced during these processes. Additionally, it includes a stability study to assess the reusability of the synthesized catalysts. This chapter corresponds to objective III.

Chapter 5: *CO₂ methanation: A bibliometric analysis and review of activated carbon-based materials (2014 – 2024) (Paper 4):* This chapter explores the potential of AC-based materials for environmental remediation and energy production, focusing on their use in converting CO₂ and H₂ into CH₄ and H₂O. The study also reviewed various applications of CO₂ methanation using AC-based catalysts and provides growing research interest, though with limited inter-institutional collaborations. This chapter corresponds to objective IV.

Chapter 6: *Molybdenum-promoted nickel catalysts for CO₂ methanation: a critical review and informetric perspective (Paper 5):* This chapter focuses on the bibliometric analysis of research on CO₂ methanation from 1994 to 2023, evaluating advancements in catalyst performance, specifically the role of Mo as a promoter in Ni-based catalysts, and identifies technical challenges and future research opportunities. This chapter corresponds to objective V.

Chapter 7: *Conclusion:* This concluding chapter summarises the study's overall findings and implications and provides recommendations for further research based on the research outcomes.

All cited articles are referenced at the end of each respective chapter.

1.8 Targeted Outputs

- Synthesis of a newly developed mesoporous Ni-Mo/AC catalyst for the conversion of CO₂ into CH₄.
- Publication of research findings in reputable peer-reviewed journals.
- Presentation of research findings at conferences.
- To ensure catalyst regeneration and reuse in CO₂ methanation.

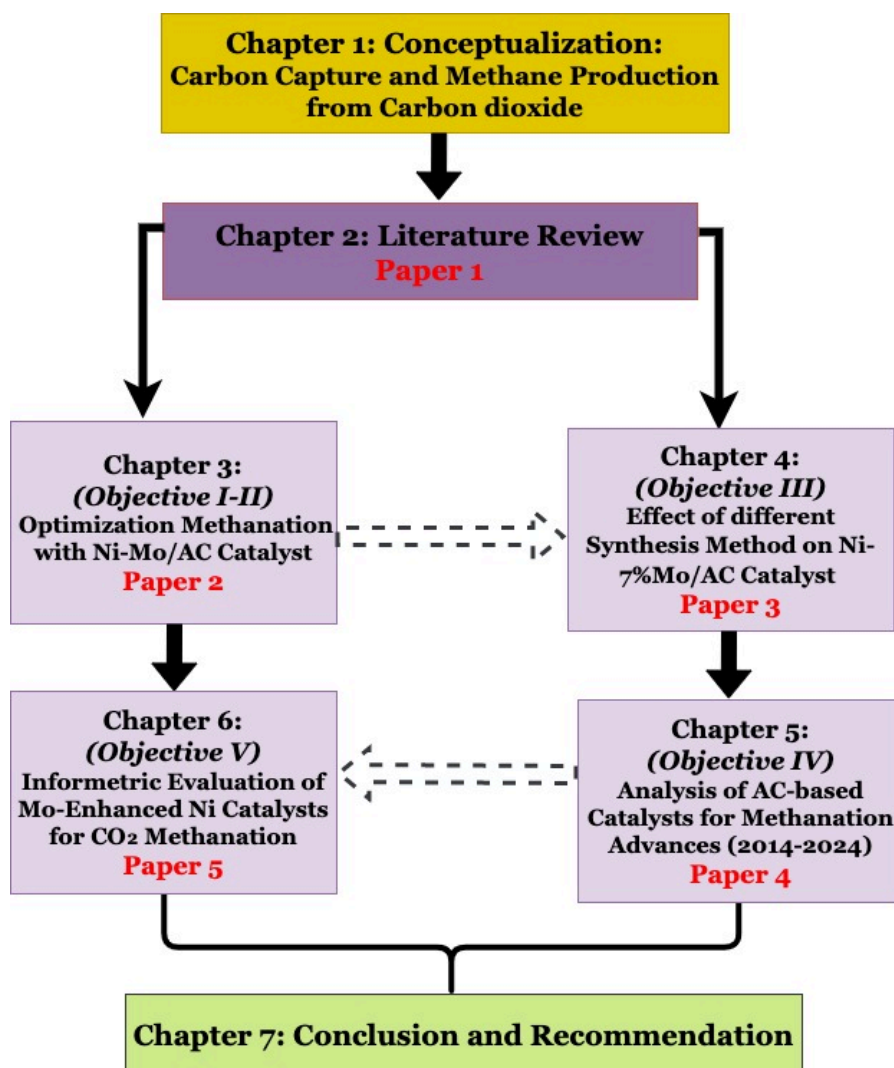


Figure 1-5. Framework of thesis layout, connecting objectives and papers to chapters.

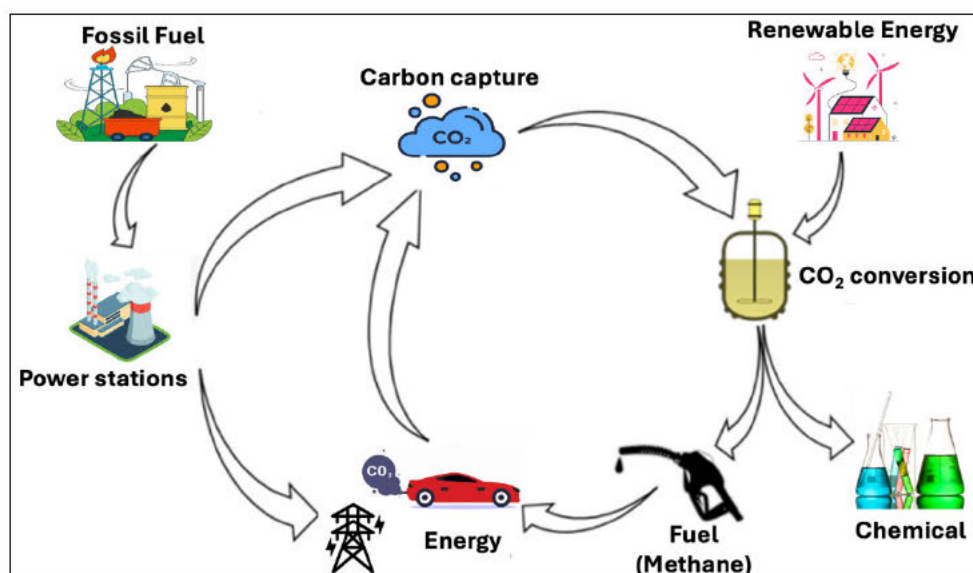
CHAPTER 2: LITERATURE REVIEW

Review of Carbon Capture and Methane Production from Carbon Dioxide

Abstract

Recently, there has been a growing interest in utilizing nickel-based catalysts within the petrochemical industry for methane production. However, several challenges remain with their application. This chapter focuses on carbon capture and methane production from carbon dioxide, aiming not merely to summarize the current understanding but to critically discuss key aspects of this process. Specifically, the chapter reviews carbon capture and utilization (CCU) technologies, CO₂ methanation, various catalytic processes, catalyst reducibility, and regeneration, as well as the concept of "Power-to-Gas" (PtG) and its impact on CO₂ reactions under different operational conditions. Additionally, the Sabatier reaction and its practical applications, the kinetics of CO₂ methanation reactions, and reactor design considerations were highlighted. The chapter also delves into the development of catalysts for CO₂ methanation, with a focus on recent advancements aimed at enhancing CO₂ conversion to methane using Ni-Mo/AC catalysts. The role of activated carbon as a catalyst support in petrochemical applications is also examined. Finally, an in-depth analysis of common catalyst preparation techniques, with particular attention to the impregnation method using incipient wetness, was provided. The chapter concluded by addressing the challenges and suggesting future directions for achieving efficient conversion of carbon dioxide into fuels and petrochemicals.

Graphical Abstract



2.1 Sustainability and Carbon dioxide Emissions

Numerous studies have established a correlation between the global climate system and greenhouse gas (GHG) emissions (Alexander, Allen and Bindoff 2013). CO₂ emissions account for an estimated 77% of greenhouse gas emissions and are therefore regarded as the primary contributor to climate change. The usage of carbon-based fuels, which today account for 80-85 % of the world's Total Primary Energy Supply (TPES), is primarily responsible for this tremendous output of CO₂ (Aresta, Dibenedetto and Angelini 2013; OECD 2016). The annual CO₂ emissions during the Industrial Revolution have increased dramatically from almost zero to about 34 GtCO₂ in 2014. Consequently, the current CO₂ concentration in the atmosphere has reached 400 ppm (Chen, Lewis and Xiang 2015).

In the coming decades, this CO₂ concentration is likely to increase, mainly due to the rapid economic growth of developing countries such as China and India, which are the world's largest energy consumers alongside the USA. Since the combustion of coal produces the most CO₂ per unit of heat generated compared to other carbonaceous fuels, coal is the raw material with the greatest environmental impact in the energy structures of these developing countries (Aresta, Dibenedetto and Angelini 2014; Wolde-Rufael and Idowu 2017).

Due to the unpredictability of economic development in key regions of the world, it is impossible to predict a clear future trend in CO₂ emissions (including South America, Russia, Eastern Europe, and other Asian nations aside from China and India, as well as almost all of Africa). In the coming years, CO₂ emissions are expected to increase by 50 to 60 GtCO₂/year, bringing the real amount of CO₂ present in the atmosphere to the unsustainable level of 500 ppm by 2050 (Senftle and Carter 2017). The Intergovernmental Panel on Climate Change (IPCC) and the International Energy Agency (IEA) emphasize that total anthropogenic CO₂ emissions must be reduced to less than 20 GtCO₂/year by 2050 in order to prevent irreversible effects on the ecosystem and global warming of more than 2 °C (Mac Dowell *et al.* 2017).

The scientific community, businesses, and governments must make a significant effort to create technology and methods that can not only help reduce CO₂ emissions but also help protect the natural resources used to produce fossil fuels, enabling them to meet the "sustainability" criteria. "Meeting the requirements of current generations without compromising the ability of future generations to satisfy their own needs" is the definition of sustainable development

(Severson and de Vos 2021). In this context, it is important to consider how social, economic, and notably environmental challenges are integral to this advancement (Figure 2.1).

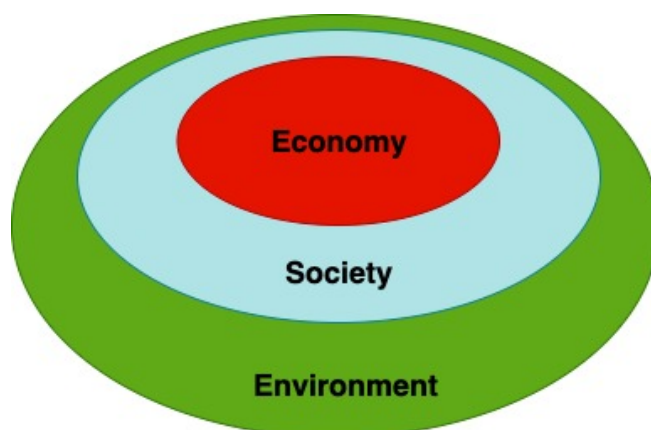


Figure 2-1. The three aspects of the sustainable development.

The development of our society has been significantly influenced by chemistry. Due to the involvement of chemical processes in technologies for its capture and utilization, its function in the creation of mitigation methods for CO₂ emissions looks to be becoming more and more important nowadays. Particularly, the term "Green Chemistry," which was coined in 1991 and whose 12 guiding principles are well-explained by (Anastas and Eghbali 2010), stresses the pressing need to develop goods and procedures that aim to reduce environmental problems and protect natural resources.

The importance of catalysis in Green Chemistry is exemplified by the fact that it serves as the foundation for effective CO₂ conversion technologies, which will be covered later. The use of catalysts makes it possible to increase selectivity (Principle II), use fewer processing and separation agents (Principle V), and reduce energy consumption (Principle VI). For these reasons, catalysts are one of the most important instruments for implementing sustainable production processes (Anastas *et al.* 2000; Anastas, Kirchhoff and Williamson 2001).

2.2 CO₂ Properties

At standard temperature and pressure, CO₂ is a gas with a density of roughly 1.98 kg m⁻³ at 0 °C. CO₂ sublimates at atmospheric pressure because it cannot exist in a liquid state below 5.1 bar. The pressure–temperature (p-T) phase diagram (Figure 2.2) makes it evident that CO₂ can be used as a green solvent for extraction applications, chromatography, and catalytic reactions because it exists as a supercritical fluid at relatively low temperature and pressure (critical point at 31 °C and 73.8 bar) (Styring, Quadrelli and Armstrong 2014).

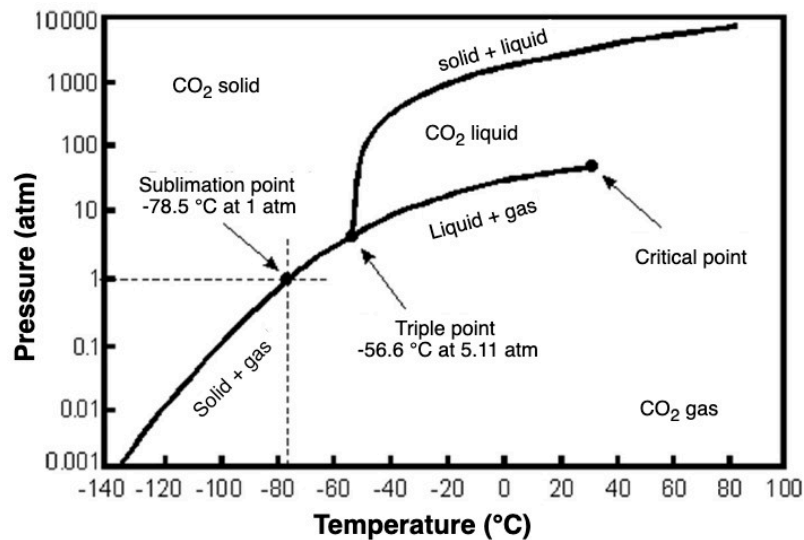


Figure 2-2. Phase diagram of Carbon dioxide at p-T. Adapted from (Glen and Hunter 2011).

CO₂ is an inert and non-combustible gas that is produced as a by-product of all combustion processes involving molecules containing hydrogen and carbon, along with water. Due to its characteristics, it is commonly employed in fire suppression and fire extinguishers systems. Due to volcanic eruptions, forest fires, and plant and animal respiration, CO₂ is naturally present in the earth's atmosphere. The natural carbon cycle has the capacity to recycle about 203 GtCO₂/year; however, since human emissions contribute only 7 Gt per year, the cycle is unable to recover this meager surplus, leading to an increase in atmospheric CO₂ concentration (Figure 2.3) (Atzori 2018).

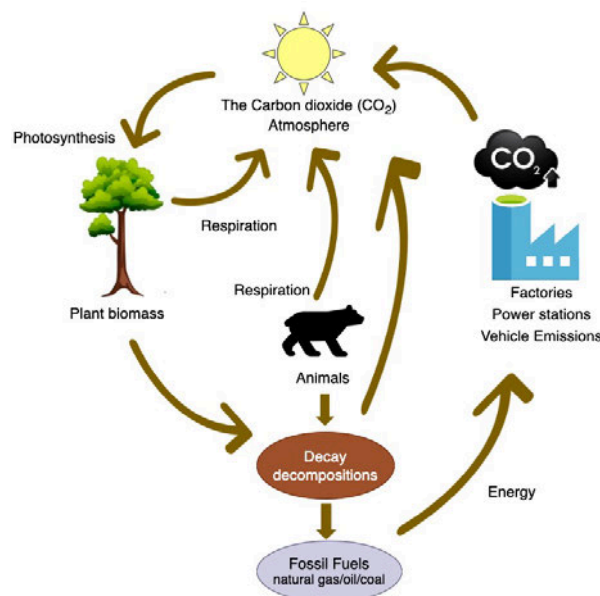


Figure 2-3. Natural carbon cycle.

The activity of the greenhouse gas is directly related to the anti-symmetric bending and stretching modes of the infrared-active vibrational modes of CO₂ (North 2015). Globally, the greenhouse effect is critical because it allows solar energy to be trapped, maintaining a steady global temperature. However, the Earth's atmosphere is becoming more concentrated with greenhouse gases, which is raising the temperature and detrimental to our biosphere. Although CO₂ is not the most potent greenhouse gas, its enormous concentration in the atmosphere relative to other GHGs, including nitrous oxide (N₂O), CH₄, and water vapour, makes it the principal agent of global warming (Kweku *et al.* 2018).

Two important characteristics predominate over the chemical reactivity of CO₂. The first is associated with the polarization of carbon-oxygen bonds caused by oxygen's stronger electronegativity than carbon's; as a result, the core carbon of CO₂ can readily react with nucleophiles such as phenolates, amines and Grignard's reagents. The capacity of some metals to coordinate CO₂ is the second characteristic. There are indeed several ways in which one or more metallic centres that either contain oxygen or carbon atoms can coordinate CO₂. This characteristic serves as the foundation for a variety of metal-induced and metal-catalyzed reactions where CO₂ can be favourably stimulated for species-specific reactions (Maitlis and Zanotti 2009).

From a thermodynamic standpoint, CO₂ is a relatively stable molecule with a heat of formation of $\Delta_f H^\circ$ of -394 kJ mol⁻¹, which makes its transformation a challenging task. However, many exothermic reactions, such as the creation of organic carbonates (by interaction between epoxides and CO₂) and the hydrogenation of CO₂ into CH₄ and CH₃OH, make CO₂ conversion fully viable (CH₃OH). It is necessary to consider changes in both enthalpy and entropy because the equilibrium position in a reaction is determined by the free energy value ($\Delta_f G^\circ = \Delta_f H^\circ - T\Delta_f S^\circ$), which must decrease in spontaneous processes. Entropy typically decreases in chemical processes with CO₂ as the reactant, as the process results in the formation of solids or liquids, and it occasionally causes a reduction in the number of molecules. As a result, the reaction temperature will rigorously determine the process's viability by causing $\Delta_f G^\circ < 0$ and shifting the equilibrium position in favour of the products (Styring, Quadrelli and Armstrong 2014).

Furthermore, kinetic considerations must be made for thermodynamically spontaneous reactions involving CO₂; in certain cases, reaction processes require the removal of a sizable

activation energy barrier. Utilizing a proper catalyst result in a notable reduction in activation energy, enabling activities to be carried out at temperatures that are manageable. Additionally, this enables the application of "Green Chemistry" catalytic concepts. Considering this, the scientific community needs to make a significant effort with the goal of discovering suitable catalysts for each process associated to CO₂ chemical recycling to fuels and chemicals.

2.3 Strategies for CO₂ Emissions Alleviation

The reduction of CO₂ emissions is a complex global objective that necessitates the involvement of several academic fields and the implementation of cutting-edge solutions from governments and companies. Since there isn't a single answer to such a complex issue, various strategies must be employed, necessitating the investment of multiple technologies to address all possible solutions (North 2015).

The reduction of CO₂ emissions can be accomplished in principle in three ways: carbon capture and utilization (CCUs) technologies, carbon capture and storage (CCS) technologies, and reduction of CO₂ emissions through enhancements in the generation and application of electric power.

2.3.1 Direct Reduction of Emitted CO₂

Enhancements in the effectiveness of electric energy generation can help address some of the climate challenges brought on by the high CO₂ emissions. For instance, the Integrated Gasification Combined Cycle (IGCC), a cutting-edge technology, can increase efficiency from its present average of 30% to around 50%, making a significant contribution to lowering CO₂ emissions. Converting all of the current power plants is not practical due to long implementation times and high costs, so a more practical approach would be to design and construct new low-emission power plants, even though there are certain technological and financial challenges that must be overcome. Additionally, transitioning from coal to a less carbon-intensive fuel, such as natural gas, can also be helpful from the perspective of resource extraction.

Additionally, reducing emissions and protecting natural resources would be possible with improved energy production efficiency. In this regard, increased building insulation, the use of fuel-efficient automobiles, and improved individual behaviour are all elements that can help create a society that is more sustainable (Aresta, Dibenedetto and Angelini 2014).

2.3.2 Carbon Capture and Storage Technologies

Concerns about climate change are greatly influenced by the amount of CO₂ released from industrial and utility plants. Table 2.1 lists the primary sources of waste CO₂; data from 2008 shows that power plants have a significant impact on CO₂ global emissions, with coal use making up the greatest share of those emissions (Wilcox and Wilcox 2012).

Table 2-1. Major sources of CO₂ emissions.

Source	Global CO ₂ emissions - 2008 (10 ⁶ t CO ₂ per year)
Ammonia production	150
Iron and steel production	1000
Coal	14200
Cement production	2000
Refineries	850
Natural gas	6320
Ethylene production	260

CO₂ is extracted directly from industrial point sources or the environment and stored in geological sites including coal beds, aquifers, gas fields and depleted oil. This process is known as carbon capture and storage (CCS) (IEA 2012). By using CCS technology, it is possible to keep CO₂ out of the atmosphere for a considerable period of time, which has obvious environmental benefits. CCS currently enables the storage of around 4.7 MtCO₂/year (IEA 2012). However, there are still several debatable areas, most notably the total energy requirements for CO₂ extraction, pumping, and storage. From this perspective, CO₂ must be transported from the sources to the final storage sites via efficient pipeline systems, whereby the length and capacity of the pipelines influence the overall costs of the system (McCoy and Rubin 2008; Huang, Rebennack and Zheng 2013). In addition, the nature of the reservoirs must be examined in detail to ensure the long-term storage of CO₂. Lastly, a significant obstacle is public acceptance, which will shape political sentiments (Wennersten, Sun and Li 2015).

The costs of CO₂ capture processes have a considerable influence on the implementation of CCS technologies. Against this background, some of the capture methods that are extensively used and studied are explained in more detail below.

2.3.2.1 Carbon Capture Process

The majority of contemporary capture agents are liquid-based, consisting of either pure liquids, mixes, or solutions in solvents such as water. Gas-liquid separation can be based on many mechanisms, such as absorption and adsorption, and CO₂-capture agent interactions can be governed by chemisorption or physisorption. Solvents such as diethanolamine (DEA) and monoethanolamine (MEA) are the most often employed chemicals in CO₂ capture methods on a commercial scale. A carbamate-ammonium ion pair is produced when these species react chemically with CO₂, and the presence of -OH groups is thought to be necessary because they create hydrogen bonds that aid in CO₂ sorption. MEA must be produced in solution with a significant amount of water (up to 70% w/w), which requires large equipment and increases the initial capital costs (CAPEX). The industrial process for MEA is carried out at 50 °C and does not require high CO₂ partial pressures. In addition, typical regeneration processes take place at 120 °C, which increases expenses (Styring, Quadrelli and Armstrong 2014). Additionally, there are large operational expenditure costs (OPEX) associated with the high temperature of the desorption-regeneration processes as a result of the chemical deterioration of MEA over time, necessitating the continual replacement of used MEA with new solvent (Zhu, Schade and Nielsen 2013; Atzori 2018). Moreover, MEA breakdown can result in the formation of chemicals such as aldehydes and ammonia, which pose a greater risk to the environment than the captured CO₂, necessitating the need for post-stripper scrubbers.

Alternative compounds can be employed even though MEA is the most frequently utilized solvent for CO₂ capture. Despite being a stable, non-toxic polymer with a low vapour pressure and high CO₂ solubility, poly-(ethylene glycol) dimethyl ether has certain drawbacks, including being expensive and having hygroscopic properties. (Aschenbrenner and Styring 2010). Alkyl carbonates are an intriguing class of compounds due to their ability to adsorb CO₂ and their ability to be created from CO₂, hence lowering their carbon footprint. A classic example is dimethyl carbonate (DMC), which is formed when CO₂ reacts with the right epoxides by transesterification to form cyclic carbonates. The adsorption capacity of DMC increases with increasing pressure and depends on the separation conditions (Gui, Tang and Fei 2010).

Ionic liquids (ILs) have recently gained increasing interest due to their very low vapour pressure, strong polarity, and resistance to chemical and heat degradation. ILs containing

amino groups can interact with CO₂ by means of C-N bond formation, the strength of which can be adjusted to improve CO₂ absorption and permit desorption processes to proceed under relatively mild settings (Bates *et al.* 2002; Mumford, Mirza and Stevens 2017). ILs operate at far lower CO₂-desorption temperatures than conventional amine sorbents and can be used in their pure liquid state, enabling smaller stripper sizes. Since the limitation of diffusion-controlled mass transfer resulting from the high viscosity of ionic liquids is probably the primary technological drawback of these materials, research has focused on porous solid polymers with properties similar to those of ionic liquids (P-ILs). In this regard, the polymerisation of 4-vinylbenzyl methacrylate, hexafluorophosphate [VBMA][PF₆], a monomer with outstanding capture properties that is solid at room temperature, represents an intriguing possibility (Figure 2.4). In addition, desorption processes can be carried out at extremely low temperatures (around 80 °C), as the separation mechanism is based on physisorption. Unfortunately, their high cost and lack of convincing evidence for commercial scale-up prevent their widespread use, although ILs and P-ILs materials appear very promising for CO₂ capture processes (Styring, Quadrelli and Armstrong 2014).

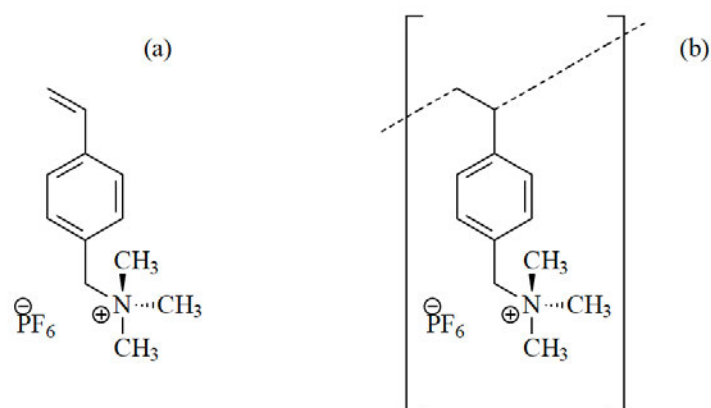


Figure 2-4. Structures of (a) [VBMA][PF₆] and its (b) solid polymer P[VBMA][PF₆] (Adapted from (Atzori 2018)).

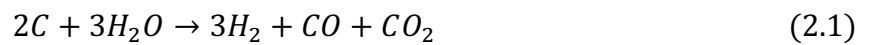
Metal-Organic Frameworks (MOF) are an additional significant class of solid porous materials that could be appropriate for CO₂ capture. Due to their enormous surface area and tunable pore structure, these materials have gained significant attention in recent decades. In addition, their adsorption capabilities can be enhanced through amine functionalisation. With pure CO₂ and high pressures, MOFs exhibit extraordinary CO₂ uptake, but their performance diminishes dramatically when exposed to a gas mixture (Bollini, Didas and Jones 2011; Yu, Huang and Tan 2012b; Schoedel, Ji and Yaghi 2016).

2.3.2.2 Carbon Capture Technology

CCS technology relies on CO₂ capture. Three methods for trapping and sequestering CO₂ are envisaged, based on the settings of a fossil fuel-based power plant, gas steam pressure, and CO₂ partial pressure. Among the carbon capture technologies are pre-combustion, oxy-fuel combustion, and post-combustion (Alrebei *et al.* 2022).

2.3.2.2.1 Pre-Combustion Capture Method

This method involves capturing CO₂ before combustion, rather than after combustion, thus making this method more feasible. Gasifiers and catalytic reactors are involved. In a gasifier with low oxygen pressure, the following equations (Equations (2.1) – (2.3)) demonstrate how pure syngas (CO, H₂) is produced. Moreso syngas is enriched by passing it through a shift reactor with a steam, as shown in Figure 2.5.



Natural gas could also be applied for steam reforming via this method; between 700 and 850 °C, an endothermic reaction occurs, culminating in the conversion of CH₄ and H₂O and the generation of syngas (CO, H₂). An exothermic reaction occurs after partial oxidation, in which CH₄ burns in oxygen to create CO₂ (Equations (2.4) and (2.5)) (Nawkarkar, Ganesan and Kumar 2022).



A key element of pre-combustion is the hydration of gas separated from air, which is the most promising technology today (Xu and Li 2014).

The CO₂ captured in this technique produces hydrogen fuel, which is used to generate electricity in several industries while emitting little CO₂ (Theo *et al.* 2016). Fertilizers and hydrogen are produced through pre-combustion capture (Babu, Kumar and Linga 2013). CO₂ is generated from this process in concentrations ranging from 5 to 60%, making it easy to

capture; however, the water gas shift reactions and gasification are costly and difficult to operate (Pires *et al.* 2011).

2.3.2.2.2 *Oxy Fuel Combustion Capture Method*

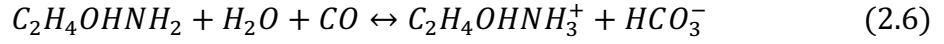
A system for air separation during oxy-fuel combustion capture is used to obtain pure oxygen, as flue gas and coal are fed into the oxy-fuel boiler (Wall *et al.* 2009; Toftegaard *et al.* 2010; Chen, Yong and Ghoniem 2012). Coal is burned at a fixed temperature and pressure. Figure 1 illustrates how the flue gases, lacking oxygen and nitrogen, are only made up of CO₂ and water vapors. Additionally, this reduces the quantity of flue gas required to remove NO_x and sulfur (Buhre *et al.* 2005; Stanger and Wall 2011). Condensing water vapor maintains the boiler's temperature. Dehydrated CO₂ is compressed and delivered to a storage facility or an industry where it is utilized in beverage carbonation, as a solvent, and as a fire extinguisher (Chen and Curcic 2016). Flue gas is recycled in its natural state to maintain the boiler's internal temperature (Toftegaard *et al.* 2010). When compared to other carbon capture technologies, it is the most efficient and adaptable (Kunze and Spliethoff 2012). There are, however, some obstacles to overcome. The air separation unit (ASU) uses cryogenic distillation, which consumes a great deal of energy to produce essentially pure oxygen. The integrated gasification combined cycle (IGCC) can be replaced by this method, which converts CO to CO₂.

A major drawback of this method is that it demands more energy to separate oxygen from the air (Yu *et al.* 2017; Dai *et al.* 2022).

2.3.2.2.3 *Post Combustion Capture Method*

After burning carbonaceous materials (such as biomass) or fossil fuels, CO₂ is removed from the flue gas using a viable adsorbent such as amine (Ben-Mansour *et al.* 2016; Dai *et al.* 2022). Currently, it is the most effective method of capturing CO₂ from natural gas plants. As separating agents, it employs amine solutions including potassium carbonate (K₂CO₃) mono-ethanolamine (MEA), methyl-di-ethanolamine (MDEA), and di-ethanolamine (DEA) (Nawkarkar, Ganesan and Kumar 2022). The novel sorbent piperazine collects contaminants efficiently because of its high volatility (Bougie and Iliuta 2011). A chemical reaction deposits CO₂ in the solution, which is then separated by flowing high-temperature (100 - 200 °C) steam over it.

An equation representing the reversible absorption–regeneration reaction is shown below (Nawkarkar, Ganesan and Kumar 2022).



However, this method has some drawbacks, such as a high parasitic load, high flue gas temperatures, and the inability to operate at low CO₂ levels. Figure 1 illustrates a direct post-combustion mechanism. Gas-fired power plants use about 4% CO₂, while coal-fired power plants utilize 7–14%, increasing electricity costs by 32% and 65%, respectively, in gas-fired and coal power plants (Dai *et al.* 2022). As a result, cutting costs while improving system performance is still a subject of great interest (Kim, Gwak and Lee 2022). Membrane technology, including ceramic or polymeric membranes, marine algae, and cryogenic distillation, can all be used for post-combustion CO₂ capture. This has many benefits, including the ability to retrofit and eliminate the need for a cryogenic separator and shift reactor. In post-combustion, CO₂ is usually absorbed or desorbed using a solution containing alkanol amine (Kazemi and Mehrabani-Zeinabad 2016; Li *et al.* 2016a; Li *et al.* 2016b).

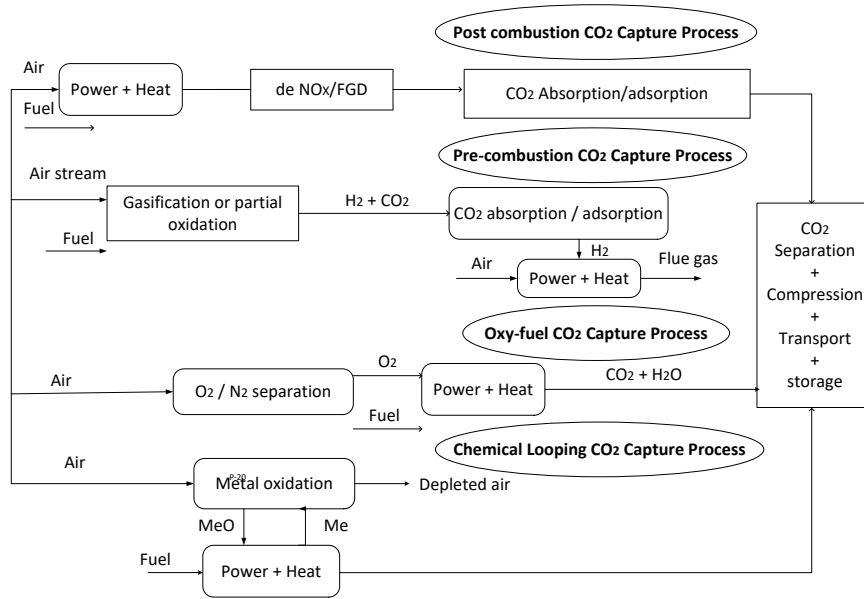


Figure 2-5. CO₂ capture technologies (Gibbins and Chalmers 2008a).

2.4 Various Combustion Technologies for CO₂ Capture

A comparison of the three CO₂ capture technologies is illustrated in Table 2.2. Coal gasification uses pre-combustion, while oxy-fuel combustion and post-combustion are applied to coal- and gas-fired plants. CO₂ capture using post-combustion technology is presently the most advanced (Bougie and Iliuta 2011; Bailey, Kurz and Sushkova 2014). According to Gibbins and Chalmers (2008b), three technologies were compared in terms of the costs of both gas-fired and coal-fired power plants (Table 2.3). CO₂ mitigation for coal-fired power plants was the

cheapest using pre-combustion technology, while oxy-fuel and post-combustion technologies were comparable. For post-combustion capture, the costs per tonne of avoided CO₂ were 50% lower for gas-fired plants than for the two other technologies. Moreover, the most inefficient method of CO₂ capture is post-combustion CO₂ capture, having an energy cost of roughly 8% for coal-fired plants and 6% for gas-fired plants (Ketzer, Iglesias and Einloft 2015).

Table 2-2. Comparison of various CO₂ capture technologies (Leung, Caramanna and Maroto-Valer 2014).

Parameter	Post-Combustion	Pre-Combustion	Oxy-Fuel Combustion
Application area	Can be utilized with current coal combustion plants.	Integrated gasification combined cycle and turbines, which can effectively use H ₂ -rich syngas.	Synergy between novel cycle and integrated gasification combined cycle has been employed.
Pros	Small concentrations of CO ₂ can be captured. Possible to retrofit to existing plants.	Lower energy penalty than post combustion methods. The pressure and temperature of the regeneration process can be altered.	The CO ₂ capture efficiency is 100%. Absence of hazardous NOx.
Cons	High costs for operation and regeneration. Excessive solvent losses.	Syngas treatment and drying before CO ₂ capture. Capital costs and investment costs are high.	High operational and capital costs. Annexing to existing plants is difficult.
CO ₂ concentration (vol.%)	4–14	15–40	75–80
CO ₂ capture efficiency (%)	85–90	85–90	90–100
CO ₂ purity (%)	99.6–99.8	95–99	87.0–94.8
Temperature and pressure	Flue gas must be cooled, and pressure is dependent on the CO ₂ capture process.	High pressure and low temperature (depending on the technique utilized).	Cryogenic temperatures are used to separate oxygen. The flue gas is recycled to lower the temperature because oxy-fuel combustion produces high temperatures.
Equipment size	Large size equipment required with high investment.	Medium equipment.	The equipment is of low size.
Combustion medium	Air is used.	Steam/air is required for gasification to generate CO ₂ .	High-purity oxygen for combustion.
Start of the art	Amine scrubbing plants (reaction with monoethanolamine) are in practice. Currently, power plants use this technology.	Integrated gasification combined cycle and ammonia production plants are running currently.	Efficient CO ₂ separation.
Acid gases	Contains H ₂ S, COS, NOx, and SOx.	Sulfur compounds need to be removed.	NOx is not present; however, gas

desulfurization is
necessary.

Table 2-3. Comparison of the costs of various capture methods (Gibbins and Chalmers 2008b; Leung, Caramanna and Maroto-Valer 2014). Costs exclude storage and shipping costs but include CO₂ compression to 110 bars.

Fuel Type	Parameter	Capture Technology			
		Pre-Combustion	Post-Combustion	Oxy-Fuel Combustion	No Capture
Gas-fired	Capital cost (USD/kW)	1180	870	1530	500
	Cost of CO ₂ avoided (USD/t CO ₂)	112	58	102	-
	Cost of electricity (c/kWh)	9.7	8.0	10.0	6.2
	Thermal efficiency (% LHV)	41.5	47.4	44.7	55.6
Coal-fired	Capital cost (USD/kW)	1820	1980	2210	1410
	Cost of CO ₂ avoided (USD/t CO ₂)	23	34	36	-
	Cost of electricity (c/kWh)	6.9	7.5	7.8	5.4
	Thermal efficiency (% LHV)	31.5	34.8	35.4	44.0

2.5 CO₂ Separation Techniques

CO₂ is separated from flue gas during combustion using a variety of advanced separation techniques (Dai *et al.* 2022). There are several techniques involved, such as absorption, adsorption, chemical looping, membrane separation, and cryogenics (Pires *et al.* 2011; Samanta *et al.* 2012; Lim *et al.* 2013). Figure 2.6 displays a flowchart outlining the methods and techniques for CO₂ capture/separation technologies.

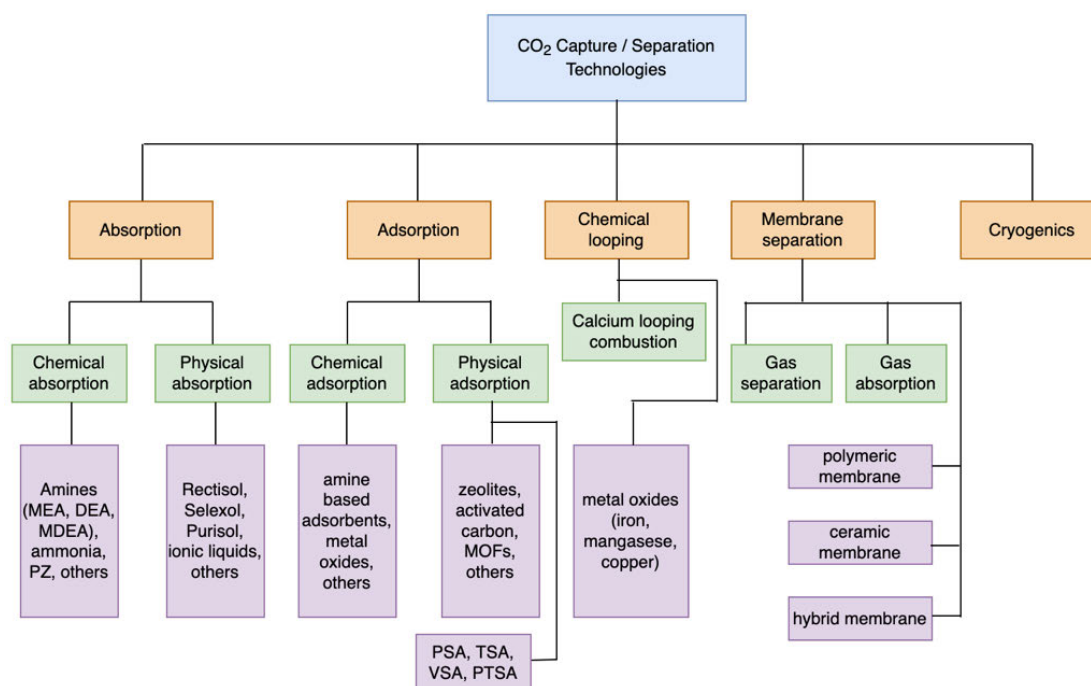


Figure 2-6. Separation techniques for CO₂ capture (Madejski *et al.* 2022).

2.5.1 Absorption

The ability of absorption to capture huge quantities of emissions from chemical factories and power plants has gained considerable attention in recent years. Chemical absorption is a reliable technique for CO₂ separation in coal-fired power plants because it is well-suited for existing plants with high operating costs and limited infrastructure (Liu *et al.* 2016c). The chemical absorption of CO₂ is a commercially viable technology due to its many advantages, including technical efficiency, handling capacity, and sophistication (Liu and Balasubramanian 2014). The potential absorbents and processes of absorption CO₂ capture are highlighted in Table 2.4.

CO₂ is separated from flue gas by absorption using a liquid sorbent (Figueroa *et al.* 2008; Edrisi *et al.* 2022). It is possible to regenerate the sorbent via a regenerative process or stripping by depressurizing and/or heating. This is the latest and most advanced method for separating CO₂ (Khurana, Goswami and Sarmah 2021). Potassium carbonate (K₂CO₃), monoethanolamine (MEA), and diethanolamine (DEA) are examples of common sorbents (Kashyap *et al.* 2019). MEA is very reactive and absorbs more quickly, and it is quite inexpensive (Khurana, Goswami and Sarmah 2021). However, their main drawback is the substantial parasitic energy load in relation to solvent regeneration, which adversely affects the total effectiveness of systems

combined with aqueous amine-based absorption processes (Heldebrant *et al.* 2017). DEA and other alkanolamines have also been employed for absorption, although they have comparable defects. Methyldiethanolamine (MDEA), a mixture of MEA and DEA, has been used with moderate success. It has higher CO₂ loading capacity, and degradation and corrosion resistance, as well as cheaper regeneration costs, but lower rates of absorption (Austgen, Rochelle and Chen 1991; Xu *et al.* 1998; Bishnoi and Rochelle 2000a, 2000b; Aroonwilas and Veawab 2007; Barzagli, Mani and Peruzzini 2010).

Veawab, Aroonwilas and Tontiwachwuthikul (2002) reported that MEA is the most efficient aqueous alkanolamine for CO₂ absorption, with a performance rate greater than 90%. Additionally, Aaron and Tsouris (2005) reviewed various CO₂ capture technologies and determined that MEA absorption is the most viable method for CO₂ capture in CCS. Applying a solvent containing 30% MEA, a 1 t CO₂/h absorption pilot plant was designed and experimentally validated in conjunction with a coal-fired power plant's post-combustion capture technology (Knudsen *et al.* 2011). In recent times, other adsorbents, including anion-functionalized ionic liquid and piperazine, have attracted a lot of attention (Gurkan *et al.* 2010). Even though piperazine rapidly reacts compared to MEA, its use in CO₂ absorption is more costly. Due to its higher volatility, it is still in the experimental phase (Bougie and Iliuta 2011). The risk of amine degradation, which could lead to equipment corrosion, solvent loss, and the formation of volatile degradation compounds, is a significant barrier to the widespread adoption of this technology for the CCS (Rochelle 2012; Fredriksen and Jens 2013), while environmental degradation has gone unnoticed.

Furthermore, amine emissions can deteriorate into nitramines and nitrosamines, which are highly toxic to human health and the environment. The chilled ammonia process captures CO₂ using aqueous ammonium salts (including ammonium carbonate) and can regenerate the CO₂ at elevated temperatures and pressures using waste heat, thereby minimizing the downstream compression (Kozak *et al.* 2009). There are fewer problems with this process than those caused by amine degradation.

Water's use as a co-solvent, which has higher thermal characteristics than other co-solvents, is one of the key precursors for the high solvent regeneration energy of MEA [20]. In the context of CO₂ absorption, the predicted regeneration energy for 30 wt. % aqueous MEA showed that more than 50% of the total energy was used to heat and vaporize the water co-solvent. The

remaining energy was used to reverse the chemical interaction between CO₂ and MEA at the same time (Tan *et al.* 2011; Asif *et al.* 2018). Considering this, it was thought that either totally or partially substituting other organic diluents for water as co-solvents could potentially reduce solvent regeneration energy, since they effectively create water-free/water-lean hybrid solvents with poorer thermal properties than water (Rivas and Prausnitz 1979; Barzagli *et al.* 2012; Liu *et al.* 2019; Alkhatib *et al.* 2021; Karlsson *et al.* 2021; Li *et al.* 2021a; Shen *et al.* 2021). Instead of vaporizing and heating the co-solvent, comparable to aqueous amines, the regeneration energy will be used more effectively to reverse acid gas chemisorption.

Additionally, hybrid water-free/water-lean solvents have been thoroughly studied in recent years, primarily for their CO₂ capture applications (Mathias *et al.* 2013; Barzagli *et al.* 2020; Alkhatib *et al.* 2021). They provide a wide range of potentially alluring substitutes to conventional aqueous amines (Heldebrant *et al.* 2017; Wanderley, Pinto and Knuutila 2021). The main objective of water-lean solvents is to preserve the chemical selectivity of water-based solvents, while enabling step gains in efficiency due to the lower specific heats of organics than water (Heldebrant *et al.* 2017). However, two problematic regions refute the claim of their attractiveness. The stated performance of these solvents when scaled up from lab-scale to industrial-scale settings has not been adequately examined due to a lack of availability of a few essential properties. This is predicted given the labor-intensive nature of experimental work, which makes it impossible to expand experimental testing to the broad range of transport and thermophysical parameters needed for precise and representative performance evaluation on an industrial scale. The second issue is that, when carried out on a lab scale, the potentiality of a particular solvent is typically demonstrated using a limited set of parameters, most notably the low enthalpy of absorption and high absorption capacity (Singto *et al.* 2016; Muchan *et al.* 2017; Wai *et al.* 2018; Liu *et al.* 2021b). These two characteristics are indeed of great concern for chemical absorption procedures, but they are still unsuitable for accurately gauging the potential of the tested solvents for their intended use. However, they ignore significant trade-offs between competing environmental, economic, and operational factors. The results of a straightforward assessment can help direct the development of novel generating solvents (Malhotra *et al.* 2017; Zhou *et al.* 2020b).

However, these difficulties can be overcome if the proper tools or novel process configurations are available. Due to recent developments in computational power and thermodynamic modeling tools, the first issue can be resolved by scaling the data from lab to industrial

operating conditions. The most appealing models for this application are molecular equations of state (EoS) centred on the Statistical Associating Fluid Theory (SAFT) (Chapman *et al.* 1989, 1990), due to their strong theoretical background, demonstrated correctness for a range of complex systems, and predictive abilities.

The solution to the second problem, which is to demonstrate the viability of a chosen solvent typically acknowledged using a limited number of requirements, may appear relatively apparent: add more evaluation criteria to the already-existing standard key performance indicators (KPIs). Moreover, making such a preference is more difficult because early design phases may not have access to information on a particular criterion (Papadokonstantakis *et al.* 2015). There must be a justification for why certain criteria should be included or excluded when narrowing the search space among the numerous properties that are available (Papadopoulos *et al.* 2014; Limleamthong *et al.* 2016; Papadopoulos *et al.* 2016). The effect of solvent characteristics on economic metrics such as total capital expenditures (CAPEX) and operating expenditures (OPEX) typically serves as the foundation for justification. Through the careful process modeling of hypothetical solvents, Mota-Martinez, Hallett and Mac Dowell (2017) ranked various solvent characteristics according to how they affected the process' overall economics. Leclaire and Heldebrant (2018) recently recommended the use of ideas from green engineering and chemistry to address problems with the advancement of CCUS technologies. They asserted that by applying the 12 + 12 principles of engineering and green chemistry (Anastas and Warner 1998), they could indirectly encourage the improvement of chemical processes' economic attractiveness and efficiency, which goes beyond their environmental motivation. Similarly to this, it may be beneficial to consider sustainability, health, and safety issues while assessing the possibility of promising solvents for the removal of acid gas (Jessop 2011; Tobiszewski *et al.* 2015). Figure 2.7 displays the schematic diagram for the absorption carbon capture process.

Table 2-4. Summary of absorption-based carbon capture.

Type	Absorbent	Reactive Separator	Operating Conditions P, C, T, G	CO ₂ Capture (%), AC (kg/kg)	Kinetics/Mass Transfer	Ref.
Single solvent	MEA	Flow (SC)	C:8 –16; T:10 –40; G:2 - 10	94, 0.4	$C_2H_4OHNH_{2(1)} + CO_{2(g)} + H_2O \leftrightarrow C_2H_4OHNH_{3(aq)}^+ + HCO_{3(aq)}^-$	(Yeh and Bai 1999; Diao <i>et al.</i> 2004; Sreenivasulu <i>et al.</i> 2015)
	K ₂ CO ₃	Fixed bed (Con-O, bench scale)	T:60 G:40 mL/min	99.4, NA	NA	(Kumar and Rao 1989; Russo <i>et al.</i> 2013)
	Ammonia	Sieve plate (CC)	C:10 - 14; T:25 - 55 °C	95–99, 1.2	$2NH_{3(g)} + CO_{2(g)} \rightleftharpoons NH_2COONH_{4(s)} + NH_2COONH_{4(s)} + H_2O_{(g)} \rightleftharpoons (NH_4)_2CO_{(s)}CO_{3(s)}$	(Yeh and Bai 1999; Diao <i>et al.</i> 2004)
	Piperazine	Stirred cell (SC, BS)	P:0.032; T:42 and 0.042	100, 0.32	1st order partial reaction occurs	(Derks <i>et al.</i> 2006)
	Ionic liquids	Double stirred cell (BS)	T:25–50; P:0.1; A:0.5–1.2	99.11 at 60 °C,	NA	(Davis Jr 2005; Rogers 2007; Wappel <i>et al.</i> 2010; Guo, Zhou and Jing 2013)
Mixed Solvents	DEA-K ₂ CO ₃	Split flow (CC, bench scale)	T:115; L:63.66 m ³ /h	99, NA	Promoter selection is very critical. It is a reversible exothermic reaction $CO_2 + K_2CO_3 + H_2O \leftrightarrow 2KHCO_3$	(Rahimpour and Kashkooli 2004)
	PEI-SiO ₂ Alcohol/ amine /water	Packed (bench scale)	L:33.66 m ³ /h	NA, NA	$\frac{q_{sensible}}{C_p \Delta m_{solution} \Delta m_{CO_2}}$	(Hoffman <i>et al.</i> 2014; Lin and Wong 2014)
	BDA-DEEA	Packed (CC, BS)	T:40 (absorption) T:90 (desorption) G: 24.78 m ³ /h	46 (HCL), 48 (HCC), 11(HCE) than MEA with 5 M	Carbamate and bicarbamate formations	(Xu, Wang and Chen 2013)
	AMP-PZ	Packed (pilot)	L/G:2.9; packing height=10 m	90, NA	-	(Xu <i>et al.</i> 1992; Cheng and Tan 2006; Notz <i>et al.</i> 2007; Freeman <i>et al.</i> 2010; Chen, Closmann and Rochelle 2011; Rochelle <i>et al.</i> 2011; Adeosun, Abbas and

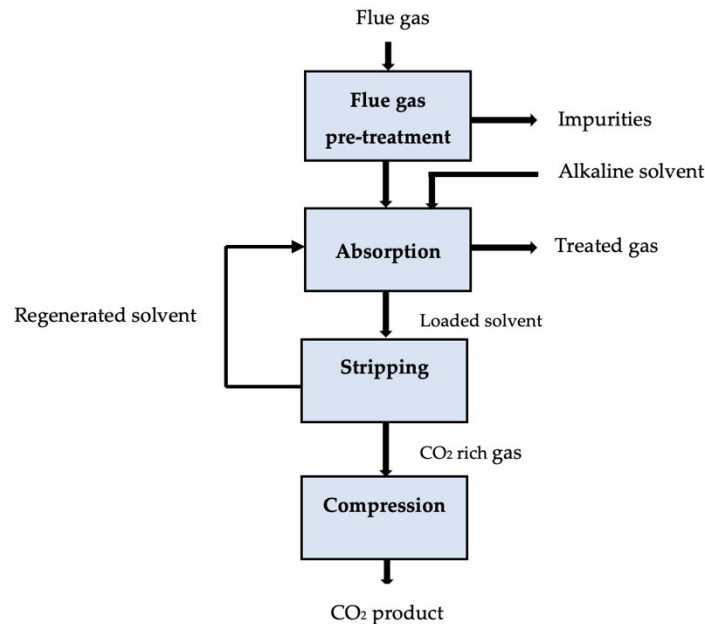


Figure 2-7. Schematic of an absorption carbon capture process (Spigarelli 2013).

2.5.2 Adsorption

The process of adsorption involves molecules in liquids and gases adhering to solid surfaces by weak van der Waals interactions (Figuerola *et al.* 2008). Unlike liquid absorbent processes, solid adsorbents bind CO_2 to their surfaces during adsorption. Selection criteria for this sorbent include a large surface area, high regeneration capability, and high selectivity. Common adsorbents include activated carbon, molecular sieves, zeolites, lithium zirconate, and hydrotalcite (Ben-Mansour *et al.* 2016). Table 2.5 highlights the potential adsorbents and adsorption parameters for CO_2 capture.

It is possible to achieve CO_2 adsorption by changing the pressure or temperature of a saturated sorbent. Pressure swing adsorption (PSA) is a commercially applied technology that recovers more than 85% of CO_2 from power plants (Takamura *et al.* 2001; Wyczalek 2005). A solid adsorbent selectively adsorbs CO_2 at high pressures, then the solid desorbs, releasing CO_2 for low-pressure transport (usually atmospheric pressure). The temperature swing adsorption (TSA) releases the CO_2 in the system by increasing its temperature through steam injection or

hot air distribution (Erlach, Schmidt and Tsatsaronis). A CO₂ purity of over 95% and recovery of over 80% are possible when using CO₂ regeneration, although regeneration is more time-consuming than PSA (Clausse, Merel and Meunier 2011). It was estimated that the operating costs of a particular TSA process ranged between USD 80 and 150 per tonne of CO₂ captured (Kulkarni and Sholl 2012). Significant attention has been paid to developing CO₂ capture sorbents from agricultural and industrial wastes to lower the overall cost of CO₂ capture. An adsorption carbon capture process is shown in Figure 2.8.

Table 2-5. Summary of adsorption-based carbon capture.

Adsorbent	Reactive Separator	Operating Conditions P, T, C, G	CO ₂ Capture (%), Ad-C (gCO ₂ /gads)	Kinetics/Mass Transfer	Ref.
TEPA-Mg-MOF-74	PBR (LS)	Regeneration temp is 250 - 300 °C	4 - 4.9 wt. %, 8.31 mmol CO ₂ /g absorbent, NA	N ₂ adsorption–desorption isotherm	(Dash, Samanta and Bandyopadhyay 2014)
ZX-APG,	PBR (3-bed, 8-step, VPSA, LS)	T:35; P: 0.007–0.008	85 - 95, NA, 73 - 82% CO ₂ purity	Langmuir adsorption isotherm is adopted	(Wang <i>et al.</i> 2013d)
Activated carbon	PBR (1 bed, 3 step, VSA, LS)	Water vapour (H ₂ O): 4.6 mol%, V _F : 44; T _{Des} :100T: 60, ICC:11.2, B _d :0.493, L _g :50, P:0.113, P _{VP} = 3, Trpt:3; SA:921.7, P _V :0.37, T _{ads} :35,	69.5, NA	Dual-site Langmuir equation has been adopted	(Xu <i>et al.</i> 2013)
NPC10	PBR (TSA, LS)	T: 25, P: 0.1, SA: 639	NA, 0.041	Langmuir adsorption isotherm	(Yang, Yuan and Tsang 2012)
Fly ash + PEI + PEG	PBR (LS, TSA)	St: 24 h, P: 0.11, T: 70	4.5 at 85 °C	$CO_2 + 2RR'NH \leftrightarrow RR'NCOO^- + RR'NH_2^+CO_2 + 2H_2O + RR'NCOO^- \leftrightarrow 2HCO_3^- + RR'NH_2^+$	(Arenillas <i>et al.</i> 2005)
ZX	MBA (LS, PSA)	Bed dimensions (m): FRR: 0.5; CT: 650; AT: 950; SA: 1873.9; 2b: 0.03, Nm: 36, W: 1.5; L:1.5; X _{pth} : 0.012 Bd: 0.65, Cs: 1.07, D _p : 3420, ε: 0.31 ks: 0.275	80, NA, 97% purity	Extended Langmuir isotherm was used	(Kim <i>et al.</i> 2013)

Rayon– HCM	PBR (TSA)	-	97, 0.2	Langmuir adsorption isotherm adopted	(Kumar 1989; An, Feng and Su 2013)

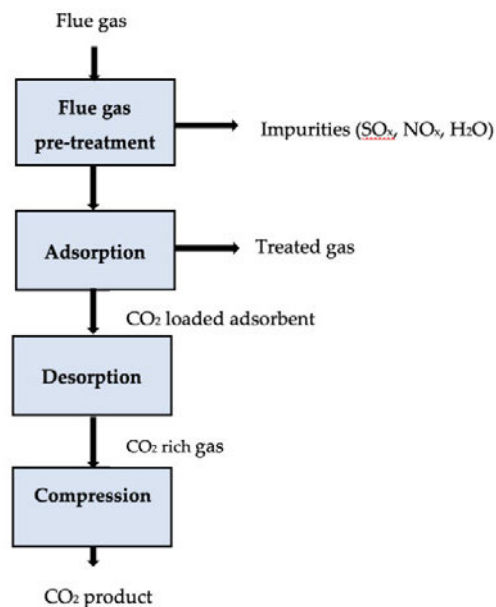


Figure 2-8. Schematic of an adsorption carbon capture process (Spigarelli 2013).

2.5.3 Chemical Looping Combustion

In contrast to oxy-fuel combustion, which uses pure oxygen for combustion, metal oxides are used as oxygen carriers in combustion. Metal oxides are reduced to metal during the process, while fuels are oxidized to create CO₂ and water. In a subsequent stage, the metal is oxidized and recycled. The removal of water by condensation from the process byproducts is easy, but the separation of pure CO₂ requires no energy. Numerous low-cost metal oxides, including Mn₂O₃, CuO, NiO, and Fe₂O₃, are suitable for this process. The potential sorbents and processes of chemical looping combustion are highlighted in Table 2.6.

Several researchers (Cho, Mattisson and Lyngfelt 2002; Ishida, Yamamoto and Ohba 2002; Adánez *et al.* 2004; Zafar, Mattisson and Gevert 2005; Guo, Zhang and Tian 2012) have examined the performance efficiency of various metal oxides in this process. According to Adánez *et al.* (2004), a metal oxide can be optimized by using support inert materials, but the selection of an inert material will vary depending on the characteristics of the metal oxide. Chemical looping combustion (CLC) was studied by Lyngfelt, Leckner and Mattisson (2001) in a boiler consisting of two fluidized beds. Lyngfelt, Leckner and Mattisson (2001) recently reviewed this technology. This process has been demonstrated to be a very promising CO₂

capture technology by both Lyngfelt, Leckner and Mattisson (2001) and Adánez *et al.* (2004). The IGCC's CO₂ separation is based on pre-combustion, but Erlach, Schmidt and Tsatsaronis (2011) found chemical looping combustion to have a 2.8% higher net plant efficiency than the former method. Figure 2.9 illustrates the basic CLC system.

Table 2-6. An overview of chemical looping combustion-based carbon capture.

Fuel Type	Operating Conditions P, T, C, G	Reactive Separator	CC (%), Purity (%)	Challenges	Kinetics/Mass Transfer	Ref.
Coal, C ₂ H ₅ OH, Isooctane, C ₃ H ₈ and CH ₄ .	T: 200–1200; molar ratios of carbon/CaSO ₄ = 0.5 and carbon/steam = 1	TGA	NA, 93 (with CaSO ₄ at 850 - 975 °C)	The ΔH_r is dependent on the fuel but not the amount of OC utilized. The yield depends on OC.	Combustion of iso-octane (–5101.58 kJ/mole) with Na ₂ SO ₄ and CaSO ₄ produces without SO ₂ formation between 200 °C and 344.3 °C.	(Zheng, Shen and Xiao 2010; Kale 2012)
Syngas, H ₂	XOC: 80–95, HR: 90–99, T: 370–1030	2-stage PBR- CLC	100, NA	PP of O ₂ in reactors; high solid inventories.	The packed bed of OC reduces the need for highly efficient cyclone to reduce costs; boron nitride (BN) used as the dense support material due to high thermal conductivity, low thermal expansion and high thermal stability.	(Cotton, Patchigolla and Oakey 2013; Hamers <i>et al.</i> 2013; Harper, Boyce and Scott 2013; Spallina <i>et al.</i> 2013)
Coal, kerosene, biomass	Bd: 4.750; Dp: 128 U _{mf} : 0.0129, Φ : 0.64	IFBR	83 - 99.3% at 800 - 950 °C, NA	Scale-up, fuel conversion, agglomeration and attrition.	ΔP_{RC} increases linearly with solid flow rate.	(Jin and Ishida 2004; Cao and Pan 2006; Wang and Anthony 2008; Moldenhauer <i>et al.</i> 2012; Tong <i>et al.</i> 2013; Yazdanpanah <i>et al.</i> 2013; Ku <i>et al.</i> 2014)
CH ₄ , coal	Iron oxide: 950 °C, FF: 1.18, CO ₂ EF: 10, DT: 5.25	CMBS or RPBR (1 MWth)	>99, >95	Reaction heat exceeds the convective heat-transfer rate to the gas flow.	The reduction kinetics and activation energy parameters are critical to find fuel conversion efficiency, temperature distribution and carbon separation efficiency.	(Gayán <i>et al.</i> 2013; Adánez-Rubio <i>et al.</i> 2014)
CH ₄ , syngas	T: 700–975; SITC:20–30; SFRR: 8–10 for CO SFRR:4–12	CC-MBR	>99% CH ₄ and 100% syngas conversion. >99.99% H ₂ purity.	The formation of FeO and FeAl ₂ O ₄ indicates further utilization of	At 900 °C, the reduction of Fe ₂ O ₃ to Fe with CO generates 37.7 KJ/mol Fe ₂ O ₃ of heat but its reduction with	(Adánez-Rubio <i>et al.</i> 2013; Gayán <i>et al.</i> 2013)

for H ₂ F _{solids} : 1.7–2.5	oxygen in iron-based OC's can be achieved. – $\phi > 1.14$.	H ₂ gas needs 61.8 KJ/mol Fe ₂ O ₃ of heat.

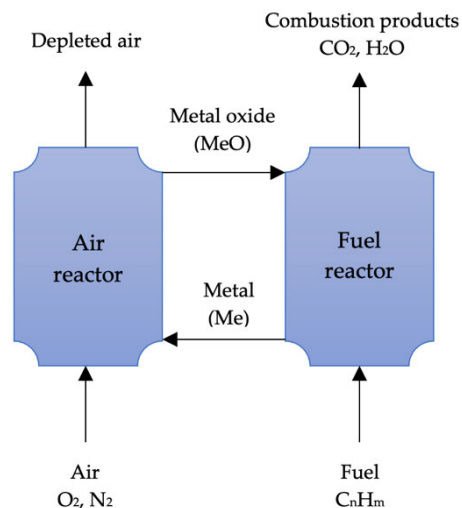


Figure 2-9. Schematic of chemical-looping combustion. Adapted from (Yang *et al.* 2008)).

2.5.4 Membrane Separation

Membrane separation uses a semipermeable membrane or barrier to physically separate CO₂ from other flue gases (Khalilpour *et al.* 2015). Membrane separation uses less energy than traditional solvent absorption methods, making it less expensive (Ansaloni *et al.* 2017). Membrane separation has successfully been used for selective gas separation in a variety of fields for the past two decades, including natural gas sweetening, air separation, hydrogen production, and biogas upgrading. Researchers are working on developing membrane-based materials to separate CO₂ released by various industries. Furthermore, this technology has produced increased efficiency in terms of both the economy and the environment (Li *et al.* 2015). Scientists have developed a variety of different membranes for CO₂ separation, including inorganic membranes, polymers, carbon molecular sieve membranes (CMSMs), microporous organic polymers (MOPs), and mixed matrix membranes (MMMs) (He, Fu and Hägg 2015). The potential sorbents and processes of membrane separation are highlighted in Table 2.7.

In addition, membrane separation technology can also separate gases in CCS processes such as pre- and post-combustion capture. It is generally considered that polymeric membranes are more flexible, durable, and efficient at capturing CO₂ from industrial processes. An upper

bound relationship analysis describes how selectivity and permeability are related to CO₂ capture by polymeric membranes (Turi *et al.* 2017). To improve results, glassy and rubbery materials with varying separation principles based on their size and diffusion ability can be used to synthesize polymeric membranes. The condensability and differences in kinetic properties of gas molecules are responsible for gas separation by glassy and rubbery polymers (Vinoba *et al.* 2017). Considering how difficult it is to examine operating conditions for rapid performance, membranes applied in gas separation systems are typically modelled to determine their working capacity (Lee *et al.* 2017). For optimal results in industrial settings, membrane performance must not be interfered with by flue gas impurities (He, Fu and Hägg 2015). Researchers were able to separate CO₂ from other gases with an efficiency of 82–88% (Brunetti *et al.* 2010; Favre 2011). In fact, despite membrane materials having poor permeability and selectivity (Bernardo, Drioli and Golemme 2009), it is also problematic to use this extraction method in flue gas with low pressure and CO₂ concentration in flue gas conditions (Wang *et al.* 2017a). A membrane carbon capture process is displayed in Figure 2.10.

Table 2-7. Summary of membrane-based carbon capture.

Membrane	Reactive Separator	Operating Parameters	Challenges	Kinetics/Mass Transfer	Ref.
Dense membranes	Hollow fiber and flat sheet	S-P, T, P, L _a , pressure ratio of the permeate side to the feed side, pore size and porosity	Lower selectivity at higher permeability	Solution–diffusion; among the mechanisms are Knudsen diffusion and the molecular sieve effect	(Olajire 2010)
Micro-porous Membranes	Hollow fiber and flat sheet	P, T, pore size and ϵ of the membrane–membrane wettability	Wetting of the membrane	Reaction kinetics depend on solvent	(Olajire 2010)
		Gas flow area	There are other compounds present in the gas stream	Even at high pressures, K _o is controlled by the resistance of the liquid film	(Luis, Van Gerven and Van der Bruggen 2012)
		Liquid flow area	Solvent volatility and limited long-term stability	Pore diffusion depends on membrane support	(Paul, Ghoshal and Mandal 2008)
Liquid in the membrane pores	Flat sheet only	G _a , L _a , VVIS, P, T	Solvent “wash-out” causes the membrane’s stability to decrease	The overall mass transfer coefficient	(Andersen <i>et al.</i> 2013)

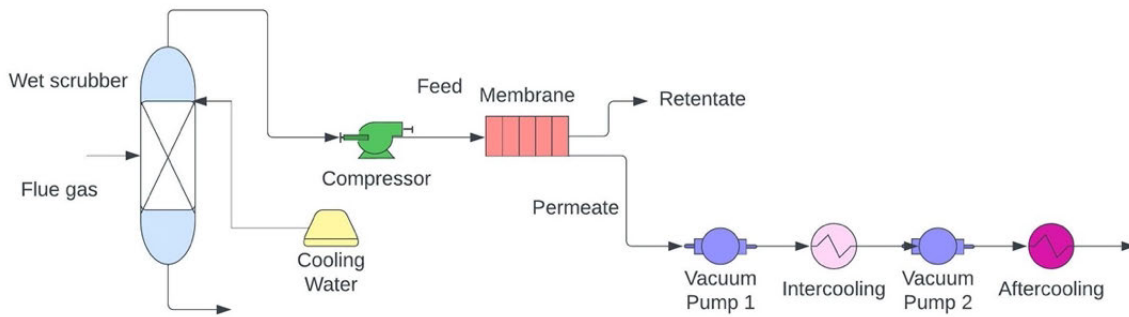


Figure 2-10. Schematic of membrane carbon capture process. Adapted from (Wang *et al.* 2017c)).

2.5.5 Cryogenic Distillation

This process separates CO₂ from gas mixtures by focusing on their boiling points at temperatures ranging from 100 to 135 °C (Figueroa *et al.* 2008; Gimžauskaitė, Aikas and Tamošiūnas 2022). In the presence of high pressures (100 - 200 atm), solidified CO₂ provides two significant benefits: a lack of solvents and liquefied CO₂ for more convenient transport and injection (Leung, Caramanna and Maroto-Valer 2014). It does, however, have some drawbacks that need to be investigated further, as do other processes. When cold and pressurized nitrogen is used as a refrigerant, ice formation compromises equipment safety, causing pressure fluctuations and pipe blockages, as well as increasing the consumption of energy (Leung, Caramanna and Maroto-Valer 2014; Knapik, Kosowski and Stopa 2018). This enhanced CO₂ separation can nullify the need for refrigerant preparation and storage (Tan *et al.* 2017; Knapik, Kosowski and Stopa 2018). However, CO₂ is separated using cryogenic distillation coupled with biogas upgrading. A comparison of different separation methods for CO₂ capture is shown in Table 2.8.

Table 2-8. Current status of different separation technologies for CO₂ capture (Hendriks 1995; Göttlicher and Pruschek 1997; Audus 2000; Takamura *et al.* 2001; Gielen 2003; Ritter 2004; Rubin, Rao and Chen 2004; Aaron and Tsouris 2005; Dillon *et al.* 2005; Wyczalek 2005; Damen *et al.* 2006; Tuinier *et al.* 2010; Bhowan and Freeman 2011; Clausse, Merel and Meunier 2011; Erlach, Schmidt and Tsatsaronis 2011; Zheng 2011; Adanez *et al.* 2012; Zhai and Rubin 2013; Leung, Caramanna and Maroto-Valer 2014; Lyngfelt and Linderholm 2014; Cuéllar-Franca and Azapagic 2015; Lyngfelt and Leckner 2015; Porter *et al.* 2015; Theo *et al.* 2016; Kanniche *et al.* 2017; Li *et al.* 2017a; Rackley 2017; Wang *et al.* 2017c; Moldenhauer *et al.* 2020; Zhang *et al.* 2020d; Castel, Bounaceur and Favre 2021; Olabi *et al.* 2022).

Parameter	Chemical Absorption	Physical Absorption	Adsorption	Chemical-Looping Combustion	Membrane Separation	Cryogenic
Separation technique	Amine, chilled ammonia, and amino acid salt solvent.	Rectisol, Selexol, etc. Mostly integrated gasification combined cycle.	Pressure swing adsorption and pressure–temperature swing adsorption.	FeO, CuO, MnO, and NiO	Polymeric, inorganic and mixed membranes.	Cryogenic distillation.
Pros	High reactivity, low cost of the solvent, and low molecular weight result in a high mass-based absorption capacity, and moderate thermal stability and thermal degradation rate.	Highly recommended for separating CO ₂ during pre-combustion processes that operate at elevated CO ₂ partial pressures. Captures CO ₂ selectively from a gas stream without a chemical reaction	Recycling is possible since it is a reversible process. It is possible to achieve high adsorption efficiency (485%). Low waste generation.	Very high CO ₂ concentration. Low-cost oxygen carrier materials. Truly and directly reduces the atmospheric CO ₂ concentration. Viable alternative for CO ₂ capture from mobile and decentralized sources.	No regeneration processes. Less solid waste produced. Less chemical consumption. High efficiency (>95% for single metal).	High capture efficiency (up to 99.9%). Mature technology. For many years, CO ₂ has been recovered in the industry by this method.
Cons	Relatively high maintenance cost.	High energy is required to compress feed gas to a high pressure. Low CO ₂ solubility. Less efficient absorption process. Large equipment sizing.	Requires adsorbent capable of operating at elevated temperatures. The significant amount of energy needed for CO ₂ desorption is high.	Currently, the process is under development, and large-scale operations have not yet been carried out.	Fouling and low fluxes are examples of operational issues. High running costs. Removal (%) decreases with the presence of other metals.	High energy requirement due to refrigeration. High capital expenditure. Need for removal of water, NO _x , SO _x , and other trace components to avoid the freezing and eventual blockage of process equipment.

						The procedure consumes a significant amount of energy.
CO ₂ concentration (vol.%)	<30.4	>59.3	28–34	3–8	11.8	<90
CO ₂ capture efficiency (%)	95	>90	<85	52–60	90	99.9
CO ₂ capture cost (USD/tonne CO ₂)	26.2	25.1	6.94	16–26	3–10	32.7
CO ₂ purity (%)	99	<99	99.98	>96	95	99.95
Status of research and development	SaskPower, Saskatchewan, Canada (Boundary Dam Carbon Capture Project) TransAlta Corporation, Alberta Canada (Project Pioneer Keephills 3 Power Plant) American Electric Power, OH, USA (Mountaineer Power Plant)	Summit Power Group, LLC, Seattle, USA (Texas Clean Energy Project) Don valley, Yorkshire, UK (Don Valley Power Project) Nuon Power, Buggenum, The Netherlands (Integrated gasification combined cycle plant)	Under developmental stage.	Less large-scale demonstration plants.	Schwarze Pumpe power station, Spremberg, Germany (Oxy-fuel technology) CS Energy: Callide Power Plant A, Queensland, Australia (Callide Oxy-fuel Project) OxyCoal, UK (Oxy-fuel technology)	Air Products and Chemicals, Inc., Pennsylvania USA

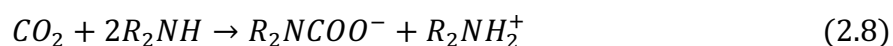
2.6 CO₂ Capture Using Dry Solid Sorbents

The selective separation of CO₂ based on interactions between gases and solids is required for CO₂ capture using a dry adsorbent (Ma'mum *et al.* 2005). In packed columns, universal dry adsorbents are typically utilized, including activated carbon and molecular sieves (Balsamo *et al.* 2013b). The surface tension and pore size of the adsorbent, as well as the process temperature and partial pressure, are critical factors in a dry adsorption process (Balsamo *et al.* 2013a). Adsorption and desorption cycles are repeated throughout the process (regeneration).

The following are the several adsorption types: (i) pressure swing adsorption (PSA) [4–6]; (ii) temperature swing adsorption (TSA) (Pirngruber *et al.* 2013; Sculley *et al.* 2013), which combines two processes—low-temperature adsorption followed by desorption or regeneration by raising the pressure; (iii) electric swing adsorption (ESA) (Datta *et al.* 2013), which entails adsorption and desorption by altering the electricity supply while a low-voltage current flows through the adsorbent; and (iv) vacuum swing adsorption (VSA) (Huang and Eić 2013). Additionally, due to their low energy needs and relative simplicity, adsorption-based technologies such as pressure/vacuum swing adsorption (PVSA) have been extensively researched (Chou and Chen 2004; Goeppert *et al.* 2011; Kim *et al.* 2014).

To effectively treat high volumes of combustion emissions from numerous sources, it is imperative to increase a dry adsorbent's CO₂ capture selectivity and adsorptive capacity. The CO₂ adsorption can be enhanced and stabilized by adding functional groups to the surface of the adsorbent material that has a high affinity for CO₂ to react with it. CO₂ can then be selectively adsorbed using the adsorbent's sizeable specific surface area and pore structure (Hicks *et al.* 2008; Wei *et al.* 2012; Auta *et al.* 2013; Nugent *et al.* 2013; Prenzel, Wilhelm and Rezwan 2014; Lee and Park 2015).

The addition of different amine groups to solid materials used as CO₂ capture sorbents is anticipated to increase polarization and CO₂ capture to achieve high selectivity and capture performance. These adsorbents have several benefits, including the potential eradication of corrosion issues and reduced costs of energy for regeneration. Under anhydrous conditions, the reactions of CO₂ with amine functional groups result in ammonium carbamates, as follows (Chang *et al.* 2009):



The reversible nature of the adsorption process and the possibility to increase adsorption efficiency by altering the composition of adsorbent materials make this process important. Therefore, by choosing a suitable adsorbent material, the CO₂ adsorption efficiency can be improved. Activated carbons (Plaza *et al.* 2010; Adelodun, Lim and Jo 2014), zeolites (Ho, Allinson and Wiley 2008), hollow fibers, and alumina are currently the major commercially available adsorbents. Each material has a unique surface area, pore structure, and surface functional groups, and their application areas are very specific. The following section discusses and provides descriptions of some typical carbonaceous and non-carbonaceous dry sorbents for CO₂ capture.

2.7 Non-Carbonaceous Adsorbents

Non-carbonaceous adsorbents include zeolites, metalorganic frameworks, silica, etc. The CO₂ uptake capacity of these materials is high; however, they are expensive and highly sensitive to moisture. As a result, zeolites can capture CO₂ molecules of 0.33 nm due to their suitable channel diameters (0.3 - 1.0 nm) (Abd *et al.* 2020).

2.7.1 Adsorbents Based on Zeolite

Adsorbents with a natural structure, such as zeolites, are made up of an interlocking structure of AlO₄ and SiO₄ tetrahedrons that share atoms of oxygen (Wang *et al.* 2012). Small pore size and high porosity are responsible for zeolite's excellent CO₂ adsorption at temperatures as low as 30 °C; however, their CO₂ capture capacity rapidly declines above this temperature and is almost non-existent above 200 °C (Wang *et al.* 2012). Zeolite's high hydrophilicity significantly reduces its CO₂ adsorption capacity when the gas contains water. In this case, high temperatures are required for the regeneration (Yu *et al.* 2012), resulting in significant energy losses as a result of the CO₂ regeneration (Lee and Park 2015).

The CO₂ selectivity of zeolites remains low despite their ability to separate gases (Xu *et al.* 2002; Siriwardane, Shen and Fisher 2003; Buckingham, Reina and Duyar 2022). The moisture content of the gas is a constraint on zeolites' capacity to adsorb CO₂ from flue gas. Water competes for adsorption with CO₂, reducing the amount of CO₂ adsorbed by Y-type zeolites

(CaY and NiY) (Gallei and Stumpf 1976). By contacting an ion and a dipole at low desorption temperatures, physisorption occurs, resulting in a linear orientation of the CO₂ molecule (Zhao *et al.* 1998; Wang *et al.* 2012).

Additionally, zeolites exhibit excellent chemical reactivity, recyclability, high stability, excellent recyclability, and structural diversity, which make them a promising candidate for the CO₂ adsorption (Kumar, Srivastava and Koh 2020). This structure consists of a network of streams into which gas molecules are adsorbable, ranging from 0.5 to 1.2 nm in size (Wang *et al.* 2012; Lee and Park 2015; Albahar 2018). Flue gas mixtures (CO₂, H₂O, CO) are not suitable for zeolites because they are not CO₂ selective, along with their limited capacity to adsorb at high temperatures (Wang *et al.* 2012; Lee *et al.* 2014b; Omodolor *et al.* 2020).

Zeolite contains exchangeable cations including K⁺, Mg²⁺, and Na⁺ that act as a balance to the negative charge that results from a SiO₄ tetrahedron replacing an AlO₄ tetrahedron. Specifically, the charge density, cation distribution, and size of the zeolites influence their adsorption and separation properties. Zeolite particles have a large pore size that allows CO₂ to diffuse into them. The adsorption of CO₂ molecules by zeolites is increased by the presence of cations in their structure via molecules and the adsorbent's interaction electrostatically (Harlick and Sayari 2007). CO₂ adsorption has been studied mostly for the zeolites 13X and 5A. Using a type 13X zeolite, Moura *et al.* (2016) investigated the effect of cation exchange on CO₂ adsorption, concluding that zeolites rich in alkali-cations, such as Li⁺ and Na⁺, could effectively adsorb CO₂. The order of decreasing adsorption capacity was Li⁺ > Na⁺ > NH₄⁺ > Ba²⁺ > Fe³⁺. According to Walton (Walton, Abney and LeVan 2006), it is believed that the ionic charge of zeolites, the ionic radius, the shielding effects, as well as the nuclear charge are the main causes of the observed decline in CO₂ adsorption capacity. According to Calleja *et al.* (1994), zeolites 13X and 5A have CO₂ adsorption capacities of 3–25 wt. % and 2–12 wt. %, respectively, at a CO₂ partial pressure of 15% and a CO₂ pressure of 100%.

2.7.2 Adsorbents Based on Metal-Organic Frameworks

The molecular organic framework (MOF) is a crystalline material containing metal ions or clusters of metal ions combined with organic molecules (ligands) (Figueroa *et al.* 2008; Zhao, Yan and Lee 2022). As the MOF has been adapted to a variety of chemical processes and applications, over 20,000 MOFs have now been created, each with distinct geometries, pore

sizes, and functions (Llabrés 2007; Ravon *et al.* 2008; Britt *et al.* 2009; Furukawa *et al.* 2010; Sumida *et al.* 2012).

Having large mesopores, high surface areas (approximately 10,000 m²/g), and an adaptability to different geometries, MOFs are ideal chemisorbents for CO₂ capture (Furukawa *et al.* 2010; Gandara-Loe *et al.* 2021). Although MOFs have some advantages when it comes to CO₂ capture at high temperatures, they also have some drawbacks. For example, moisture is absorbed while CO₂ is being captured, the manufacturing process is difficult, and the MOFs are not very durable (Lee and Park 2015).

In a study by Szczeniak and Choma (2020), copper-based MOFs (Cu-BTC), with benzene-1,3,5-tricarboxylate, had an uptake capacity for CO₂ of 9.59 mmol/g adsorbent and a surface area of 1760 m²/g at 1 atm at 273 K. The CO₂ capacity of most MOFs decreases noticeably as the temperature increases during the CO₂ capture phase. At 298 K, 313 K, and 328 K, the temperatures for CO₂ capture, Aarti *et al.* (2016) reported 4 mmol/g adsorbent for Cu-BTC-PEI-2.5, 2.61 mmol/g adsorbent for Cu-BTC-PEI-2.5, and 1.66 mmol/g adsorbent for Cu-BTC-PEI-2.5, respectively, due to MOFs' structural stability's degradation with temperature.

There has been a breakthrough in developing microporous coordination polymers (MCPs) to decrease the production cost of MOFs. As the name implies, MCPs are composed of repeating channels of metal ions linked by ligands whose function is to link ions. MCPs have porous structures because of their inherited organic functionality (Caskey, Wong-Foy and Matzger 2008). The magnesium-based MOF Mg-MOF-74 was found to have better CO₂ adsorption with 8.61 mmol/g adsorbents at 1 bar partial pressure and 298K (Bao *et al.* 2011). Magnesium dioxybenzenedicarboxylate (Mg/DOBDC) is an MCP composed of Mg²⁺ ions connected to 2,5-dioxide-1,4-benzene-dicarboxylate (Caskey, Wong-Foy and Matzger 2008). Researchers have claimed that the high performance can be attributed to the improved ionic behavior of the magnesium oxide Mg-O bond when CO₂ partial pressures are as low as 0.1 bar. As opposed to MgO, exothermic carbonation does not form magnesium carbonate (MgCO₃) from Mg/DOBDC. MCP networks are inflexible and prevent insertion into the MgO bonds likely due to their inflexibility. Due to the highly ionic nature of the Mg-O bonds in Mg/DOBDC, the material can capture CO₂ reversibly. Low CO₂ partial pressures can be improved by these techniques (Caskey, Wong-Foy and Matzger 2008).

The ability of many early MOF adsorbents to adsorb large amounts of CO₂ was demonstrated. To be used as CO₂ adsorbents, MOFs must be stable in an aqueous medium. Mahdipoor *et al.* (2021) reported an MOF CO₂ adsorbent containing iron-based on poly terephthalate (BDC). Observations revealed that the *amino*-functionalized MOF MIL 101(FE) is water- and ethanol-stable, and capable of capturing 13 mmol/g CO₂ per adsorbent. Additionally to the physical CO₂ adsorption by the amino MIL 101(FE) MOF's structure, the chemisorption of CO₂ by the MIL 101(FE) MOF structure affects the total CO₂ adsorption by the MOF (Mahdipoor *et al.* 2021).

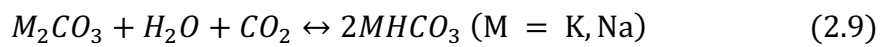
2.7.3 Mesoporous Silica Materials

Mesoporous silica has also been proposed as a viable candidate material for capturing CO₂ because of its large surface area and high capacity to be synthesized with a variety of pore hole sizes (Yu, Huang and Tan 2012a). The modification of mesoporous silica for CO₂ capture has been proven to be an effective method for developing adsorbents, despite its low adsorption capacity (Yu, Huang and Tan 2012a). The possibility of chemically treating their surface OH groups to promote their CO₂ selectivity and adsorption capacity may be further investigated to process flue gases at low pressures using CO₂ (Yu, Huang and Tan 2012a).

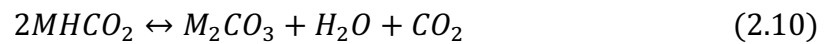
Sánchez-Zambrano *et al.* (2018) investigated the chemical modifications of mesoporous silica treated with 3-aminopropyl triethoxysilane (APTES), and then impregnated it with polyethyleneimine (PEI) to find out how the modifications affected kinetic mechanisms, site energy distributions, and CO₂ adsorption under post-combustion conditions (Figuerola *et al.* 10). As determined by microcalorimetry, the functionalization process resulted in new adsorption sites. When amine groups were added to the support, physisorption accounted for the vast majority of adsorption, and CO₂ capture capacity and selectivity increased as the temperature increased (50 and 75 °C). Due to sites that could not be restored due to strong chemical bonds formed by adsorption products, using a turbomolecular vacuum pump was the only way to regenerate after adsorption at 25 °C with CO₂. In the first stage of CO₂ capture, these sites became available for regeneration, but only at higher temperatures (Sánchez-Zambrano *et al.* 2018). Although mesoporous silicas are highly effective adsorbents for CO₂ capture due to their large pores with a tunable size, high surface area, and mechanical and thermal stability, they do not possess sufficient CO₂ adsorption abilities to be of any use, especially at a 1-atmosphere pressure (Yu, Huang and Tan 2012a).

2.7.4 Alkali Metal-Based Materials

Alkali metal carbonates, including those made of Na, K, and Al, have been reported to be efficient dry adsorbents for CO₂ capture from flue gas operating below 473 K in relatively moderate conditions (Duan *et al.* 2012; Zhao *et al.* 2013). Various inorganic supports, including alumina, silica, ceramics, zirconia, and carbon materials, are added with alkali metal carbonates during this procedure; Equation (2.9) explains how moisture and CO₂ react, facilitating CO₂ adsorption, and how decarbonization (Equation (2.10)) regenerates the absorbent (10) (Samanta *et al.* 2012):



−141 kJ/mol and $\Delta H = -135$ kJ/mol for M = K and Na, respectively



As shown in Equation (2.9), alkali–metal bicarbonates are typically formed when CO₂ and H₂O react with carbonate sorbents between 333 and 383 K, which then regenerate alkali–metal carbonates at 373–473 K, releasing CO₂. Theoretically, Na₂CO₃ and K₂CO₃ have CO₂ adsorption capacities of 41.5 and 31.8 wt. %, respectively.

The use of lithium-based materials such as lithium-based silicate (Li₄SiO₄) and lithium-based zirconate (Li₂ZrO₃) for direct CO₂ capture from flue gas at temperatures of 700–900 K is another promising method for capturing CO₂ (Essaki, Kato and Uemoto 2005). Li₄SiO₄, specifically, is a promising CO₂ captor because of its low volume change during CO₂-adsorption–desorption and its high CO₂ sorption capacity of 36.7% (Venegas *et al.* 2007).

In a study conducted by Kato *et al.*, Li₄SiO₄ and Li₂ZrO₃ were examined at low CO₂ concentrations, i.e., 50 ppv. They found that Li₄SiO₄ was 30 times more capable of absorbing CO₂ than Li₂ZrO₃. Additionally, zirconia materials are more expensive than silica materials (Pacciani *et al.* 2011). Recently, Seggiani, Puccini and Vitolo (2013) reported that Li₄SiO₄, with the addition of 30% Na₂CO₃ or K₂CO₃, demonstrated a CO₂ sorption capacity of 23 wt. % at an ideal sorption temperature of 853 K and low CO₂ partial pressure of 0.04 bar, equating to a Li₄SiO₄ conversion of almost 80%. Li₈SiO₆ was proposed by Durán-Muoz *et al.* as a substitute dry adsorbent for CO₂ capture. It demonstrated a high sorption capacity of roughly

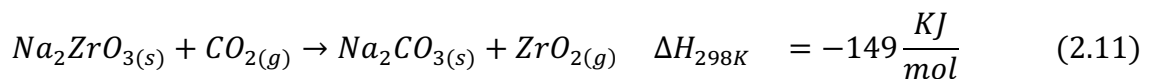
51.9 wt. % over a wide temperature range, with an efficiency of 71.1% (Durán-Muñoz, Romero-Ibarra and Pfeiffer 2013).

It is technically and economically desirable to use alkali–metal-based materials to capture CO₂ post-combustion at low temperatures and in low concentrations, since they do not require additional cooling processes; although, the long-term stability and sustained performance of such adsorbents under real flue gas conditions must be addressed.

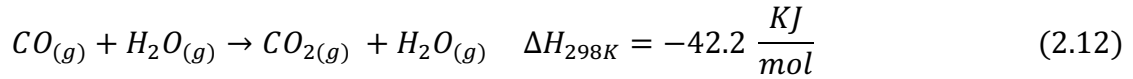
2.7.5 Alkaline Metal-Based Ceramics

In addition to alkaline ceramics, binary metal oxides are also referred to as alkaline oxides because they contain more than one alkaline element. Metal-based alkaline ceramics include Li₅AlO₄, Li₂CuO₂, Li₂ZrO₃, and Li₄SiO₄. Notably, these alkaline metal ceramics can be regenerated at elevated temperatures. Consequently, they are ideal for adsorption and desorption cycles, such as those associated with post-combustion capture. The robustness of alkaline metal ceramics allows them to be made without refractory supports, resulting in a simpler synthesis method (Memon *et al.* 2017). Alkaline ceramics are synthesized in a variety of ways, depending on the desired type. When synthesizing zirconates, co-precipitation, sol-gel, or soft chemistry methods are preferred for achieving the desired morphology of an adsorbent. A sorbent needs to have a morphology with a large surface area and a small particle size to capture CO₂ to its maximum capacity (Memon *et al.* 2017). The sol-gel method can be used to create a mesoporous structure for silicates that is advantageous (Memon *et al.* 2017).

These materials, including zirconate Na₂ZrO₃, are important for process intensification (Alcántar-Vázquez *et al.* 2015), owing to their catalytic activity (Memon *et al.* 2017). Following CO₂ chemisorption, the carbonated derivate, Na₂CO₃, is formed. Equation (2.11) depicts the reaction pathway for Na₂ZrO₃ (Alcántar-Vázquez *et al.* 2015; Memon *et al.* 2017).



Sutton, Kelleher and Ross (2001) described alkaline metal-based ceramics as catalysts of the water gas shift reaction (WGSR).



Compared to other ceramics made of alkaline metal, lithium cuprate (Li_2CuO_2) has demonstrated the ability to adsorb CO_2 over a wide temperature range (120 to 690 °C), and it retains its efficacy as a CO_2 adsorbent at low CO_2 partial pressures (Palacios-Romero and Pfeiffer 2008; Oh-ishi *et al.* 2014). At CO_2 concentrations less than 15%, the alkaline metal zirconate (Li_2ZrO_3) exhibits excellent CO_2 selectivity and CO_2 acceptor performance in flue gas streams (Memon *et al.* 2017). In summary, Li_2CuO_2 and Li_2ZrO_3 are two CO_2 adsorbents that have been subjected to extensive research and have been demonstrated to be promising dependable CO_2 adsorbents (Memon *et al.* 2017).

Much of the research on alkaline ceramics in recent years has focused on CO_2 capture at high temperatures. The CO_2 adsorption capacities of two alkaline yttrium oxides ($NaYO_2$ and $LiYO_2$) at high temperatures were recently evaluated. Since lithium ions are not as close together as sodium ions are in an octahedron, $LiYO_2$ has a greater capacity for CO_2 capture than $NaYO_2$. However, both ceramics were capable of adsorption/desorption for at least ten cycles (Bernabé-Pablo, Duan and Pfeiffer 2020). Table 2.9 lists the basic CO_2 adsorption capacities of the main adsorbent types that are commonly addressed in the literature.

Table 2-9. The CO_2 adsorption capacity of the most common adsorbents (D'Alessandro, Smit and Long 2010; Hao, Li and Lu 2011; Wang *et al.* 2017b).

Adsorbent	Examples	Temp. (K)	Pressure (atm)	SBET ($m^2 g^{-1}$)	Capacity ($mmol g^{-1}$)
Zeolite-based	NaY, NaX, 13X, ZIF-70, ZIF-69	273–384	1	15–1730	≤ 5.4
Amine-based	Silica monolith/TEPA, MCM-41/PEI	298–384	1	16–367	≤ 5.9
MOF-based	MOF-53, MOF-177	198–304	1–96	270–4500	≤ 48.7
Calcium-based	$Ca(OH)_2$, CaO	195–348	1	-	≤ 11.6
Alkali ceramic-based	Na_2ZrO_3 , Li_2ZrO_3	500–600	1	-	≤ 6.5
Carbon-based	Activated. Carbon BPL, MAXSORP, Activated carbon	195–348	1	1150–3250	≤ 8

2.8 Carbonaceous Adsorbents

Even though carbon is the only component of carbonaceous materials, they offer several advantages, such as high thermal/chemical stability, heat and electrical conductivity, bio-affinities, elasticities, and strengths (Park and Kim 1999; Seo and Park 2004; Bilalis, Katsigiannopoulos and Avgeropoulos 2014). Being lightweight, having a very high specific surface area, and having a large pore volume make them especially suitable for applications involving the storage of gases or adsorption (Gupta and Saleh 2013; Seema *et al.* 2014). Additionally, they offer benefits for CO₂ capture: (i) they are not moisture-sensitive; (ii) they are reasonably priced; (iii) their desorption/adsorption temperatures are below 373 K; (iv) they may be employed at atmospheric pressure; and (v) their energy usage is minimal. Each of these factors has had an impact on recent research in this field.

2.8.1 Activated Carbons

The textural characteristics and surface groups of carbon-based adsorbents are highly correlated with CO₂ adsorption capability (Bai *et al.* 2013; Yu *et al.* 2014). Due to their materials' wide range of pore sizes, from micropores to macropores, activated carbons are not suitable for selective gas adsorption. Adsorption temperatures of less than 25 kJ/mol are typically seen in pristine carbon-based adsorbents, which have weak CO₂ affinities (Guo, Chang and Xie 2006). At 298 K and 0.1 pressure, the standard CO₂ adsorption capacity of activated carbon is ~5 wt. % (Sevilla and Fuertes 2012; Wang *et al.* 2020b).

By modifying the activation and preparation conditions, the pore structures of activated carbons can be easily regulated (Yoo *et al.* 2011; Wang and Kaskel 2012). Additionally, the activated carbon's surface functional groups can be easily modified utilizing a variety of treatment methods (Seo and Park 2010; Kim and Park 2011). Incorporating different basic groups into activated carbon has been extensively researched for improving the CO₂ affinity by enhancing the CO₂ adsorption capacity (Meng and Park 2012b; Pramanik *et al.* 2020).

NiO-loaded activated carbons (NiO-ACs) were synthesized by Jang *et al.* utilizing a post-oxidation technique that involved nickel electroless plating at 573 K in an air stream. The NiO-AC samples' ability to adsorb CO₂ increased as oxidation duration increased. The maximal CO₂ adsorption capacity was 49.9 cm³/g, above the 41.2 cm³/g capacity of unaltered activated carbon at 298 K and 1 bar. They reported that the acid-base characteristics of the NiO caused

it to serve as an electron donor on the carbon surface, increasing the CO₂ adsorption, which acts as an electron acceptor (Jang and Park 2012).

2.8.2 Graphene

A graphene derivative known as graphene oxide (GO) can be created using different functional groups on the edges and basal planes (Chua and Pumera 2014). Researchers have extensively studied modifying the surfaces of GO with functional groups for applications including gas storage, separation, conversion of energy, and synthesizing newly developed GO-like derivatives with lightweight frameworks (Liu *et al.* 2014d; Liu *et al.* 2014e; Mittal *et al.* 2015).

Thermally exfoliated graphene nanoplates were reported by Meng and Park (2012a) as being innovative, highly effective sorbents for CO₂ capture. At 298 K and 30 bar, the produced graphene nanoplates demonstrated remarkable capture efficiencies of 248 wt. %. The graphene nanoplates' wider inter-layer spacing and substantial inner void volume were attributed to the higher CO₂ capture capacity (Liu *et al.* 2014e).

2.8.3 Ordered Porous Carbons

Since they are widely used as electrode materials, catalyst supports, and other types of materials, ordered porous carbon materials have drawn a lot of study interest (Dubey *et al.* 2014; How *et al.* 2014; Moradi 2014). There are numerous ways to make ordered porous carbons, including (i) direct synthesis utilizing organic self-assembly, which uses a mixture of carbon precursors and blocks co-polymers as soft templates, and (ii) nano-casting, employing silica materials as structure-controlling hard templates (Karthikeyan *et al.* 2015; Liu *et al.* 2020c).

Yoo *et al.* (2013) examined the impact of the phenolic resins' carbonization temperature on the total pore volumes and the specific surface areas of ordered nanoporous carbons (ONCs). Due to its greater specific surface area and smaller micropore size distribution, ONC carbonized at 1173 K had the highest CO₂ adsorption capacities at 298 K (15.8 wt. % at 1 pressure and 68.5 wt. % at 30 bar) (Yoo, Lee and Park 2013).

2.8.4 Activated Carbon Fibres (ACFs)

ACFs are attractive adsorbent materials because of their numerous micrometer porosities, nanostructures, and other characteristics, including narrow pore size distributions and large specific surface areas (Kim and Park 2007; Im, Park and Lee 2009). Compared to granular and powdered adsorbents, ACFs are more flexible due to their fibrous structure (Yoon *et al.* 2004).

For large-scale CO₂ capture testing, Thiruvengkatachari *et al.* created huge honeycomb-shaped carbon fiber composite (HMCFC) adsorbents (the adsorbent mass in one column was 4.486 kg). For a simulated flue gas with 13% CO₂, 5.5% O₂, and the remaining N₂ at 293 K, the average CO₂ adsorption capacity was 11.9 wt. %. Additionally, they demonstrated that the thermal decomposition process and combined vacuum improve the CO₂ collection efficiency of the HMCFC adsorbents (Thiruvengkatachari *et al.* 2013).

2.9 Carbon Capture and Utilization Technologies

The CO₂ acquired through the use of proper capture agents can be transformed using CCU technologies with the dual purpose of lowering greenhouse gas emissions while simultaneously utilizing wastes such as CO₂ for technological and chemical purposes. Notably, CCU and CCS belong to a family of technologies that aim to reduce CO₂ emissions into the atmosphere and do not compete with each other. Although both have advantages, CCUs seem to be better in the medium to long-term (Atzori 2018). In addition, CO₂ conversion into fuels and chemicals can aid in meeting sustainability standards since it provides an efficient method for preserving non-renewable fossil natural resources. Companies that commit resources to CCU technologies can reap significant benefits, including improved public perception, lower carbon disposal costs and the opportunity to earn carbon reduction credits (Centi and Quadrelli 2009).

CCU technologies cannot be regarded a sustainable process despite this. In this regard, it is essential to differentiate between "avoided" and "used" CO₂ (Roh *et al.* 2018). CO₂ emissions cannot be completely prevented when using CO₂ in chemical reactions. Indeed, both CO₂ capture and utilization procedures demand energy (which is still mostly produced from fossil fuels), therefore CO₂ production could exceed consumption. Therefore, perpetual and renewable energy sources including geothermal, hydro, solar, and wind energy should be favoured, and the sustainability of all chemicals utilized in the utilization process should be carefully evaluated.

Even if CO₂ transformation technologies are currently available, CO₂ consumption today accounts for a very small percentage of total emissions (0.62%). Therefore, a net increase in the conversion of "waste carbon" into "spent carbon" is required for CO₂ exploitation to be significant. In general, there are three ways in which CO₂ can be used:

- technological applications.
- conversion into chemicals.
- conversion into fuels.

Continuous-point sources are probably best suited for CCU technologies if CO₂ conversion facilities are located close to the source, reducing the need for transport and storage. From this perspective, it should be better to capture CO₂ from a reasonably constant source, such as the atmosphere, even though CO₂ recovery is difficult to implement in this situation as a result of the low concentration of CO₂ in the air (Aresta, Dibenedetto and Angelini 2014).

It is critical to emphasize that the concentration and impurity specifications of the CO₂ feed must be specified based on the CCU application. Table 2.10 lists these characteristics for the major emitting sources (Esposito *et al.* 2019).

Table 2-10. Features of the main sources of CO₂.

Source	CO ₂ concentrations (%)	Typical impurities
Natural gas streams	0 - 8	H ₂ S, O ₂ , N ₂ , C ₁ -C ₄ hydrocarbons
Fermentation	> 99	H ₂ S, H ₂ O
Steel making	18 - 20	O ₂ , NO _x , SO _x , N ₂
Power generation	10 - 15	NO _x , SO _x , H ₂ O, N ₂
Atmosphere	0.04	NO _x , SO _x , O ₂ , N ₂ , particulates
Natural deposit	90 - 100	He, O ₂ , N ₂
Cement production	> 99	O ₂ , N ₂

Contaminants like NO_x, SO_x, and O₂, which are typically present in the flue gases from power plants, may be detrimental because they might poison the catalysts required for the subsequent conversion of CO₂. Given that the necessary purification and separation procedures can significantly increase the total cost of the CCU technologies, the appropriate sources of CO₂ should be carefully considered in this context.

2.9.1 CO₂ Utilization for Technological Applications

CO₂ is utilized in approximately 18Mt/year in technical applications. Table 2.11 provides an overview of the various industrial sectors that employ CO₂. Technological applications can be recycled and reused because they do not convert CO₂ into other compounds, except for water treatment and agricultural applications. CO₂ replaces organic and inorganic molecules for many of the uses listed in Table 2.11, significantly reducing the environmental impact and improving the environmental performance of processes (Aresta 2003).

Table 2-11. CO₂ technological applications

Industrial sector	Use
Metal fabrication	• Manufacturing operations, moulding, welding
Water treatment	• Neutralization of alkaline industrial effluent
Agriculture	• Uses in greenhouses. • Addictive to irrigation water • Fumigating agent in silos
Food industry	• Carbonated beverages
Other applications	• Food processing and conservation • Refrigerators • Fire extinguishers, glass industry, lasers, and electronic industry • Plastic blowing agent and rubber

The other technical uses of CO₂ are directly related to the relatively simple conditions under which it exists as a supercritical fluid. Substituting toxic chemical compounds with CO₂ produces numerous benefits. Supercritical CO₂ is utilized in a variety of chemical applications, including decaffeination of coffee beans, fragrance extraction, dyeing, as a solvent or reactant, as an agent for polymer modification, waste treatments, and material preparations (Medina-Gonzalez, Camy and Condoret 2012).

2.9.2 CO₂ Conversion to Chemicals

Since the second 19th century, CO₂ has been used as a building block in chemical synthesis. In general, the conversion of CO₂ into chemicals can be categorized as either catalytic or thermal. Thermal processes primarily involve the conversion of CO₂ into inorganic carbonates salicylic acid, and urea, but the generation of organic carbonates and methanol plays an important part in catalytic transformations.

Currently, the major chemical application of CO₂ is in the synthesis of urea (CH₄N₂O), which can be used as a reactant or as fertilizer in the production of polymers. About 155 Mt/year of CH₄N₂O are generated, with an expected annual growth rate of 5 -7 % over the next 20 years [33]. CO₂ and NH₃ react to form ammonium carbamate (NH₂CO₂) (exothermic step), followed by its dehydration to CH₄N₂O (endothermic step) in a well-established two-step thermal process (Figure 2.11). As the entire process is exothermic ($\Delta_r H = -101 \text{ kJ mol}^{-1}$), the heat generated can be efficiently captured and utilized (Brinckerhoff 2011).

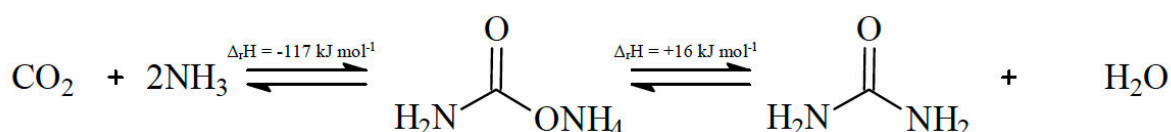


Figure 2-11. Thermal two-step process for the synthesis of urea (Brinckerhoff 2011).

The production of salicylic acid is a significant process that can also take place without the use of catalysts. With an approximate annual output of about 90 kt, salicylic acid is now produced from a comparatively little amount of carbon dioxide. The technique involves the interaction of phenol salts with CO₂, which is a moderately exothermic reaction (Figure 2.12). The procedure is carried out commercially under pressure at temperatures between 100 to 160 °C (Omae 2012; Luo *et al.* 2016).

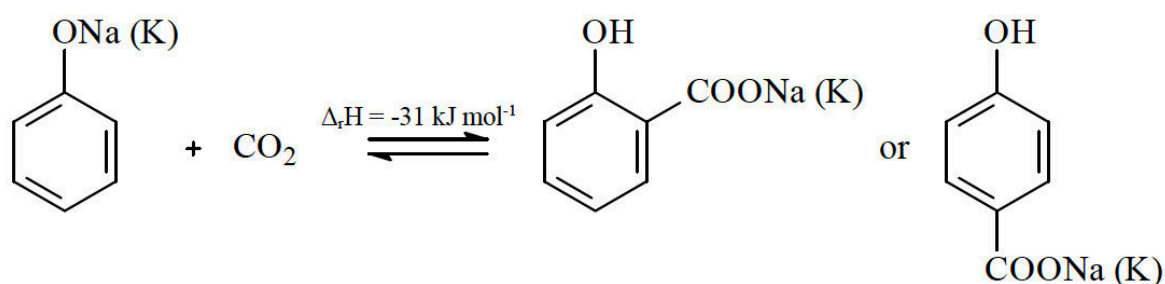


Figure 2-12. Synthesis of salicylic acid (Omae 2012; Luo *et al.* 2016).

Inorganic carbonates are produced through the thermal process of carbonation. Currently, the inorganic carbonate market is valued at about 200 Mt/year, with CaCO₃ holding the top spot. The storage of CO₂ as magnesium carbonates and calcium is possible through "mineral carbonation," which is a major application of carbonation technologies. CO₂ storage via carbonation of rocks such as wollastonite (a calcium inosilicate) and olivine (a magnesium iron silicate) are an intriguing geological storage alternative, particularly in places where subsurface storage is impractical. In addition, the exothermic process of mineral carbonization offers the

possibility of collecting the recovered heat and using it in a useful way. However, chemical and mechanical pre-treatments of the mineral are required to speed up the reaction and enable its commercial usage, as natural carbonation is a relatively slow process (Bobicki *et al.* 2012).

The most proven and commercially viable catalytic process for the chemical recycling of CO₂ into chemicals is the synthesis of organic carbonates from CO₂ and epoxides. Depending on the type of catalysts, it is possible to obtain cyclic carbonates (North, Pasquale and Young 2010) or aliphatic polycarbonates (Kember, Buchard and Williams 2011) (Figure 2.13).

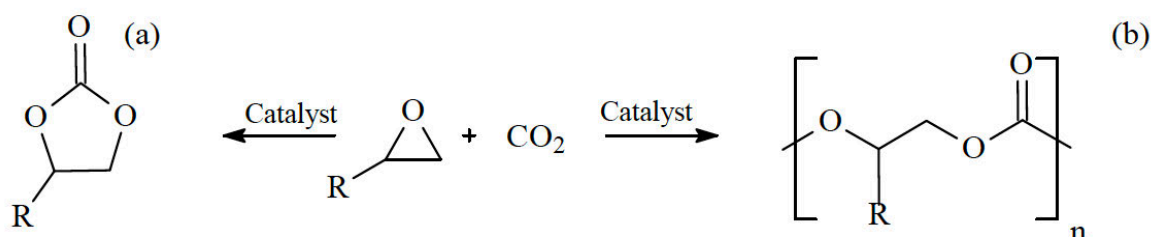


Figure 2-13. The catalytic conversion of carbon dioxide into (a) organic carbonates and (b) aliphatic polycarbonates (Kember, Buchard and Williams 2011).

The market for cyclic carbonates is currently expanding (by 100 kt annually) due to their use in a number of applications, including solvents (Schäffner *et al.* 2010; Díaz-Álvarez *et al.* 2011), DMC (dimethyl carbonate) and polymer manufacturing reactants, and electrolytes for lithium-ion batteries (Xu 2004)

The latter is produced commercially by transesterifying cyclic carbonates with CH₃OH, and it is extensively utilized in the production of aromatic polycarbonates (605 kt/year) as a substitute for phosgene (COCl₂) (Dai *et al.* 2009). As aliphatic polycarbonates have interesting properties such as transparency and impact resistance, which make it possible to use them instead of conventional polymers made from fossil fuels, researchers are currently looking into their potential applications (Lee *et al.* 2012).

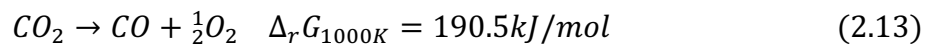
Another intriguing method of converting CO₂ is catalytic hydrogenation, which, when carried out with the right catalysts, produces CH₃OH. CH₃OH serves as both a fuel and a chemical. Therefore, it might play a significant part in the recycling of CO₂. DMC, methylamine acid acetic, and Formaldehyde are all produced using CH₃OH, which is also utilized as a methylating agent in many industrial processes. Additionally, it can be applied directly as an antifreeze or solvent as well as in wastewater treatment. Although the majority of CH₃OH

production, approximately 4 kt per year relies on syngas (Omae 2012), there is a growing interest in manufacturing CH₃OH from CO₂ due to its potential for higher selectivity.

2.9.3 CO₂ Conversion to Fuels

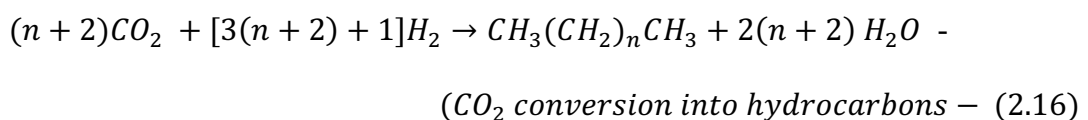
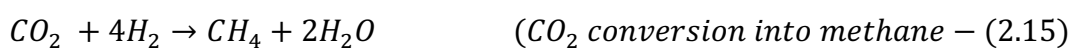
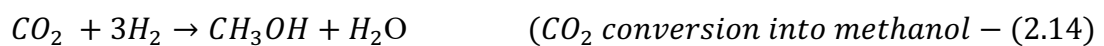
CCU technology can benefit from the conversion of CO₂ into chemicals. As opposed to fuels, their market is considerably smaller. To have a significant impact on sustainability, the production of fuels also requires a considerable amount of CO₂ because the amount of CO₂ released during the combustion of fuels is significantly higher than the amount that can be converted into chemicals.

One of the methods for converting CO₂ into fuels is CO₂ deoxygenation to CO, which can be accomplished by radiative or thermal processes that require a lot of energy (eqn 2.13).



The CO that is produced can be burned with air to produce energy and CO₂. According to several studies, the reaction can occur at room temperature when CO₂ is coordinated to a metallic centre (Grills and Fujita 2010; Jacquet *et al.* 2013; Nielsen *et al.* 2018). Combining the oxidation of organic substrates with the extraction of oxygen from CO₂, with a focus on epoxidation processes, will yield substantial benefits (Aresta and Dibenedetto 2002).

The key processes in converting CO₂ to fuels in a commercial setting necessitate the use of hydrogen and effective catalysts. It is worth noting that while H₂ can be directly used as an energy carrier, converting it to carbon-based fuels offers certain advantages, particularly due to its lower energy density compared to CH₃OH, CH₄, and hydrocarbons. From a thermodynamic perspective, it is always feasible to reduce CO₂ to any carbon-based fuel ($\Delta_r H < 0$). To activate CO₂, however, it is necessary to overcome the high energy barrier's severe kinetic limits, making the creation of extremely effective catalysts vital.



CO₂ can be chemically recycled into fuels through both indirect and direct methods. In the first scenario, CO₂ must first be converted to CO/syngas using the methane dry reforming, Reverse Water Gas Shift (RWGS) (Zhang *et al.* 2020b), or gasification. Next, CO/syngas must be converted into CH₃OH or hydrocarbons. In contrast, the second technique involves the direct interaction of CO₂ with hydrogen, which, depending on the catalyst, can occur via many ways. The discovery of adequate catalysts for the direct conversion of CO₂ to fuels is a difficult objective that requires extensive research.

Cu/ZnO-based catalysts are utilized to produce CH₃OH from CO₂, with water formation and the increased H₂ consumption being the main drawbacks in comparison to the conventional synthesis from syngas. As was already indicated, CH₃OH may be utilized effectively as fuel, and various relevant researchers have emphasized its significant significance in a future sustainable economy (referred to as the "methanol economy") (Olah, Goeppert and Prakash 2009, 2018). Additionally, CH₃OH can be converted into other significant species that are relevant to the energy sector, such as olefins (MTO process) or hydrocarbons (MTG process), by dehydrating it into DME with the help of suitable acidic catalysts (typically ZSM-5), (Figure 2.14) (Keil 1999; Bjørgen *et al.* 2007; Olah, Goeppert and Prakash 2009).

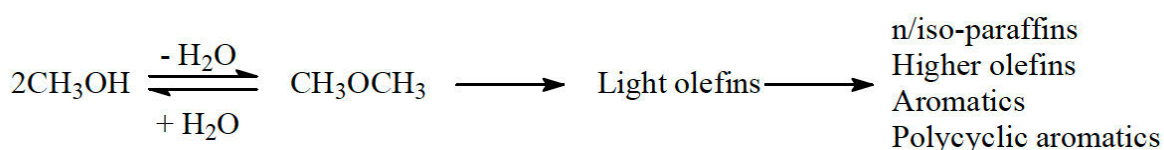


Figure 2-14. Methanol as a feedstock for MTG, MTO, and DME processes.

Another intriguing mechanism of CO₂ conversion is the Sabatier reaction, which is the result of CO₂ hydrogenation to CH₄. Even with the use of a variety of catalysts based on Ni, Rh, and Ru, formulation changes are still necessary to improve CO₂ conversion in moderate temperature conditions. Higher amounts of hydrogen are needed to produce CH₄ because it has a lower energy density than CH₃OH. Nevertheless, a major focus of the CCU technologies framework is the development of effective methods for producing CH₄ from CO₂ since the methanation reaction permits a higher degree of conversion of CO₂ and enables CH₄ to be used immediately in the conventional energy distribution grid without modification (Frontera *et al.* 2017).

FT catalysts based on iron or cobalt are utilized in the FT process, which converts CO₂ directly into higher hydrocarbons (similar to the conventional process starting with syngas). According

to reports in the literature, the main product of CO₂ hydrogenation with Co-based catalysts is CH₄ (Zhang *et al.* 2002; Pham *et al.* 2011); on the other hand, iron-based catalysts yield a mixture of hydrocarbons that is quite identical to that obtained when employing syngas as the feedstock (Riedel *et al.* 1999).

The main challenge continues to be the high energy and hydrogen consumption, even though chemical recycling of CO₂ to fuels may be the best option to achieve the sustainability criteria. The total amount of CO₂ emitted during the production of a biofuel may be more than the amount of CO₂ utilized as feedstock because this energy is currently produced using fossil fuels. Currently, over 90% of hydrogen is created from fossil fuels extremely using energy-intensive techniques, making it unable to sustainably catalyze CO₂ reduction into fuels. The primary resources on which scientists, businesses, and governments should focus their investments for a sustainable future are perennial energy sources including geothermal hydro wind, and solar energy. Through photo-electrochemical and electrochemical processes, these renewable energy sources can convert water to hydrogen, albeit technological advancements are still required to make these processes competitive with the traditional method. The economic studies of H₂ production using various technologies (Table 2.12) (Aresta, Dibenedetto and Angelini 2014) make it abundantly evident that the cost of producing hydrogen using renewable energy sources like solar and wind energy remains higher than that of producing fossil fuel.

Table 2-12. Production cost for 1kg of H₂ using several technologies.

Technology	Cost
Electrolysis with SPC	3.50 €
Electrolysis with wind	3.80 – 5.20 €
Gas reforming	1.10 – 1.15 €
Electrolysis with electricity from oil power station	2.20 – 3.50 €
Electrolysis with photovoltaic	2.8 – 4.0 €
Electrolysis with nuclear	1.45 – 1.50 €

To transform solar energy into H₂ using water electrolysis, photovoltaic (PV) technologies have a lot of potential. This is particularly true with regard to the considerable efficiency gains that can be achieved by switching from conventional monocrystalline Si-based technologies to those based on thin-film technology. The overvoltage for hydrogen production and the

electrolysis efficiency are two crucial parameters for PV systems that must be resolved for this technique to reach a technological maturity level that will make it economically competitive.

2.10 Fundamentals of CO₂ Methanation

2.10.1 Power to Gas (PtG)

Power storage has become more challenging as a result of the growing installed base of renewable energy generation technologies (photovoltaic, wind, etc.) (Figure 2.15) (Yao *et al.* 2016). The fact that the power generated from renewable sources is delivered as a fluctuating and intermittent output during the actual production presents a significant problem. Therefore, it is vital to create technology for storing and using surplus power. The most popular option for long-term energy storage, however, is the use of chemical energy carriers with high energy densities.

Power to gas (PtG) is a promising method of storing electricity in the form of chemical energy within chemical bonds. Since CH₄ is now consumed in large quantities across a wide range of businesses and is readily available through the CH₄ grid, PtG is most popular for this product. The concept is to convert CO or CO₂ to CH₄ and then inject the resulting methane into the existing methane grid.

Power-to-X technologies, such as power-to-gas (PtG) and power-to-liquids concepts, have been viewed as the best options thus far for converting intermittent renewable energy to carbon-neutral fuels (Buffo *et al.* 2019; McDonagh 2019; Rego de Vasconcelos and Lavoie 2019). There are some commercial cases, such as the methanation pilot by Audi, the methanol synthesis plant by Carbon Recycling International, and the Power-to-Liquids facility by Sunfire, that have shown power-to-X technology at a scale suitable for commercialization. The largest gas-to-power plant in Germany is owned and operated by Audi. It began operating in 2013 and uses three alkaline electrolyzers to produce the necessary hydrogen while receiving its CO₂ from a biogas facility (Bailera *et al.* 2017).

PtG is one of the power-to-X technologies that could be helpful in balancing variable renewable energy. One possible application of the renewable electrical energy of PtG is the production of SNG compatible with the existing natural gas grid using CO₂ and hydrogen produced by water electrolysis. Another advantage of developing PtG is the possibility of using power-to-X

technologies to produce high-quality chemicals from synthesis gas, CO₂ and H₂. PtG technologies, such as power to hydrogen and power to CH₄, have been studied for a long time, and some institutions or scientists have started looking into the technical requirements and molecular phenomena for commercial installation (Sterner and Specht 2021). The hydrogen generated from PtG needs to be processed, packaged, transported, and stored just like any other chemical before it can be used to synthesize other compounds. Although H₂ is a valuable gas produced by PtG technology, the main difficulty of temporary H₂ storage needs to be addressed (Žalec *et al.* 2022). However, the chemical storage of hydrogen, especially in SNG, could be an option for the storage of H₂ produced with PtG technology, as it offers better storage performance (Wilcox and Wilcox 2012; Senftle and Carter 2017; Fendt *et al.* 2019; Bassano *et al.* 2020). In addition, there are several potential ways for hydrogen storage, including underground storage, cryogenic compressed liquid hydrogen tanks, physical storage, and compressed gas tanks (Styring, Quadrelli and Armstrong 2014; Hassan *et al.* 2021) [13-15]. However, the cost of operation, installation and security must be taken into account.

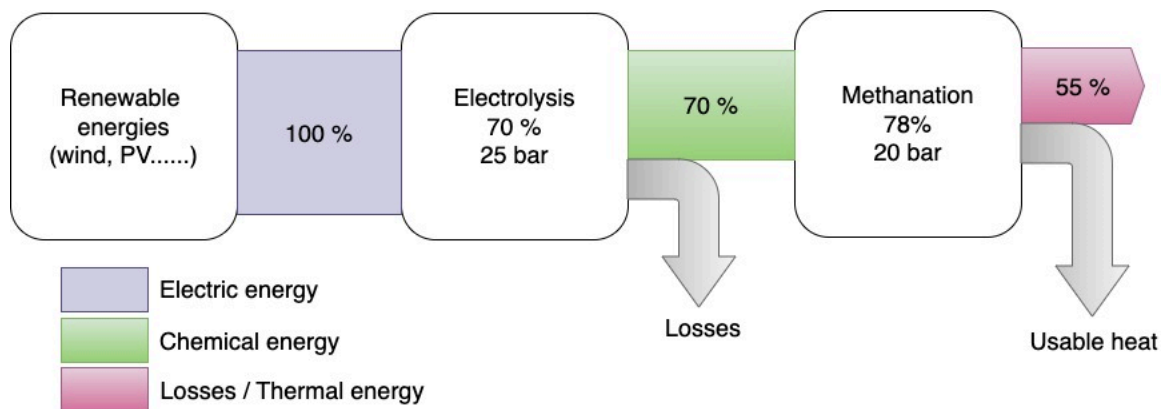


Figure 2-15. Sankey diagram of the PtG Process efficiency (Götz *et al.* 2016).

As shown in Figure 2.15, the efficiency of water electrolysis and methanation is a drawback that needs to be removed from the PtG chain (Götz *et al.* 2016). The compressed hydrogen produced by electrolysis will consume 30% less total energy than renewable electricity. Alkaline electrolysis, proton exchange membrane (PEM) electrolysis, and solid oxide electrolysis are currently the three most effective electrolysis techniques. Alkaline electrolysis currently has the advantage in terms of economics, but if PEM electrolysis's cost can be brought down in the future, it will be the best option for flexible industrial production. In Figure 2.15, the feasibility of currently accessible electrolysis technology is taken into account (alkaline electrolysis (AEL) and PEM). The methanation process is another link in the chain that could

use enhancement. The equilibrium of the reaction sets a limit on the efficiency, however the heat generated by the reaction can be used as a heat source for other operations (Schaaf *et al.* 2014a). The power-to-gas chain is shown in Figure 2.16 below. from the production of power to electrolysis, methanation, and the use of the SNG product.

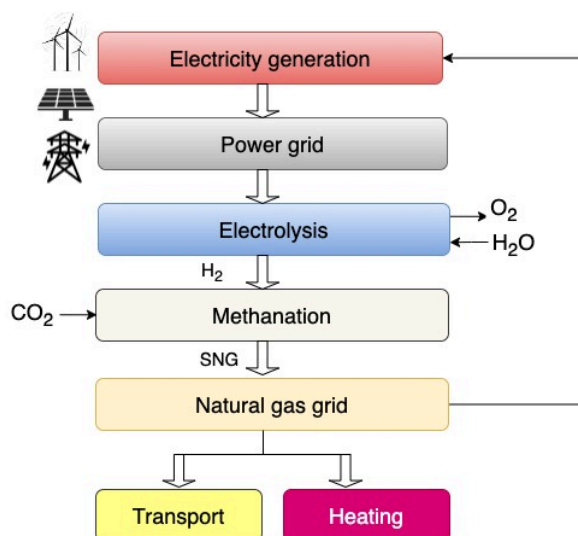


Figure 2-16. Power-to-Gas.

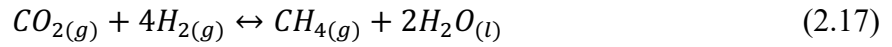
As shown in Figure 2.16, renewable energy can be converted into CH_4 (i.e., power-to-methane) and used for power generation, transportation, and home heating. CH_4 can be linked to the existing natural gas infrastructure by CO_2 methanation and co-electrolysis from industrial exhaust.

2.10.2 Sabatier Reaction

The hydrogenation of organic compounds is a method extensively used in the chemical sector. It specifically alludes to the interaction of molecular hydrogen with an additional element or organic compound. In a catalytic setting, the significant proportion of those reactions take place. An organic compound is often hydrogenated to decrease, oxidize, or alter its saturation state. A compound can undergo reduction, oxidation, or saturation, which refers to the presence or absence of double and triple bonds in the substance.

CO_2 and CO methanation are two of the most well-known hydrogenation processes. Specifically, the synthesis of CH_4 and H_2O (reduction) from the reaction of either CO or CO_2 with hydrogen (reduction). The Sabatier process, also known as the hydrogenation of CO_2 , is one of the hydrogenation processes that has likely received the most research. It was discovered

in the 1910s (Sabatier 1922) and is attributed to the French scientist Paul Sabatier, a pioneer in the catalytic hydrogenation techniques. This chemical reaction occurs as follows:



The Sabatier process is extremely exothermic, releasing $\Delta H = -165 \text{ kJ/mol}$ of energy for the reaction with CO_2 and $\Delta H = -201 \text{ kJ/mol}$ for the reaction with CO (Barbarossa and Vanga 2011). It is thermodynamically favourable ($\Delta H = -113,5 \text{ kJ/mol}$) throughout a broad temperature and pressure range (Barbarossa and Vanga 2011). In contrast, the reduction of completely oxidized carbon to CH_4 is kinetically constrained (Wei and Jinlong 2011). To achieve appropriate conversion rates and selectivity to CH_4 , a catalyst is required. Although CO_2 methanation is a simple and direct reaction, the mechanism by which CO_2 is converted to CH_4 during catalysis is complex. The approach includes two general pathways. One refers to the conversion of CO_2 to CO and the subsequent production of CO into CH_4 (Weatherbee and Bartholomew 1982). The second process is the direct conversion of CO_2 to CH_4 without intermediaries (Fujita *et al.* 1987).

As shown in Figure 2.17, the thermodynamic equilibrium of CO_2 methanation favours low temperatures and high pressure, but equilibrium conversions at low temperatures are difficult to achieve for exothermic reactions (Chang *et al.* 2003). When operating at high temperatures, the catalyst may sinter, which further reduces structural strength and deactivates the catalyst (Chen *et al.* 2011). The formation of gum and carbonyl at high CO concentrations can lead to the deactivation of the catalyst (Chen *et al.* 2011).

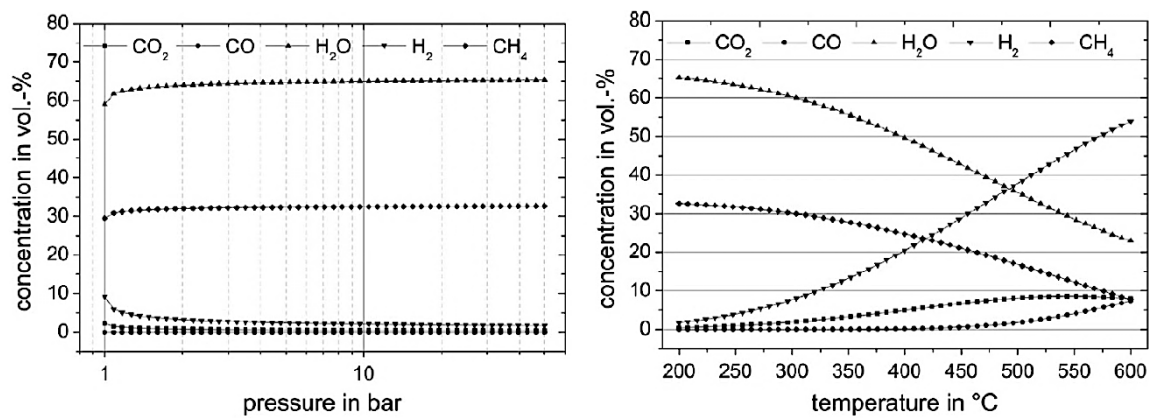


Figure 2-17. Concentration of CO_2 methanation at equilibrium as a function of pressure (at 300°C and 1 bar). $\text{H}_2:\text{CO}_2$ ratio of feed is 1:4 (Rönsch *et al.* 2016).

As a process, the Sabatier reaction has been extensively studied in both academia and the corporate sector due to its diverse applications and the fact that it involves some of the most prevalent and abundant chemical compounds on the planet. The primary focus of research is on the materials that can stimulate this process.

For energy-efficient and cost-effective CO₂ removal and CH₄ production, the Sabatier reaction faces a number of technological obstacles. The formation of many byproducts during the Sabatier reaction is the first issue. CO, CH₃OH, and solid carbon are some of the probable byproducts. Although methanation catalysts have the capability to convert these byproducts to CH₄ through alternate chemical pathways, solid carbon can render the metal catalyst inactive. Figure 2.18 shows how the product distribution in the Sabatier reaction varies with temperature.

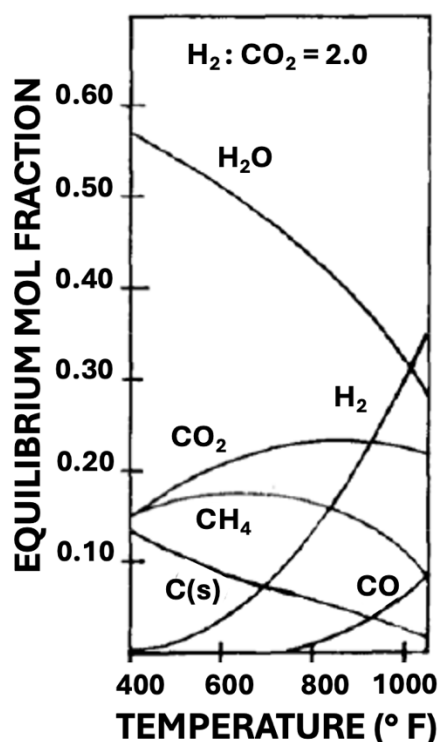


Figure 2-18. Product distribution at an H₂/CO₂ feed ratio of 2:1 over 0.5 wt.% Ru/Al₂O₃ catalyst as a function of reactor temperature in the Sabatier reaction (adapted from (Lunde and Kester 1974). At 345 °C, CH₄ production is at its peak. As the temperature rises, CO is produced at 425 °C.

The Sabatier reaction uses a ruthenium-based catalyst, which is a second drawback of the process. Ruthenium is a highly reactive catalyst for methanation (Falbo *et al.* 2019), but it is both poisonous and expensive (Bratsos *et al.* 2007). Additionally, nickel is an active catalyst for methanation that during synthesis poses health risks.

The production of hydrogen for the Sabatier reaction is the third and most difficult problem. Steam reforming of fossil fuels, mainly CH_4 , coal or oil, produces 95% of the hydrogen consumed worldwide (Sheet 2005). Under intense heat and pressure, the fossil fuel combines with the water during steam reforming to produce CO_2 and H_2 . Overall, fossil fuels like CH_4 would react with H_2O to make H_2 and CO_2 , which would then react with additional CO_2 to form less CH_4 than was initially present. For the Sabatier reaction to be advantageous from an economic, energy, and environmental standpoint, additional strategies for hydrogen synthesis must be developed because this circular reaction route is expensive and wasteful.

2.10.3 Application of Sabatier Reaction

A number of chemical processes depend on the hydrogenation of CO and CO_2 to CH_4 .

2.10.3.1 *Production of Methane as an Energy Carrier*

Natural gas, which mostly consists of methane and has a high specific heating value as well as a smoke- and ash-free decomposition, is an excellent fuel for transportation and the production of electricity. Gas pipelines make it simple to transport and distribute, and compression and liquefaction allow it to be stored in caverns or tanks. As was previously mentioned, it is also a typical source for synthesis gas and hydrogen due to its inexpensive cost and widespread availability in most Middle east and Western nations. However, in nations with scarce or expensive access to natural gas, the production of SNG through the methanation of syngas generated from other fuels can be a feasible economic and political choice.

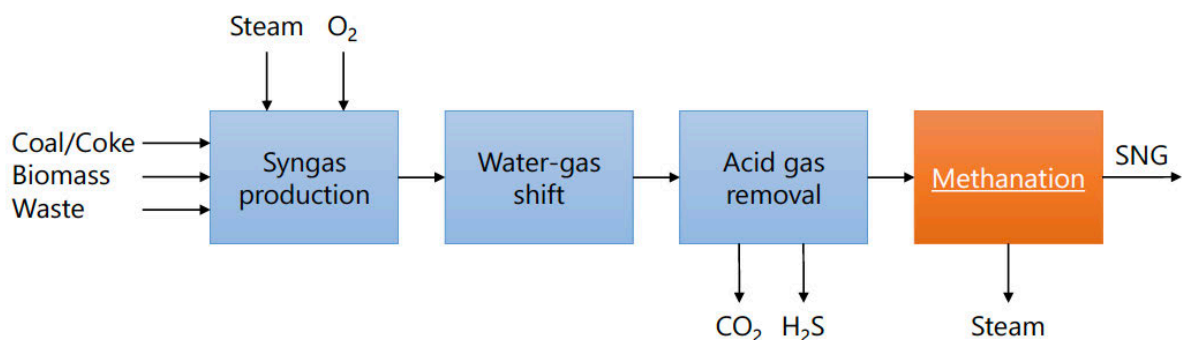


Figure 2-19. Simplified process diagram for the production of SNG from solid fuels (Kern 2019).

Figure 2.19 shows a simple process flow diagram. Since SNG production is also a synthesis gas process, it is closely related to the Haber-Bosch process. Using steam and/or oxygen from an air separation unit, carbonaceous feedstock is gasified/reformed to produce hydrogen and

carbon oxides. Typically, the gasifier/operating reformer's parameters are chosen so that the raw syngas already contains a large quantity of CH₄ (Kopyscinski, Schildhauer and Biollaz 2010). Typically, the stoichiometric ratio for SNG methanation processes is $(\text{H}_2 - \text{CO}_2)/(\text{CO} + \text{CO}_2) = 3$. Since most feedstocks do not contain hydrogen, the composition of the synthesis gas must be adjusted by partial CO conversion using water gas shift and CO₂ removal. Raw SNG is dried after methanation to obtain a high calorific value for pipeline gas quality. The CO₂ produced by the SNG process is generally pure and can be used for carbon storage, increased oil recovery, etc. (Panek and Grasser 2006). The strong exothermicity of methanation and its appropriate temperature control are used to produce high-pressure steam, which is often used for power generation.

The first patents for the production of CH₄ as SNG were filed as early as 1905 (Elworthy and Elworthy 1909), but it was not commercialised because the gas demand at that time was covered by town gas from natural gas, coke oven gas or coal (Hiller *et al.* 2000). However, the rise in oil and gas costs and the anticipated natural gas crisis in the 1960s and 1970s led to a surge in SNG technology research in the UK and the USA (Smil 2015). Numerous businesses developed SNG processes using coal or naphtha as the feedstock during this time period, and up to 40 big SNG facilities were planned in the US alone (Mills and Steffgen 1974). During this period, a great deal of basic research on methanation was conducted. However, just one factory: the Great Plains Synfuels Plant in Beulah, North Dakota, USA was ultimately built in 1983, aside from a number of pilot and process research plants. This SNG facility produces approximately 1.5109 Nm³ a⁻¹ of SNG utilizing a Lurgi-developed technology (Hiller *et al.* 2000).

Coal-to-SNG plants are extremely capital-intensive (about 2 billion US dollars in the given scenario (Panek and Grasser 2006), mainly due to the complexity of coal gasification plants (Rostrup-Nielsen, Sehested and Nørskov 2002). In addition, the economic success of SNG is closely linked to the availability and price of natural gas. When oil and gas prices collapsed in the mid-1980s, the first SNG plant in North Dakota went bankrupt shortly after its construction (Panek and Grasser 2006; Yang and Jackson 2013). With the help of government subsidies and long-term gas price agreements, the plant remained in operation; however, no further plants have been built since. As gasoline prices began to rise again around the turn of the millennium, interest in SNG rekindled in the United States, and numerous SNG plants were again proposed. Plans for SNG plants in the United States were again abandoned as non-conventional natural

gas extraction techniques such as shale hydrofracking have increased the availability of natural gas and lowered its price (Stevens 2012).

During the same period, numerous large coal gasification plants were built in China. In 2013, nine plants with a total capacity of 37-109 Nm³ a⁻¹ per year were approved by the national government (Yang and Jackson 2013). China has an abundance of coal reserves, but only small reserves of natural gas. As coal mining primarily takes place in remote regions far away from urban centres, SNG is considered a viable energy source for transportation to cities.

From an ecological point of view, however, this development is viewed very negatively (Yang and Jackson 2013). Compared to fossil fuels, the conversion of coal to SNG has a much larger carbon and environmental footprint. The lifecycle greenhouse gas emissions of SNG are approximately six times that of normal natural gas, at 460 g CO² equivalent per MJ⁻¹. When SNG is utilized to generate electricity, the emissions are 40 to 80 % higher than when coal is directly burned in power plants. And when SNG is used as a vehicle fuel, the lifecycle emissions are double those of gasoline. In addition, without effective off-gas treatment, coal gasification emits mercury and hydrogen sulfide. In conclusion, SNG production results in a massive specific water usage of approximately 0.23 l MJ⁻¹. As coal mining occurs in arid locations such as Inner Mongolia and Xinjiang, water scarcity and contamination may cause further environmental issues.

2.10.3.1.1 *Energy transport*

The NFE initiative ("Nuclear Far Energy") of the German nuclear research facility Juelich described in (Harms, Höhle and Skov 1980) was another method for storing and transporting energy via CH₄. The main objective of this research was to develop a closed-loop chemical system capable of transferring thermal energy from an external consumer to a high-temperature nuclear reactor. The syngas transferred through the pipeline would be produced by endothermic steam reforming of methane, with the process heat provided by nuclear energy. At peripheral sites, the syngas would undergo methanation to produce steam and heat; the methane produced would then be fed back into the steam reformer. The NFE project (Barnet 1997) was also discontinued as a result of the fall in natural gas prices following the resolution of the oil crisis and the discontinuation of nuclear reactor initiatives in Germany.

2.10.3.1.2 *Energy storage*

The Sabatier process can also have a significant impact in the fields of energy storage and carbon dioxide management. Despite attempts to minimize CO₂ emissions from industry, transportation, and energy production, we are still unable to reach the tough global CO₂ output targets set at the international level. A great deal of emphasis has been placed on carbon storage via innovative CO₂ capture techniques. However, CO₂ storage is still energy-intensive and inefficient, necessitating the development of new strategies. The chemical transformation of CO₂ into renewable fuels constitutes these solutions. These include CH₃OH, liquid hydrocarbons, and methane, as previously stated. Consequently, the Sabatier process, which not only reduces CO₂ but also produces CH₄, could be a potential answer. In the modern western world, this substance is utilized extensively in both households and industry. It also has the advantage of an existing distribution network, particularly in Europe. Concerning energy storage, the conversion of hydrogen to the more "practical" (as indicated above) CH₄ has advantages. After the proliferation of renewable energy sources, electrolysis may produce a substantial volume of hydrogen each year, which is more difficult to store and transport than CH₄. Therefore, a stable Sabatier process is required to convert hydrogen to natural gas.

2.10.3.1.3 *Biomass-to-SNG*

Several European nations have investigated a more environmentally friendly usage of SNG technology over the past two decades (Kopyscinski, Schildhauer and Biollaz 2010). As an alternative to coal, biomass extracted from wood is regarded a suitable fuel. The first small-scale plants were built in Guessing, Austria (BioSNG) and Gothenburg, Sweden (GoBiGas) (Rönsch *et al.* 2016). Due to the chemical complexity and variable quality of the feedstock, the conversion of biomass into synthesis gas and SNG poses additional problems in the design of processes and plants. To prevent deactivation of the sensitive methanation catalysts, the synthesis gas must be efficiently cleaned of sulfur compounds, olefins and tar (Baumhagl 2014). Due to the much smaller scale of biomass-to-SNG plants compared to coal-based processes (planned energy output of 10-200 MW due to the higher calorific value of SNG compared to 1.5 GW in the Great Plains Synfuel Plant), standard gas cleaning technologies such as Rectisol are not economically viable. Therefore, other approaches, such as hydrotreatment or adsorptive desulfuration, must be introduced to preserve the catalyst (SCHILDHAUER and BIOLLAZ 2016). Several European nations have investigated a more environmentally friendly usage of SNG technology over the past two decades (Kopyscinski,

Schildhauer and Biollaz 2010). As an alternative to coal, biomass obtained from wood is considered a suitable fuel. The first small-scale plants were built in Guessing (Austria) (BioSNG) and Gothenburg (Sweden) (GoBiGas) (Rönsch *et al.* 2016). Due to the chemical complexity and variable quality of the feedstock, the conversion of biomass into synthesis gas and SNG poses additional problems in the design of the process and equipment. To prevent deactivation of the sensitive methanation catalysts, the synthesis gas must be efficiently purified of sulfur compounds, olefins and tar (Baumhakl 2014). Due to the much smaller scale of biomass-to-SNG plants compared to coal-based processes (planned energy output of 10-200 MW due to the higher heating value of SNG compared to 1.5 GW at the Great Plains Synfuel Plant), standard gas cleaning technologies such as Rectisol are not economically viable. Therefore, other approaches, such as hydrotreatment or adsorptive desulfuration, must be introduced to preserve the catalyst (SCHILDHAUER and BIOLLAZ 2016).

2.10.3.2 *Removal of Carbon monoxide from Hydrogen-Rich Streams*

The technological removal of small amounts of CO from hydrogen-rich gas streams was historically the first and is currently the most widespread application of methanation. Since many transition metals strongly adsorb CO, its presence as an impurity can cause catalysts to be strongly deactivated. Contrarily, at the conditions of the majority of catalytic hydrogenation reactions, methane is chemically inert. At high hydrogen pressures and temperatures below around 400 °C, the methanation reaction is virtually irreversible, making it possible to attain very low CO levels.

2.10.3.2.1 *Ammonia Synthesis*

One of the most important applications of methanation since the opening of the first commercial ammonia factory in 1913 is Haber-Bosch ammonia synthesis, the catalytic process with the largest hydrogen consumption worldwide (Rostrup-Nielsen, Sehested and Nørskov 2002). To prevent oxygen-containing molecules such as H₂O, O₂, CO and CO₂ from oxidizing or poisoning the iron catalyst used in the hydrogenation of nitrogen to ammonia, their concentration must be reduced to 2-10 ppm (Hiller *et al.* 2000).

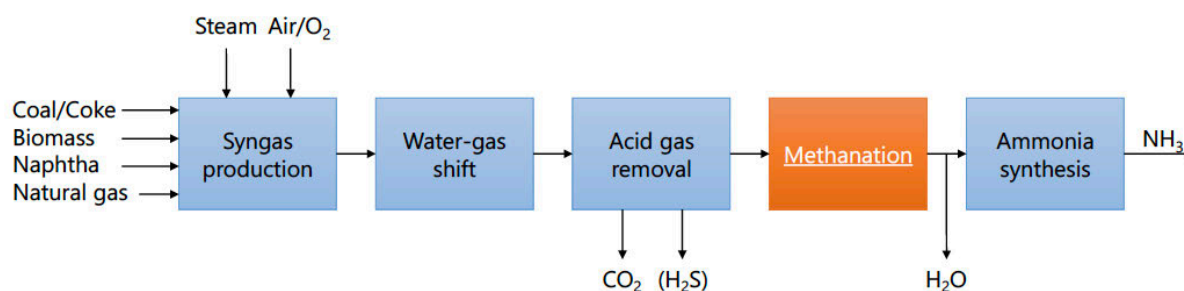


Figure 2-20. Simplified flow diagram of ammonia synthesis (Kern 2019).

The flow diagram of a typical ammonia plant is shown in Figure 2.20. Most ammonia plants either perform steam reforming of natural gas or partially oxidize naphtha and heavy oil (vacuum residue) to produce hydrogen (vacuum residue). After the reformer/gasifier, the raw synthesis gas comprises between approximately 10 ± 3 vol% of CO₂ and 20 ± 5 vol% of CO approx. (Hiller *et al.* 2000). A water-gas shift to CO₂ is used to increase the H₂ content while lowering the CO content of the syngas. The CO₂ in the syngas is then extracted, along with other possible impurities like H₂S, by an absorptive washing phase, such as with amines (MEA wash), aqueous potassium carbonate solution (Benfield), or methanol (Rectisol).

CO cannot be entirely converted due to the chemical equilibrium limitations of the water-gas shift reaction. Therefore, before the actual ammonia synthesis, a methanation phase is carried out at a temperature of about 300 °C to reduce the carbon oxide concentration below the expected standard, and the water produced is condensed.

2.10.3.2.2 Fuel cells

Hydrogen fuel cell technology is a still-emerging area of application for CO removal by methanation. In proton exchange membrane fuel cells (PEM cells), the platinum catalyst is susceptible to CO poisoning, which leads to a sharp drop in the power output of the fuel cell. Depending on the type of catalyst, the CO content in the feed should be below about 10-100 ppm to ensure efficient operation (Baschuk and Li 2001; Park, Lee and Lee 2009). Partial oxidation of light hydrocarbons or alcohols or low temperature steam reforming followed by water gas shift are considered potential sources of hydrogen for remote or mobile areas where the use of cryogenic and/or compressed hydrogen is undesirable. The hydrogen-rich synthesis gas from these reformers consists mostly of CO₂, but it also contains between 1-2 vol of CO (Takenaka, Shimizu and Otsuka 2004).

Currently, partial oxidation by air and methanation are being studied as two different ways to remove the CO from the hydrogen input. Methanation has the benefit of not requiring additional air dosing, which simplifies the system and reduces complexity. It also has the advantage of preventing explosions and excessive N₂ dilution of the H₂ stream. Since methanation consumes hydrogen, the main difficulty with this method is the selective conversion of a small amount of CO in the presence of a significant excess of CO₂, which requires catalysts that strongly inhibit the latter reaction. In addition, very high catalytic activities are required in a compact on-board reactor at low operating temperatures to achieve the desired final concentration of CO (Lindermeir *et al.* 2007; Cipiti and Recupero 2009).

2.11 Catalysis

As shown in Figure 2.21, a catalyst is a material (or enzyme) that speeds up a chemical reaction by reducing the activation energy. As a result, a catalyst affects a chemical reaction's kinetics rather than its thermodynamics. The number of catalytically active compounds at the end of a reaction is the same as it was at the beginning since a catalyst is not consumed in comparison to the reaction's initial substances. A catalyst can be employed repeatedly to catalyze the same reaction under normal conditions (Nørskov *et al.* 2014; Hagen 2015; Rothenberg 2017). Toxic catalysts, such as sulphur in hydrogenation processes over nickel or H₂S in FT synthesis over iron, might, however, cause them to lose their activity (Bartholomew 2001). As a superordinate concept, catalysis can be separated into three distinct and more specific fields: homogeneous, heterogeneous, and biocatalysis. The term "biocatalysis" refers to chemical reactions that are primarily facilitated by enzymes. The catalyst is in the same phase as the reactants and products in homogeneous catalysis (e.g., liquid-liquid). As opposed to heterogeneous catalysis, which describes a reaction in which the catalyst is in a separate phase from the reactants and products (e.g., gas and solid). Since nearly 90% of all chemical reactions are heterogeneously catalyzed, heterogeneous catalysis is particularly crucial in the industrial setting. This preference can be explained, in part, by the ease with which products and catalysts can be separated, as opposed to in homogeneous catalysis (Nørskov *et al.* 2014; Hagen 2015; Rothenberg 2017).

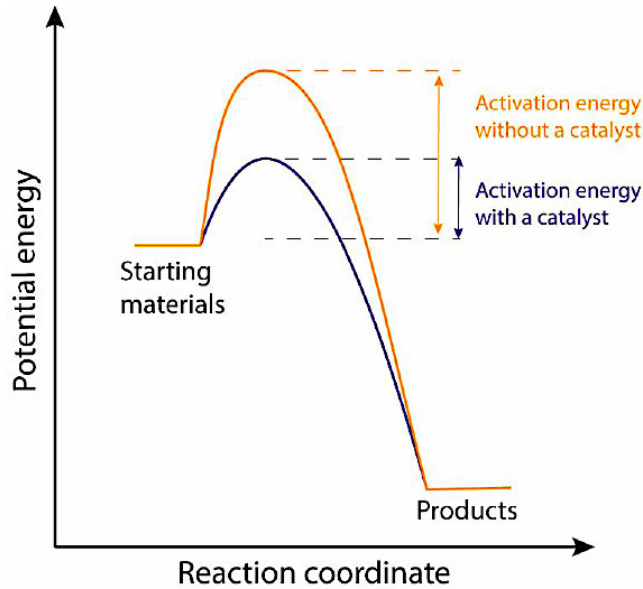


Figure 2-21. The influence of catalyst on chemical reaction by activation energy reduction. Adapted from (Hagen 2015).

2.11.1 Key Properties of a Catalyst

The following three characteristics highlight the qualities of an excellent catalyst:

- i. High activity: A catalyst's activity defines how effective it is; the higher the activity, the more effective the catalyst. It is frequently necessary to have a high surface area with an active phase that is evenly scattered and exposed to the reactants. Surface area is significantly influenced by the preparation technique used. Therefore, the catalyst surface needs to have a lot of active sites in order to speed up a process. A fast reaction time and slow reaction rate maximize the product throughout.
- ii. High selectivity: If a catalyst is selective, it produces a large proportion of the desired product with minimal by-products; hence, there is an additional economic incentive to design selective catalysts. As a result, process efficiency is enhanced, and pollution is reduced. Less waste necessitates less disposal or recycling. Therefore, the intended product yield is maximized, by-products are minimized, and purifying expenses are kept to a minimum.

$$S = \frac{i}{\text{rate of reaction}} \quad (2.18)$$

where S = selectivity, i = desired product and rate of reaction .

- iii. High recycling potential (regeneration): The lifespan of the catalyst must also be addressed. This implies that a small amount of catalyst must endure a large number of cycles for the process to be economically viable.

2.11.2 Types of Catalytic Processes

Catalytic processes can be broadly classified into three groups: enzymatic catalysis, homogeneous catalysis, and heterogeneous catalysis. The following factors typically affect a catalytic process's efficiency: yield, selectivity of the product, economic viability, and reactant conversion.

Conversion of X

$$X_i(\%) = \frac{n_i^{in} - n_i^{out}}{n_i^{in}} \times 100^a \quad (2.19)$$

Selectivity for S

$$S_i(\%) = \frac{X_i n_i^{in}}{\sum_i X_i n_i^{in}} \times 100 \quad (2.20)$$

Yield of Y

$$Y_i(\%) = X_i \times S_i \times 100 \quad (2.21)$$

2.11.2.1 Homogeneous Catalysis

Homogeneous catalysis refers to a process in which a catalyst is in solution with at least one of the reactants, which in the modern chemical industry is about 17%. Homogeneous catalysis often function under more favourable conditions than heterogeneous catalysis employing a liquid-phase organometallic catalyst. The organic ligands surrounding the metal ion provide a specific and tunable steric environment near the catalytic sites, which favours the synthesis of a particular product and thus leads to high selectivity. However, the difficulty of catalyst recovery has been one of the major obstacles to the economic viability of the process. Hydroformylation, often known as the oxo process, is an important industrial synthesis that utilizes homogeneous catalysis to produce aldehydes from alkenes.

2.11.2.2 Enzymatic Catalysis

Enzymatic catalysis, which employs enzymes as active catalysts, is the least frequent type of catalysis. The culinary and pharmaceutical industries, e.g., in the production of beer, cheese and medicines, benefit greatly from enzymatic processes. Similar to the homogeneous process, the recovery of enzymes has proven to be a challenge, and the functionality of enzymes is extremely sensitive to operating parameters such as temperature and pH value.

Enzymes, as biological catalysts, are essentially proteins. Similar to the catalytic action of acids and bases, but substantially more complex. They catalyze chemical reactions with high selectivity and efficiency. They are present in all living species and catalyze the majority of cellular reactions, such as the breakdown of lipids, carbohydrates, and proteins.

The fact that enzymes are frequently highly selective is one of their outstanding qualities. When an enzyme acts on carbohydrates, it is designed specifically so that even the smallest alteration in the molecule's stereochemical arrangement renders it incompatible with other enzymes and prevents hydrolysis. The majority of enzymes are sensitive to a wide range of compounds that may impede or occasionally boost the activity, and they function best within a restricted pH range. At temperatures above 313K, most enzymes lose their effectiveness quickly. Based on the kind of substrate and the reaction that the enzyme catalyzes, enzymes are divided into groups. Oxidoreductases, transferases, hydrolases, lyases, isomerases, and ligases are the six major divisions. Enzyme catalytic sites are located inside a three-dimensional array of hydrophobic amino acids and are frequently coordinated with metal complexes (e.g., those of Mg and Cu).

2.11.2.3 Heterogeneous Catalysis

Due to the relatively simple recovery of the catalyst after its use and the simple separation of the liquid product mixture, heterogeneous catalysis is the most widely used and financially most attractive catalytic technique. Heterogeneous catalysis, in which the reaction takes place in several phases, is used in almost 80% of catalytic processes in the chemical industry (Figure 2.22). The catalyst and the reaction mixture are usually liquid or gaseous, similar to the Haber-Bosch process.

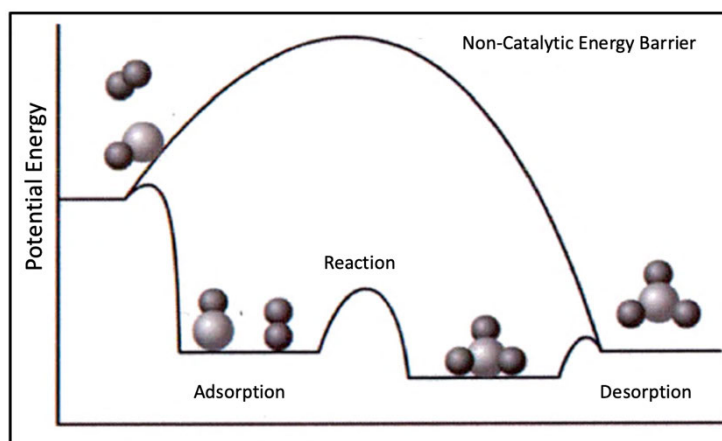


Figure 2-22. The effect of catalysts on activation energy. The presence of a catalyst initiates a new, lower-energy chemical pathway (Murzin and Salmi 2016).

The structure and geometry of the microenvironment of a heterogeneous catalytic process are crucial. In heterogeneous catalysis, unlike in homogeneous catalysis, the catalyst and reactants are in separate phases. The catalyzed reaction happens at the interface between two phases, such as a solid catalyst in a reaction involving liquid or gaseous reactants. In general, such reactions are known to facilitate the adsorption and reaction of reactants at the catalytic surface. The active site chemistry, the support material, and the position of the metal on and/or within the pore structure of the support, such as TiC_2 and Al_2O_3 , are the primary determinants of the catalyst's properties.

The catalyst is the heart of any reactor. A heterogeneous catalyst consists of a support (often oxides) and scattered metal particles. The most common oxide supports include titanium dioxide (TiO_2), silicon dioxide (SiO_2) and aluminium oxide (Al_2O_3). The large surface area of these supports and their ability to prevent sintering of the catalytically active particles are key features of these supports (Nørskov *et al.* 2014). However, the support is not only responsible for the dispersion of the particles, but it can also be involved in a chemical process. It is known that contacts between the support and nanoparticle contribute significantly to the total reaction. In heterogeneous catalysis, the catalytic activity may be affected by various metal-support interactions. For example, electron rearrangement can result in charge transfer processes that affect the total conversion at the interface between support and metal. In addition to these phenomena of charge transfer, further modifications can be caused by additional interactions. It is important to note that these metal-support interactions can be modified by a variety of parameters, resulting in improved performance (van Deelen, Hernández Mejía and de Jong

2019). In sections 2.11.3, additional information is provided regarding how a support affects the catalytic reaction and the reducibility of heterogeneous catalysts.

The space-time yield (STY) measures the catalytic activity of a heterogeneous catalyst, which is defined as follows:

$$STY = \frac{\text{product quantity}}{\text{catalyst volume} * \text{time}} \quad (2.22)$$

Space-time yield is measured in $\text{mol}_{\text{pro}} \text{ l}^{-1}_{\text{cat}} \text{ h}^{-1}$ or $\text{g}_{\text{prod}} \text{ kg}^{-1}_{\text{cat}} \text{ h}^{-1}$ (Hagen 2015; Porosoff, Yan and Chen 2016). The advantage of providing the space-time yield as the output is that it can be compared across various types of reactors with various catalysts, as the mass/volume of the catalyst is taken into account. In contrast, this also indicates that the concept of a space-time yield lacks specificity, as it captures the total activity without providing crucial details about the active sites.

i. From a reactor to the active sites

Although the catalyst itself has a significant impact on the yield of a chemical reaction, other components, including a suitable reactor, also have an impact on the overall yield. A catalytic reaction is affected at three separate levels. The chemical reactor is often the largest component, followed by the reactor's catalyst. The catalytically active sites on the catalyst are the smallest unit determining the catalytic activity, as shown in Figure 2.23 (Rothenberg 2017).

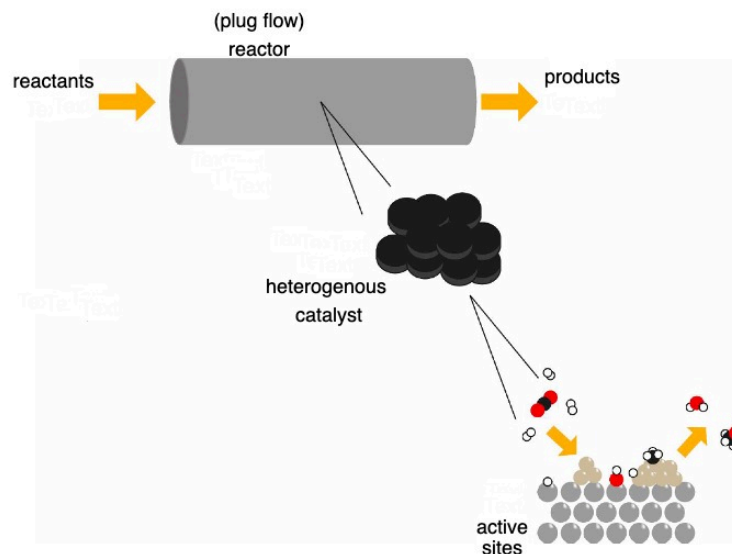


Figure 2-23. Different levels in heterogeneous catalysis. Reactor as the "black box", heterogeneous catalyst in the reactor as macroscopic level and the active sites on the catalyst as the microscopic level. Adapted from (Rothenberg 2017).

ii. Reactor

Various reactor designs are better suited for different chemical reactions. The plug flow reactor (PFR) is a common reactor for heterogeneous catalysis. PFRs are simple reactors made up of one or more parallel tubes that house the catalyst. The catalysts are arranged in a loose configuration inside the reactor to prevent mass flow irregularities. The reactants are added to the tube(s) on one end of the reactor, and the products and unreacted species exit the reactor through the other end.

A continuously stirred tank reactor is another common form of reactor (CSTR). In comparison to the PFR, a mechanical stirrer continuously mixes the reactants and catalyst in a CSTR. As a result, unlike in a plug flow reactor, the concentration of the reactants and products is the same throughout the reactor (Hill and Root 2014; Hagen 2015).

In addition to sorption-enhanced reactors (Bayat *et al.* 2014; Arora, Iyer and Hasan 2018) and looped recycling reactors (Rahimpour *et al.* 2003), additional improved reactor types include sorption-enhanced reactors. Both reactor types are PFR-based. In sorption-enhanced reactors, one or more products are continuously extracted from the reaction chamber (Bayat *et al.* 2014; Arora, Iyer and Hasan 2018). Unreacted gases are removed from the products and reintroduced into a recycling reactor (Rahimpour *et al.* 2003).

At this point, it should be noted that selecting a good chemical reactor is also crucial because changes made at the reactor level might improve reaction yield.

iii. Active site

As stated previously, both support and nanoparticles play a major role in the reaction, although they do not contribute equally to the catalytic activity. This results in the concept known as catalyst active sites. The interaction between reactants and a catalyst's active site might be regarded as a microscopic interaction. The surface of a heterogeneous catalyst is not a uniform plane with sites always having identical shape and physical properties. There are various surface spots on a catalyst's surface. Different surface sites of a catalyst are depicted in Figure 2.24 (Rothenberg 2017).

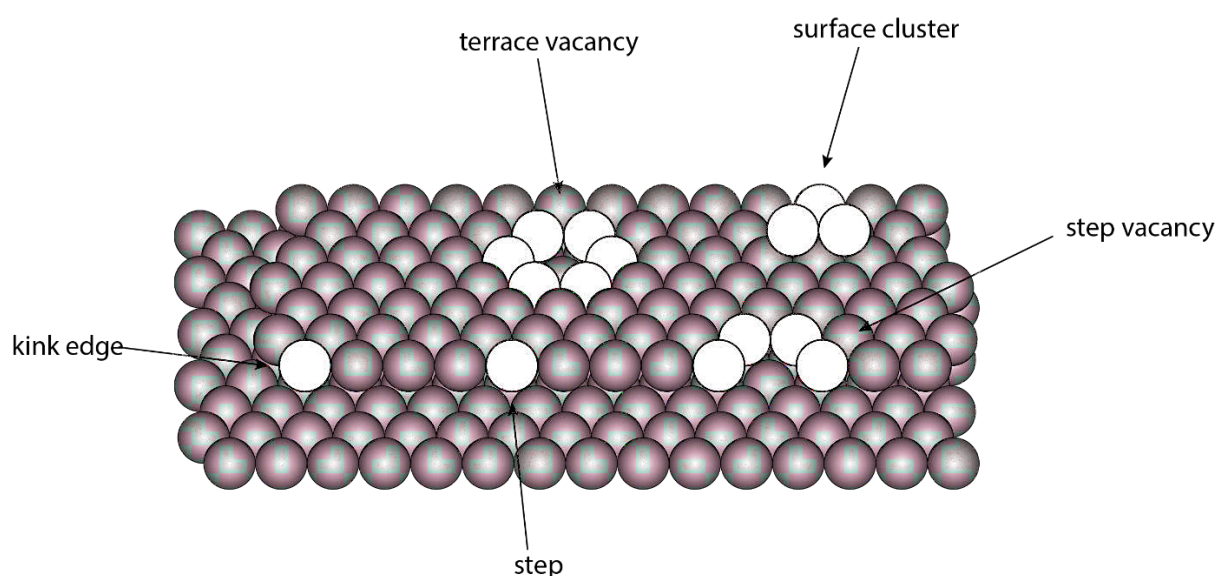


Figure 2-24. Different irregular sites on a heterogeneous catalyst. Adapted from (Rothenberg 2017).

These surface sites are not as completely coordinated as the atoms in the bulk. This lack of coordination allows atoms and molecules to interact with one another. As these surface irregularities are not coordinated in the same way, they offer distinct opportunities to engage with reactants and intermediates. This demonstrates how easy the surface of a catalyst can be modified to alter its activity (Nørskov *et al.* 2014; Rothenberg 2017).

Typically, the turnover frequency (TOF) is used to define the activity of such active sites, as shown in the following equation:

$$TOF = \frac{\text{rate}}{\text{number of active sites}} \quad (2.23)$$

The turnover frequency is expressed in s^{-1} . The turnover number (TON) is strongly related to the turnover frequency (TOF), which specifies the TON until the active sites/catalyst degrade (as summarized in Equation (2.23) [43].

$$TON = TOF * lifetime \quad (2.24)$$

Since there is often little information about the total number of active sites in heterogeneous catalysis, the activity is often expressed as the space-time yield (see equation 2.22) (Hagen 2015).

2.11.3 Reducibility of Heterogenous Catalyst

While certain supports are actively involved in catalysis, others are chemically inert (Rothenberg 2017). As a result, the reducibility principle was developed. In terms of thermodynamics, all oxides are reducible. However, in practice, reducible and non-reducible oxides are distinguished (Pinto *et al.* 2019). Reduced support loses oxygen when compared to non-reducible support under standard conditions. The cation then stabilizes the remainder of the negative charge (electrons) (leading to a change in the oxidation state). The band gap must be narrow ($< 3\text{eV}$) for this stabilization to occur. TiO_2 , WO_3 , and Fe_2O_3 are examples of oxides that can be reduced.

As an alternative, there is the category of non-reducible supports, including Al_2O_3 , SiO_2 , and MgO . These supports are less prone to losing oxygen atoms than reducible metal oxides because the substantial band gap between the valence and conduction bands prevents the stabilization of the extra electrons. However, by adding dopants, a non-reducible oxide can be modified into a reducible oxide (e.g., heteroatoms) (Ruiz Puigdollers *et al.* 2017; Pinto *et al.* 2019).

Reducible oxides may facilitate a catalyzed reaction in heterogeneous catalysis. These oxides have a variety of effects on the catalytic reaction as a whole, depending on whether they are based on the strong interaction between the metal and the support (such as via strong-metal support interactions, SMSI), or on the support's structure (such as changes brought on by oxygen loss) (Wang, Jiang and Wang 2019).

The overall catalytic activity of a commercial CuO/ZnO/Al₂O₃ catalyst for methanol production is significantly influenced by its reducibility [59]. The metal may undergo electronical alterations as a result of the addition of negative charges or electrons produced by the reduction of ZnO (Bainbridge *et al.* 2017).

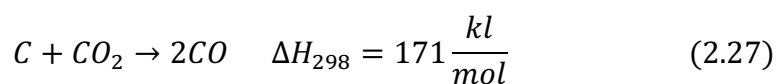
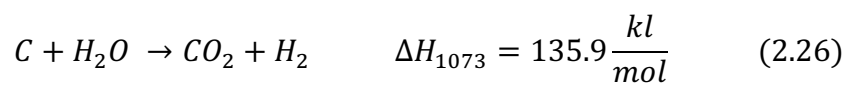
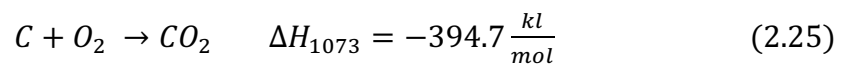
2.11.4 Regeneration of Heterogeneous Catalyst

The loss of catalytic activity in most processes is unavoidable, despite the efforts of researchers to prevent it. When the activity has dropped to a critical level, one must choose between four options: (i) restoring the activity of the catalyst, (ii) using it for another application, (iii) reclaiming and recycling the vital and/or costly catalytic components, or (iv) discarding the catalyst. The first option (regeneration and reuse) is nearly always preferable; catalyst disposal is typically the last resort, especially when environmental concerns are taken into account.

Reactivating a catalyst is contingent upon the reversibility of the deactivation process. For instance, carbon and coke formation can be reversed rather simply by gasification with hydrogen, water, or oxygen.

Coke deposition on the surface of the catalyst prevents its active sites from accessing the reactant. Sintering influences catalyst activity in addition to nanomaterial coking. Sintering, on the other hand, is typically irreversible, but metal redispersion is feasible in certain noble metal systems under specific conditions. Others cannot be removed without deactivating or damaging the catalyst further.

Combustion and gasification of the deposited carbon nanomaterial are common processes applied for catalyst regeneration during CO₂ methanation. In combustion, oxygen is utilized (Villacampa *et al.* 2003), but in gasification, steam (Aiello *et al.* 2000) or CO₂ is utilized (Huang and Tan 2014). Any one or combination of the following reactions may be used to regenerate a catalyst.



2.11.4.1 *Regeneration of Heterogeneous Catalyst by Gasification*

Typically, the gasification process regenerates a catalyst deactivated by coke or carbon; the rate of gasification is dependent on the kind of gas employed and the reactivity and structure of carbonaceous species (Nzihou, Stanmore and Sharrock 2013; Mahamulkar *et al.* 2016). Oxygen is mainly employed during gasification. Oxygen, for instance, can effectively remove coke by producing CO_x, which also promotes the sublimation of MoO_x and/or formation of inert Al₂(MoO₄)₃. Catalyst regeneration in an oxygen atmosphere can convert molybdenum carbide back to its oxide phase and redisperse the Mo nanoparticles into an isolated single Mo atom tethered to a Brønsted acid site, as is the case with a fresh catalyst treated in O₂. It was observed that prolonged exposure to O₂ at 753 K caused Mo migration on the zeolite's extraframework and decreased benzene yield (Kostyniuk, Bajec and Likozar 2021). This technique, however, has the disadvantage of exothermicity. The exothermic nature of the material causes it to overheat, which enables sintering. In these instances, a mixture of oxygen and an inert gas or oxygen and steam is employed to control the temperature during the gasification of carbonaceous materials. The gasification procedure did not remove the sulphur toxicity from the catalyst surface. In a reforming or hydrogenation reaction, the high-temperature gasification of sulphur with oxygen or steam results in sulphate, which then reverts to NiS when exposed to hydrogen. Moreover, high temperatures induce sintering. By treating the metal or metal oxide phase with oxygen, chlorine, nitric oxide, and hydrogen, deactivated catalysts can be regenerated through sintering. An example of such regeneration is the redispersion of the agglomerated Pt phase supported on alumina by oxygen and chlorine treatment at high temperatures. Also applicable to other alumina-supported noble metal catalysts are similar procedures. However, these conditions may not apply to Pt on other supports or to other supported metals.

2.11.4.2 *Regeneration of Heterogeneous Catalyst by Combustion*

The combustion of produced coke on a catalyst with oxygen eliminates deposited carbon more efficiently than steam-based gasification. The process heat generated by this method supports continuous methane decomposition and is significantly faster than gasification. Low metal support interaction (MSI) enhances carbon deposition on the backside of the metal catalyst, which facilitates the combustion-based regeneration of low metal %wt. loaded catalysts (Cunha-Silva *et al.* 2009). Saraswat and Pant (2013) studied the regeneration of a spent Ni-Cu/SiO₂ catalyst by passing O₂ and N₂ in a volumetric ratio of 1:3 at 550 °C. Based on their

findings, they concluded that catalyst recovery could only be accomplished at high temperatures. After reducing the reaction temperature from 550 °C to 500 °C, they also noticed a decline in catalyst activity from 88% to 80%. This was due to the fact that carbon deposition only occurred on the surface of the catalyst that was more exposed to gasification.

2.11.4.3 *Regeneration of Heterogeneous Catalyst by Hydrogenation*

Regeneration of heterogeneous catalysts by hydrogenation entails the use of hydrogen gas (H₂) to eliminate fouling materials or restore the catalyst's active sites. This approach is especially effective for catalysts used in petrochemical refining and ammonia manufacturing, where foulants such as coke, sulphur, and metals might deactivate the catalyst.

Coke removal is also possible using non-oxidative processes, such as pyrolysis with inert gas (Fau, Gascoin and Steelant 2014; Zhou *et al.* 2020a) and hydrocracking with hydrogen or alkanes (Chandler, Seufitelli and Resende 2020; Pisarenko *et al.* 2022). Schulz and Wei (1999) observed that coke deposited on HZSM-5 catalysts could be removed completely by inert gas treatment at 287 °C, but only partially at higher reaction temperatures of 327–377 °C. Magnoux, Cerqueira and Guisnet (2002) discovered that N₂ treatment could partially remove coke deposited on USHY catalysts, resulting in an increase in residual coke aromaticity and catalytic deactivation. In other words, whether the catalytic activity can be recovered or not following treatment with inert gas at high temperature remains uncertain.

2.11.5 Mechanisms and Surface Interactions in Heterogenous CO₂ Reduction

In heterogeneous CO₂ reduction, there are various mechanisms governing the surface interactions of the reactants (Figure 2.25). The Langmuir-Hinshel-wood model proposes that CO₂ and H₂ react on the surface of the catalysts (solid state), generate intermediates and products, and then desorb from the surface of the catalyst (Hagen 2015; Rothenberg 2017). The Eley-Rideal model states that only one of the starting materials is adsorbed on the surface, while the other reacts directly with the adsorbed species from the gas phase (Hagen 2015; Rothenberg 2017).

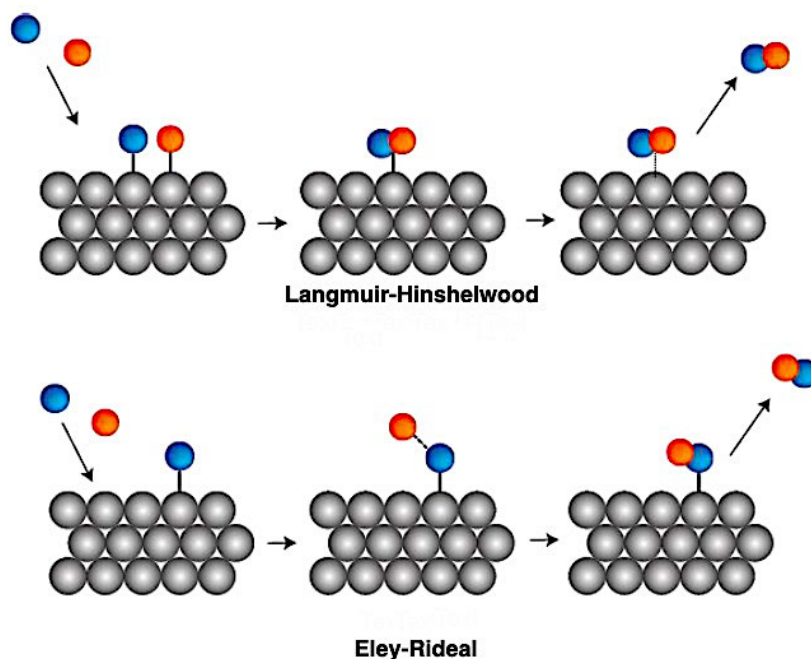


Figure 2-25. Top: Representation of the Langmuir-Hinshelwood mechanism in heterogeneous catalysis. Bottom: Representation of the Eley-Rideal mechanism in heterogeneous catalysis. Both concepts are redrawn from literature (Rothenberg 2017).

2.11.5.1 *Physisorption and Chemisorption*

In both reaction processes, adsorption is essential because at least one of the starting components must be adsorbed on the surface of the catalyst. Adsorption can be further classified into physisorption and chemisorption depending on the interaction intensity between adsorbate and catalyst. Physisorption is a weak interaction between the adsorbate and the surface of the catalyst (Králík 2014; Hagen 2015). The bonding is comparable to Van der Waals interactions with a low heat of adsorption ($10 - 40 \text{ kJ mol}^{-1}$). Chemisorption, on the other hand, has a relatively high heat of adsorption (about $20 - 400 \text{ kJ mol}^{-1}$) (Králík 2014). Due to the interaction's strength, it can be defined as a normal chemical bond between the species and the surface of the catalyst. Unlike physisorption, chemisorption frequently results in the dissociation of molecules on the surface. Chemisorption is typically an exothermic reaction (Králík 2014; Hagen 2015).

2.11.5.2 *Hydrogen Dissociation*

Hydrogen is one of the molecules that must be adsorbed onto the surface of a heterogeneous catalyst for CO_2 reduction. Hydrogen's dissociation is required for its chemisorption onto a catalyst (Chen, Giordano and Pacchioni 2013). On nonreducible supports like MgO or ZrO_2 ,

the dissociation of H_2 is observed to be heterolytic. In this instance, the proton is adsorbed by the oxygen anion, whereas the hydride ion is adsorbed on the metal (Tosoni *et al.* 2018).

When a pure metal or a reducible transition metal oxide is considered, the process differs. The dissociation is homolytic in these two cases. The dissociation results in the formation of two OH groups in the case of a reducible transition metal oxide. While two adsorbed hydrogen atoms are produced on a metallic surface (Chen, Giordano and Pacchioni 2013).

2.11.5.3 CO_2 Activation by Adsorption

More attention needs to be given to the adsorption of CO_2 on the catalyst, especially in a Langmuir-Hinshelwood process where all starting materials are initially adsorbed on the catalyst surface. The CO_2 is activated in the initial phase of CO_2 adsorption by electron transfer from the surface to the molecule. The Walsh diagram (Figure 2.26) (illustrating this geometry shift) is the result of this electron transfer (Iota and Yoo 2001).

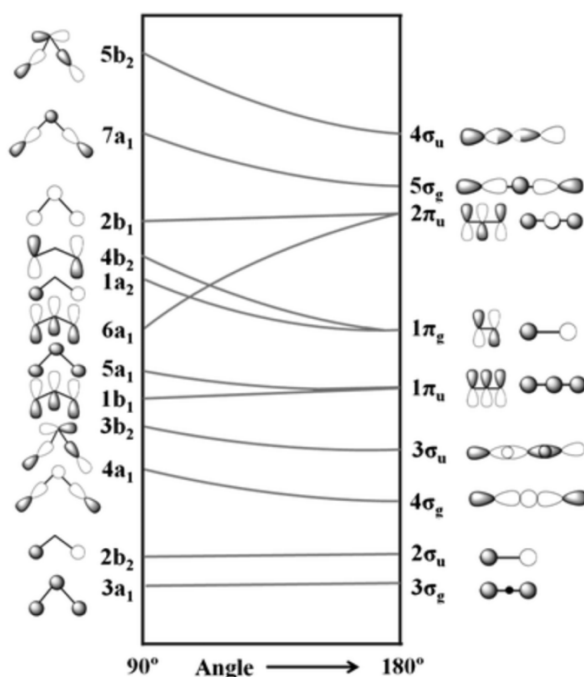


Figure 2-26. Walsh diagram of carbon dioxide. The left axis represents the orbital energies for a bent CO_2 molecule, while the right axis represents the orbital energies for a linear CO_2 molecule. Adapted from (Freund and Roberts 1996).

A neutral CO_2 molecule possesses 16 valence electrons, with two degenerate molecular orbitals ($1\pi_g$) serving as the HOMO (highest occupied molecular orbital). When CO_2 is activated, the extra electron occupies the previously LUMO (lowest unoccupied molecular orbital) state. In

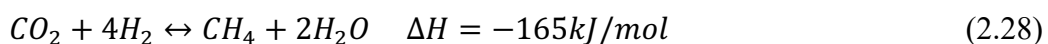
linear geometry, the additional electron is located in the $2\pi_u$ orbital, which is energetically superior to the corresponding orbital in the bent state ($6a_1$). Thus, the addition of an electron/activation of CO_2 results in a structural transformation from a linear to a bent molecule (Freund and Roberts 1996).

2.11.6 CO_2 Reduction

The formation of numerous species contributes to the reduction of CO_2 . These include higher hydrocarbons, simple C_1 species like CH_4 or CH_3OH , and many more (Fierro 1993). As previously stated, the sole aim of the present study is to convert CO_2 into potential renewable energy carriers such CH_4 , CH_3OH , and CH_3OCH_3 .

2.11.6.1 CO_2 Methanation

The methanation of CO_2 is a heterogeneously catalyzed reaction that proceeds in the presence of a transition metal catalyst in accordance with the overall reaction equation.

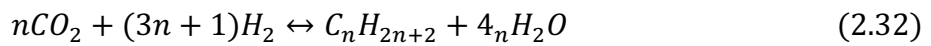


Nearly all transition metals display methanation activity, with the following order of active materials: $\text{Ru} > \text{Ni} > \text{Co} > \text{Rh}$ (Tsiotsias *et al.* 2020a; Xu *et al.* 2021a). Ru is the most reactive metal, but it is extremely scarce and therefore quite expensive. Although Fe has a high hydrogenation activity, it has a low selectivity for CH_4 . Ni is the preferred catalytic metal due to its abundance, good activity at low prices, and strong selectivity for CH_4 (Kawi *et al.* 2015; Seo 2018). Promoters can be added to the catalyst to boost the stability against sintering (e.g., MgO) (Jin, Li and Liang 2021) or to alter the selectivity (e.g., K) (Tsiotsias *et al.* 2020b). A promising system is the bimetallic NiFe catalyst, which was discovered through first-principles-based catalyst screening investigations and experimentally demonstrated to be more active than the pure metals (Nørskov *et al.* 2009; Liu *et al.* 2020a).

Typically, the active metal is dispersed on a porous ceramic support with a large surface area to produce small metal crystals with a large metal surface area. SiO_2 , CeO_2 , and Al_2O_3 are commonly used as support materials (Águila, Gracia and Araya 2008; De Piano *et al.* 2024). In addition to the dispersion of the active metal, the support can be of great importance for the methanation mechanism (Li *et al.* 2022b). To form various carbonates and bicarbonates, CO_2 is adsorbed on basic adsorption sites on the support, which can be found on $\gamma\text{-Al}_2\text{O}_3$ or CeO_2 .

(Proaño *et al.* 2019; Alkhoori *et al.* 2023). The activity of CO₂ methanation on Ni catalysts with basic sites on the support is usually higher than that of the same catalyst on an acidic support, suggesting that the support or the metal/support interface is involved in the mechanism (Shen *et al.* 2020).

The CO₂ methanation is a highly exothermic reaction, with an enthalpy of standard reaction $\Delta R H^\circ = -164.7 \text{ kJ mol}^{-1}$. It is bound by thermodynamic equilibrium constraints, which necessitate low temperatures for high CH₄ conversion and selectivity (De Piano *et al.* 2024). Side reactions include (reverse) water-gas-shift reaction (reaction 2), CO methanation (reaction (Altomare *et al.*)), Boudouard reaction (reaction (Altomare *et al.*)), and n-alkane chain development (reaction 5), with C₂H₆ and C₃H₈ as the primary components [12, 32]. The average operating range for CO₂ methanation is between 573 to 823K and 1 to 100 bar (Kreitz 2021; Spennati, Riani and Garbarino 2023).

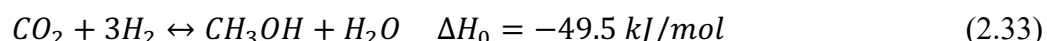


There are numerous reactors designs available, including fixed-bed (adiabatic, polytropic), fluidized-bed, and three-phase (Rönsch *et al.* 2016; El Sibai, Rihko Struckmann and Sundmacher 2017). To prevent the formation of hotspots, all reactor designs (except for adiabatic reactors) emphasize the removal of reaction heat. Hotspots must be avoided for two reasons: safety and security. At temperatures over 823K, the catalyst begins to deactivate due to coke formation (Schueth 2011) and metal crystal sintering (Hardiman 2007). Due to thermodynamic equilibrium, high temperatures lower the potential for conversion and promote the formation of CO (Qi *et al.* 2022). In the fluidized-bed and three-phase reactors, it is possible to obtain almost isothermal conditions, but these reactors have other challenges, such as catalyst attrition in the fluidized bed and liquid phase stability (Grace 2016). Fixed-bed reactors with a tube bundle layout that are cooled by thermal oil or molten salt are the most common type utilized in industry (Jiang *et al.* 2015). Fixed-bed reactors typically produce a polytropic profile with a distinct hot spot at the reactor entry (Matthischke, Roensch and Güttel 2018). Microstructured fixed-bed reactors that increase heat and mass transfer due of their shorter

characteristic length are extremely promising (Commence *et al.* 2005). These microstructured reactors are best suited for decentralized applications and are more likely to be operated transiently.

2.11.6.2 *CO₂ Reduction to Methanol*

The conversion of CO₂ to CH₃OH is a potential alternative to CO₂ methanation (Saravanan *et al.* 2021).



The weak driving force caused by the low heat of the reaction makes the reaction more difficult. In accordance with Le Chatelier's concept, "the reaction yield can be increased by increasing the pressure" (Wang *et al.* 2011). Therefore, CH₃OH synthesis from CO₂ is carried out on a Cu/ZnO/Al₂O₃ catalyst at temperatures between 200 and 300 °C and pressures between 50 and 100 bar. Although this catalyst is used in industry (Behrens *et al.* 2012; Studt *et al.* 2015), the exact mechanism and effect of ZnO are not yet well known (Studt *et al.* 2015). It is generally accepted that copper (Cu) is the active phase of such a catalyst and that the Cu area is proportional to the activity of the catalyst (Behrens *et al.* 2012; Studt *et al.* 2015). It appears that the introduction of ZnO serves several purposes. Zinc oxide is a structural promoter that, according to scientific studies, leads to well-dispersed copper particles. In addition, there seems to be a strong interaction between copper and zinc (Cu/Zn alloy formation, strong interaction with the metal support), which also affects the catalytic activity (Behrens *et al.* 2012; Studt *et al.* 2015). Hansen *et al.* (2002) have shown that a Cu/ZnO catalyst changes during reaction conditions, which emphasizes the need for *in situ* measurement methods. A temperature-programmed reduction (TPR) study of a CuO/ZnO catalyst showed that ZnO not only acts as a dispersant but also enhances the reduction of Cu. The activation energy (E_a) for the reduction of CuO is always lower when ZnO is present in the system (e.g., E_a for the reduction of pure CuO is 84 kJ mol⁻¹ and for CuO - ZnO mixtures is 77 kJ mol⁻¹) (Fierro *et al.* 1996).

Porosoff, Yan and Chen (2016) reported in their review that pressures as high as 360 bar were necessary for a Cu/ZnO/Al₂O₃ catalyst to get a comparably high reaction yield (pace-time yield of 7729 g_{MeOH} kg⁻¹_{cat} h⁻¹). New catalysts or elaborated reaction principles must be developed because these high pressures make the economically unfavourable methanol synthesis from CO₂ possible. Sorption-enhancement is one method that might be improved. By modifying the

sorbent, sorption enhancement can be used to synthesize methanol and successfully enhance its catalytic system.

Olah, Goeppert and Prakash (2011) introduced the idea of the "methanol economy," which has been used to illustrate the significance of methanol as a future energy source. The fundamental principle of this concept is that CH_3OH will eventually replace present fossil fuels as a CO_2 -neutral fuel, ensuring a closed carbon cycle (see Figure 2.27).

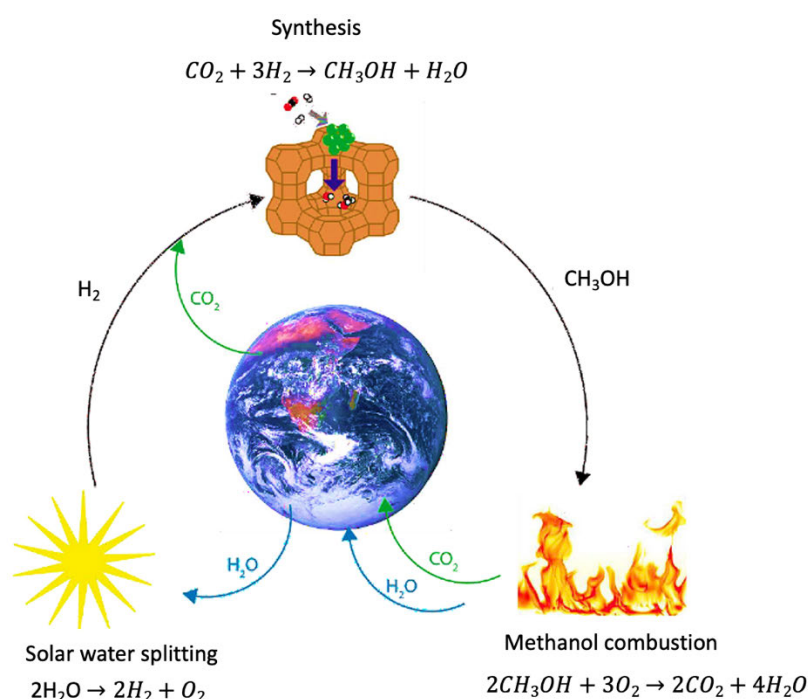
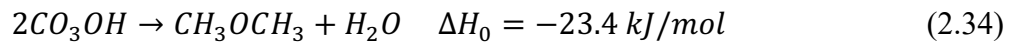


Figure 2-27. Closed carbon cycle with methanol based on the idea of (Olah, Goeppert and Prakash 2011).

According to Olah, Goeppert and Prakash (2011), CH_3OH and dimethyl ether ($\text{C}_2\text{H}_6\text{O}$) would be ideal replacements for gasoline, diesel fuel, and natural gas, enabling them to serve as, for example, future transportation fuels. Important to note is that the methanol fuel cell permits the generation of power from methanol. It is essential to realize that the concept of the methanol economy takes into account molecules that can be synthesized from CH_3OH and $\text{C}_2\text{H}_6\text{O}$ in addition to methanol and dimethyl ether. For example, MTO (methanol to olefins) permits CH_3OH to be converted to ethylene (C_2H_4) or propylene (C_3H_6). In addition, CH_3OH is a critical starting material that enables the synthesis of numerous compounds, including polymers, adhesives, and formaldehyde (Liu *et al.* 2021a; Malik, Abatzoglou and Achouri 2021).

2.11.6.3 *CO₂ Reduction to Dimethyl Ether*

Dimethyl ether (C₂H₆O) can be synthesized from CH₃OH by condensation, as shown in the following equation (Catizzzone *et al.* 2017):



Following the initial CO₂ reaction, the entire reaction equation yields (He and Liu 2017):



A bifunctional catalyst is needed to produce C₂H₆O from CH₃OH. Cu/ZnO/Al₂O₃ and zeolites could be used to create a bifunctional catalyst that converts CO₂ to CH₃OH (for CH₃OH to CH₃OCH₃) (Catizzzone *et al.* 2017).

According to equation (2.35), a process typically favoured at low temperatures is the conversion of CH₃OH to CH₃OCH₃. Pressure changes do not affect the dehydration of CH₃OH because the number of moles remains constant, unlike CH₃OH synthesis from CO₂, which requires high pressures for reasonable yields (Catizzzone *et al.* 2017). Al₂O₃ is used as a catalyst for the reaction since it works well at acidic sites. Since adsorption of water is considered to poison the catalyst, γ -Al₂O₃ primarily adsorbs the resulting water, thus deactivating the catalyst. (Catizzzone *et al.* 2017; ZADAM 2021). Since C₂H₆O has a higher calorific value than CH₃OH and is nontoxic and environmentally benign, interest in it as a potential storage material is growing (Yoo *et al.* 2006; Serov and Kwak 2009).

Furthermore, DME is considered to have similar properties as LPG (liquefied petroleum gas) so the infrastructure (land- and ocean-based) existing for LPG could be used with minor modifications. Thus, the transition from natural gas to DME is not time-consuming, and significant cost savings are possible. Comparatively environmentally friendly to other fuels, DME combustion has low SO_x and NO_x emissions and is devoid of soot (Styring, Dowson and Tozer 2021).

2.11.7 Reaction Pathways in CO₂ Hydrogenation to CH₄ and CH₃OH

There are a number of possible pathways by which the conversion of carbon dioxide to CO, CH₃OH, and CH₄ might occur, some of which are shown in Figure 2.28.

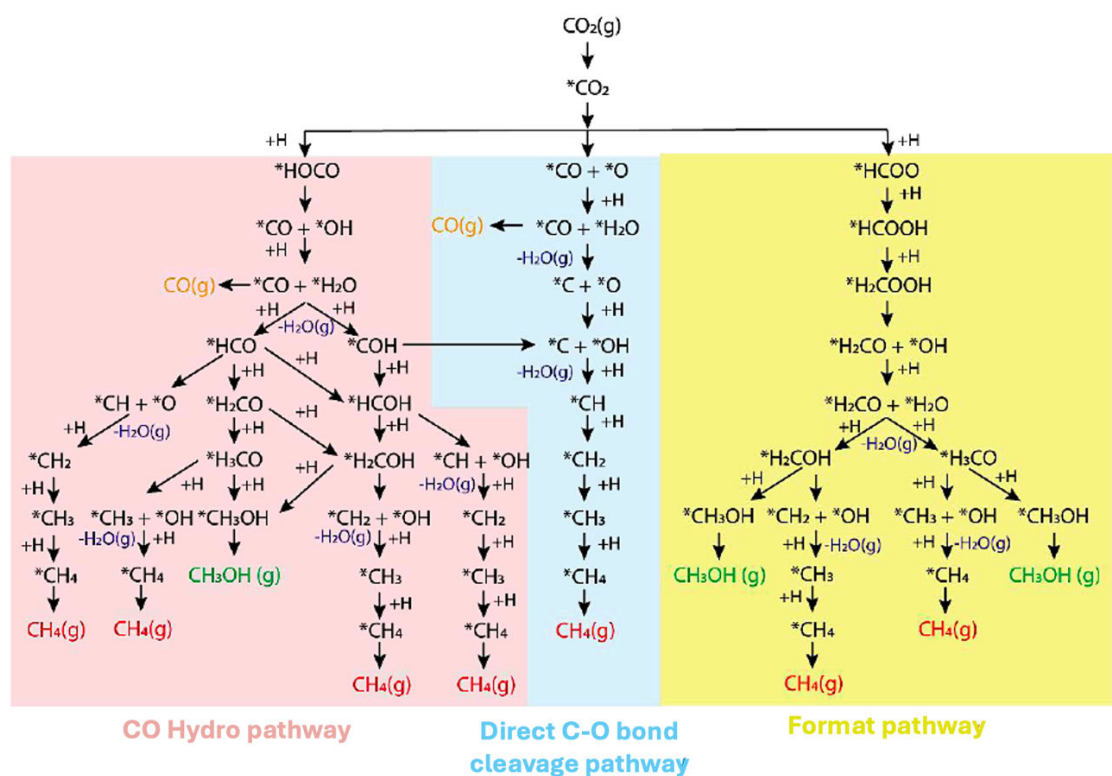


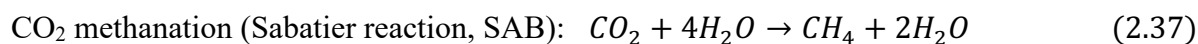
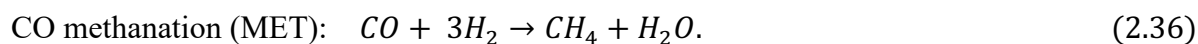
Figure 2-28. Summary of possible reaction pathways for the hydrogenation of carbon dioxide to methane and methanol. Adapted from (Kattel, Liu and Chen 2017).

Figure 2.28 depicts the complexity of CO₂ reduction to C₁ species (Kattel, Liu and Chen 2017). Taking into account the production of higher carbon species or the adsorption of different intermediates at different sites on the catalyst can adversely affect the complexity depicted in Figure 2.28.

It becomes considerably more complicated when the detailed reaction mechanism is taken into account in addition to the reaction intermediates and their adsorption sites. The reverse water gas shift reaction over nickel, for instance, can proceed in one of three methods, including over HOCO* or by directly cleaving the bond (Kattel, Liu and Chen 2017). CO can be formed using the Eley-Rideal, Langmuir-Hinshelwood, or hot atom processes, according to (Lin, Stocker and Schatz 2017). The simple conversion of CO₂ to CO, together with the potential paths and mechanisms involved, demonstrates how challenging a detailed analysis can be.

2.11.8 Thermodynamics of CO₂ Conversion to Methane

The stoichiometry and standard heats of reaction for the hydrogenation of CO and CO₂ to produce methane and by-product water are given in Equations 2.36 and 2.37:



Since both reactions are highly exothermic and result in a decrease in the number of molecules, they are favourable at low temperatures and high pressures. The water-gas shift (WGS) process, which converts CO into CO₂ or vice versa, connects the two methanation reactions:

Consequently, the CO₂ methanation is commonly viewed as a mixture of the reverse of the WGS reaction and the CO methanation reaction, which is thermodynamically accurate. The reverse reaction of methanation is known as methane steam reforming, and it is one of the most important industrial processes to produce synthesis gas and hydrogen. The Boudouard reaction, in which two CO molecules disproportionally transform into carbon dioxide and solid carbon, is another crucial reaction in the syngas system.

The thermodynamic conditions, or temperature, pressure, and reaction system composition, determine the direction in which a specific equilibrium reaction will proceed. The tendency of a thermodynamical system to decrease its energy serves as the driving force for chemical reactions. In case of constant temperature and pressure, the respective change in Gibbs free energy due to given reaction ΔG_R is a quantitative measure for its thermodynamic feasibility. ΔG_R is linked to the change in enthalpy ΔH_R and entropy ΔS_R via the relationship:

Figure 2.29 depicts the change in Gibbs free energy as a function of temperature for the four aforementioned chemical reactions. As it is evident from the negative values of ΔG_R in the low temperature range, CO and CO₂ methanation, water-gas shift and carbon formation give a decrease in free energy and so are thermodynamically favourable. ΔG_R increases with increasing temperature and becomes positive at approximately 600 °C, indicating that at high temperatures the respective reverse reaction is favoured. As indicated by the steady slope of each curve across the entire temperature range, the change in entropy and enthalpy resulting from each reaction remains relatively constant.

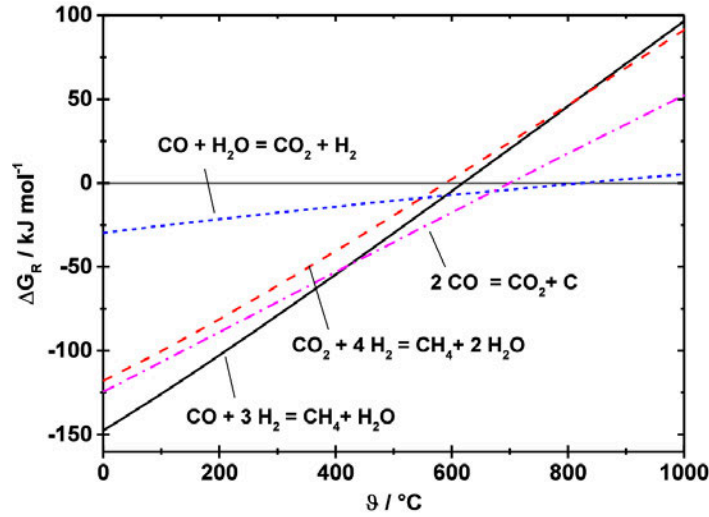


Figure 2-29. Gibbs free energy change due to reaction for the CO methanation, CO₂ methanation, water-gas shift and Boudouard reaction as function of temperature. Calculated from ideal gas phase thermochemistry data taken from (Risch 2021).

As indicated by the most negative value of ΔG_R , the hydrogenation of CO to CH₄ and H₂O is the most favourable reaction at temperatures below 400 °C. If water is present in a system, for instance as a byproduct of methanation, the water-gas shift reaction of CO₂ to CO₂ is likely to occur simultaneously. If CO₂ is employed as a feedstock, the reaction with hydrogen to methane is thermodynamically much more favourable than the reverse water-gas shift reaction, as the positive change in Gibbs free energy for the latter reaction results in an increase in the total energy of the system. At temperatures above approximately 600 °C, the situation reverses, and CO formation becomes more favourable. The formation of carbon through the dissociation of CO is most likely to occur between 400 and 700 °C, where this reaction delivers the highest change in free energy.

The equilibrium constant $K_{eq,j}$ and the change in the Gibbs free energy of a particular reaction j are related by:

$$\Delta G_{R,j} = -RT \ln K_{eq,j} \quad (2.38)$$

The equilibrium constant of a particular gas phase reaction j is determined by the product of the activity a_i of the molecules participating in the reaction multiplied by the relevant stoichiometric coefficients $\nu_{i,j}$. For the gas phase, the activity is determined by dividing the fugacity f_i by the reference pressure p^+ ($= 1 \text{ atm}$).

$$K_{eq,j} = \prod_i a_{i,eq}^{\nu_{i,j}} = \prod_i \left(\frac{f_{i,eq}}{p^+} \right)^{\nu_{i,j}} \quad (2.39)$$

At low pressure and temperatures well below the boiling point, a gas mixture can be considered ideal, and the fugacity is roughly equal to the partial pressure p_i . Therefore, the equilibrium constant can be expressed as:

$$K_{eq,j} = \prod_i \left(\frac{p_{i,eq}}{p^+} \right)^{V_{i,j}} = \left(\frac{p}{p^+} \right)^{\sum_i V_{i,j}} \frac{\prod_i y_{i,eq}^{v_{i,j}}}{k_{y,eq,j}} \quad (2.40)$$

Where $K_{y,eq,j}$ is the equilibrium constant expressed in terms of the molar fraction of the gas phase, y_i . The pressure dependence of the reaction equilibrium is determined by the factor $\left(\frac{p}{p^+} \right)^{\sum_i V_{i,j}}$.

Figure 2.30 illustrates the equilibrium gas phase composition as a function of temperature for the feed of stoichiometric mixtures of CO or CO₂ with H₂ at atmospheric pressure. It also shows how temperature and pressure affect the degree of conversion and selectivity to CH₄ and how these variables are affected by each other. It is assumed that carbon formation is suppressed kinetically and therefore not taking place. The curves were numerically generated using the Gaseq software by minimizing the total Gibbs free energy while adhering to the restrictions of mass conservation (Risch 2021).

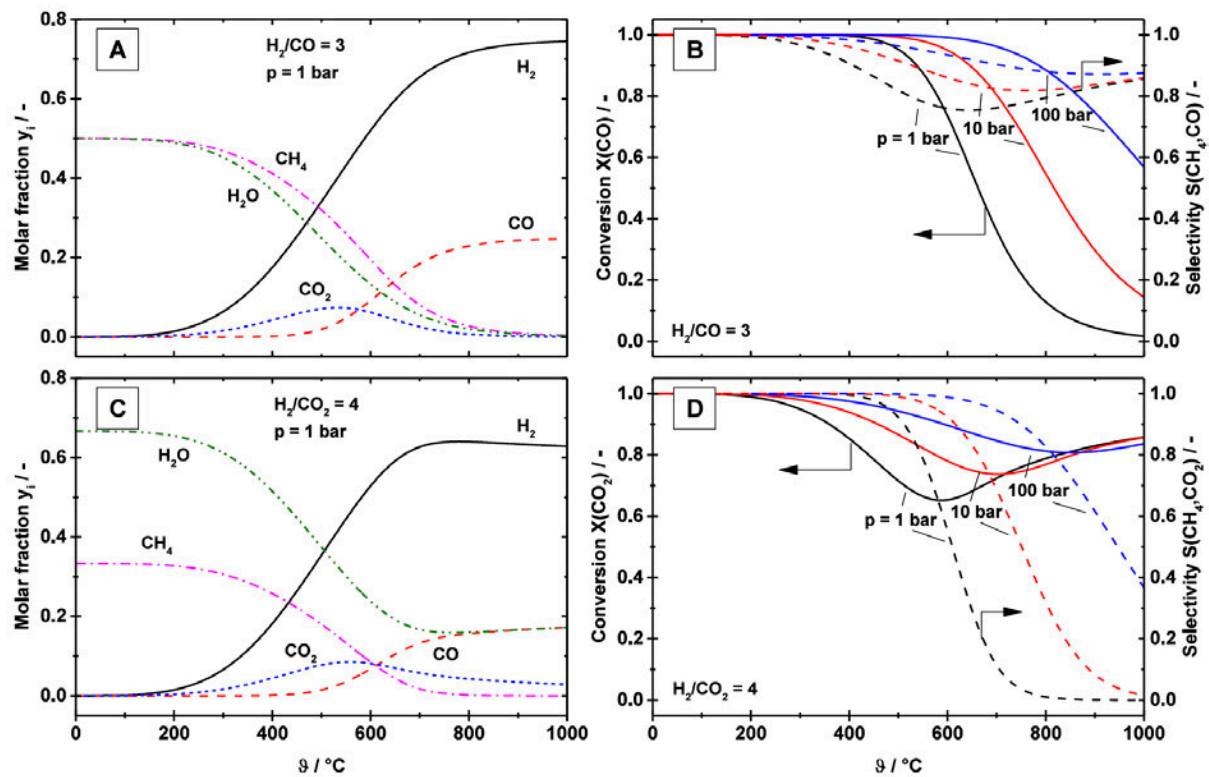


Figure 2-30. Equilibrium composition, degree of conversion and selectivity to CH₄ for feed of pure stoichiometric mixtures of H₂/CO (A, B) and H₂/CO₂ (C, D). Adapted from (Kern 2019).

According to the composition curves, the most stable products for both carbon oxide feeds at low and high temperatures, respectively, are CH_4 and H_2O and H_2 and CO . A sizable portion of CO_2 may also be generated in the intermediate region of roughly 300 - 800 °C. These patterns lead to various conversion/selectivity characteristics for the two carbon oxides: At atmospheric pressure, a complete conversion of CO is thermodynamically possible up to around 400 °C; after that, the conversion steadily decreases until it reaches values below 0.1 at temperatures above 800 °C. Because CO_2 is produced as a byproduct at temperatures above around 200 °C, the thermodynamic selectivity for methane already starts to fall below 0.99. The selectivity rises again to 0.90 at 1000 °C as CO_2 formation becomes less possible, passing a minimum of 0.75 at roughly 650 °C. The curves' pattern is reversed for CO_2 hydrogenation. Only incomplete conversion is possible at around 200 °C, with a minimum of about 0.6 at 600 °C. In contrast, the selectivity for CH_4 is greater than 0.99 at temperatures below about 400 °C and zero at temperatures above about 800 °C as a result of CO formation.

An increase in pressure results in a noticeable shift to higher temperatures, as shown by the extra curves for 10 and 100 bar, and it also raises the possible degree of conversion and theoretical selectivity. According to the stoichiometric coefficients $\sum_i \nu_{ij}$ the hydrogenation of both carbon oxides to methane results in a net consumption of two molecules per converted CO_x molecule, or -2. Accordingly, the equilibrium constant $K_{y,\text{eq},j}$ of both methanation processes is pressure dependent by p^2 , favouring the conversion of CO_x to CH_4 at higher pressures. The water-gas-shift reaction, in contrast, is pressure independent, i.e. $\sum_i \nu_{ij}$ is 0. As a result, pressure also causes the selectivity to CH_4 to rise. On the other hand, because the partial pressure of the reactants is dropped by diluting the feed with inert gas, conversion and selectivity are reduced.

The possible degree of conversion is generally unaffected by variations in the H_2/CO ratio, while the selectivity to CH_4 rises as H_2 content does. With increasing H_2 content, the equilibrium conversion for CO_2 hydrogenation increases at a specific temperature and pressure. Clearly, no complete conversion is achievable under sub-stoichiometric circumstances. With a higher H_2/CO_2 ratio, the selectivity to CH_4 only slightly improves. Water vapor addition decreases methane selectivity because it speeds up the water-gas shift process. When both CO and CO_2 are present in the feed, it is preferable that CO be reacted to CH_4 at low temperatures while CO_2 is converted to CO at high temperatures.

The complexity of the reaction system rises when the creation of solid carbon is also taken into account. More information about the effects of the reactant ratio, feed dilution with inert gas, co-feed of CH₄, H₂O, and mixed feed of CO and CO₂ on the reaction equilibrium is provided in the literature, for example in (Gao *et al.* 2012). The system's C/H/O ratio has a significant impact on the thermodynamic stability of carbon (Baumhagl 2014). Carbon is stable between roughly 450 and 800 °C starting with a stoichiometric H₂/CO mixture at atmospheric pressure. With increasing pressures, this window diminishes, and above around 10 bar, carbon deposition is essentially suppressed. However, even at high pressures, carbon formation is still possible in a wide temperature range between 250 and 850 °C if the H₂/CO-ratio is reduced below approximately 2.6-2.8 (Mills and Steffgen 1974). While CH₄ addition has the opposite effect, adding steam to the feed helps in reducing the carbon stability.

2.12 CO₂ Methanation Reaction Kinetics and Reactor Designs

2.12.1 CO₂ Methanation Reaction Kinetics

In reactor design and the field of chemical engineering in general, closed-form kinetic methods are used to predict the performance of a reactor (Güttel 2013). The power-law protocol is the simplest kinetic equation, which for the methane production rate r_{CH_4} is:

$$r_{CH_4} = k c_{H_2}^\alpha c_{CO_2}^\beta \quad (2.41)$$

where the rate constant k and exponents are regression-fit to match steady-state kinetic measurements of experimental data. Weatherbee and Bartholomew (1982) provide a summary of CO₂ methanation examples using this method. Using a Langmuir- Hinshelwood-Hougen-Watson (LHHW) rate expression, which is derived from an underlying mechanism, is a physically sound method. The LHHW method is derived from one potential pathway for CH₄ production, assuming the most abundant surface intermediates (MASIs) and equilibrated and rate-determining stages (RDS). The LHHW ansatz devised by Koschany, Schlereth and Hinrichsen (2016) for the CO₂ methanation is represented by Equation (2.41).

$$r_{CH_4} = \frac{k P_{H_2}^{0.5} \left(1 - \frac{P_{CH_4} P_{H_2O}^2}{P_{CO_2} P_{H_2}^4 K_{eq}} \right)}{\left(1 + K_{OH} \frac{P_{H_2O}}{P_{H_2}^{0.5}} + K_{H_2} P_{H_2}^{0.5} + K_{mix} P_{CO_2}^{0.5} \right)^2} \quad (2.42)$$

When an equilibrium component is included in the numerator and adsorption terms are contained in the denominator. By assuming different processes, MASIs or RDSs (Rate-Determining Surface Species) (Güttel 2013; Guo *et al.* 2022), many LHHW expressions are

typically developed. Then, all these expressions are regressed by fitting the rate constants and their temperature dependency to steady-state data. Considered to include the correct mechanism is the approach that describes the experiments the best. Numerous studies (Koschany, Schlereth and Hinrichsen 2016; Vazquez *et al.* 2018; Onrubia-Calvo *et al.* 2022; Quindimil *et al.* 2022) have developed LHHW methods for CO₂ methanation and CO methanation. Typically, multiple LHHW kinetics based on distinct mechanisms and assumptions (MASI, RDS) can accurately represent the same set of data. Therefore, it is impossible to differentiate between the underlying mechanisms (Güttel 2013). Power-law and LHHW techniques can be categorized as postdictive kinetics, and they are frequently ill-suited to generate predictions for alternative settings or provide insights into the actual mechanism (Green 2020; Kreitz 2021). Nevertheless, reaction kinetics based on the LHHW technique are utilized most frequently in transient reactor simulation studies or in the design of catalysts suited for dynamic operation (Ibrahim and Idem 2007; Tripodi *et al.* 2017). However, extrapolating these closed-form rate expressions outside their regression range can result in error (Ibrahim and Idem 2007; Tripodi *et al.* 2017). This can be especially problematic during transient operation, when significant concentration gradients and total dropouts of a single reactant are to be anticipated. In addition, the coverage of adsorbates varies slightly during transients, which challenges the idea that a single MASI or RDS can be applied to all potential operating conditions. Moreover, adsorbates are stored on the catalyst's surface as well as on the basic sites of the support for CO₂, as shown by several experimental experiments for both CO and CO₂ methanation (Burattin, Che and Louis 2000; Saib, Claeys and Van Steen 2002; Koirala, Pratsinis and Baiker 2016). Closed form rate expressions fall short of describing this reservoir, and as a result, they are unfit to characterize the catalyst's transient behaviour (Burattin, Che and Louis 2000). Microkinetic models, which consider all fundamental steps of a process, must be used in conjunction with a multiscale modelling approach in order to accurately describe the behaviour of the catalyst and reactor during transient operation (Chen *et al.* 2017). Therefore, understanding the mechanism of CO₂ methanation is initially important. First-principles approaches can be used to access the binding energy of adsorbates or the saddle point of transition states on a metal surface using density functional theory (DFT) calculations, or surface science methods combined with operando methods (Alfonso 2008; Goodwin *et al.* 2018; Ewald and Hinrichsen 2019). DFT techniques have already been used to examine the mechanism of methanation (Ren *et al.* 2015; Xu *et al.* 2021b). The formate, carboxyl, and redox/carbide routes are three potential pathways that have been addressed in the literature although the mechanism for the methanation of CO₂ has not yet been determined

(Frontera *et al.* 2017; Kreitz, Wehinger and Turek 2019). The activation of the CO₂ molecule differs between these pathways (see Figure 2.31a). The formate pathway activates CO₂ at the C atom, whereas the carboxyl pathway activates CO₂ at the O atom. In the redox/carbide route, CO*2 spontaneously dissociates into CO*. It is difficult to interpret the methanation mechanism because the various channels are not distinct systems and there are numerous potential connections between them.

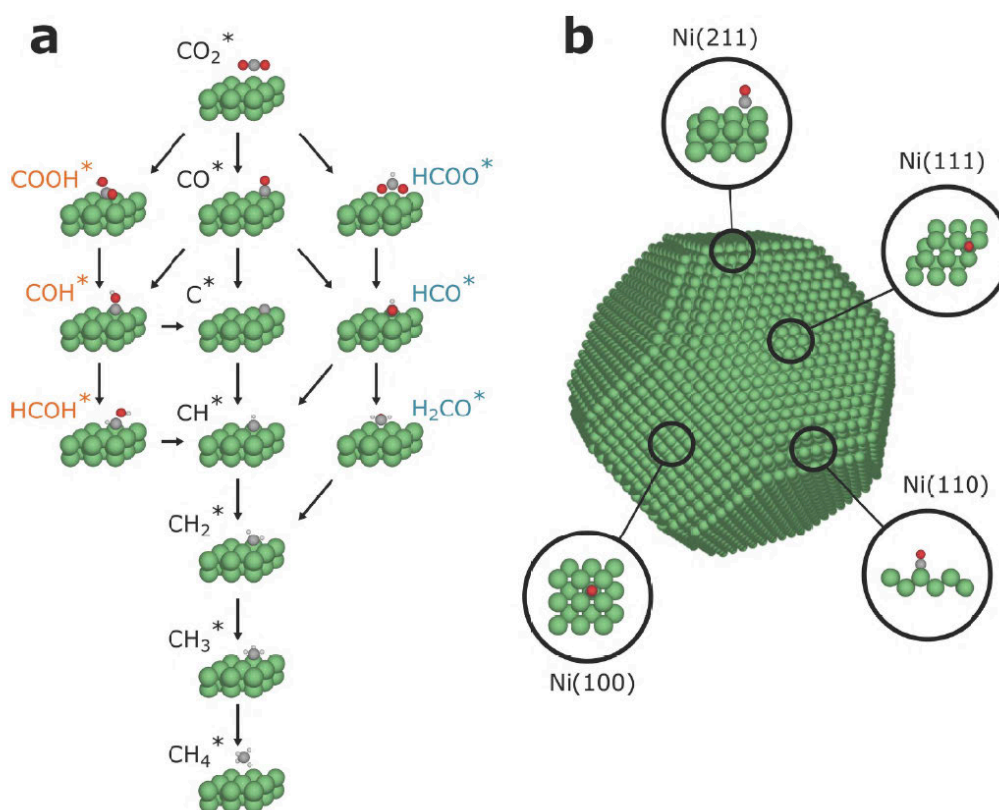


Figure 2-31. (a) Schematic drawing of the discussed reaction network for the CO₂ methanation: the formate path (orange, left), the redox path (black, centre), and the carboxyl path (blue, right). All adsorbates are shown in their most stable position on the Ni(111) surface. Adapted from Vogt *et al.* [100] (b). Equilibrium shape of a Ni crystal with 16,000 atoms and a size of 6.8 nm consisting of the Ni(111), Ni(100), Ni(110), and Ni(211) facet created via Wulff construction. Adapted from (Kreitz 2021).

The active site for methanation is another topic of discussion. The four most essential facets of a Ni crystal are (111), (100), (110) and (211) (see Figure 2.31b), and their catalytic activity has been the subject of debate. (111) and (100) are terrace sites with the highest proportions of the equilibrium shape. Steps (211) and an open facet (110) separate the terrace sites from one another (Kreitz 2021). Beierlein *et al.* (2019) concluded from CO₂ methanation tests on Ni/-Al₂O₃ catalysts that it is a structure-insensitive reaction and should proceed on the terrace sites. In contrast, Vogt and Weckhuysen (2019) report that the Ni/SiO₂ system is sensitive to its structure. Similar CO methanation primarily takes place at Ni(211) step sites (Vogt *et al.* 2019).

2.12.1.1 Kinetic Models

The mechanism of CO₂ methanation has been studied in great detail, but the kinetic model is still up for debate (Garbarino *et al.* 2014). Different hypothesized processes have been made as a result of various experimentally applied reaction conditions, the types of assumed and measured reaction intermediates, the assumed rate-determining step, the methane formation process, and the interpretation of kinetic results (Koschany, Schlereth and Hinrichsen 2016).

Kinetic models often ignore the effect of the reverse water gas shift (RWGS) because they usually consider only CO₂ methanation for their kinetic studies. Along with the CO₂ methanation rate, an appropriate rate for the RWGS must also be specified. As far as the author is aware, only a handful of authors have published RWGS rates in combination with methanation rates. The only examples of integrating RWGS or WGS in the literature are provided by Kopyscinski *et al.* (2010) and Zhang *et al.* (2013b) for CO methanation and by Xu and Froment (1989) for steam reforming. Without the assumption of a rate-determining step, the kinetic techniques described in the literature use a simple power law to describe the reactions. It has also been used to calculate rates using the complicated Langmuir-Hinshelwood (L-H) rate expression, which considers the surface coverage of the species involved. The power law cannot be applied to all experimental settings, while the L-H models include a large number of kinetic parameters, including adsorption constants for some or all adsorbed species (Kopyscinski 2010). Ni/SiO₂, Ni/Cr₂O₃, and Ni/Al₂O₃ are just a few examples of the many catalysts for which complicated mechanistic models have been established (Zhao and Lercher 2013). The models published in the literature are summarised in Table 2.13.

Table 2.13. Kinetic models for CO₂ methanation on nickel-based catalyst.

Kinetic model equation	Catalyst Experimental conditions		Apparent E _A (kJ/mol)	Ref.
$r_{CH_4} = \frac{k \cdot p_{CO_2}^{0.33} \cdot p_{H_2}^{0.5}}{(1 + K_{CO_2} \cdot p_{CO_2}^{0.5} + K_{H_2} \cdot p_{H_2}^{0.5} + K_{H_2O} \cdot p_{H_2O})^2}$	Ni/Al ₂ O/La ₂ O ₃	240 – 320 °C 1 bar	72.5	(Kai, Takahashi and Furusaki 1988)
$-r_{CH_4} = \frac{k \cdot p_{CO_2}^{0.33} \cdot p_{H_2}}{(1 + K_{CO_2} \cdot p_{CO_2} + K_{H_2} \cdot p_{H_2} + K_{H_2O} \cdot p_{H_2O})}$	Ni	250 – 350 °C	n/a	(Inoue and Funakoshi 1984)
$r_{CH_4} = \frac{k \cdot p_{CO_2} \cdot p_{H_2}}{(1 + K_{H_2} \cdot p_{H_2} + K_{CO_2} \cdot p_{CO_2})}$	58 wt% Ni/SiO ₂	275 – 320 °C 17 bar	n/a	(Chiang and Hopper 1983)
and				
$r_{CH_4} = k \cdot p_{CO_2}^{0.66} \cdot p_{H_2}^{0.21}$ $r_{CH_4} = \frac{k \cdot p_{CO_2}}{(1 + K_{CO_2} \cdot p_{CO_2})}$	28 wt% Ni/SiO ₂	200 – 230 °C 17 bar	106	(Van Herwijnen, Van Doesburg and De Jong 1973)
$r_{CH_4} = k \cdot p_{CO_2}^{0.5}$	62 wt% Ni/Cr ₂ O ₃	160 – 180 °C 1 bar	n/a	(Šolc 1962)
$r_{CH_4} = \frac{k \cdot p_{CO_2}^{0.5} \cdot p_{H_2}^{0.5}}{\left(1 + K_1 \cdot p_{CO_2}^{0.5} \cdot p_{H_2}^{0.5} + K_2 \cdot \frac{p_{CO_2}^{0.5}}{p_{H_2}^{0.5}} + K_3 \cdot p_{co}\right)^2}$	3 wt% Ni/SiO ₂	227 – 327 °C 1 bar	94	(Weatherbee and Bartholomew 1982)
$r_{CH_4} = \frac{k \cdot p_{CO_2} \cdot p_{H_2}^4}{(1 + K_{H_2} \cdot p_{H_2} + K_{CO_2} \cdot p_{CO_2})^5}$	60 wt% Ni/SiO ₂	260 – 400 °C 1 bar	55 - 58	(Dew, White and Sliepcevich 1955)

All these studies investigated the gas outlet concentrations under various experimental conditions and determined the methanation rate based on the conversion of CO₂ or the gas outlet concentration of CH₄.

As stated previously, the majority of kinetic experiments employed highly diluted gas compositions, with CO₂ conversions often less than 10%, which is not industrially relevant. In addition, the influence of produced CH₄ and H₂O species on the kinetics was studied using an integrated reactor that enabled CO₂ conversions of up to 90% (Kai, Takahashi and Furusaki 1988; Xu and Froment 1989). The application of modern analytical techniques, to the best of the author's knowledge, has not significantly altered this picture; rather, it has validated and added new pertinent information about the mechanism of CO₂ methanation.

2.12.1.2 *Kinetics Rate Equations*

A mathematical equation that takes into account a kinetic term, a potential term (driving force term), and an adsorption term can be used to express the rate of C (Hougen and Watson 1943). This is demonstrated by Equation (2.43):

$$r = \frac{(\text{kinetic term})(\text{potential term})}{(\text{adsorption term})^n} \quad (2.43)$$

$$r_A dW = F dx_A \quad (2.44)$$

Where,

r_A = reaction rate of reactant A

W = catalyst mass

F = Total reactant A flow rate

x_A = conversion of reactant rate

In certain studies, it was hypothesized that the adsorption and desorption stages are considerably faster than the carbon hydrogenation surface reaction (Van Ho and Harriott 1980; Singh and Vannice 2001). In an additional study, the rate-determining step is temperature-dependent (Weatherbee and Bartholomew 1982).

According to Le Chatelier's Principle, the formation of hydrocarbons and CH₃OH leans toward higher operating pressure, as higher pressure tends to move the equilibrium to the right-hand

side of the processes. Experiments have showed that an increase in pressure will increase CH₄ production because it enhances the adsorption of H₂ and CO₂ molecules onto catalysts. However, after a certain pressure, the effect of increasing pressure on CO₂ equilibrium conversion diminishes (Stangeland *et al.* 2017).

When binding sites are saturated, the formation of water molecules as a byproduct of CO₂ hydrogenation may impede catalyst activity and decrease reaction rates (Puga 2016). However, increasing the hydrogen partial pressure could inhibit the adsorption of water molecules on the catalyst, so mitigating their negative effects (Stangeland, Li and Yu 2018). Therefore, methane synthesis is enhanced by a higher ratio of H₂ to CO₂ (Saebea *et al.* 2022).

2.12.2 Reactor Designs Commonly Used in CO₂ Methanation

Methanation includes fast, highly exothermic processes that produce enormous amounts of heat that must be evacuated; therefore, reactor and process design are crucial. It's crucial to manage the heat in the reactor. There are many methods and tools available (Rönsch *et al.* 2016; Bremer, Rätze and Sundmacher 2017), however the majority of them are unable to stop hotspots from forming inside the catalyst bed and reactor. Therefore, for large-scale syngas (CO, H₂) methanation processes (Coal to SNG), high temperature catalysts and adiabatic fixed bed reactor systems with intercooling and gas recycling are a known technology (Sudiro and Bertuccio 2010). The main disadvantage of these systems is the high temperature increase (up to 700 °C), which restricts CO₂ conversion and CH₄ yield and might cause catalyst sintering and deactivation owing to carbon deposition. Low temperatures (between 200 and 400 °C) are preferred from a thermodynamic standpoint. While adiabatic fixed bed reactors with intercooling are still the main focus of current research (Bremer, Rätze and Sundmacher 2017; Matthischke, Roensch and Güttel 2018), other ideas such as fluidized bed reactors for better heat distribution (Werther 2000; Behjat, Shahhosseini and Hashemabadi 2008), three phase methanation (Lefebvre *et al.* 2015; Lefebvre, Bajohr and Kolb 2019), and structured reactors (Neuberg *et al.* 2019; Stiegler *et al.* 2019) with good heat conductivity are also of interest.

However, the PtG process requires a reactor and process design suitable for a small scale (e.g., a biogas plant) and dynamic operation. Most approaches could be considered for large, continuous methanation reactors (fast shutdown and start-up). The latter is critical if intermittent renewable power generation results in the electrolyzer not producing enough H₂.

2.12.2.1 *Adiabatic Fixed-Bed Reactors*

In fixed-bed reactors, the reaction occurs as a heterogeneously catalyzed gas reaction on the surface of catalysts, which is referred to as the "fixed bed" in the reactor (Figure 2.32). The catalyst is present as a uniform fixed bed encased in an insulating jacket (Olson 1950). Normal operation in fixed-bed reactors involves a succession of two to five adiabatic reactors, with intercooling and gas circulation similar to multi-tube reactors. In such reactors, the catalyst must be able to withstand temperatures between 250 and 700 °C. Possible cracking or sintering is the primary hazard with fixed-bed reactors. Such reactors operate at GHSV = 2000 - 5000 h⁻¹ (Lefebvre 2015), which is a fast rapid rate.

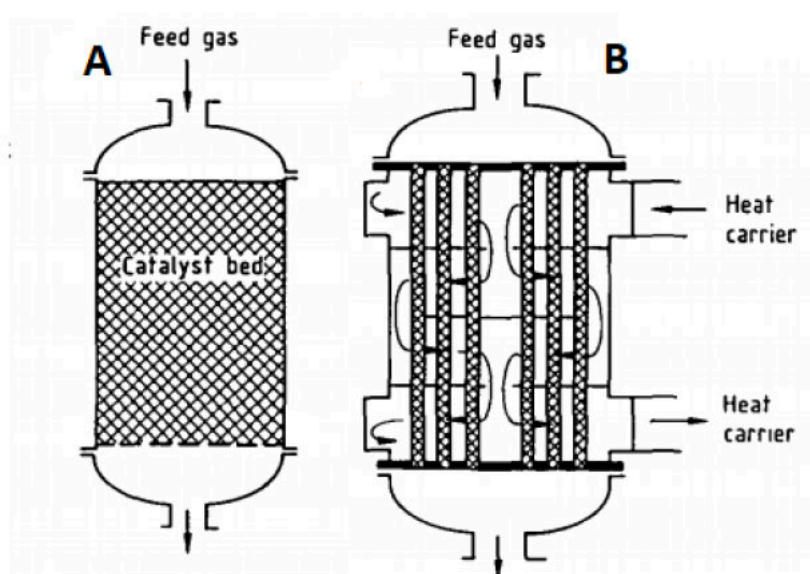


Figure 2-32. Catalytic fixed-bed reactors. (A) Adiabatic fixed-bed reactor; (B) Multi-tubular fixed-bed reactor (Nelabhotla, Pant and Dinamarca 2021).

2.12.2.2 *Fluidized Bed Reactors*

During the production of SNG, methanation reactors produce significant amounts of heat. The primary objective in the design of catalytic reactors is to accomplish effective heat removal in order to reduce the deactivation of the catalyst due to thermal stress and to prevent the yield of methane from decreasing as the chemical equilibrium approaches. And this enables the use of a single reactor with a more simplistic design. In fluidized-bed reactors (Figure 2.33), the mixing of fluidized solids enables an isothermal, one-step process that facilitates control. In addition, the movement of the catalyst particles through the bed and the possibility of combining the water gas shift and methanation reaction in a single apparatus permits a long catalytic stability due to the catalyst's internal regeneration. Fluidized-bed reactors have the

drawbacks of requiring an erosive-resistant catalyst and being difficult to scale up (Werther 2000; Helmi *et al.* 2016).

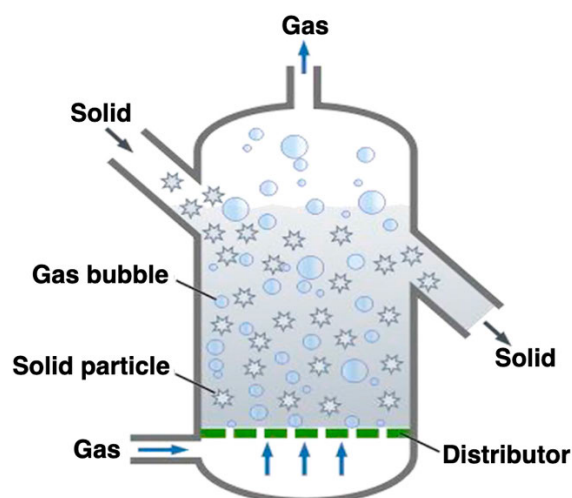


Figure 2-33. Fluidized-bed reactor (Sahoo and Ram 2015).

2.12.2.3 Three-Phase Reactors

In both fixed-bed and fluidized-bed reactors, catalyst deactivation is a significant problem. This deactivation occurs due to sintering issues in fixed-bed reactors and attrition in fluidized-bed reactors. To circumvent these issues, three-phase reactors (Figure 2.34) with a solid catalyst (size 100 μ m) in a temperature-stable inert liquid are regarded as a superior choice for methanation. The existence of a liquid phase with high heat efficiency enables efficient temperature control: the reaction heat can be eliminated entirely, and the reactor can function nearly isothermally, resulting in a straightforward process design. In three-phase methanation reactors, however, gas-liquid mass transfer resistances are a significant problem. The GHSV of such reactors ranges between 500 and 1000 h^{-1} (Lefebvre 2015).

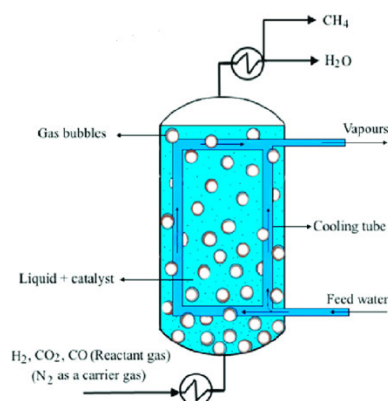


Figure 2-34. Three-phase reactor (Younas *et al.* 2016).

2.12.2.4 Structured Micro-Reactors

Structured reactors, such as milli-fixed bed, micro-channel, and monolith reactors, have evolved in recent years as a solution for adiabatic fix-bed reactors' temperature hot spots and excessive pressure drops. Due to the internal metallic structure of structured microreactors, heat conduction in the metal offers an advantage over other reactors with superior radial heat transport in the conductive metal. Very small reactors are structured micro-reactors. They possess a high ratio of surface area to volume. Catalyst deposition on the metal and replacement of deactivated catalysts are disadvantages of micro-reactors (Sanz *et al.* 2013). Figure 2.35 depicts three types of structured micro-reactors, each with its own internal structure.

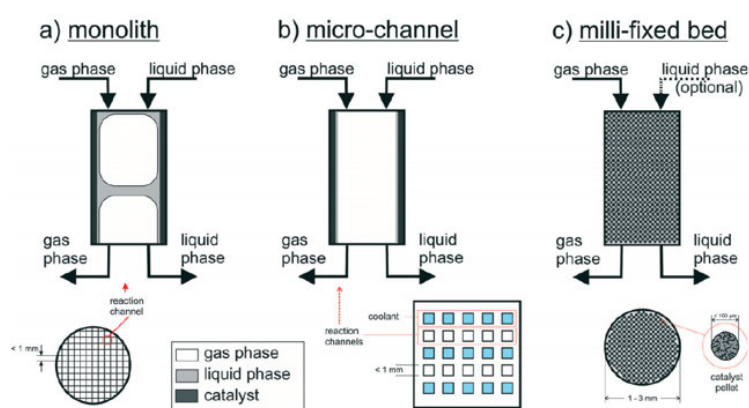


Figure 2-35. Structured micro-reactors (Sanz *et al.* 2013).

Table 2-14. Comparison of methanation reactors.

	Fixed bed	Fluidized bed	Three phase reactors	Structured micro-reactors
Scaling up	Easy	Difficult	Easy	-
Catalyst stability	Not stable	Stable	Not yet determined	-
Coke formation	Possible	No	Not yet determined	-
Hot spots	Yes	No	No	-

2.13 CO₂ Methanation Mechanism

The reaction pathways for CO₂ methanation depend not only on the catalyst (e.g., support, promoter, active metal), but also on the operating conditions. There is no unifying mechanism; rather, several chemical routes assuming distinct fundamental stages and adsorbed surface intermediates have been proposed (Fujita *et al.* 1993). This disparity is attributable to the variation in experimental conditions, including temperature, pressure, reactor type, and catalyst type (Kopyscinski 2010). There are two primary types for the proposed CO₂ methanation

method. Mechanism (A) involves the direct dissociation of CO₂ into adsorbed CO and surface carbon (C*), which is then hydrogenated to produce CH₄. Mechanism (B) involves the formation of carbon hydroxyl or formate species by hydrogen-assisted dissociation (e.g. HCOO, COH, etc.)

2.13.1 Direct CO₂ dissociation to adsorbed CO and surface carbon (C*) – Mechanism A

Several authors (Dew, White and Sliepcevich 1955; Falconer and Zağlı 1980; Goodman *et al.* 1980; Weatherbee and Bartholomew 1982; Kai, Takahashi and Furusaki 1988; Fujita *et al.* 1991; Koschany, Schlereth and Hinrichsen 2016) have argued that the mechanism "A" involving surface carbides serves as an intermediary in CO₂ methanation. According to this mechanism, CO₂ will dissociate, and carbon and carbenes (CH₂) will then hydrogenate to form methane and water, respectively. Adsorbed oxygen will also hydrogenate to form water. It is assumed that dissociative adsorption of carbon dioxide and hydrogen exists. Adsorbed CO₂ is desorbed as CO, according to Falconer and Zağlı (1980); this finding was in line with earlier studies that suggested CO dissociation as an intermediary step for CO₂ methanation (Weatherbee and Bartholomew 1982). Similar to this process, a kinetic approach was developed by Weatherbee and Bartholomew (1982), assuming that the rate-determining phase is CO dissociation.

Different Langmuir-Hinshelwood (L-H) rate expressions can be found using the sequence in Table 2.15, depending on the rate-determining step (RDS) assumption. Multiple rate-determining steps can be proposed because different mechanistic regimes with distinct rate-controlling processes may exist during the reaction depending on the conditions. It is evident that more mechanisms can be developed, and matching rate equations can be established if more irreversible steps are assumed. This mechanism could yield several similar rate equations, requiring surface species identification to supplement process assumptions derived from steady-state laboratory observations.

Table 2-15. Direct CO₂ dissociation to adsorbed CO and surface carbon (C*) – Mechanism A.

Reaction		Description	Step
$H_2 + 2^* \leftrightarrow 2 H^*$			A1
$CO_2 + ^* \leftrightarrow CO_2^*$	RDS	Adsorption of CO ₂	A2
$CO_2^* + ^* \leftrightarrow CO^* + O^*$	+O*	Dissociation of CO ₂	A3
$CO^* + ^* \leftrightarrow C^* + O^*$	+O*	Dissociation of CO to surface C	A4

$C^* + H^* \leftrightarrow CH^* + *$	+ *	RDS	Hydrogenation of C	A5
$CH^* + H^* \leftrightarrow CH_2^* + *$	+ *	RDS	Hydrogenation of CH	A6
$CH_2^* + H^* \leftrightarrow CH_3^* + *$	+ *	RDS	Hydrogenation of CH ₂	A7
$CH_3^* + H^* \leftrightarrow CH_4^* + *$	+ *		Hydrogenation of CH ₃	A8
$CH_4^* \leftrightarrow CH_{4(g)} + *$	+ *		Desorption of CH ₄	A9
$O^* + H^* \leftrightarrow OH^* + *$	+ *		OH formation	A10
$OH^* + H^* \leftrightarrow H_2O^* + *$	+ *		H ₂ O formation	A11
$CO^* \leftrightarrow CO_{(g)} + *$	+ *	RDS	Desorption of CO	A12
$H_2O^* \leftrightarrow H_2O_{(g)} + *$	+ *		H ₂ O desorption	A13

Recently, attempts have been made to identify spectrophotometrically the surface species involved in CO₂ methanation. Initially, carbonyl species were proposed as intermediates for CO₂ methanation after the complete dissociation of CO over the Rh/ γ -Al₂O₃ catalyst (Beuls *et al.* 2012). Rh-(CO)₂ and Rh-CO species are formed by the adsorption/dissociation of CO₂ on metallic centres, as shown by diffuse reflectance Fourier transform spectroscopy (DRIFTS) experiments. The latter is dissociatively adsorbed and forms CO* and O* (see Table 2-1, A3). CO* then dissociates at metallic centres to form C* and O* (see A4). The C* is then hydrogenated to CH₄ (steps A5 to A8) (Beuls *et al.* 2012). Similarly, carbonyl species (CH*) were discovered during methanation via Ru/TiO₂ using DRIFTS (Panagiotopoulou and Verykios 2017) and Raman (Martínez Tejada *et al.* 2016). Reportedly, the main constituents of the intermediate species are carbonyl Ru_x-CO and (TiO₂) Ru-CO. It has been proposed that the carbonyl species should be generated in parallel with the reverse water gas shift (RWGS) reaction. The RWGS reaction has the potential to produce CO at temperatures above 270 °C. Ru-Co centres increase and can absorb the formed CO at metallic centres. Subsequently, the carbonyl species can dissociatively adsorb to C* and O*. In addition, C* can hydrogenate to CH₄ at higher temperatures or be the cause of carbon deposition. In this context, Raman has also been used to detect CH_x/C_nH_x/C_xH_xO/CH_x-CO intermediates (Martínez Tejada *et al.* 2016).

2.13.2 Hydrogen-Assisted Dissociation of Carbon Oxide Bonds – Mechanism B

According to this mechanism, the dissociation of the two carbon-oxygen bonds is favoured by the adsorbed hydrogen. It has been suggested that the dissociation energy is lowered by hydrogen (Beuls *et al.* 2012). A proposed set of basic steps is shown in Table 2.16, which is an analog of the so-called hydrogen-assisted pathway for CO methanation via the intermediate of an oxygen-containing compound, e.g., COH_x (Ibraeva *et al.* 1991; Schild *et al.* 1991; Fujita and Takezawa 1997; Marwood, Doepper and Renken 1997). Surface formate (e) is formed

when adsorbed CO_2^* and adsorbed hydrogen reacts (e.g., HCOO^* or COOH^*), from which CH^* , CO^* , and/or COH^* were subsequently formed. The latter can be present as formyl (HCO^*) or as carbon-hydroxyl (COH^*). Even the formation of H_2COO^* has been suggested. The COH^* species subsequently disintegrate into OH^* and C^* or CH^* . After the hydrogenation of the latter two species, methane is formed.

Table 2-16. Hydrogen assisted of carbon-oxygen bond dissociation. Mechanism B.

Reaction			Description	Step
$\text{H}_2 + 2^* \leftrightarrow 2\text{H}^*$				B1
$\text{CO}_2 + ^* \leftrightarrow \text{CO}_2^*$	RDS		Adsorption of CO_2	B2
$\text{CO}_2^* + \text{H}^* \leftrightarrow \text{COOH}^* + ^*$	RDS		Formation of formates	B3
$\text{COOH}^* + ^* \leftrightarrow \text{CO}^* + \text{OH}^*$	+ OH^*	RDS	Dissociation of formates	B4
$\text{COOH}^* + \text{H}^* \leftrightarrow \text{COH}^* + \text{OH}^*$	+ OH^*	RDS	Dissociation of formates	B5
$\text{COH}^* + \text{H}^* \leftrightarrow \text{CH}^* + \text{OH}^*$	+ OH^*	RDS	Dissociation of formyl	B6
$\text{COH}^* + ^* \leftrightarrow \text{C}^*$	+ OH^*	RDS	Dissociation of formyl	B7
$\text{CH}^* + \text{H}^* \leftrightarrow \text{CH}_2^*$	+ *	RDS	Hydrogenation of CH^*	B8
$\text{CH}_2^* + \text{H}^* \leftrightarrow \text{CH}_3^*$	+ *	RDS	Hydrogenation of CH_2^*	B9
$\text{CH}_3^* + \text{H}^* \leftrightarrow \text{CH}_4^*$	+ *		Hydrogenation of CH_3^*	B10
$\text{CH}_4^* \leftrightarrow \text{CH}_{4(g)}$	+ *		Desorption of CH_4	B11
$\text{O}^* + \text{H}^* \leftrightarrow \text{OH}^*$	+ *		OH^* formation	B12
$\text{OH}^* + \text{H}^* \leftrightarrow \text{H}_2\text{O}^*$	+ *		H_2O^* formation	B13
$\text{H}_2\text{O}^* \leftrightarrow \text{H}_2\text{O}_{(g)}$	+ *		H_2O desorption	B14
$\text{CO}^* \leftrightarrow \text{CO}_{(g)}$	+ *		Desorption of CO	B15

* Empty active site, x* adsorbed species, RDS rate determining step

According to (Solymosi, Erdöhelyi and Bánsági 1981; Walter *et al.* 1994), early attempts have been made to detect surface chemicals using DRIFTS for CO_2 methanation over Ru/TiO_2 and $\text{Rh}/\text{Al}_2\text{O}_3$ (Marwood, Doepper and Renken 1997). According to certain theories, CO_2 reacts with a hydroxyl group on the surface to form the surface-bound hydrogen carbonate molecule HCO_3^- (OH).

Carbonate species are hydrogenated after being reduced to formates HCOO^- . The same surface chemicals were found in FTIR experiments on CO_2 hydrogenation over Pd/ZrO_2 , but the HCO_3^- as formate precursor was not detected (Schild, Wokaun and Baiker, 1990). Similarly, species were recently discovered using FTIR spectroscopy to study CO_2 methanation on $\text{Ni}/\gamma\text{-Al}_2\text{O}_3$ (Pan *et al.* 2014).

Formates and carbonates have been proposed as primary and intermediate adsorption species, respectively. According to infrared (IR) research, intermediate hydrogen carbonates (HCO_3^-) and carbonates (CO_3^{2-}) are involved in the methanation of carbon dioxide via $\text{Ni/Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$. To produce formates, formaldehyde-like and methoxy species and finally methane, these species are further reduced and hydrogenated by H atoms formed by hydrogen dissociation on the surface of the NiO particles (Aldana *et al.* 2013). Comparable results from infrared studies of CO_2 methanation on NiUSY zeolites were discovered (Westermann *et al.* 2015), providing evidence that formate species produce CO at temperatures below 200 °C.

Direct CO_2 Dissociation to Adsorbed CO and Subsequent Hydrogen-Assisted Dissociation of the Carbon-Oxygen Bond – Mechanism AB

In the literature, adsorbed oxygen-containing species (e.g., HCOO^- , HCOH , CHO) or the formation of surface carbon, which reacts extremely slowly with hydrogen, are mentioned as mechanisms for CO_2 methanation.

2.14 Effect of Operating Conditions on CO_2 Reactions

Parameters of operating conditions are crucial aspects that might directly influence the performance of catalytic reactions. This section therefore examines in detail the role of operating parameters such as temperature, the feed ratio of $\text{H}_2:\text{CO}_2$ and the GHSV in CO_2 methanation. A thorough comprehension of these critical aspects helps enhance reactor design, process optimization, kinetic evaluation, and industrial scale-up.

2.14.1 Effect of Reaction Temperature

As a thermochemical reaction, temperature has a significant influence on the efficiency and product selectivity of CO_2 methanation. Therefore, the temperature dependence of CO_2 methanation and numerous side reactions was investigated using the program HSC Chemistry Version 6.0. Figure 2.36 illustrates the temperature-dependent changes in Gibbs free energy (G) values for primary CO_2 methanation and several side reactions. In most cases, a negative Gibbs free energy value indicates a spontaneous reaction. Therefore, the methanation of CO_2 should preferably take place at temperatures below or equal to 600 °C, as shown in Figure 2.36.

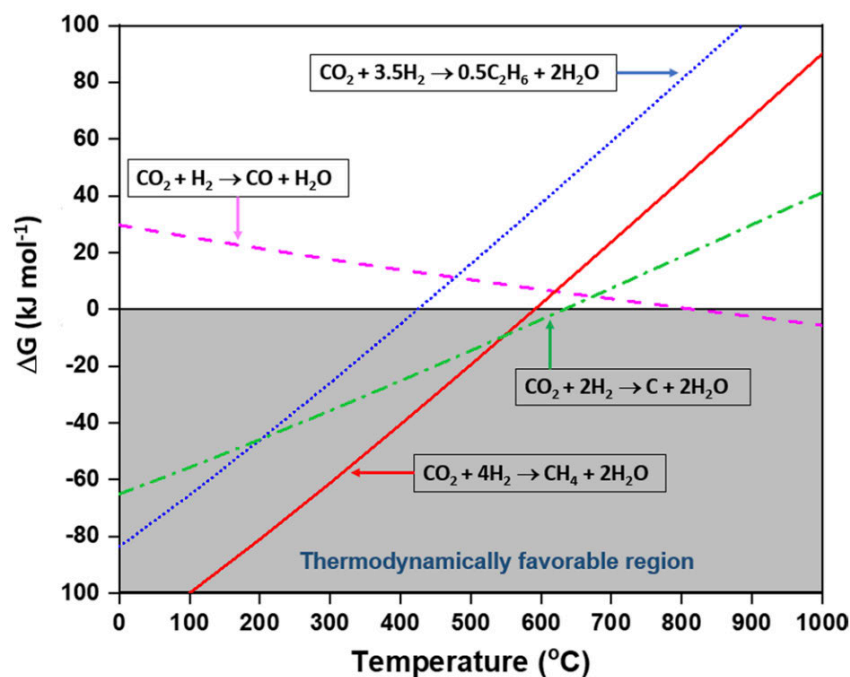


Figure 2-36. The profiles for CO₂ methanation and other side reactions vary as a function of Gibbs free energy (ΔG) and temperature. The equilibrium of the reaction shifts towards the products and vice versa when the Gibbs free energy value is less than zero, which is indicated by the gray colour. Adapted from (Pham *et al.* 2022).

To prevent the very toxic nickel carbonyl formation caused by CO, CO₂ methanation was preferably carried out over a nickel-based catalyst at temperatures below 200 °C (Schaaf *et al.* 2014a). In fact, 550 °C was given as the maximum temperature to avoid catalyst deactivation due to metal sintering or carbon formation. Stangeland *et al.* (2018) studied the effect of temperature on nickel supported on alumina with 12 and 20% and 0.5% ruthenium promoter for methanation of carbon dioxide. With the increase of temperature from 250 to 400 °C, the amount of CO₂ converted increased and reached a maximum of 85% at 400 °C for 12% Ni/Al₂O₃. Moreover, the methane selectivity was more than 99.5% between 250 and 400 °C. However, the reverse water-gas shift reaction caused the output of carbon monoxide to increase slightly with increasing temperature. In addition, 12% Ni/Al₂O₃ showed consistent catalytic performance with only slight deactivation.

Abate *et al.* (2016a) synthesized nickel-aluminium hydrotalcite catalysts for the methanation of CO₂ using a co-precipitation method and evaluated their catalytic performances at different reaction temperatures between 250 and 400 °C. At 300 °C, all catalysts converted CO₂ at a maximum rate of 86 %. The CH₄ yield also tended to increase to 86% when the temperature was increased from 250 to 300 °C, as the higher temperature provided the required energy for CO₂ dissociation and thus improved the activity of the catalyst. However, both trends decreased

again when the temperature was increased above 300 °C. The low selectivity of less than 4% allowed the detection of the small amount of carbon monoxide produced in the reverse water-gas shift side reaction.

Table 2.17 shows the estimated activation energy values for CO₂ consumption derived from the Arrhenius equation using carbon dioxide conversion data at different temperatures. It is evident that a catalyst with a low apparent activation energy has a better catalytic performance than a catalyst with a high apparent activation energy. As a result, the apparent activation energy value can be used to reflect the catalyst's reactivity. Table 2.17 shows that the apparent activation energy values described in the literature for the methanation of CO₂ are between 43 and 129 kJ mol⁻¹, depending on the type of catalyst used.

Table 2-17. Values of the apparent activation energy of different catalysts used for the CO₂ methanation process.

Catalyst	Synthesis method	Apparent activation energy, Ea (kJ mol ⁻¹)	Surface area (m ² g ⁻¹)	References
4%Ru/Al ₂ O ₃	Impregnation	84	172	(Quindimil <i>et al.</i> 2022)
12%Ni/Al ₂ O ₃	Impregnation	129	160	(Quindimil <i>et al.</i> 2020)
15%Ni/Ce ₈₀ Zr ₂₀	Impregnation	82.9	45.3	(Xu <i>et al.</i> 2020a)
2%Co/NiO-MgO	Impregnation	43	68	(Varun, Sreedhar and Singh 2020)
2%Co-8%Ni/Al ₂ O ₃	Evaporation-induced self-assembly	64.7	206	(Xu <i>et al.</i> 2018)
8%Ca-10%Ni/Al ₂ O ₃	Evaporation-induced self-assembly	53.6	210.7	(Xu <i>et al.</i> 2017)
12.5%Ni/γ-Al ₂ O ₃	Impregnation	92	n.m	(Hubble, Lim and Dennis 2016)
10%Ru/γ-Al ₂ O ₃	Impregnation	66	n.m	(Duyar <i>et al.</i> 2015)
3%Rh/TiO ₂	Impregnation	71.2	n.m	(Karelovic and Ruiz 2013b)
5%Pd/γ-Al ₂ O ₃	n.m	98.4	140	(Karelovic and Ruiz 2013a)

2.14.2 Effect of Pressure

To understand how pressure affects the general properties of CO₂ methanation, calculations were performed for ΔG and K_{eq} at different pressures. Figure 2.37 shows the LnK_{eq} value for CO₂ methanation at different P. The LnK_{eq} values increase logarithmically with increasing pressure and that they correlate with an increase in the spontaneity of the reaction. This

behaviour can be described by the principle of Le' Chatelier (Tahir-Kheli and Tahir-Kheli 2020). Since CO₂ methanation reduces a mixture of five molecules to three, an increase in pressure leads to a reduction in volume, which favours the product over the reactant. Due to the logarithmic nature of the increase, the effect of pressure on CO₂ methanation decreases with increasing pressure. Therefore, the pressure range of 1 atm to 30 atm is generally used for CO₂ methanation processes. Increasing the reactor pressure increases $\text{Ln}K_{\text{eq}}$; the K_{eq} value represents higher CO₂ conversion and CH₄ yield up to 30 atm. According to a previous study (Lefebvre, Bajohr and Kolb 2019), the H₂ partial pressure at the reactor input will also affect the reaction rate from a kinetic point of view. Increasing the $P_{\text{H}_2,\text{in}}$ from 1 bar to 4 pressure at 300 °C can increase the reaction rate in a fixed bed reactor by up to 70%. The CO₂ reaction rate is significantly less influenced by the CO₂ partial pressure $P_{\text{CO}_2,\text{in}}$ at the same temperature: An increase in $P_{\text{CO}_2,\text{in}}$ from 0.75 bar to 1.25 bar leads to an increase in the CO₂ reaction rate of only 17%.

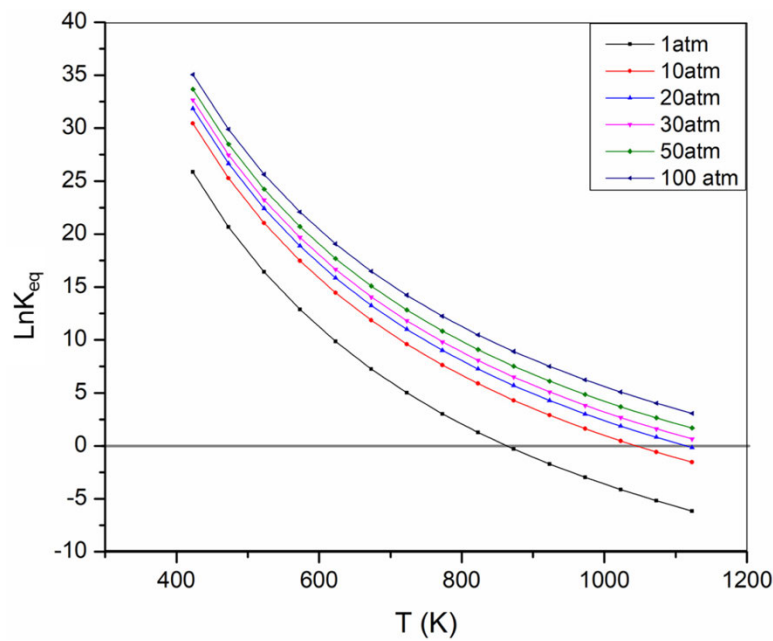


Figure 2-37. $\text{Ln}K_{\text{eq}}$ versus T plot for CO₂ methanation (R1) at different pressure (H_2/CO_2 ratio = 4) (Mohd Ridzuan *et al.* 2022).

Although the kinetic and thermodynamic aspects of a reaction indicate higher rate and better conversion at higher pressure, it should be emphasized that extreme reaction conditions are less preferred in industry due to equipment limitations and high energy consumption (Götz *et al.* 2016; Ghaib and Ben-Fares 2018). Therefore, taking into account the thermodynamic aspect and equipment limitations, the commonly used operating window is between 1 atm and 30 atm, using atmospheric pressure in a two-phase reactor and higher pressure in a three-phase reactor to improve gas solubility (Esa and Sapawe 2020). The use of a pressure slurry reactor, as

proposed by Gao *et al.* (2015), has the potential to improve the methanation process as it can be operated at high pressure, which increases CO₂ conversion (Zhang *et al.* 2014b).

2.14.3 Effect of Gas Hourly Space Velocity (GHSV)

The volumetric flow rate of the reactants divided by the total volume of the catalyst, measured under standard conditions (25 °C and 1 atm), is referred to as the GHSV. The GHSV is usually expressed in h⁻¹ (inverse time) when the amounts of catalyst and reactants are the same units. For a granular catalyst, the GHSV is usually expressed in SmL (gcat.h)⁻¹. A lower GHSV indicates that the reactants are in contact with the catalyst for a shorter period of time.

According to Hoekman *et al.* (2010), the short residence time could lead to a significant decrease in carbon dioxide conversion due to the increasing gas hourly space velocity. Pastor-Pérez *et al.* (2018) investigated how the gas hourly space velocity affected the efficiency of CO₂ methanation on 3% Fe or 15Ni/CeO₂-ZrO₂ catalysts. The catalyst was tested with different values of GHSV ranging from 6250 to 25,000 mL g⁻¹ h⁻¹ while other process factors were manipulated for comparison. With the reduction of the GHSV from 25,000 to 6250 mL g⁻¹ h⁻¹, the carbon dioxide convergence was subsequently increased slightly to 97.2 %. At 300 °C, the CO₂ conversion was still at a respectable level of about 60.4 % at a GHSV of 25,000 mL g⁻¹ h⁻¹. For the design of reactors with a compact configuration, maintaining catalytic performance at high hourly gas space velocities is essential.

In a separate study, Abate *et al.* (2016b) also evaluated the effect of GHSV on the performance of nickel catalysts with mixed oxide support (Ni/-Al₂O₃ZrO₂-TiO₂-CeO₂) synthesized by a wet impregnation method. The catalytic activity decreased significantly from the equilibrium conversion with increasing GHSV. It was shown that the GHSV had no significant effect on the methane selectivity of Ni/- Al₂O₃- ZrO₂- TiO₂-CeO₂, as the selectivity of CO remained low at less than 4% regardless of the values.

2.14.4 Effect of Initial CH₄ Concentration

The CH₄ component of the gas mixture does not have a major effect on the conversion, although at temperatures above 400 °C carbon deposition increases due to the methane cracking reaction (Mirkarimi *et al.* 2023). Jürgensen *et al.* (2015) investigated the effect of CH₄ in the biogas feed using thermodynamic calculations. When the CH₄ content was increased

from 0% to 64% at 1 bar, the CO₂ conversion decreased from 96% to 92%. However, increasing the pressure immediately neutralized this effect. As the CH₄ mole fraction in the biogas input stream increased from 0% to 64% at a constant pressure of 10 bar, the conversion rate decreased from 98% to 97%. At a pressure higher than 8 bar, the CH₄ concentration in the feed stream has a negligible effect on CO₂ conversion. The findings clearly show that CH₄ removal prior to the Sabatier reaction is not necessary when the operating pressure is increased. Again, it was suggested that the CH₄ cracking reaction is the main cause of carbon deposition.

2.14.5 Effect of Ratio of H₂ to CO₂

In addition to the reaction temperature and the GHSV, the feed ratio of H₂ to CO₂ has a significant effect on the activity and stability of the catalysts in CO₂ methanation. This process requires a stoichiometric ratio of 4:1 between hydrogen and carbon dioxide, as indicated in equation (1). Since the H₂/CO₂ ratio plays a crucial role in CO₂ methanation, the influence of different hydrogen/carbon dioxide ratios on CO₂ methanation has been widely reported in the literature.

Zhou *et al.* (2015) conducted a study in which they used the impregnation method to prepare CeO₂-Ni/Al₂O₃ catalysts. The authors then evaluated the effectiveness of these catalysts in the methanation of CO₂ at 400 °C, varying the ratio of H₂:CO₂ from 1:1 to 7:1. By increasing the molar ratio of H₂ to CO₂ from 1:1 to 4:1, the conversion of carbon dioxide and the selectivity for methane increased from 53.5 to 72.6 % and from 76.5 to 97.2 %, respectively. It is worth noting that a H₂/CO₂ ratio of exactly 5 was used to achieve a selectivity of 100% for CH₄. Conversely, CO₂ conversion and CH₄ selectivity in the empirical data showed a comparable upward trend when the H₂:CO₂ ratio increased. At an H₂/CO₂ ratio of 4, this tendency became even more pronounced in the feed mixture. Due to the greater surface interaction between adsorbed CO₂ and excess H₂, increasing the H₂/CO₂ ratio could improve the performance of CO₂ methanation.

By manipulating operating factors such as temperature, hourly gas space velocity and hydrogen to carbon dioxide ratio, Jaffar, Nahil and Williams (2019) achieved an optimization of the carbon dioxide methanation process. A range of H₂ to CH₄ ratios (from 2:1 to 4.5:1) was observed when investigating 10% Ni/ Al₂O₃. CH₄ yield increased by 88.9 to 96.1 %, CO₂ conversion improved by 29.1 to 71.7 %, and CH₄ concentration increased by 5.9 to 9.0 mmol

when the H₂:CO₂ feed ratio was adjusted from 2:1 to 4:1. A decrease in CO₂ conversion and CH₄ formation was observed at a feedstock ratio of 4.5:1, which is consistent with the results of (Aziz *et al.* 2014) and (Zhou *et al.* 2016). To maximize CO₂ conversion and CH₄ concentration, a H₂ to CO₂ ratio of about 4:1 was found to be optimal.

2.15 Various Attempts to Improve CO₂ Conversion to Methane over Ni-Mo/AC

An ongoing area of research with potential applications for carbon capture and utilization is the use of catalysts to convert CO₂ to CH₄, particularly Ni-Mo activated carbon catalysts (AC). The conversion of CO₂ to CH₄ with these catalysts has been improved in several ways. The main techniques and strategies include the following:

2.15.1 Catalyst Composition Optimization

An important component affecting CO₂ conversion is the composition of the catalyst. Optimizing the composition is critical, and this includes the metals chosen and the amount with which they are loaded onto the support AC. The selectivity and catalytic activity of a catalyst can be greatly controlled by changing the Ni-Mo ratio and improving the metal loading. Among the most important factors to consider is the interaction of the metal with the support material. Maximizing catalytic activity and selectivity requires an ideal balance between the Ni and Mo loading and the appropriate ratio. Properly optimized catalysts can increase CO₂ consumption efficiency and help develop systems for long-term carbon capture and utilization. In addition, mesoporous carbon nitride catalysts supported by nickel nanoparticles (Ni/CN) have shown promising results for CO₂ methanation. Methane selectivity and CO₂ conversion of up to 44% have been demonstrated with the Ni/CN catalyst (Refaat *et al.* 2023).

2.15.2 Support Modification and Promoters

Catalytic activity can be improved by adjusting the AC support's properties and adding promoters. The catalyst's acidity and basicity can be modified through surface functionalization, doping, or the addition of promoters such as alkali metals, which facilitate CO₂ adsorption and activation. These modifications may improve the overall catalytic performance. Ni-Fe catalysts for the CO₂ methanation process have been investigated in relation to the effects of support modification on their catalytic activity. The findings indicated that the catalyst's activity can be improved by changing the support (Frontera *et al.* 2017).

2.15.3 Reaction Conditions and Syngas Co-Feeding:

CO₂ conversion to CH₄ is greatly influenced by reaction conditions, including temperature and pressure. Increasing the temperature and pressure can facilitate the conversion. Co-feeding CO₂ with hydrogen (H₂) or carbon monoxide (CO) can lead to the production of syngas, which contains CO and H₂ and can later be converted to methane. This technique increases methane production and CO₂ utilization.

2.16 Catalyst Development for CO₂ Methanation Reaction

2.16.1 The Active Phase

Fischer, Tropsch and Diltney (1925) conducted the first systematic study with powdered unsupported metals in 1925. The authors found that, in addition to Mo and Ag, virtually all transition metals in the VIII group are active for methanation. The relative mass-based catalytic activity was as follows: Ru > Ir > Rh > Ni > Co > Os > Pt > Fe > Mo > Pd > Ag.

In the 1970s, Vannice conducted another in-depth study on supported catalyst made of alumina and silica. Based on the active surface area determined by CO and H₂ chemisorption, the relative activity on alumina supports were as follows: Ru > Fe > Ni > Co > Rh > Pd > Pt > Ir (Vannice 1975). The sequence of silica supports was as follows: Co > Ru > Fe > Ni > Rh > Pt > Ir > Pd (Vannice 1977).

Numerous studies, also using additional catalyst supports including ceria, zirconia, and titania have experimentally confirmed the high methanation activity of the five most active metals, namely the three base metals Ni, Fe, and Co and the noble metals Rh and Ru (Takenaka, Shimizu and Otsuka 2004; Yaccato *et al.* 2005).

Vannice was one of the pioneers who postulated the Sabatier principle, which stipulates a possible correlation between the strength of a metal's CO interaction and its methanation activity. By plotting the activity against the heat of adsorption for CO, which increases with the number of groups of metals in the periodic table, he obtained a volcano-shaped curve (Yaccato *et al.* 2005). By combining kinetic studies with theoretical DFT calculations, Bligaard *et al.* revised this concept (Bligaard *et al.* 2004). According to their findings, the energy shift caused by CO dissociation is actually linked to the methanation activity of transition metals at low temperatures (in their case 275 °C). With a low activation energy barrier, CO is readily

dissociated at the metal surface of low dissociation energy metals (such as Re or Fe). However, in the subsequent reaction steps, methane can only be produced due to the strong adsorption of the atomic degradation products C and O. For example, metals such as Pd, Pt and Ir, which have a strong interaction with CO but a weak interaction with C and O, are limited in their ability to split CO due to a high activation barrier. Intermediate dissociation energies, such as those exhibited by Co and Ru, are optimal for splitting CO to achieve maximum methanation activity. For Ni, Rh and Fe, their estimates provide slightly higher dissociation energies than necessary.

Ruthenium, the most active and least expensive metal in the group of potential catalysts, and nickel are used as catalysts in industry. Although Fe and Co, among other basic metals, also function as FT catalysts and produce a larger amount of hydrocarbons, especially under elevated pressure conditions, nickel catalysts show favourable activity at comparatively lower feedstock costs than Ru, Rh and Co and exhibit high selectivity to CH₄ (Mills and Steffgen 1974; Andersson *et al.* 2006).

The most methanation-active metal is ruthenium, but its supply is scarce, and its price is about a hundred times higher than that of nickel. Ruthenium is not only FT-active but can also form long-chain paraffin waxes at low temperatures and high pressure. Ru is mainly used for low temperature methanation and gas purification (Bakar, Ali and Toemen 2012).

Several bimetallic alloys have also been found as promising methanation catalysts (Tsiotsias *et al.* 2020a), based on the volcano curve for monometallic catalysts. From the point of view of availability and cost of raw materials, Ni-Fe alloys with Fe concentration up to 50 mol% are considered a viable option (Kustov *et al.* 2007; Yan *et al.* 2024). The addition of Fe increases the activity and, at the same time, reduces the raw material costs (Tian *et al.* 2013).

As previously mentioned, sulphur components in the feedstock can poison metallic catalysts, necessitating additional gas cleaning procedures. Sulphur -resistant catalysts can be replaced with molybdenum sulphide and tungsten (Liu *et al.* 2013; Zhang *et al.* 2019a). However, due to the lower specific activity of these catalysts, larger reactors and higher reaction temperatures are required.

2.16.2 The Promoter

Promoters can be broadly categorized into two types: (i) An electron promoter to modify the catalyst's electron mobility. (ii) A structural promoter that alters the catalyst's chemical composition, mechanical strength dispersion state pore structure, and crystal texture to enhance dispersion and thermal stability. Some oxide promoters can function as both.

In addition, transition metals, rare earth metals and alkali and alkaline earth metals are used as promoters (Tsotsias *et al.* 2020b). They can be deposited as oxides on the surface of the catalyst or integrated into the crystal lattice in the form of ions (Zhang *et al.* 2021). These substances increase the metal dispersion and thermal stability structurally or electronically. The alteration of the acidic/basic sites on the catalyst surface by selective blocking is another strong effect (poisoning). Table 2.18 shows the results of the most studied CO₂ methanation promoters. Normally, the weight percentage (wt.%) of the promoter is much lower than that of the active metal or support (Jacobs *et al.* 2002).

Table 2-18. Common promoters used in catalysts for CO₂ methanation and their effects.

Promoter	Effect	Ref.
Mo	- Higher sulfur resistance - Higher methane selectivity than Ni, therefore higher methane yield.	(Argyle and Bartholomew 2015)
Zr	- higher reducibility of Ni - higher dispersion of active metal	(Stangeland <i>et al.</i> 2017)
Ce	- Stabilization of Al₂O₃ support when H₂O is present. - Lower S deposition on active metal - Lower metal particle sintering - Higher activity at low temperature - Higher dispersion of active Ni phase	(Gao <i>et al.</i> 2015; Gac <i>et al.</i> 2019; Alarcon <i>et al.</i> 2020; Chein and Wang 2020)
Mn	- Higher number of moderate basic sites - Higher dispersion of active metal - Higher reducibility of Ni and stabilized metal surface of NiO	(Pastor-Pérez <i>et al.</i> 2020)
Mg	- Higher adsorption capacity for CO₂ - Facilitated CO₂ activation. - Stabilization of Al₂O₃ support when H₂O is present. - Higher thermal stability - Resistance to water	(Kim, Lee and Park 2010; Tada <i>et al.</i> 2012; Boggula <i>et al.</i> 2020)
Ru	- Lower carbon deposition and metal particle sintering - Facilitated CO₂ and H₂ activation. - Higher activity at low temperature - Higher basicity - Higher reducibility of Ni	(Tsotsias <i>et al.</i> 2020a)
Co	- Higher dispersion of active metal - Lower activation energy required for CO₂ activation. - Lower carbon deposition and sintering of metal particles.	(Pastor-Pérez <i>et al.</i> 2020; Tsotsias <i>et al.</i> 2020a)

Fe	• Facilitated CO₂ adsorption. • Higher activity at low temperature • Facilitated CO₂ adsorption. • Higher reducibility of Ni • Higher activity at low temperature	(Pastor-Pérez <i>et al.</i> 2020; Tsiotsias <i>et al.</i> 2020a)

MgO is an efficient promoter for enhancing resistance to carbon deposition and minimizing sintering of Ni particles (Hu *et al.* 2012; Liu *et al.* 2014a). MgO-promoted Al₂O₃ (Mg₂Al(O)) supported with Ni (Liu *et al.* 2014a) and Ni/Mg/Al hydrotalcite-like compounds (Zhang *et al.* 2018a) exhibited excellent catalytic activity and thermal stability in methanation reaction, demonstrating the effectiveness of adding promoters to fine tune the properties of composite oxide catalyst support to enhance the thermal stability for efficient SNG production.

The addition of La₂O₃ can improve the activity of catalysts by increasing H₂ uptake, decreasing NiO particle growth, and dispersing Ni (Qin *et al.* 2014; Riani *et al.* 2021). Tada *et al.* (2014a) found La-electron-promoter to be able to increase the electron density in Ru species, which improved the dissociation of the C-O bond on Ru due to back donation of electrons from Ru to carbon monoxide, and consequently led to high carbon monoxide methanation activity over Ru-La/TiO₂. By altering the interaction between Ni and Al₂O₃ (Liu *et al.* 2014b; Tada *et al.* 2014a), the addition of CeO₂ can increase the reducibility of the methanation catalyst. Pt doping can also aid in the reduction of Ni species (Yoshida *et al.* 2015) of TiOx, including ZrO₂ (Guo *et al.* 2014; Zhang *et al.* 2014b) were discovered to successfully inhibit the development of the NiAl₂O₄ spinel phase and reduce the strength of the Ni-Al₂O₃ interaction, which increased the exposure of Ni species and increased the capacity for carbon monoxide adsorption. Additionally, electron transfer from TiOx may intensify Ni's electron cloud, which would aid in the dissociation of CO (Zeng *et al.* 2014). Ni methanation catalysts promoted by MoO₃ also displayed the same phenomenon. The dispersion of Ni and the carbon monoxide-promoted dissociation were both improved by Zr doping (Zhang *et al.* 2014c). Recent research has shown that the addition of V₂O₃ improves the activity and coking resistance of Ni-Al₂O₃ for the methanation of CO and CO₂. (Liu *et al.* 2014c) This is because V₂O₃ causes the formation of Ni₃V₂O₈ (Liu *et al.* 2014c). Na, which may also promote the use of Ni/Al₂O₃ catalysts for the methanation of syngas. Many research efforts have been made up to this point in finding new promoters to enhance the functionality of the methanation catalysts. However, it doesn't appear that a magic promoter is yet in view. In Table 2.19, the promoting factors are listed and contrasted with some representative examples of promoted catalysts and their impact on catalytic performance from the literature.

Table 2-19. Summary of typical promoted catalysts in CO₂ methanation (note: Based on the methane yield, promoting factors are determined).

Promoter	Catalysts	Operating conditions	Outcomes	Promoting factor	Ref.
Lanthanide	5 wt% lanthanide series (La, Ce, Pr, Eu & Gd)	T = 200 - 350 °C, P = atmospheric, H ₂ /CO ₂ = 4	XCO ₂ = 98.2%; SCH ₄ = 100% at 300 °C	1.2 (at 300 °C)	(Ahmad <i>et al.</i> 2017)
Alkaline earth metals	12 % Ni/Al ₂ O ₃	T = 250 - 450 °C, P = atmospheric, H ₂ /CO ₂ = 4	(5%Pr/Ni/Al ₂ O ₃)	0.8 (at 350 °C) / 1.6 (at 400 °C)	(Bacariza <i>et al.</i> 2017)
	5%Ni/USY zeolite		XCO ₂ = 40%; SCH ₄ = 75% at 400 °C		
	2.5 %Mg				
Alkali metals	20 %Ni/Al ₂ O ₃	T = 200 - 600 °C, P = atmospheric, H ₂ /CO ₂ = 4	XCO ₂ = 80%; SCH ₄ = ca. 100% at 300 °C	5.4 (at 300 °C)	(Le <i>et al.</i> 2018)
	Alkaline (Mg, Ca, Sr, Ba)	T = 100 - 350 °C, P = atmospheric, H ₂ /CO ₂ = 4	(5%Ba/Ni/Al ₂ O ₃)	2.0 (at 250 °C)	
	33 %Ni/CeO ₂ (or SiO ₂)		XCO ₂ = 60%; SCH ₄ = ca. 100% at 250 °C		
	0.20 wt.% alkalimetals (Li, Na, K, Cs)		(0.1%Na/Ni/SiO ₂)		
	0.1–1 wt% Na				
	37 %Ni/Mg/Al mixed metal oxides (MMO)		T = 100 - 350 °C, P = atmospheric, H ₂ /CO ₂ = 4		
Ni/Mg/Al molar ratio = 0.98/1.00/21.00					
Mn	1.7 wt% Mn	T = 250 - 500 °C, P = atmospheric, H ₂ /CO ₂ = 4		XCO ₂ = 66%; SCH ₄ = 99% at 300 °C	2.9 (at 300 °C)
	0.5 %Ru/TiO ₂	T = 170 - 450 °C, P = atmospheric, H ₂ / CO ₂ = 4	XCO ₂ = 60%; SCH ₄ = 95% at 400 °C	2.8 (at 300 °C)	(Le <i>et al.</i> 2018)
	0.20 wt.% alkalimetals (Li, Na, K, Cs)		(0.2%Na/Ru/ TiO ₂)		

Fe ₂ O ₃	5 wt% Fe	T = 200 - 500 °C, P = atmospheric, H ₂ / CO ₂ = 3.5	XCO ₂ = 70.6%; SCH ₄ = 98.9% at 350 °C	1.1 (at 300 °C)	(Moghadd am <i>et al.</i> 2018a)
	15 % Ni/Al ₂ O ₃				
La ₂ O ₃	5 wt% La ₂ O ₃	T = 200 - 500 °C, P = atmospheric, H ₂ / CO ₂ = 4	XCO ₂ = 65%; SCH ₄ = 100% at 350 °C	4.3 (at 300 °C)	(Quindimil <i>et al.</i> 2018)
	10wt% La ₂ O ₃				
V ₂ O ₅	7.8 % Ni/Na-BETA 3wt% V ₂ O ₅	T = 260 - 420 °C P = atmospheric, H ₂ / CO ₂ = 4	XCO ₂ = 90%; SCH ₄ = 98% at 380 °C	3.9 (at 320 °C)	(Lu <i>et al.</i> 2015)
	15 % Ni/Mg-Al ₂ O ₃	T =250 °C, P = atmospheric, H ₂ /CO ₂ = 4	XCO ₂ = 61%; SCH ₄ = 100% at 250 °C	1.2 (at 300 °C)	(Zhang <i>et al.</i> 2018a)
CeO ₂	2 wt%Ru/Al ₂ O ₃ 30wt%CeO ₂	T = 250 - 500 °C P = atmospheric, H ₂ /CO ₂ = 4	XCO ₂ = 90%; SCH ₄ = 100% at 350 °C	10.3 (at 300 °C)	(Tada <i>et al.</i> 2014b)
	5%Ni/Na-USY (Si/Al = 3) 3% Ce	T = 250 - 450 °C, P = atmospheric, H ₂ /CO ₂ = 4	XCO ₂ = 22%; SCH ₄ = 84% at 350 °C	3.0 (at 300 °C)	
	NiAl/CeO ₂ 5% Ce	T = 150 - 450 °C, P = atmospheric, H ₂ /CO ₂ = 4	XCO ₂ = 91%; SCH ₄ = 99% at 250 °C	1.2 (at 225 °C)	(Tada <i>et al.</i> 2014b)
	20 %Ni/Bentonite	T = 260 - 420 °C,			(Guo <i>et al.</i> 2019)
ZrO ₂	12 %Ni/Al ₂ O ₃ 3wt% ZrO ₂	T = 180 - 360 °C, P = atmospheric H ₂ /CO ₂ = 3.5	XCO ₂ = 69.8%; SCH ₄ = 100% at 360 °C	6.4 (at 300 °C)	(Cai <i>et al.</i> 2011)
	15 % Ni/Al ₂ O ₃ 2 wt% CeO ₂	T = up to 450 °C, P = atmospheric H ₂ /CO ₂ = 4	XCO ₂ = 85%; SCH ₄ = 100% at 350 °C	1.1 (at 350 °C)	(Nie <i>et al.</i> 2017)

2 wt%Ru/Al ₂ O ₃ 20wt%CeO ₂	T = 20 - 700 °C, P = atmospheric, H ₂ /CO ₂ = 5	XCO ₂ = 76%; SCH ₄ = ca. 100% at 300 °C	-

2.16.3 The Support

The performance of a heterogeneous catalyst depends strongly on the support material. Support materials often improve the activity of the catalyst through mechanisms such as facilitating electron transfer between the metal and the support, improving metal-support interactions, and introducing additional defect sites onto the support (Aziz *et al.* 2014; Pan *et al.* 2014). The above improvements are achieved in two ways: first, by using different preparation techniques to disperse the metal component on the support (Younas *et al.* 2016), thereby increasing the amount of accessible metal atoms on the surface for catalysis; second, by using the interaction between the metal and the support to stabilize the newly formed small metal crystallites (Iizuka, Tanaka and Tanabe 1982). Surface contacts can be facilitated by electronic interactions between supports and active metal species, which allow a partial transfer of electrons from the support materials to the metal to enrich its electron population. To stimulate further methane reactions, electrons are attached to the dissociated and adsorbed CO species on the metal surface during methane production from CO₂ (Tada *et al.* 2012).

Al₂O₃, SiO₂, ZrO₂, TiO₂, CeO₂ and other typical metal oxides as well as composite oxides (perovskite, solid solution, and hexaaluminate), structured metal oxides, carbon and zeolites have been used in the past as supports for methanation catalysts. Excellent reviews of CO₂ methanation catalysts have been published in various places (Vannice 1976; Gao *et al.* 2015; Rönsch *et al.* 2016; Su *et al.* 2016; Stangeland *et al.* 2017). In the present review, we consider only the most commonly used supports and focus on identifying methods that could improve CO₂ methanation catalysts at low temperatures.

2.16.4 Interaction Between Metal and Support

Various types of metal oxide support have been reportedly used for carbon dioxide methanation, including titania (TiO₂) (Karelovic and Ruiz 2013b; Zhou *et al.* 2016; Unwiset *et al.* 2020), zirconia (ZrO₂) (Li *et al.* 2018b; Jia *et al.* 2019), ceria (CeO₂) (Tada *et al.* 2012; Wang *et al.* 2016). In the case of supported catalysts, depending on the properties of the supports, interactions between the active metal and the support may vary in strength, affecting the catalytic activity, stability, and selectivity.

The method of catalyst preparation is one of the most important factors that directly affects the strength of metal–support interaction. Bian *et al.* (2018) synthesized nickel-silica (NiSi)

catalysts with 15% Ni loading by two methods: ammonia and impregnation evaporation, designated NiSi-P and NiSi-I, respectively. The Ni–O–Si content of NiSi-P appears to be higher than that of NiSi-I, as determined by the Fourier transform infrared spectra of both samples. This indicates that the NiSi-P catalyst operates on a more robust metal–support interface, which is consistent with the results of the temperature-programmed H₂ reduction experiment. Thus, the peaks of H₂ reduction of NiSi-P were greater than those of NiSi-I (397 °C and 535 °C versus 539 °C and 684 °C, respectively). The increased level of interaction between the metal and the support resulted in a higher temperature for H₂ reduction. In addition to the high Ni⁰ surface area and small particle size, Bian *et al.* (2018) found that the higher performance of NiSi-P over NiSi-I was partly due to the improved metal–support interaction.

2.16.5 Catalyst Deactivation

The gradual loss of catalytic activity with time-on-stream is known as catalyst deactivation. Most catalyst-based thermal processes, such as CO₂ methanation, are significantly hampered by catalysts' accelerated deactivation over time. The industrial use of CO₂ methanation may be threatened by catalyst deactivation; as a result, it is essential for catalyst design and actual implementation to comprehend the fundamental causes of catalyst deterioration. As stated by Ghaib, Nitz and Ben-Fares (2016), sintering, poisoning, and fouling are three common causes of catalyst deactivation.

One of the most common causes for catalysts deactivation is sintering. According to Argyle and Bartholomew (2015), the catalyst surface area typically decreases due to the growth of crystallites at the active sites, while the support surface area decreases as a result of the collapse of the support. Chen *et al.* (2020b) evaluated the CO₂ methanation capabilities of nickel supported on hydrothermally synthesized zeolite and nickel supported on conventional silica (Ni/SiO₂). Ni/SiO₂ had the least stability of all the tested catalysts. The rapid deactivation of the nickel sample was attributed to the sintering and loss of Ni particles on the support surface, which was further enhanced by the production of Ni(CO)_x species. The production of the unfavourable Ni(CO)_x species can be attributed to two factors: the considerable pore size and the generation of CO during the hydrogenation of CO₂ on Ni metal. As a result, more carbon was deposited on the surface of the catalytic support.

Bai *et al.* (2014) also studied the deactivation of Ni/Al₂O₃ catalyst for methanation of carbon dioxide. They discovered that the considerable decrease in the surface area of the active metal was due to the sintering of the metal as a result of the collapse of the porous support, agglomeration of encapsulation, and Ni crystallites. As a result of the decrease in the surface area of the active metal, the activity of the catalyst was drastically reduced.

Poisoning is another important factor that contributes to catalyst deactivation along with sintering. In catalytic reactions, impurities, reactants, or products that strongly chemisorb to active sites can poison active metals by blocking those sites from further adsorption and surface reactions. According to Bartholomew (2001), impurities such as acetylene (C₂H₂), halides ammonia (NH₃), zinc (Zn), arsenic (As), mercury (Hg), sulphur (S), lead (Pb), and phosphorus are frequently found in feedstocks that lead to catalytic deactivation in carbon dioxide methanation. Deactivation by poisoning has primarily been researched on sulphur compounds like hydrogen sulphide (H₂S) because they are frequent impurities in gaseous reactants (Legras *et al.* 2014; Liu *et al.* 2020b). This type of poisoning is primarily caused by the dissociative adsorption of H₂S on metal surfaces. Corresponding chemical, thermal or mechanical methods for deactivating catalysts have subsequently been documented (Argyle and Bartholomew 2015). The potential reversibility or irreversibility of these effects is briefly summarized in Table 2.20.

Table 2-20. Types, nature and mechanisms of catalyst deactivation in methanation activity.

Mechanism	Description	Example	Nature	Ref.
Fouling	The blockage of the sites and pores onto the catalyst active surface due to carbon deposition that results in activity loss	$2CO_{(g)} \leftrightarrow CO_{2(g)} + C_{(s)}$	Physical	(Bartholomew 2001)
Attrition or fouling	The crushing of the catalyst particles due to mechanical fluidization, which reduces the internal surface area of catalytic materials	In a fluidized-bed or slurry-bed reactors, the catalyst particles are crushed into fines powder, which may block the active sites is carried away with the product flow	Physical	(Bartholomew 2001)
Thermal degradation (Sintering)	The loss of active surface of catalysts due to crystallite growth of either the active phase or support material by sintering, chemical transformations, or evaporation	Thermal degradation usually occurs during reduction or calcination of synthesized samples at high temperatures.	Physical	(Zhang <i>et al.</i> 2013a)

Poisoning	Strong chemisorption of pollutants species on the catalytic active sites due to unwanted chemical reactions.	• $H_2S_{(g)} + NiO_{(s)} \leftrightarrow NiS_{(s)} + H_2O_{(l)}$ • $2H_{2(g)} + C_4H_{5(g)} \leftrightarrow H_2S_{(g)} + C_4H_{10(g)}$ • Tars • Ammonia • Chlorine compounds • Alkalis	Chemical	(Struis <i>et al.</i> 2009)
Vapours soilds reactions	Formation of inactive phases on catalytic actives sites due to chemical reactions with, support materials, promoter, or fluid.	Carbon monoxide react with active phase of Ni-based catalysts to form nickel carbonyls species at temperatures below 230 °C $Ni(S) + 4CO_{(g)} \rightarrow Ni(CO)_4_{(g)}$	Chemical	(Harms, Hoehlein and Skov 1980)

Gac *et al.* (2019) investigated the role of contamination in the deactivation of the cerium-promoted alumina-supported nickel (Ce-Ni/Al₂O₃) catalyst. A trace amount of hydrogen sulfide impurity was added to the gaseous reactant mixture during the CO₂ methanation process. They discovered that adding a cerium promoter to a nickel catalyst supported by alumina increased the activity of CO₂ methanation. In 20 hours onstream at 475 °C, the high methane selectivity of about 97.1 % and the CO₂ conversion of 80.0 - 87.5 % remained stable. The conversion of CO₂ and CH₄ selectivity rapidly decreased to 10% and 0%, respectively, as 8 ppm H₂S was added to the reaction system for 20 hours. This occurred in the order of 20%Ni/Al₂O₃ < 5%Ce-20%Ni/Al₂O₃ < 40%Ni/Al₂O₃ < 5%Ce-40%Ni/Al₂O₃. Conversely, the CH₄ selectivity was improved, and CO emerged as the main product once it was completely eliminated. The deactivation of the catalyst is thus caused by the formation of the carbonyl group and subsequent hydrogenation to CH₄, hindering the first stage of CO₂ methanation. Although sulphur adsorption was temperature dependent, sulphur poisoning was nearly irreversible at moderate reaction temperatures commonly used in methanation reactions (Dou *et al.* 2021).

Alarcon *et al.* (2020) studied the deactivation process of the cerium oxide-promoted Ni/Al₂O₃ catalyst for the methanation of carbon dioxide in the presence of harmful hydrogen sulphide impurities at a concentration of 1 to 5 parts per million. Compared to its unpromoted counterpart, the promoted catalyst showed good heat stability for 138 hours. However, when hydrogen sulphide was added to the solution, both the unpromoted and promoted catalysts became unstable and converted only 25% and 10% of the CO₂, respectively. The more stable catalyst that was promoted suggests that nickel-cerium oxide is more resistant to hydrogen

sulphide poisoning. This behaviour was associated with the development of the $\text{Ce}_2\text{O}_2\text{S}$ phase, which may have prevented the formation of the undesirable nickel sulphide form.

In addition, the phenomenon of fouling can also lead to catalytic deactivation. When a solid, such as carbon, is deposited on the active surface of the catalyst, this is called fouling. Adsorption of reagents to the active sites for a particular surface reaction has been significantly suppressed because carbon deposits can block the sites, reducing catalytic activity. Deposited carbon, typically generated by Boudouard and methane pyrolysis reactions (see equations), can inevitably lead to fouling-induced deactivation. Both (5) and (8) are correct. Although coke deposition during methanation of carbon monoxide has been extensively documented in the literature (Li *et al.* 2017b; Gong *et al.* 2018). Due to the combination of CO methanation and reverse water gas shift, which helps to remove carbon from the catalyst surface, fouling is not a major problem in CO_2 methanation (Mebratu *et al.* 2019; Elia *et al.* 2021). Various strategies have been employed to prevent the deactivation and poisoning of catalysts, such as the addition of certain promoters and modifications to the catalyst production process, as already described in section 2.8.3.

2.16.6 Catalyst Regeneration

In contrast to carbon production, the overall deactivation rate is determined by sulphur poisoning. Methanization and sulphur poisoning in general can lead to the formation of sulphides, sulphates and other structures. Several authors (Bartholomew, Agrawal and Katzer 1982; Argyle and Bartholomew 2015; Nieß *et al.* 2022) have proposed regeneration by oxidation or reduction as a last resort to extend catalyst lifetime. However, there are other consequences that make this extremely difficult to do effectively. The elimination rate is clearly too low for technological applications based on reduction. Increasing the temperature could be beneficial, but only with catalysts that are thermally stable. The same applies to oxidative treatment, which can also lead to the formation of the most stable structure, NiSO₄ (Neuberg *et al.* 2019). One such technique that could be used is vapour treatment. Advanced techniques have been evaluated, such as the regeneration of a thiopene-poisoned Ni/SiO₂ catalyst through a series of oxidation-reduction treatments at low O₂ partial pressure and 1 atm H₂. In each case, a temperature higher than 700 °C would be required, which would lead to sintering of the Ni metal particles.

In addition, certain *ex-situ* treatments with oxidizing agents such as permanganate, hypochlorite and N₂O have been documented.

2.16.7 Catalytic Activity of Different Transition Metals

Several authors have documented research on the catalytic activity of transition metal catalysts using AC support in the process of CO₂ methanation (Younas *et al.* 2018; Ha, Ha and Brown 2019; Wang *et al.* 2019c; Gonçalves *et al.* 2020; Sukkathanyawat *et al.* 2020). From literature, Ru, Ni, Fe, and Rh have been found to be more active in CO₂ conversion and CH₄ selectivity (Younas *et al.* 2018; Ha, Ha and Brown 2019; Wang *et al.* 2019c; Gonçalves *et al.* 2020), while others like Cu showed little activity in CO₂ conversion (Sukkathanyawat *et al.* 2020). Table 2.21 shows catalytic activity of common transition metal catalysts supported on AC in terms of CO₂ conversion and CH₄ selectivity.

Table 2-21. Catalytic activity over 0.5%metal/AC transition metal catalysts for CO₂ methanation.

Catalysts	Synthesis Method	Reaction Conditions			CO ₂ Con. (%)	CH ₄ Yie. (%)	CH ₄ Sel. (%)	Ref.
		Temp. (°C)	H ₂ : CO ₂ : Ar (N ₂ , He)	GHSV/h ⁻¹				

Ni/AC	IWI	100 - 450	1:4:5	4000 mL gcatl h ⁻¹	71.5	68.6	96	(Ha, Ha and Brown 2019)
Ru/AC	MWI	240 - 460	4:1	6000 mL·g ⁻¹ h ⁻¹	91	89.2	98	(Wang <i>et al.</i> 2019c)
Fe/AC	UAM	200 - 450	1:4:5	60 000 mL·g ⁻¹ h ⁻¹	77	75.5	98	(Gonçalves <i>et al.</i> 2020)
Co/AC	SG	350 - 450	-	15000 h ⁻¹	78	70	75	(Asundi <i>et al.</i> 2014)
Cu/AC	SGM	250 - 350	2:1	-	19.4	0.83	4.26	(Sukkathanya wat <i>et al.</i> 2020)
Pt/AC	WC	250 - 350	-	5000 h ⁻¹	75	70	68	(Asundi <i>et al.</i> 2014)
Rh/AC	IWI	160 – 220	4:1	5000 h ⁻¹	80	75	75	(Younas <i>et al.</i> 2018)
V/AC	CP	250 - 400	1:4:5	10000h ⁻¹	74	68	66	(Asundi <i>et al.</i> 2014)
Zn/AC	SG	220 - 360	4:1	15000 h ⁻¹	70	65	64	(Giglio <i>et al.</i> 2014)
Zr/AC	CP	300 - 500	1:4:5	5000 h ⁻¹	62	60	63	(Giglio <i>et al.</i> 2014)
La/AC	IWI	350 - 500	4:1	10000 h ⁻¹	68	63	61	(Giglio <i>et al.</i> 2014)

IWI – Incipient wetness impregnation; MWI – Modified wetness impregnation; UAM – Ultrasonic assisted melt infiltration;
SG – Sol-gel; WC – Wet chemistry; CP – Co – precipitation.

2.16.8 Promotion of Ni/AC with the Second Transition Metal

The promotion of nickel-based catalysts supported on activated carbon (Ni/AC) with second transition metals has gained significant attention in catalytic processes, particularly for CO₂ methanation. This approach aims to enhance catalytic performance by improving the yield and selectivity for methane. The second transition metals often used in conjunction with nickel can alter the electronic properties of the catalyst, enhance metal dispersion, and facilitate the reaction kinetics, leading to greater efficiency in converting CO₂ to CH₄. Research has shown that the inclusion of second transition metals, such as cobalt, molybdenum, ruthenium, or palladium, can promote synergy in catalytic activity. This can result in increased surface area and more active sites for the reaction, thus improving overall performance. The synthesis methods and reaction conditions vary widely, highlighting the need for optimization of parameters such as temperature, gas composition, and flow rate to maximize yield and selectivity. From Table 2.22, results of 10Ni5Mo/AC catalyst promoted with different transition metals are given but, in my opinion, they are not conclusive as different metal loading and transition metal synergism could give totally different results.

Table 2-22. The catalytic performance of Ni/AC catalyst for CO₂ methanation with a second transition metal.

Catalysts	Synthesis Method	Reaction Conditions			CO ₂ Con. (%)	CH ₄ Yie. (%)	CH ₄ Sel. (%)	Ref.
		Temp. (°C)	H ₂ : CO ₂ : Ar (N ₂ , He)	GHSV/H ⁻¹				
15Ni5Fe/AC-R	IWI	250 - 450	1:4:5	60000 mL g ⁻¹ h ⁻¹	77	75.5	98	(Gonçalves <i>et al.</i> 2020)
20Ni5Ce/AC	IWI	250 - 450	4:1	36000 cm ³ h ⁻¹ gcat ⁻¹ (h ⁻¹)	78.7	77.9	99	(Hu <i>et al.</i> 2019)
15Ni10Ca/AC	IWI	200 - 500	4:1	-	76	75.53	100	(Feng, Yang and Chu 2016)
NiCo/AC	IWI	300 - 400	4:1	10,000 h ⁻¹	93	85	90	(Sastre Cuadrillero 2015)
NiRu/AC	CP	270 - 350	1:4:5	5000 h ⁻¹	85	80	90	(Sastre Cuadrillero 2015)
10Ni5Mo/AC	IWI	350 - 450	1:4:5	10,000 h ⁻¹	85	80	94	(Sastre Cuadrillero 2015)
NiPd/AC	IWI	300 - 450	4:1	10,000 h ⁻¹	90	80	85	(Sastre Cuadrillero 2015)
NiCu/AC	IWI	300 - 400	1:4:5	10,000 h ⁻¹	82	78	72	(Sastre Cuadrillero 2015)
Ni Zn/AC	CP	220 - 360	4:1	15,000 h ⁻¹	70	65	64	(Sastre Cuadrillero 2015)

2.16.9 Carbonaceous Catalysts

Numerous carbon materials have been used as catalytic supports for CO₂ methanation, including carbon nanotubes (Kwak, Kovarik and Szanyi 2013; O'Byrne *et al.* 2013; Wang *et al.* 2013c; Chew *et al.* 2014; Feng *et al.* 2014; Li *et al.* 2018a; Wang *et al.* 2018a), activated carbon (Swalus *et al.* 2012; Feng, Yang and Chu 2016), carbon felt (Wang *et al.* 2019b), biochar (Wang *et al.* 2019c), and carbon nanofibers (Roldán, Marco and García-Bordejé 2015, 2017), as listed in Table 2.23. In most cases, carbon supports provide hydrogen adsorption sites but cannot activate CO₂. It is advantageous to use carbon-based supports because they have high hydrogen storage capacity, high thermal conductivity that reduces tunable surface properties, local temperature gradients, large specific surface area, and low tendency to coke.

Table 2-23. Carbonaceous support-based catalytic system for CO₂ methanation.

Catalysts	Active metal loading, (wt%)	Temp. (°C)	Pressure (bar)	XCO ₂ (%)	SCH ₄ (%)	Ref.

Ni/OCF	10	125	1	50	100	(Wang <i>et al.</i> 2019b)
Ru/N-ABC	2	380	10	94	100	(Wang <i>et al.</i> 2019c)
Ru/N-CNF	5	350	-	63	100	(Roldán, Marco and García-Bordejé 2017)
Ru/N-CNF	5	375	-	63	100	(Roldán, Marco and García-Bordejé 2015)
K+-Fe/CNT	10	340	2	35	26	(Wang <i>et al.</i> 2013c)
Fe/N-CNT	9.5	360	25	25	40	(Chew <i>et al.</i> 2014)
Ni/N-CNT	10	360	1	90	99	(Wang <i>et al.</i> 2018a)
NiMn/(SGO)-CNT	15Ni 4Mn	350	1	78	100	(Li <i>et al.</i> 2018a)
Ni-Ce/CNT	12Ni 5Ce	350	1	-	85	(Feng <i>et al.</i> 2014)
PdLa ₂ O ₃ /MWCNT	11Pd 2.3La ₂ O ₃	500	-	35	1	(Kwak, Kovarik and Szanyi 2013)
Fe@CNT	1.1	370	1	-	29.3	(O'Byrne <i>et al.</i> 2013)
Ni-Ca/AC	15Ni 10Ca	360	1	76	100	(Feng, Yang and Chu 2016)
Rh/ γ -Al ₂ O ₃ + Ni/AC	1Rh 1Ni	125	2	50	100	(Feng, Yang and Chu 2016)

2.17 Application of Activated Carbon as Catalysts Support

The reactivity and overall activity of a catalyst are determined by its physical properties, chemical composition, and surface area. By printing an active substance or phase onto a suitable support, it is possible to increase the mechanical strength and surface area of the carrier. In addition, the incorporation of the highly dispersed active phase into the micropores of the support contributes to its stabilization. Due to the synergistic relationship between the active phase and the support, the catalytic activity of the active phase is enhanced. It helps to inhibit the agglomeration rate. The optimal dispersion of the active phase on the support, defined as the ratio between the number of surface atoms of the active phase and the total number of atoms present, is the most important feature in the development of catalysts.

AC, which is widely used due to its non-toxicity, affordability, and ease of synthesis, is one of several materials that can act as a support. It minimises the recombination of e-h⁺ pairs by acting as a sink for the resulting electron-hole pairs. Iron, copper, and zinc are examples of impurities that significantly impair their performance and are known as catalyst poisons. Both the inner surface and the pore structure of AC are highly customizable, which is a great advantage when used as a catalyst support. A small part of the structure consists of disordered graphitic components. Electron transfer takes place in the corners of the carbon sheets, which determines their catalytic activity. Therefore, it is crucial to consider the existence and arrangement of these active sites. By incorporating heteroatoms such as nitrogen and sulphur into the lattice, the catalytic activity of the graphite structure can be altered. The presence of acidic or basic surface oxide complexes also influences the activity. Compared to silica and

alumina supports, (a) AC is inexpensive, (b) its pore size distribution is tailored to specific reactions, (c) it is stable at high temperatures, and (d) it has strong resistance to acidic or basic solutions.

Hydrolysis, esterification, hydrogenation, and esterification are among the chemical processes in which AC, and its composites can be used as catalysts or catalyst supports. The hydrolysis of pure cellulose to glucose was unachievable with conventional catalysts such as Amberlyst-15, Nafion and H-mordenite. However, the carbon catalyst, which has an amorphous structure and highly reactive groups such as -COOH , -OH and $\text{-SO}_3\text{H}$, successfully facilitated this conversion. Due to its low activation energy, the carbon catalyst accelerated the hydrolysis process. Due to its propensity to absorb 1,4-glucan, the catalyst shows excellent performance (Suganuma *et al.* 2008). The cellulose is hydrolyzed to glucose as shown in Figure 2.38.

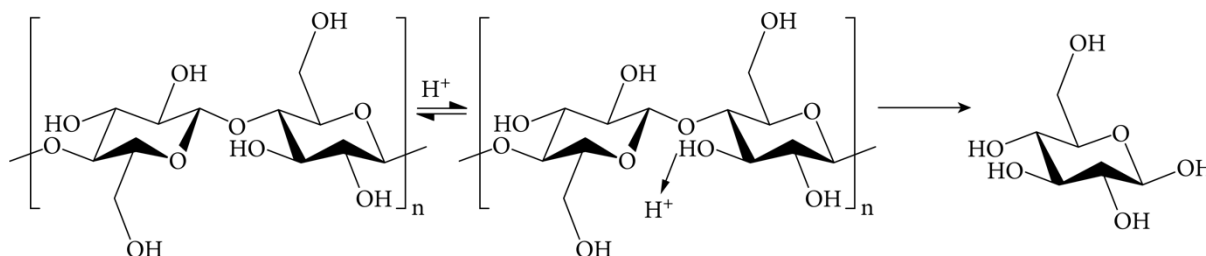


Figure 2-38. Cellulose hydrolysis to glucose production (Lam and Luong 2014).

Hydrodeoxygenation reactions represent another branch in which carbon serves either as a support or as a catalyst. These reactions facilitate the conversion of carbohydrates into unsaturated molecules through the action of a catalyst that favors the cleavage of C-O over C-C, minimizing the use of H_2 . MXenes supported on activated carbon facilitate the conversion of vegetable oils to diesel-range hydrocarbons, including rapeseed, olive, and soybean oils (Han *et al.* 2011).

Molecular hydrogen is applied to compounds in hydrogenation processes. In industrial hydrogenation, the nitro groups in nitroaromatic compounds are reduced to lessen the possibility that other chemicals, such as aniline, will be produced. In 1977, the hydrogenation of nitrobenzene with a Pt catalyst on an AC support was studied (Perez, De Lecea and Solano 1997). Results presented show that catalytic activity of Pt got enhanced by its impregnation onto AC. The results show that the impregnation of Pt on AC increases its catalytic activity. It was found that the dispersion of Pt on AC, the pore structure of AC, the chemical composition of the AC surface and the temperature depend significantly on the catalytic activity. It was

found that there is a linear relationship between the activity and the Pt dispersion (measured at the corresponding reduction temperature).

In addition, AC acts as a support material when phenol is oxidized. Shukla and his colleagues have developed a catalyst that can be used to initiate the oxidation of phenol. The catalyst was produced by impregnating AC with Co(II) ions. The Co(II) ions were evenly distributed on the surface of the AC. The results indicate that Co/AC has considerable efficiency in oxidizing phenol with sulfate radicals. Within 60 min, it was possible to achieve 100% degradation and 80% TOC (total organic carbon) elimination (Shukla *et al.* 2010).

2.18 Catalyst Preparation Methods

Catalytic CO₂ methanation is successfully controlled by the physicochemical properties of the catalysts. It is possible to ensure high CO₂ conversion and catalytic stability by designing a catalyst system with preferred properties. The modification of catalysts has received much attention in recent literature, and various synthesis techniques including co-precipitation, impregnation, and solgel have been applied. As a result, it is possible to positively modify the properties of catalysts such as morphology, metal dispersion, metal-support interaction, and reducibility to enhance the activity and stability of CO₂ methanation.

2.18.1 Impregnation Method

The impregnation method is considered one of the most popular methods for the preparation of catalysts because it is simple and conventional. As shown in Figure 2.39, the impregnation process usually consists of three basic processes (Tsao and Yang 2018). The process begins with the impregnation of a solution containing a metal precursor onto a metal oxide support with a large surface area. To distribute the active metal evenly on the surface of the support during the impregnation process, a magnetic stirrer, an ultrasonic accelerator, or a rotating vacuum evaporator can be used. The solvent is then evaporated in a freeze dryer or oven. Finally, to produce the catalyst, the metal precursor is calcined in a reactor or muffle furnace with the addition of oxygen or air.

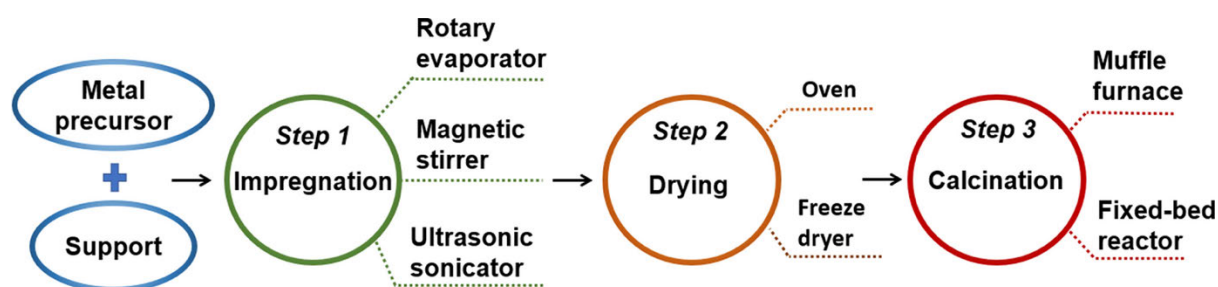


Figure 2-39. Basic steps for catalyst synthesis of impregnation method (Pham *et al.* 2022).

Romero-Sáez *et al.* (2018) prepared Ni-ZrO₂/CNT-nickel zirconia on carbon nanotube catalysts by sequential and co-impregnation methods. In this technique, the impregnated solution was thoroughly mixed with a stirrer before excess solvent was removed using a rotating vacuum evaporator. The material was then processed at approximately 350 °C in an argon atmosphere. Compared to other studied catalysts, Ni-ZrO₂/CNT prepared by sequential impregnation showed the highest activity of 55.3% and the highest methane selectivity of 97.5% at 400 °C. Interestingly, Ni-ZrO₂/CNT prepared by successive impregnation was reportedly stable even after 50 hours of operation.

Martin *et al.* (2019) also synthesized nickel and rhodium catalysts for the methanation of carbon dioxide using the impregnation technique. Unlike the method of Romero-Sáez *et al.* (2018), the catalysts were thoroughly mixed before being freeze-dried with liquid nitrogen. Similar carbon dioxide conversion values were measured for both catalysts: 44% for Ni/CeO₂ and 46% for Rh/CeO₂. However, Rh/CeO₂ had 41% higher methane selectivity than Ni/CeO₂. The Rh nanoparticles of Rh/CeO₂ were smaller than those of Ni/CeO₂ (6 nm) at less than 4 nm, as shown by transmission electron microscopy images, indicating the intense metal-support interaction in Rh/CeO₂, which justifies the higher methane selectivity during carbon dioxide methanation.

In another study, Zhou *et al.* (2016) evaluated the effects of ultrasound-assisted impregnation of 2.5% Ce-Ni/Al₂O₃. Due to the enhanced metal oxide dispersion on the surface, the catalyst prepared with ultrasound in only 25 min showed higher CO₂ conversion of 72.6% and CH₄ selectivity of 97.3%. Due to the accumulation of active components and the destruction of the channel structure of the catalyst, prolonged use of ultrasound for more than 25 minutes may result in poorer catalytic performance.

2.18.2 Sol-Gel Method

In addition to conventional impregnation, the sol-gel technique is a versatile method for producing catalytic materials. The texture and surface properties of catalysts are apparently very controllable by this technique. Therefore, the sol-gel synthesis method (Figure 2.40) is widely used in thermal catalytic processes, such as autothermal reforming (Nimmas *et al.* 2020), steam reforming (Carrera Cerritos *et al.* 2011; Fornari *et al.* 2017; Martin *et al.* 2019), and dry reforming (Aghamohammadi *et al.* 2017; Araújo *et al.* 2020; Abdullah, Ainirazali and Ellapan 2021). The sol-gel method is often used to produce catalysts for the methanation of CO₂, similar to other thermochemical processes.

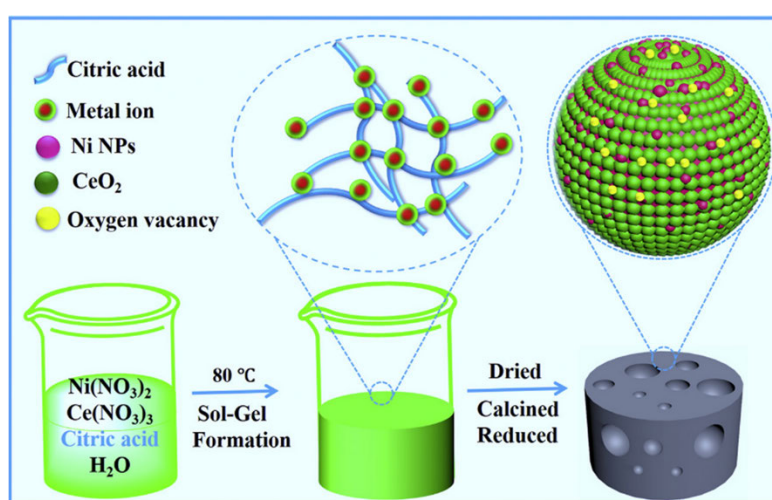


Figure 2-40. The sol-gel method for creating a nickel catalyst with nanostructure supported on ceria (Pham *et al.* 2022).

Moghaddam, Rezaei and Meshkani (2020) synthesized a number of nickel-supported alumina catalysts ($\text{Ni}/\text{Al}_2\text{O}_3$) with a specific nickel content of 15–30 wt, using a novel sol gel method for CO₂ methanation that is surfactant-free. Notably, using the surfactant-free sol gel method resulted in an increase in the surface area of catalysts between 269 and 297 m² g⁻¹. Meanwhile, the addition of Ni led to an increase in the size of nickel crystallites to 4 nm, a decrease in the intensity of the metal-support contact and an improvement in the reducibility of the catalyst. Moreover, 30% $\text{Ni}/\text{Al}_2\text{O}_3$ showed remarkable catalytic activity at 350 °C, with CO₂ conversion and CH₄ selectivity of 74% and 99%, respectively.

Unwiset *et al.* (2020) used the solgel method in another study to synthesize a series of TiO₂-supported nickel catalysts with different nickel concentrations of 3, 6, 12, and 20 wt%, and they investigated the catalyst activity in the methanation of CO₂. Interestingly, this solgel

method improved catalytic activity when nickel was added to titania by adjusting the structural and surface properties. Moreover, when the Ni content was increased from 3 to 20 wt%, the conversion of CO₂ improved significantly, reaching 52.1% for carbon dioxide conversion and 97.2% for methane selectivity at 20% Ni/TiO₂.

Ye *et al.* (2020) also used the sol-gel approach to fabricate the nanostructured nickel support on ceria, Ni/CeO₂ as seen in Figure 2.40, and investigated it for CO₂ methanation. The CO₂ conversion and CH₄ selectivity of Ni/CeO₂ prepared by the sol-gel method were 82.5 % and 94.8 % higher than those of the catalyst obtained by impregnation, respectively. The high performance of Ni/CeO₂ prepared by the sol-gel method was attributed to the formation of nanostructures that maximized nickel ceria contacts with a synergistic metal–support effect. In addition, the significant improvement in thermal and metallic stability was greatly facilitated by the intense interaction between Ni and CeO₂.

2.18.3 Co-Precipitation

The co-precipitation method is one of the most appealing and effective ways to make catalysts for thermal reactions. The co-precipitation method typically entails the basic solution-assisted hydroxide precipitation of metals from metal precursors. By controlling the release of cations and anions, which is a crucial step in the synthesis of monodispersed nanoparticles, the particle growth and nucleation in this method could be directly controlled (Burda *et al.* 2005). The co-precipitation method also attracted attention for its affordability, speedy execution, ease of use in industrial applications, and large-scale transportability (Laurent *et al.* 2008; Pereira *et al.* 2012; Wu, Jiang and Roy 2016).

Hwang *et al.* (2013a) investigated the effects of precipitants on the properties and CO₂ methanation activity of iron-doped nickel on alumina (5%Fe-30%Ni/Al₂O₃) synthesized by coprecipitation. These precipitants included ammonium hydroxide (NH₄OH), ammonium carbonate ((NH₄)₂CO₃), sodium carbonate (Na₂CO₃) and sodium hydroxide (NaOH). The catalyst prepared with ammonium carbonate had the highest CO₂ conversion and CH₄ yield of 58.5% and 58.2%, respectively, which was attributed to the reduction in metal particle size (Ocampo *et al.* 2011; Hwang *et al.* 2013b). In addition, the size of metal particles in 5%Fe-30%Ni/Al₂O₃ varied with the type of precipitant used, with ammonium carbonate producing the largest metal particles.

He *et al.* (2014) also developed an alumina-based nickel hydrotalcite catalyst (Ni-Al- HT) and investigated its performance in the methanation of CO₂. At about 350 °C, the Ni-Al-HT catalyst showed a temperature advantage of 82.5 % efficiency in CO₂ conversion and 99.5 % selectivity in CH₄. This was in comparison to the Ni/Al₂O₃ catalyst produced by impregnation. According to the authors, the catalyst synthesized by coprecipitation showed improved CO₂ activation and methanation activity compared to the catalyst synthesized by impregnation, which is due to the formation of robust basic sites on its surface. Another reason for the effective catalytic performance was the higher Ni dispersion of the co-precipitated Ni-Al- HT.

2.18.4 Mechanical Mixing

As an alternative to co-precipitation, techniques based on mechanical mixing of the components are used. Their advantage is that they emit hardly any emissions and wastewater. The primary step in the process is the dispersion and homogeneity of the catalyst precursors, which is followed by drying and/or calcination. Compared to coprecipitation or calcination of heteronuclear complexes, this method is simple and easy to understand.

2.19 Market Value of CO₂ Conversion to Methane

Current power plants with a maximum capacity of 5 MW are used to estimate the market value of the methanation process. Electrolyzers and methanation collectors make up most of these plants. It is assumed that the methanation part based on these plants costs between 208 and 440 CHF/kW (Zapf 2017). For further calculations, the most optimistic estimate of 208 CHF/kW is used and the resulting investment amounts to 4,405 million CHF, taking into account the predicted economies of scale due to the considerable size of the project.

Expenditure on depreciation and interest amounts to 148 million CHF/a. Due to a lack of expertise, little useful data is currently available, particularly over longer periods. However, a range of 1-3% of the investment costs is what the various plant manufacturers expect. The total amount required to operate the plants is 220 million CHF, plus an additional safety margin of 5%. This expenditure covers the cost of replacing the cooling media, catalysts, and essential water management. The extraction of CO₂ (32.6 €/t CO₂) from the exhaust gases of the cement industry costs a further 88 million CHF/a (Hermann, Emele and Loreck 2014; Schaaf *et al.*

2014b). In total, the methanation plant's operating expenses amount to 457 million CHF/kWh, which translates to about 0.04 CHF/kWh (Table 2.24).

Table 2-24. The cost of methanation with a 419 MW installed capacity (Baier, Schneider and Heel 2018).

Capital expenditures (CapEx)	
Investment costs/power	208 CHF/kW
Investment costs	4,405 million CHF
Operational expenses (OpEx)	
CO ₂ separation	88 million CHF/a
Material, repairs, personnel, etc. (5% capex)	220 million CHF/a
Depreciation and interest	148 million CHF/a
Total	457 million CHF/a
Costs/energy consumed	0.04 CHF/kWh

It is essential to point out that the cost estimate is not influenced by the waste heat generated during methanation at 300 °C. This is because the methanation is expected to be heated with the waste heat from a cement kiln. In addition, the water produced by catalytic reactions during methanation is not considered. Ideally, this relatively pure water can be fed back into the electrolysis process and used as a water source. A heat and mass flow exchange between two complicated systems further complicates the system from a technical point of view. It must therefore be clarified elsewhere to what extent heat and water can be used as input for electrolysis and how great the resulting advantage is. The possible implementation of an intermediate H₂ storage to decouple the methanation processes from the electrolysis could be a viable solution to address the challenges related to electricity use and modulating operation.

2.20 Research Progress in Converting CO₂ into Valuable Fuels

One of the most stable compounds with carbon in its greatest valence state is CO₂. Due to its low electron affinity, electrophilic reactions are challenging. Thus, a nucleophilic assault on the carbon atom is necessary for the conversion of CO₂. As is well known, the dissociation energy required to rupture the C=O bond within a CO₂ molecule is greater than 750 kJ mol⁻¹ (Zhang *et al.* 2018b). From a thermodynamic perspective, this is an uphill reaction. To provide the necessary energy for such a reaction to be completed, high temperatures, high pressures, or extremely effective catalysts are frequently required.

To date, a range of methods have been employed to reduce CO₂, including the thermal catalysis (Kunkes *et al.* 2015; Rui *et al.* 2017; Currie *et al.* 2019; Song *et al.* 2019; Jiang *et al.* 2020), photocatalysis (Wang *et al.* 2014; Li, Peng and Peng 2016; Meng *et al.* 2018; Ran, Jaroniec and Qiao 2018), electrocatalysis (Kornienko *et al.* 2015; Gao *et al.* 2016b; Huang and Buonsanti 2018; Wang *et al.* 2019a), and photoelectrochemical (PEC) reactions (Kim *et al.* 2018; Chen *et al.* 2019; Kalamaras *et al.* 2019; Leung *et al.* 2019), in which heat, light, or electricity are utilized to supply the reaction's necessary energy. Eight electrons are required for each CO₂ molecule to convert into a hydrocarbon molecule completely. Due to the large number of compounds that are created during the reduction process, the purification procedure is complicated, and the yield of the desired products is decreased. Table 2.25 presents a clear comparison of the performance of different CO₂ conversion methods employed in recent years. Extremely concentrated and efficient enzymatic processes were added to the aforementioned reduction technologies to boost the efficiency and accuracy of the CO₂ conversion (Sultana *et al.* 2016; Rudroff *et al.* 2018). These reactions were inspired by natural photosynthesis. The schematic of the most modern CO₂ chemical conversion techniques is shown in Figure 2.41.

As a result of the use of different CO₂ conversion strategies, such as thermal catalysis, photocatalysis, electrocatalysis, photoenzymatic catalysis, photoelectroenzymatic catalysis, and photoelectrochemical (PEC), a range of yields and products were obtained. Table 2.26 the numerous value-added products made using different CO₂ utilization strategies and the catalysts used throughout the conversion process.

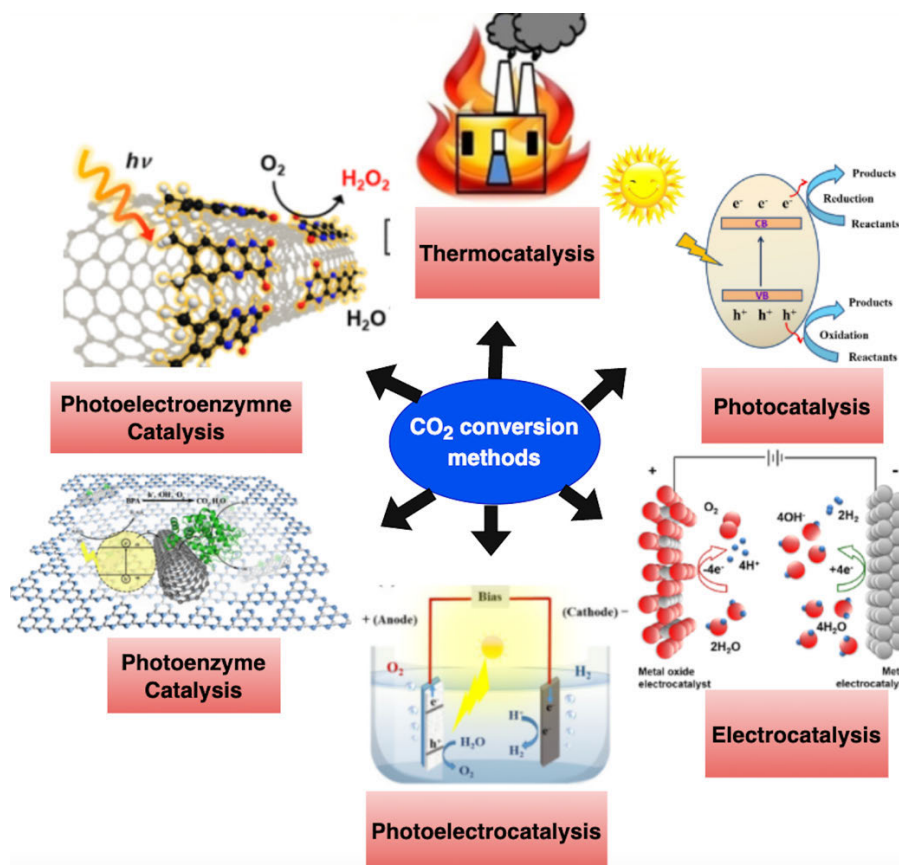


Figure 2-41. A schematic of the CO₂ chemical conversion methods (Xu *et al.* 2020b).

Table 2-25. Performance evaluation of various CO₂ reduction systems.

Materials	Method of CO ₂ Conversion	Efficiency	Reference
CuO + Cu ₂ O	Photo electrocatalysis	CH ₃ OH, 95%, 85 mM at −0.2 V vs. standard hydrogen electrode (SHE) after 1.5 h	(Rajeshwar <i>et al.</i> 2013)
C ₆₀ polymer film	Photocatalysis	HCOOH, 239.46 μM after 2 h	(Yadav <i>et al.</i> 2020)
Ni-Ru/Al ₂ O ₃	Thermal catalysis	CO ₂ conversion: 82.7% CO ₂ selectivity: 100%	(Zhen <i>et al.</i> 2014)
Polyoxometalates (POMs)	Electrocatalysis	38.9 mA cm ^{−2}	(Wang <i>et al.</i> 2018b)
Co-Pi/Fe ₂ O ₃	Photoelectro/enzymatic catalysis	HCOOH, 6.4 μM h ^{−1}	(Nam <i>et al.</i> 2016)
Plain graphite rod	Photo/enzymatic catalysis	HCOOH, 15.49 μM mg Enzyme ^{−1} min ^{−1}	(Srikanth <i>et al.</i> 2014)

Table 2-26. List of catalysts utilized in CO₂ conversion processes to manufacture valuable products.

Catalysts	Products	Methods	Reference
CuInS ₂ thin film	Methanol	Photoelectrochemical	(Yuan and Hao 2013)
Sulfur modified copper	Formate	Electrochemical	(Vickers 2017; Chen <i>et al.</i> 2020a)

Indium W ₁₈ O ₄₉	Formate and acetate	Electrochemical Photocatalytic	(Zha, Li and Li 2020) (Xi <i>et al.</i> 2012)
p-type GaP	Methanol	Photoelectrochemical	(Barton, Rampulla and Bocarsly 2008)
Zn ₂ GeO ₄ nanoribbon	Methane	Photocatalytic	(Liu <i>et al.</i> 2010a)
Bi ₂ WO ₆ nanoplate	Methane	Photocatalytic	(Zhou <i>et al.</i> 2011)
HNb ₃ O ₈ nanobelt	Methane	Photocatalytic	(Li <i>et al.</i> 2012)
TiO ₂	Methanol and methane	Photocatalytic	(Kočí <i>et al.</i> 2009)
PET supported TiO ₂	Carbon monoxide	Photocatalytic	(Jensen, Mikkelsen and Krebs 2011)
Nickel (Ni)	Methane	Thermal (Reforming)	(Zhang <i>et al.</i> 2020a)

2.21 Technologies for CO₂ Capture at Various Technological Readiness Levels (TRL)

The global concern over the effects of industrial operations, such as chemical processes, on the environment has increased interest in green technologies. This issue has fueled significant growth in research and new technologies across many fields since the turn of the 21st century. Due to their significant contributions to high greenhouse gas emissions, the power generation, agricultural, and chemical industries stand out numerically in developing green technologies. It is crucial to track how new technologies are being developed and how old ones are being improved. This allows for future projections for a given area of Research, Development and Innovation (RDI).

A tool called technological maturity analysis, created by NASA in 1990 and modified by The Electric Power Research Institute (EPRI), can rank existing technologies by highlighting the stage they are at. This system is called the Technology Readiness Level (TRL) system (Freeman and Bhowan 2011). TRL has a straightforward nomenclature (TRL1, TRL2, TRL3, etc.) and enables analysis of the stages of technological development. As illustrated in Table 2.27, these stages advance progressively, and each one is necessary for the next.

Table 2-27. Stages of TRL development as defined by EPRI. Source: adapted from (Freeman and Bhowan 2011).

	TRL Level	Technology Mature Level
Demonstration	6	Integrating pilot testing into an appropriate environment
	7	Full-functioning prototype, miniature demonstration
	8	Commercial implementation and full-scale deployment
	9	Standard trade services
Development	3	Component-level proof-of-concept evaluation
	4	A laboratory setting for system validation

	5	Validation of a subsystem in an environment
Research	1	Observation of fundamental ideas, initial conception
	2	Application-based formulation

TRL analysis assesses current technologies, aids in decision-making, and provides for forecasts of time, cost, and environmental implications. Politicians and businesspeople use it as a tool today across the globe, notably in RDI.

Carbon capture, storage and use (CCSU) technologies are typically expensive technologies, hence it is crucial to conduct a technological maturity analysis to identify potential solutions that can direct RDI investments by analyzing the TRL levels the technology can achieve (Roh *et al.* 2020).

The International Energy Agency (2020) conducted a survey of opinions on CO₂ capture systems based on TRL levels. Table 2.28 presents information from this review's four categories of technologies: adsorption, absorption, membrane separation, and chemical capture.

Table 2-28. TRL assessments for adsorption, absorption, membrane separation, and chemical capture technologies (2020) conducted by the International Energy Agency (2020).

Technology Category	TRL Level	Considerations
Absorption	9	It is one of the most advanced technologies. As a result of the research time, this technology has been applied to small and large power plants, fuel converters, and industrial production facilities. The technology is used in natural gas and ethanol processing, where CO ₂ can be captured in large plants. There are many possible applications for this technology. One of its main advantages is its simplicity of operation.
Adsorption	9	Among existing separation technologies, it is considered the most effective and is relatively new. In terms of advances, they depend on existing separation technologies. A small number of its commercial applications have been developed, while most are in demonstration or development phases.
Membrane separation	6–7	

Chemical capture	4–6	Due to the time and research intensity involved, the capture involving chemical reactions is provided in the TRL. Its magnitude is explained by the requirement for extensive pilot-scale testing given that it is still relatively new.

TRL studies have been carried out using information from technology suppliers. Data from Kearns, Liu and Consoli (2021) were used as a comparative source.

The main drawback of the TRL scale, according to Freeman and Bhowan (2011), is the absence of requirements at each stage of development to move on to the next stage. Specifically, the amount of effort needed to move from TRL1 to TRL2 and beyond is unknown.

2.22 Production of Methane (CH₄) Based on CO₂ (Methanation): Challenges and Prospects

Chemical feedstocks such as CO₂ can be used to transform renewable energy. One promising approach to combating CO₂-induced climate change is CO₂ methanation for value-added products, where water electrolysis is a potential energy storage technique for generating H₂ with renewable energy and would contribute to the creation of a carbon-based cycle that is sustainable. Due to their inherent intermittency, renewable energy sources are currently limited by the need for scalable storage methods (Sun *et al.* 2020). Therefore, the most practical and easiest method of storing significant volumes of intermittent energy generated from renewable sources for extended periods is the generation of synthetic natural gas or liquid fuels. PtG is one concept that has gained a lot of attention over the years (Figure 2.42) (Mutz *et al.* 2015). In this method, CO₂ interacts with H₂, which is created by water electrolysis using renewable solar or wind energy to generate CH₄ as a substitute for natural gas. In Copenhagen, a commercial-scale PtG plant with 1.0 M2 of capacity was successfully operating in 2016, exploiting the change of the energy system towards a sustainable system (Younas *et al.* 2016). Five projects, using CO₂ methanation at a commercial or pilot plant size with capacities varying from 25 kW to 6300 kW, were implemented in Germany between 2009 and 2013 (Rönsch *et al.* 2016). In fact, natural gas, or methane, is Germany's main source of heat and a significant contributor to natural gas supplies. Due to their robust dynamic properties, natural gas power plants now generate a larger portion of Germany's electricity than the country's present coal-fired power plants do (Billig *et al.* 2019). Because it has a higher H:C ratio than its conventional

counterpart, its use in automobiles instead of gasoline minimizes CO₂ emissions. The following reactions in Table 2.29 take place in the methanation reactor (Bailera *et al.* 2017):

Table 2-29. CO₂ methanation: main reactions and side reactions (Xing *et al.* 2020).

Reaction Equation	Response Type	$\Delta H_R^{298K}/\text{kJ} \cdot \text{mol}^{-1}$
$\text{CH}_4 \rightleftharpoons \text{C} + 2\text{H}_2$	Methane pyrolysis	-75
$\text{CO}_2 + 2\text{H}_2 \rightleftharpoons \text{C} + 2\text{H}_2\text{O}$	CO ₂ reduction	-90
$\text{CO} + \text{H}_2 \rightleftharpoons \text{C} + \text{H}_2\text{O}$	CO reduction	-131
$2\text{CO} \rightleftharpoons \text{C} + \text{CO}_2$	Boudouard reaction	-172
$\text{CO}_2 + 4\text{H}_2 \rightleftharpoons \text{CH}_4 + 2\text{H}_2\text{O}$	CO ₂ methanation	-165
$2\text{CO} + 2\text{H}_2 \rightleftharpoons \text{CH}_4 + \text{CO}_2$	reverse dry reforming	-247
$\text{CO} + 3\text{H}_2 \rightleftharpoons \text{CH}_4 + \text{H}_2\text{O}$	CO methanation	-206
$\text{CO}_2 + \text{H}_2 \rightleftharpoons \text{CO} + \text{H}_2\text{O}$	reverse water gas shift	41

It is difficult to apply CO₂ because of its inertness, which prevents it from being converted into chemicals with added value. The use of specific catalysts can, however, help to resolve this problem (Wannakao *et al.* 2015). According to Park *et al.* (2015), utilizing a double-layered TiO₂/Cu-TiO₂ catalyst instead of a typical TiO₂ catalyst resulted in a two-fold improvement in the yield of CH₄ production from CO₂ (film catalyst). To clean syngas in ammonia factories, carbon oxides were also hydrogenated to methane. Additionally, this might result in carbon-neutral fuel (methane) (Rafiee *et al.* 2018). The conversion of CO₂ to CH₄ can also occur biologically, for example, using methanogens. Methane-producing organisms are produced via the anoxic enrichment of waste-activated sludge (methanogens). The effectiveness of methane generation was improved by almost 70-fold when the organism's activated cultures were used (Yasin *et al.* 2015).

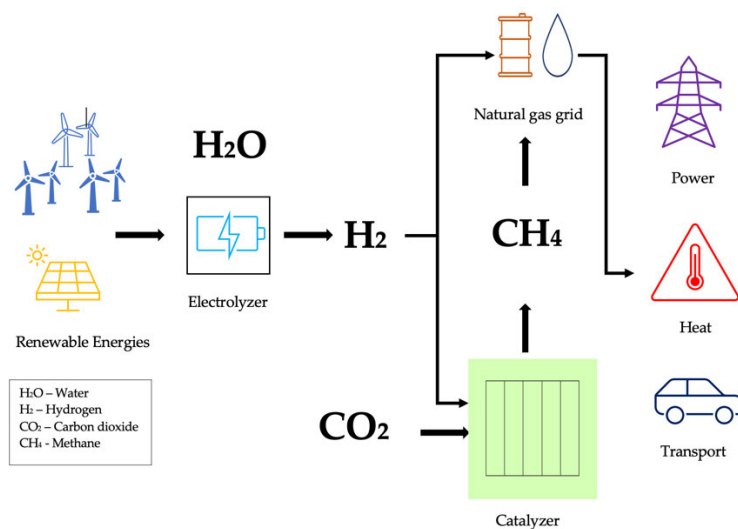


Figure 2-42. Schematic illustration of “power to gas” (PtG) technology (adapted from Younas (Younas *et al.* 2016)).

Due to the increasing demand for storing renewable energy and mitigating global warming, CO₂ methanation has gained renewed attention due to the French chemist Paul Sabatier's discovery in 1902 (Li *et al.* 2018c). Storing energy from renewable resources such as wind and solar, the efficient conversion of biogas to biomethane, and the conversion of CO₂ into chemical feedstocks and fuels are all made possible by the Sabatier reaction (Tomsett *et al.* 1986; Li *et al.* 2022c).

Figure 2.43 illustrates the exothermic nature of CO₂ methanation, which has a high equilibrium conversion between 25 and 400 °C (Herrmann *et al.* 2022; Liu *et al.* 2022). By using the right catalysts, CO₂ methanation can achieve 99% CH₄ selectivity, avoid product separation, and circumvent the challenges of dispersed product distribution. Because of this thermodynamic characteristic, CO₂ methanation is more important in terms of energy effectiveness and economic viability.

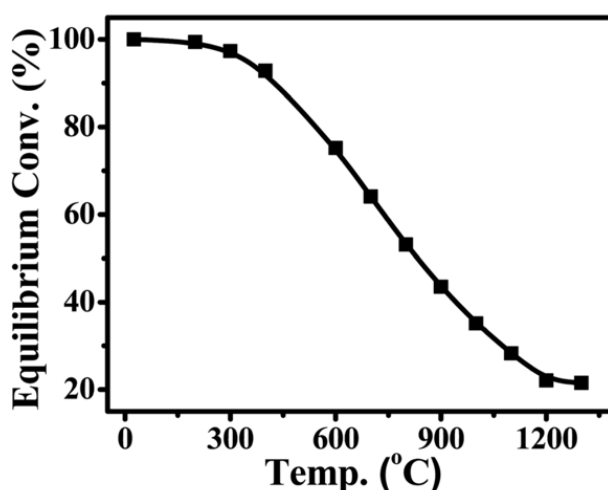


Figure 2-43. A plot of equilibrium CO₂ conversion in methanation at various temperatures (based on literature data) (Du *et al.* 2018; Burger, Donaubaue and Hinrichsen 2021).

2.22.1 Challenges

In CO₂ methanation, deactivating metal catalysts is a major challenge. There are two different ways that methanation catalysts can be deactivated: (a) chemically and (b) physically.

In contrast to Co/Al₂O₃, which deactivated quickly in the same amount of time, the Co/ZrO₂ catalysts showed a greater CO₂ methanation activity and practically consistent performance even after 300 h on stream. Through thermogravimetric analysis and hydrothermal (H₂O) treatment verification experiments, the deactivation of the Co/Al₂O₃ catalyst was further

researched. An excessive amount of CoAl_2O_4 was produced because of the addition of extra H_2O to the reaction system, which hastened the deactivation of the $\text{Co}/\text{Al}_2\text{O}_3$ catalyst. As a result, the product H_2O encourages the production of the inactive phase CoAl_2O_4 , which causes $\text{Co}/\text{Al}_2\text{O}_3$ catalysts to deactivate quickly. One of the causes of deactivation is the deposition of carbon, but the primary cause is the creation of the CoAl_2O_4 spinel structure in the inactive phase.

Active metal sintering and carbon deposition are the main causes of physical deactivation. Ni/YSZ catalysts were synthesized by Kesavan *et al.* (2018) using several techniques. Thin coatings of carbon are generated on NiO particles with a spherical shape, and graphitic laminations are formed on NiO particles that are exposed to surfaces on the Ni/YSZ catalyst created by the impregnation procedure. When NiO/ Ni^{2+} oxidation with a high $\text{CO}_2:\text{H}_2$ ratio was used, the Ni/YSZ(EDTA) catalyst displayed outstanding stability, and operant XAS demonstrated that it was not deactivated. Increasing the H_2/CO_2 ratio or adding steam can prevent carbon from depositing on the catalyst because hydrogen reacts with the carbon deposits to keep them from deactivating the catalyst.

Increased metal dispersion via strong metal–support contact, the addition of catalyst promoters, the development of novel synthesis techniques, and other typical techniques are used to reduce metal sintering (Schubert *et al.* 2016). When the active Co particles are separated by graphite-like carbon, metal sintering is averted effectively. In a study by Li, Lu and Ma (2014), NiO–MgO@ SiO_2 catalysts were successfully prepared and maintained their activity after 100 h on stream. Therefore, particles with the right size are beneficial to CH_4 formation.

2.22.2 Prospects and Future Work Considerations

Increasing atmospheric CO_2 concentrations are believed to be one of the primary drivers of climate change. Although CO_2 capture technologies are quite advanced, using captured CO_2 remains a significant difficulty that will require extensive future research. In the short to medium term, the creation of new life cycle assessments (LCA), techno-economic tools, and benchmark assessments will make it possible to evaluate CO_2 conversion pathways consistently and transparently. Current barriers to furthering CO_2 conversion include energy and water usage, the need for costly catalysts, and problems with gas infrastructure. Cost-effective CO_2 conversion techniques are especially needed, and their pilot-scale testing is essential for their commercial application. A thorough introduction to the various CO_2

conversion processes aids in comprehension of the mechanisms and the selection of suitable methods for using captured CO₂. It is preferable to use the prospective integrated approaches to close the current gaps for widespread industrial applications. Additionally, it is advantageous to demonstrate research and development (R&D) initiatives for CO₂ conversion and analyze CO₂ utilization markets to determine the likelihood of the full-scale implementation of these technologies.

Economic viability, whether it is attained through technical progress or legislative changes, is crucial to promoting the development of the industrial feasibility of CO₂ conversion technology. Because of this, future key research objectives should be concentrated on CO₂ conversion and CCS legislation, policy, and assessments, as well as the integration of CO₂ use with other strategies to minimize costs and energy consumption, especially at a larger scale. Public education and publicity on the capture, sequestration and conversion to methane (CSCM) should be highlighted, and global collaborations need to be further strengthened in the meantime, to increase the general public's awareness of the environmental repercussions. Additionally, it should be highlighted that CCS is necessary to achieve our climate goals, and that CO₂ is not a substitute for it. To keep the rise in the global mean temperature below 1.5 °C, governments should strengthen their commitment to CSCM and play a critical role in supporting its deployment (e.g., through laws, financial options, and tax incentives). The encouragement of private sector funding for larger-scale demonstration programs and the commercialization of CO₂ technologies is another successful approach. The market for CO₂-based products may soon be impacted by regulations and policies as CO₂ becomes a resource that diverse sectors of the global economy want.

The following are general directions for future CO₂ methanation research:

1. To increase the H/C ratio of catalyst surface and facilitate C–C coupling for high-value-added products.
2. To promote CO₂ adsorption and activation by enhancing the oxygen vacancies and support basicity.
3. To investigate potential novel catalytic materials and enhance the stability of the catalyst.
4. To develop more effective catalysts for CO₂ hydrogenation at low temperatures and with little energy consumption.

5. To analyze the process intensification and optimization of CO₂ conversion technologies, which are crucial to understanding how various operating parameters interact, improve process effectiveness, and reduce costs.

2.23 Concluding Remarks and Outlook

The comprehensive chapter presented in this section has highlighted the significant advances and ongoing challenges associated with CO₂ methanation. The transformation of CO₂ into valuable methane through various catalytic methods demonstrates the dual benefits of reducing greenhouse gases and generating alternative fuel sources. Nonetheless, the diversity of catalyst options, process optimization requirements, and energy demands highlights the complexity of achieving efficient, scalable methanation systems.

One of the most critical future directions involves enhancing catalyst efficiency and durability, particularly by exploring novel bimetallic and supported catalysts that can operate under lower energy inputs while maintaining high methane selectivity. Investigating the mechanisms underlying catalyst deactivation, especially due to carbon deposition, remains vital. Future research should also address the development of catalysts that are both cost-effective and environmentally friendly, as these materials will be essential for the large-scale adoption of CO₂ methanation in industrial applications.

Process optimization, including temperature and pressure control as well as reaction kinetics analysis, is another essential area of future study. Advanced reactor designs, such as integrated and modular systems, can potentially enhance conversion rates and reduce operational costs. Digital tools like machine learning and AI-driven process monitoring are promising for achieving real-time optimization, further boosting the efficiency of CO₂ methanation under fluctuating operational conditions.

Finally, expanding interdisciplinary collaborations among research institutions, industry stakeholders, and government entities is crucial to advancing the technology readiness level (TRL) of CO₂ methanation systems. Policy and regulatory support, combined with incentives for adopting carbon utilization technologies, can catalyze the transition from laboratory-scale research to commercial viability. Altogether, continued innovation in catalyst development,

process efficiency, and collaborative frameworks will play a crucial role in realizing the potential of CO₂ methanation as a sustainable solution for global carbon management.

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CHAPTER 3: EXPERIMENTAL METHODOLOGY

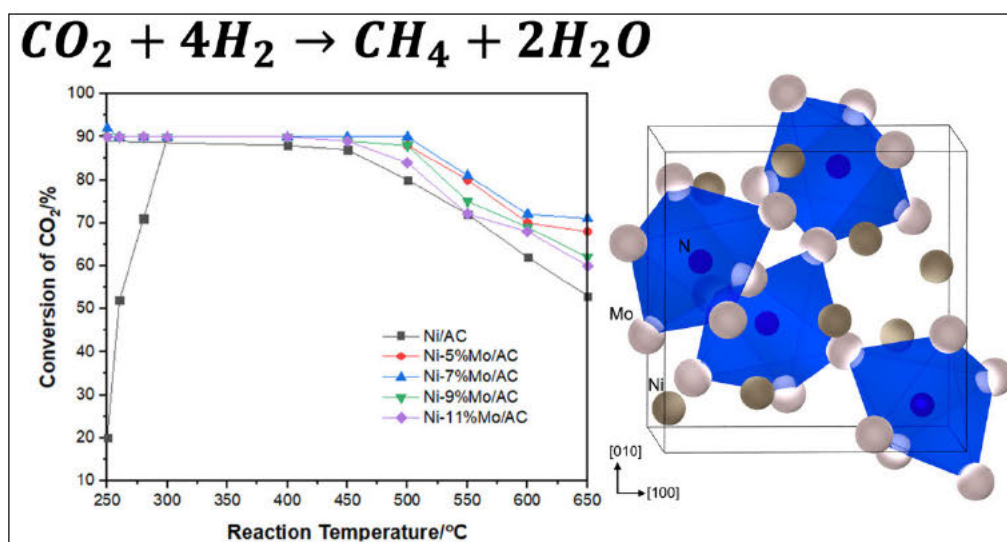
Effects of Molybdenum Addition to Activated Carbon Supported Ni-Based Catalysts for CO₂ Methanation

Abstract

This chapter delves into the synthesis of novel mesoporous activated carbon (AC)-supported bimetallic Ni–Mo catalysts (Ni–xMo/AC, where Ni = 13 wt.% and x = 5, 7, 9, 11 wt.%) using the incipient wet impregnation method. The synthesis was conducted under carefully controlled conditions, including a 10-hour ageing period and 1-hour calcination at 500 °C. The method involved impregnating the AC support with varying concentrations (5–11 wt.%) of molybdenum (Mo) as a promoter. The resulting catalysts were thoroughly characterized to assess their structural, morphological, and chemical properties. A suite of analytical techniques: X-ray diffraction (XRD), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), and N₂ adsorption analysis was employed to confirm the successful incorporation of Mo into the AC support framework. The introduction of Mo as a promoter notably influenced the catalysts' crystallinity, structure, and chemical state. The catalytic performance was evaluated in a fixed-bed reactor under conditions of 250–650 °C, 1 atm pressure, gas hourly space velocity (GHSV) of 1200 mL h⁻¹ g⁻¹, and a H₂/CO₂ ratio of 4:1. Among the synthesized catalysts, the Ni–7%Mo/AC catalyst exhibited the lowest carbon deposition rate, superior stability, and highest activity. The results indicate that the inclusion of Mo enhances the thermal stability of the Ni/AC catalyst and strengthens the interaction between nickel and the support, thereby reducing catalyst sintering.

Keywords: CO₂ methanation; nickel; molybdenum; activated carbon, Ni/AC catalyst; Mo/AC catalyst.

Graphical Abstract



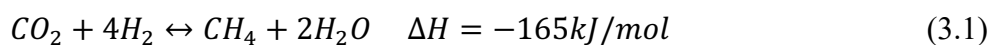
3.1 Introduction

Energy demand is increasing due to human population expansion and activities like industrial operations (Xu *et al.* 2016; Esquivel-Patiño, Serna-González and Nápoles-Rivera 2017; Ray and Deo 2017). However, despite extensive research and the use of sustainable and renewable energy sources, the main sources of energy remain carbon-based fossil fuels, including natural gas, coal, and oil (Martin *et al.* 2017; Guilera, Morante and Andreu 2018; Moghaddam *et al.* 2018b; Bao *et al.* 2019). Processing these non-renewable resources produces substantial environmental pollution, primarily from gaseous emissions, including CH₄, NO_x, and CO_x, sometimes known as greenhouse gases (GHGs), responsible for numerous climatic problems. Carbon dioxide (CO₂) stands out among them. It accounts for over 80% of GHG emissions (Kudapa 2022), which has sparked greater interest in developing processes and methods to capture, reduce, or convert CO₂ to a source of renewable energy (Tahir *et al.* 2016; Ray and Deo 2017; Moghaddam *et al.* 2018b; Farooqui *et al.* 2019). The atmospheric lifetime of CH₄ is much shorter than that of CO₂ (around 12 years compared with centuries for CO₂). Therefore, CO₂ methanation provides an avenue for the reduction of CO₂ (Wuebbles and Hayhoe 2002).

Transitional modifications are required in the current energy system to stabilize atmospheric CO₂ concentration and regulate CO₂ emissions. The two main approaches are CO₂ utilisation and CO₂ capture and storage (CCS). Although CCS technology can effectively reduce CO₂ emissions, several disadvantages limit its efficiency, including the need for a CO₂ sequestration site near the CO₂ source or the prohibitive cost of transporting captured CO₂ (Olajire 2013). However, CO₂ utilization is viewed as an intriguing and supplementary alternative to CCS. The primary atmospheric pollutant, CO₂, can be transformed by this process into chemical compounds or fuels, primarily urea, salicylic acid, and polycarbonate (Song 2006; Wang and Gong 2011b; Olajire 2013). The conversion of CO₂ into alternative energy vectors like methane, methanol, and dimethyl ether appears more logical, given that the amount of carbon released during the combustion of fossil fuels is expected to be between 100 - 1000 Gt CO₂ by 2100. Presently, CO₂ emissions are between 35-40 Gt CO₂/y (Ocampo, Louis and Roger 2009; Ocampo *et al.* 2011; Wang and Gong 2011b; Masson-Delmotte 2018; Rajendran *et al.* 2019).

The most favourable reaction thermodynamically among the many conversion options is CO₂ methanation. The Sabatier reaction allows for the catalytic conversion of CO₂ (collected from

combustion or other processes) into methane or synthetic natural gas (SNG) when mixed with H₂ produced from renewable energy sources (Bareschino *et al.* 2021):



This reduces anthropogenic CO₂ emissions while storing excess renewable energy in the form of SNG, which is easily transportable via the current gas grid. In general, nickel-based catalysts (Aziz *et al.* 2015b; Alrafei *et al.* 2020) and noble metal-supported catalysts (Rh, Ir, Pt, Pd, Ru) (Aziz *et al.* 2014; Kattel *et al.* 2016; Jiang *et al.* 2019; Nguyen *et al.* 2019) have shown good selectivity and conversion for CO₂ methanation. Nickel-based catalysts dominate industrial CO₂ methanation applications due to their low cost and comparable performance (Alipour, Rezaei and Meshkani 2014; Habibi, Arandiyan and Rezaei 2016). However, metal sintering and coking are significant drawbacks for Ni-based catalysts, reducing their activity (Shamskar, Rezaei and Meshkani 2017). Support for Ni-based catalysts is an effective method for dispersing nickel species and modifying the reducibility of oxide precursors (Gac *et al.* 2018). As a result, the type of support significantly impacts how well-supported nickel catalysts perform for the CO₂ methanation (Bian *et al.* 2018).

Using bimetallic catalysts is one of the most significant ways to increase the stability and activity of CO₂ methanation processes. Several studies have shown that modifiers inhibit the coke formation (Jawad, Rezaei and Rownaghi 2020). In the CO₂ methanation reaction, the transition-metal carbides, particularly molybdenum carbide (Mo₂C) and tungsten (W), were shown to exhibit outstanding catalytic selectivity and activity (Zhang *et al.* 2020c). However, the tungsten carbide (WC) and Mo₂C catalysts can only show stable activity at high pressure. These catalysts' reactivity rapidly declines over a short period at low pressure due to CO₂ oxidation (Cheng and Huang 2010; Zhang *et al.* 2020c). According to Daroughegi, Meshkani and Rezaei (2021), adding Mo to Ni/Al₂O₃ catalysts improved the contact between support and Ni species and inhibited the formation of Ni particles. Daroughegi, Meshkani and Rezaei (2021) also showed that the addition of 5 wt% Mo improved the CO₂ methanation activity and reduced the formation of CO as a reaction intermediate (Boudouard reaction, r.2). Thus, this facilitates the synthesis of CO₂ methanation product including (CH₄). This showed that the addition of Mo promoter enhances the performance of the Ni/Al₂O₃ during the CO₂ methanation. However, the addition of molybdenum carbide (Mo₂C) specie increased catalyst deactivation by coking.



Zhang *et al.* (2014c) also reported that incorporating Mo enhances the Ni/AC catalytic activity at a low temperature of 250 °C. The use of AC for CO₂ methanation has been rare. However, in a study by Chang, Tsay and Liang (2001), the CO₂ hydrogenation process using rice husk ash as a precursor to producing AC support revealed that Ni species had good contact with the support and good hydrogenation activity. Several research groups (35-42) have recently studied and created a large surface area and pore-structured AC for CO₂ methanation. According to their findings, AC has a high capacity for CO₂ adsorption under ambient conditions. In a different study, Ha *et al.* (2015) reported on a theoretical investigation of the activation of CO₂ on three metals (Ni, Co, and Cu) supported by AC. According to the computations, CO₂ is adsorbed chemically onto Ni-supported AC. Ni/AC is an active catalyst for CO₂ methanation due to the high surface area of AC, which can store large amounts of both H₂ and CO₂ (Le *et al.* 2017a).

This work reports the CO₂ methanation activity of Ni-Mo/AC catalysts impregnated with different Mo loadings using the incipient wetness impregnation approach. The prepared catalysts were characterized using transmission electron microscopy (TEM), scanning electron microscopy/energy dispersive X-ray spectroscopy (SEM/EDS), X-ray powder diffraction (XRD), and N₂ physisorption techniques. Catalyst performance, CO₂ methanation activity, and CH₄ selectivity over Ni-xMo/AC were measured using the fixed bed reactor apparatus in response to Mo loading and reaction temperature.

3.2 Experimental Method

3.2.1 Catalyst Synthesis

3.2.2.1 Ni – Mo/ AC Catalyst Synthesis

Due to their high activity in methane conversion, Ni - AC catalysts were synthesized via incipient wetness impregnation using Ni(NO₃)₂·6H₂O (99% pure, Merck) as the nickel precursor using AC catalyst as the support (Zhang *et al.* 2014c). After impregnation, the samples were dried at 100 °C for 10 h to remove residual water and calcined in air at 500 °C for 1 h (heating rate: 2 °C min⁻¹) to decompose the nickel (II) nitrate to nitrate oxide (NO) as shown in Figure 3.1. The nickel content in each catalyst was 13 wt%. For comparison, the same procedure was used to prepare the Ni - Mo based AC catalysts using (NH₄)₆Mo₇O₂₄·4H₂O as

a precursor to molybdenum and AC as support. The catalysts were denoted as Ni-xMo/M, where x indicated the wt. % of molybdenum. Table 1.1 lists the materials and gases used.

Table 3-1. Properties of the materials utilized for this study.

Gas/Material	Chemical formula	Purity (%)	Supplier
Ammonium heptamolybdate	$(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$	98	Merck
Nickel (II) nitrate hexahydrate	$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	99	Merck
Activated carbon	AC	99.8	Merck
Carbon dioxide	CO_2	99.99	Afrox
Hydrogen	H_2	99.999	Afrox
Nitrogen	N_2	99.999	Afrox

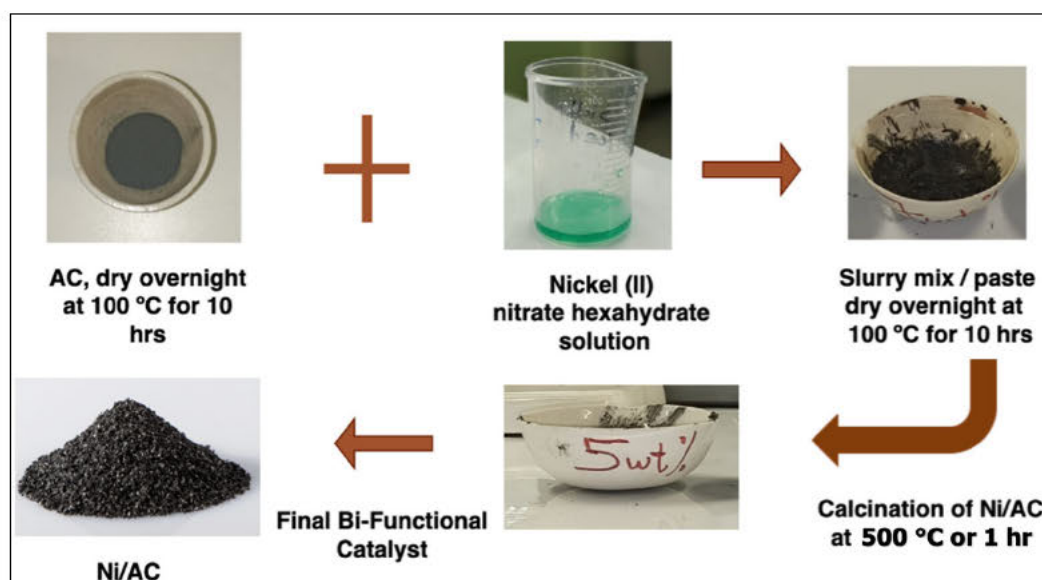


Figure 3-1. Synthesis of the Ni/AC catalyst. The Ni-Mo/AC catalyst was prepared using the same procedure.

3.2.2 Catalyst Characterization

The synthesized catalysts were examined using XRD, BET, SEM/EDX, and TEM to determine their crystallinity and phases, textural properties, morphology, and elemental composition, as well as their reducibility, thermal stability, dispersion, and metal particle size.

3.2.2.1 Textural Properties

The BET surface area, average pore size, and pore volume of the produced catalysts were measured at 77 K using a Micromeritics Tristar 3000 V6.05 A after degassing at 150 °C for 2 hours (Denardin and Perez-Lopez 2019).

3.2.2.2 Phase Identification

Shimadzu's XRD-6000 X-ray powder diffractometer was used to conduct X-ray diffraction (XRD) measurements on the materials' crystalline phases. Cu-K radiation (40 kV, 200 mA) was used, and the scan rate was set to 8°/min from 20° to 80° while the materials were under atmospheric pressure.

3.2.2.3 The Metal Dispersion of the Catalyst

A transmission electron microscope (TEM) was used to create two-dimensional images to visualize the dispersion of Ni particles and their particle size. The instrument used was JEOL JEM 2100 at 200KV, a thermo Fischer detector. Samples were dissolved in ethanol and sonicated for ±20mins and dispersed on a carbon-coated copper grid for analysis.

3.2.2.4 Morphology and Elemental Composition of the Catalyst

The morphology and elemental composition of the catalyst were studied using scanning electron microscopy with energy-dispersive X-ray (SEM/EDX), which generates 3-D images. A Phillips XL30 ESEM microscope operating at 200 kV was utilised for this procedure. Preparing catalysts involved dispersing in ethanol, placing the resulting alcoholic suspension to a standard 3 mm lacy carbon-coated copper grid, and allowing the alcohol to evaporate at ambient temperature. Samples were sputtered with gold before measurements were taken.

3.2.3 Catalytic Tests

The CO₂ hydrogenation to CH₄ was conducted in a fixed-bed reactor (inner diameter: 8.5 mm, length: 575 mm, outer diameter: 12.7 mm) at 250 - 650 °C under standard atmospheric pressure. The reaction temperature was measured by inserting a thermocouple into the catalyst bed. For each run, typically 0.5 g of powdered catalyst (particle size: 3.7-5.5 nm) was loaded into the fixed bed reactor and reduced in situ under a continuous flow of pure H₂ at a rate of 50 ml min⁻¹. The reduction temperature was set up to increase from ambient temperature to 500 °C and remained at this temperature for 2 hours. The temperature was lowered to 250 °C after

reduction while maintaining the same hydrogenation flow rate, and the catalyst was subjected to CO₂/H₂/N₂ feed gases having a molar ratio of 9:36:10 and a gas hourly space velocity (GHSV) of 12000 ml h⁻¹ g⁻¹ at atmospheric pressure. The catalytic activity was measured at temperatures 250, 300, 350, 400, 450, 500, 550, 600, and 650 °C. After stabilizing the catalytic system, three CH₄, CO₂, and CO measurements were taken at each temperature, and the average value was computed. The output gases were run via a cold trap to condense water before being analyzed. The water level in the cold trap was sufficiently low to restrict gas absorption. Using an online GC (Shimadzu GC-2016) fitted with a thermal conductivity detector (TCD) and a 2 m TDX01 column, effluent gases were analyzed. Carbon balances calculated during catalytic testing were consistently between 97 and 99 %. According to equations (3.3) and (3.4), the CO₂ conversion (X_{CO_2}) and methane selectivity (S_{CH_4}), respectively, were calculated (Rahmani, Rezaei and Meshkani 2014; Kesavan *et al.* 2018). Figure 3.2 displays the experimental setup for evaluating the catalyst's performance. According to equations (3.3) and (3.4), the CO₂ conversion (X_{CO_2}) and methane selectivity (S_{CH_4}), respectively, were calculated (Rahmani, Rezaei and Meshkani 2014; Kesavan *et al.* 2018). Figure 3.2 displays the experimental setup for evaluating the catalyst's performance.

$$X_{CO_2} (\%) = \left(1 - \frac{CO_{2out}}{CO_{2in}} \right) \times 100 \quad (3.3)$$

$$S_{CH_4} (\%) = \left(\frac{CH_{4out}}{CH_{4out} + CO_{out}} \right) \times 100 \quad (3.4)$$

Where the percentages of CH₄, CO, and CO₂ identified by GC analysis are CO_{2 out}, CH_{4 out}, and CO _{out}, respectively.

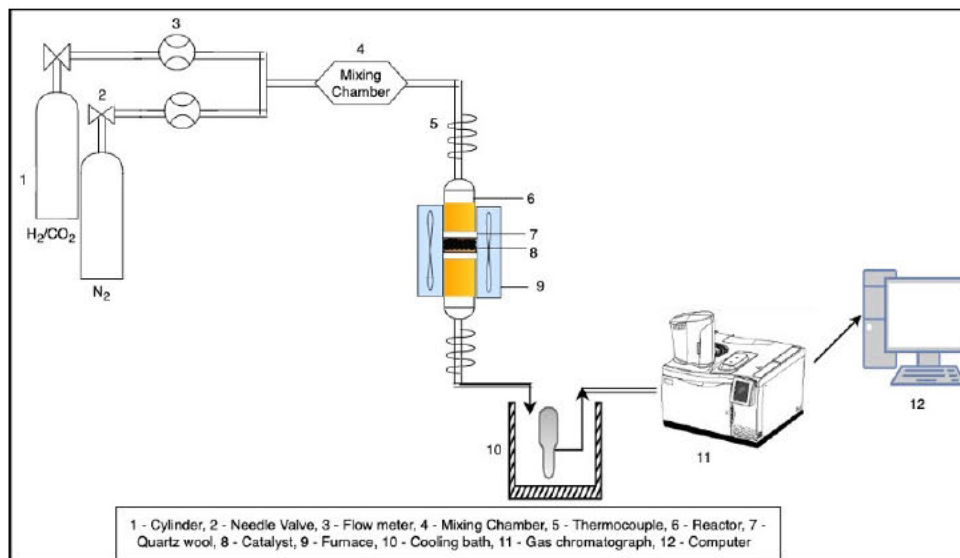


Figure 3-2. Experimental setup for evaluating catalyst performance.

3.3 Results and Discussion

3.3.1 Catalyst Characterization

3.3.1.1 BET Analysis

Figure 3.3 depicts the N₂ physical adsorption – desorption isotherms. The N₂ physical adsorption instrument was used to investigate the physical properties of Ni/AC and Ni-Mo/AC.

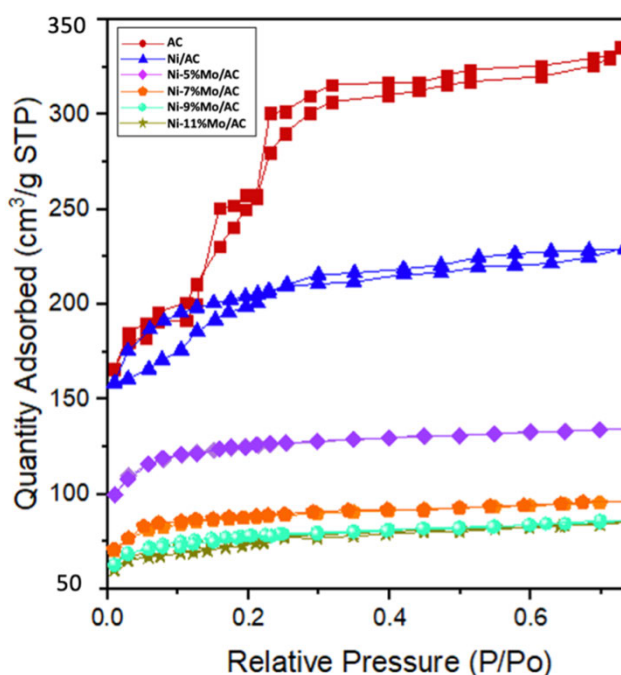


Figure 3-3. N₂ adsorption-desorption isotherms of Ni/AC and Ni-Mo/AC.

The N₂ adsorption-desorption isotherm curves for AC typically displayed IV-type isotherms (Biz and Occelli 1998). In the structured mesoporous material, the equivalent pressure produced by capillary condensation causes the adsorption isotherms to increase drastically. The sudden increase in adsorption isotherms indicates the regularity of the mesoporous material's opening. Figure 3.3 shows the typical IV isotherms for the N₂ physical adsorption-desorption isotherms of the Ni-Mo/AC and Ni/AC catalysts. All adsorption curves exhibited a significant rise in the relative pressure range (P/Po) between 0.2 and 0.4, indicating that Ni-Mo/AC and Ni/AC catalysts are typical mesoporous materials. Nevertheless, the slopes of the adsorption curves in the relative pressure range were distinct for each sample, showing that the mesoporous structures displayed distinct regularities. Therefore, adding Mo considerably lowers the Ni/AC pore structure's hexagonal long-range regularity.

According to the findings of the BET study in Table 3.2, all of the catalysts had a surface area of more than 200 m² g⁻¹. The reference AC support's structural parameters were 762.5883 m² g⁻¹ of surface area, 0.26 cm³ g⁻¹ of pore volume, and 13.07 Å of pore size. The AC's texture was significantly changed after being impregnated with nickel and molybdenum.

The pore volume and surface area of the Ni/AC catalyst decreased by 3.85% and 17.04%, respectively, when the AC was impregnated with nickel. The pore size of Ni/AC increased by 15.23% when AC was impregnated with nickel. Compared to the AC support, the surface area and pore volume of the Ni-5%Mo/AC catalyst also decreased by 48.88% and 42.30%, respectively. It was found that Ni-9%Mo/AC catalysts showed a slight increase in surface area, pore volume and pore size compared to Ni-7%Mo/AC.

According to the trend above, the reference AC support consists of a mesoporous material with a large surface area (Ha, Ha and Brown 2019; Hu *et al.* 2022). The NiO and MoO₃ oxides are impregnated into the AC to modify their properties. The catalyst's pore volume and surface area decrease as its MoO₃ content increases, but its pore size is only slightly enhanced. This indicates that the MoO₃ addition reduced the Ni-Mo/AC catalysts' surface area and pore volume because MoO₃ particles may have blocked some pores (Zhang *et al.* 2014c).

The surface area of nickel was further increased by adding Mo, with the Ni-9%Mo/AC catalyst having a surface area of 274 m² g⁻¹. According to the definition of mesoporous materials, the produced catalyst consisted of mesopores based on the average pore size value in Table 3.2 (Daramola, Matamela and Sadare 2017). It is also clear that adding Mo to the AC support increased the catalyst pore size and surface area. Table 3.2 describes the physicochemical parameters of the Ni/AC and Ni-Mo/AC catalysts.

Table 3-2. Physicochemical properties of Ni/AC and Ni-Mo/AC catalysts.

Catalyst	BET surface area (m ² /g)	Pore volume (cm ³ /g)	Average pore size (Å)
AC	763	0.26	13.07
Ni/AC	633	0.25	15.06
Ni-5%Mo/AC	390	0.15	31.62
Ni-7%Mo/AC	240	0.09	30.29
Ni-9%Mo/AC	274	0.11	31.19
Ni-11%Mo/AC	244	0.09	31.17

3.3.1.2 XRD Phase Analysis

Figure 3.4 shows the results of powder X-ray diffraction for Ni/AC, Ni-5%Mo/AC, Ni-7%Mo/AC, Ni-9%Mo/AC, and Ni-11%Mo/AC catalysts. As demonstrated in Figure 3.4, the diffraction peak at 2θ of 38° , attributed to the Mo species, shows that the Mo-based catalysts were successfully formed. Diffraction patterns are consistent with monoclinic NiMoO_4 (JCPDS No. 031-0902) and graphitic carbon (JCPDS No. 75-1621). The peak of the prepared catalysts, attributed to the AC support, was at 2θ of 25.3° with a shoulder peak at 2θ of 26.9° .

The (002) and (101) activated carbon planes correspond to the two notable broad peaks at 2θ around 26° and 44° (Liu *et al.* 2010b; Kang, Ye and Chang 2013; Konwar *et al.* 2015). The monoclinic NiMoO_4 crystal structure may be seen in the diffraction peaks at $2\theta = 28.9$ and 38.8 , respectively, which correlate to the planes of (220) and (003) (Bhaskar *et al.* 2001; Fontaine *et al.* 2010; Tougerti *et al.* 2013). As a result, the appearance of peaks demonstrates that the catalysts successfully formed the carbon-based support (Saleh 2020). The ultrasmall size of nanoclusters is evident from the observation that NiMoO_4 's peaks are less intense and broader.

In addition, as the molybdenum trioxide (MoO_3) content increased, the diffraction peaks (220) and (003) almost disappeared, and the peak intensities of other peaks became weak. Due to its long-range hexagonal structure, MoO_3 reduces long-range regularities of pore structures (Tu *et al.* 2020). This can lead to a reduction in the surface area of the catalyst.

Ni/AC catalysts had no detectable MoO_3 diffraction peaks. However, all catalysts showed clear nickel diffraction peaks ($2\theta = 44.18$ and 63.24) (Zhang *et al.* 2014c), indicating a strong MoO_3 dispersion on the catalytic surface. The intensity of the diffraction peaks of the metallic nickel increased as the Mo concentration increased, indicating that the particle size of the metallic nickel first decreased and then increased.

It is generally accepted that the particle size of a metallic nickel affects the ability of the supported Ni methanation catalyst to catalyze reactions. The catalyst activity would increase if the metal nickel particles were smaller and had a better surface dispersion (Liu *et al.* 2006). According to the XRD results, a Mo spot promotes the refinement of the metallic nickel grains to some extent and improves the catalytic activity.

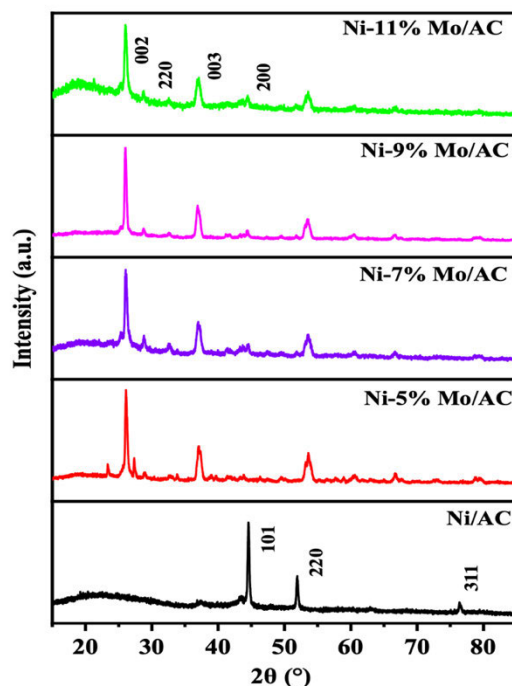


Figure 3-4. X-ray diffraction pattern of the produced catalysts after 500 °C calcination.

3.3.1.3 TEM Analysis

Figure 3.5 displays the findings from TEM imaging of the mesoporous surfaces of the reduced Ni/AC and Ni-7%Mo/AC catalysts, as well as the distributions of active Ni species. The dispersion of active metal particles on the support surface is essential to increase the catalytic activity. As shown in Figure 3.5(A), there were no black spots on pure AC since there was no metal loading. However, as shown in Figure 3.5(B), there were black spots attributable to Ni particles in Ni/AC. As shown in Figure 3.5(C), Ni-Mo alloy particles were also clearly visible as dark spots on TEM images of Ni-Mo/AC. Therefore, it is evident that the active metal particles were evenly distributed on the catalyst support surface.

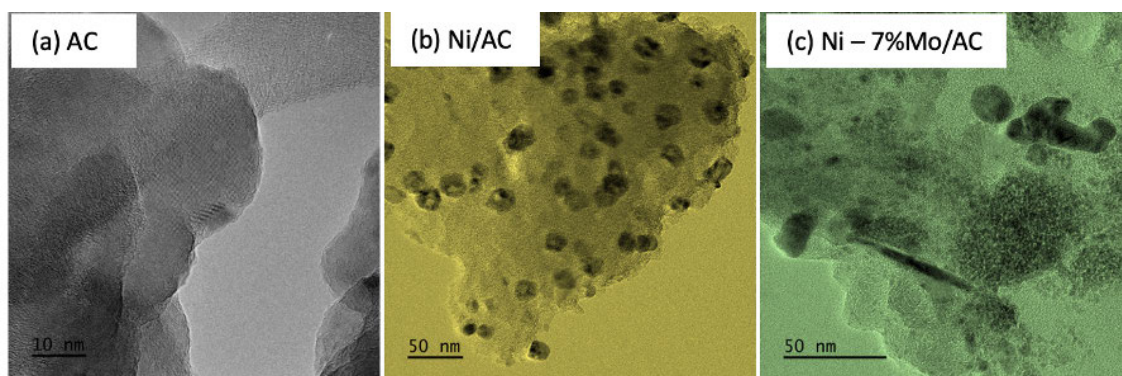


Figure 3-5. TEM Images of Ni, Ni/AC and Ni – 7%Mo/AC catalysts.

3.3.1.4 SEM – EDX

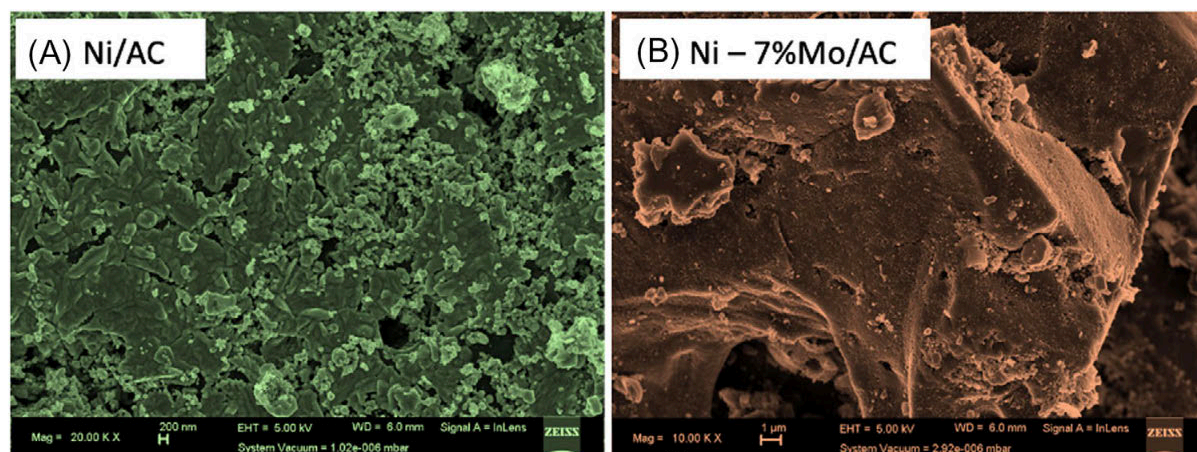


Figure 3-6. SEM images of Ni/AC and Ni–7%Mo/AC catalysts.

Using the SEM-EDS technique, the metal particles on the catalyst surface (Figure 3.6) were analyzed, and the results are shown in Figure 3.7. Figures 3.7(A) and (B) illustrated that the metal particles in regions A and B included large particles of the metal element (Ni) and small particles of the metal element (Mo), while region 3.7(C) contained one kind of metal element (Mo). Studies have shown that the incorporation of Mo in nickel-based catalysts results in the formation of Ni-Mo alloy, which is a viable catalyst for the CO₂ methanation (Zhang *et al.* 2013c; Bian *et al.* 2016; Li *et al.* 2019a; Park, To and Myung 2023). Therefore, the relatively large particles on Ni–7%Mo/AC catalyst surface and the metal particles on Ni/AC catalyst surface should be the metal Ni particles and the relatively small particles on Ni–7%Mo/AC catalyst surface should be the Ni–Mo alloy. The Ni-Mo alloy particles could effectively prevent Ni particles from migrating and accumulating around the metallic nickel particles. Studies have also shown that adding Mo significantly improves the Ni/AC catalyst's heat resistance performance, according to the catalyst's heat resistance assessment (Frontera *et al.* 2018; Fan and Tahir 2021; Xu *et al.* 2023).

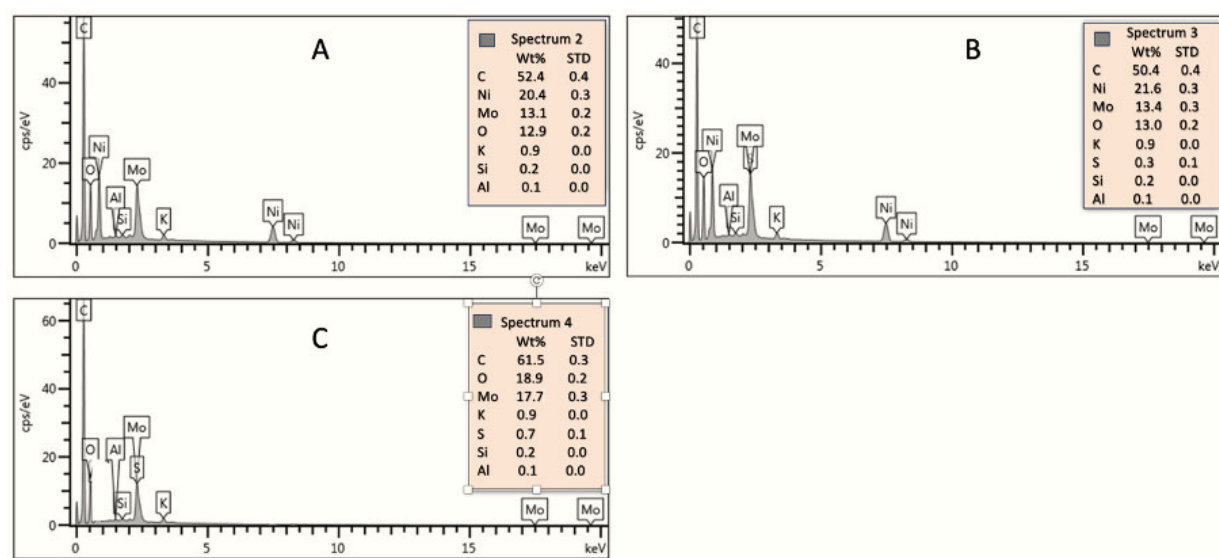


Figure 3-7. SEM-EDS of the Ni/AC and Ni-7%Mo/M catalysts.

3.3.1.5 XPS Analysis

XPS was used to analyze the chemical composition of the catalyst surface and better understand how the influence of Mo affects the electronic properties of nickel. The concentration of nickel atoms on the catalyst's surface and the particle size of the metal nickel both influence the catalytic activity of the catalyst (Wang *et al.* 2000). Based on the XPS results, the nickel atom concentration on the surface (n_{Ni}/n_{Si}) of Ni/AC and Ni-7%Mo/AC catalysts were 7.2% and 13.3%, respectively. MoO_3 could thus be added to increase the concentration of nickel atoms on the catalyst surface. The Ni-7%Mo/AC catalyst exhibited a 62.6% increase in nickel atom concentration. The dissociative adsorption of CO_2 on the surface of the nickel atom produces adsorbed carbon (*C_{ads}*) for the CO_2 methanation reaction, in which *C_{ads}* reacts with H to produce CH_4 (Zagli, Falconer and Keenan 1979; Bang *et al.* 2012). *C_{ads}* formation-controlled CO_2 methanation. The higher the concentration of nickel atoms on the catalyst surface, the more active sites were developed, and the dissociation of CO generated more *C_{ads}*. The findings of the catalyst activity assessment were consistent with the improvement in the methanation activity of CO_2 .

The Mo 3d XPS spectra of the Ni-7%Mo/AC catalyst are presented in Figure 3.8b. They indicate the presence of Mo 3d in several regions located at 232.8, 229.4, and 228.3 eV. Based on the literature, the peaks at region Mo^{6+} (232.8 eV), Mo^{4+} (229.4 eV) and Mo^{2+} (228.3 eV) are probably attributed to molybdenum oxidized phases (Ji *et al.* 2008), resulting from the passivation step (Xiao *et al.* 2002; Wang *et al.* 2022a). This meant that the Ni species had a

strong metal-support interaction between NiO and MoO₃. It was likely that the presence of Mo caused a significant metal-support interaction between the support and the NiO species. The promoting effect and the highly dispersed NiO species on the surface of the Ni-7%Mo/AC catalyst, which is the active component for CO₂ methanation, can be linked to the increased activity of Ni-7%Mo/AC.

Over the sample of Ni/AC, it is found that the corresponding Ni^{2p} spectra are shown in Figure 3.8a, where 852.6, 854.8, and 856.3 corresponded to Ni⁰, Ni²⁺ and Ni^{δ+} (Wang *et al.* 2022a). It was discovered that the catalytic activity of the catalysts at low temperatures of 250 °C was significantly enhanced by reducing the binding energy of Ni 2p^{3/2}. Moreover, it is known that nickel atoms have 9.4 electrons in their 3d electron orbit and 0.6 electrons in their 4s electron orbit (Li *et al.* 2019c). This indicated that there was a 0.6 electron hole in the 3d electron orbit of the nickel atoms. The electron hole is capable of accepting electrons from other atoms (ions). During the activation phase, MoO₃, which had shifted to the surface of the Ni atoms, was largely reduced to Mo<6⁺ due to the catalytic activity of Ni and the H spillover.

This enhanced the electron cloud density of nickel atoms, Ni⁰ → Ni^{δ-}. The Ni-C bond was strengthened, while the Ni-C-O bond was weakened during the methanation reaction due to an increase in electron cloud density of the nickel atoms. This facilitated CO₂ dissociation, resulting in an increase in catalyst activity (Wang *et al.* 2000). Based on the findings of XRD, the metal-nickel particle sizes of the Ni-Mo/AC and Ni/AC catalysts did not differ significantly. Therefore, it can be concluded that adding MoO₃ could significantly promote the activity of Ni/AC catalyst activity at low temperatures of 250 °C due to the transfer of electrons from MoO₃ to the metallic nickel. Moreover, the presence of Mo and Ni oxides is due to the oxidation of the catalyst transfer caused by the active metal properties of nano-sized Ni and Mo, which facilitate the formation of an oxide layer on the surface. The Binding energies of the Mo 3d and Ni 2p orbitals for Ni/AC and Ni-Mo/AC catalysts are presented in Table 3.3.

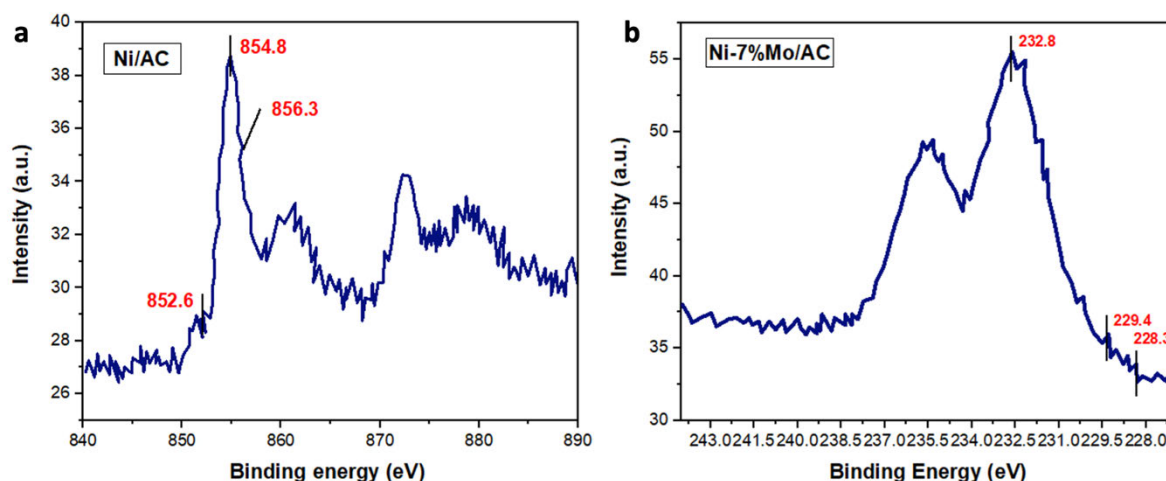


Figure 3-8. XPS spectra of Ni 2p, Mo 3d level for (a) Ni/AC (b) Ni-7%Mo/AC catalysts.

Table 3-3. Binding energies of the Mo 3d and Ni 2p orbitals for Ni/AC and Ni-Mo/AC catalysts.

Catalyst	Mo 3d				Ni 2p _{3/2}		
	Mo ⁰	Mo ²⁺	Mo ⁴⁺	Mo ⁶⁺	Ni ⁰	Ni ^{δ+}	Ni ²⁺
Ni/AC	-	-	-	-	852.6	856.3	854.3
Ni-7%Mo/AC		228.3	229.4	232.8	-	-	-

3.3.2 Catalyst Activity

3.3.2.1 Influence of Mo Content

At 250 °C and atmospheric pressure, the effect of Mo content on the catalytic activity of a Ni/AC catalyst was studied. The findings are presented in Table 3.4.

Table 3-4. Catalytic performance of Ni/AC and Ni-Mo/AC catalysts with varying Mo content.

Catalysts	CO ₂ conversion (%)	CH ₄ selectivity (%)
Ni/AC	11	7
Ni-5%Mo/AC	89	79
Ni-7%Mo/AC	92	80
Ni-9%Mo/AC	90	78
Ni-11%Mo/AC	87	79

Parameters: $n(\text{H}_2):n(\text{CO}_2):n(\text{N}_2) = 36:9:10$, 0.5 g catalyst, 12000 ml h⁻¹ g⁻¹; 250 °C; 1 atmosphere pressure.

According to Table 3.4, the Ni-Mo/AC catalysts were more active than the Ni/AC catalysts. The catalytic activity for Ni-Mo/AC catalysts is in the following order: Ni-7%Mo/AC > Ni-9%Mo/AC > Ni-5%Mo/AC > Ni-11%Mo/AC. Mo could increase the Ni/AC activity at 250 °C

and atmospheric pressure. CH₄ selectivity increased from 7% to about 95%, while the conversion of CO₂ increased from 11% to 92%. The Ni-7%Mo/AC catalyst had the best activity, with 92% CO₂ conversion and 95% CH₄ selectivity. The activities of Ni-Mo/AC catalysts were almost identical. As a result, adding Mo can increase the Ni/AC catalyst activity at low temperatures, and 7 wt% Mo was the optimal concentration.

The particle sizes of metallic nickel did not differ significantly between Ni/AC, Ni-5%Mo/AC, Ni-9%Mo/AC, and Ni-11%Mo/AC catalysts. At 250 °C, Ni-Mo/AC catalysts were considerably more active than Ni/AC catalysts. Therefore, the difference in activity between Ni-Mo/AC and Ni/AC catalysts was not primarily due to particle size at 250 °C. The critical factor causing Ni-Mo/AC catalysts to be more active at low temperatures may be the electron transfer from MoO₃ to nickel metal (Calvino-Casilda *et al.* 2010; Yazdani *et al.* 2015; Chen, De Crisci and Xing 2016). Several studies have shown that the process of electron transfer from MoO₃ to metallic nickel (Ni) is the main cause of activity enhancement of Ni-Mo catalysts, especially when used with AC at low temperatures (Maluf and Assaf 2009; Wang, Ling and Jiang 2016; Yin *et al.* 2017). The catalyst is activated by this electron transfer mechanism, which increases its efficiency in facilitating a number of chemical reactions, especially hydrogenation and removal of sulphur compounds (Zhang *et al.* 2019c; Khalil, Kadja and Ilmi 2021).

The Arrhenius equation was used to calculate the apparent activation energy (E_a) of Ni/AC and Ni-Mo/AC catalysts. The following activation energy values were derived from the graph plotted in the linearized coordinates ln K vs. 1/T(K⁻¹): E_a = 115 kJ/mol for Ni/AC, 102.5 kJ/mol for Ni-5%Mo/AC, 54.6 kJ/mol for Ni-7%Mo/AC, 83.7 kJ/mol for Ni-9%Mo/AC, and 109 kJ/mol for Ni-11%Mo/AC (Figure 3.9). The lower apparent activation energy of Ni-7%Mo/AC (54.6 kJ/mol) compared to that of Ni/AC (115 kJ/mol) strongly supports that the high dispersion of Ni on the small Ni-7%Mo/AC results in a large phase interface and high density of oxygen vacancies, which facilitates CO₂ conversion by reducing the apparent activation energy of CO₂ methanation (Shen *et al.* 2020). This indicates that CO₂ methanation can be significantly accelerated with the Ni-7%Mo/AC catalyst at low reaction temperatures. Consequently, the addition of Mo significantly lowers the activation barrier for the CO₂ methanation reaction (by about 5.1 kJ/mol) compared to Ni/AC.

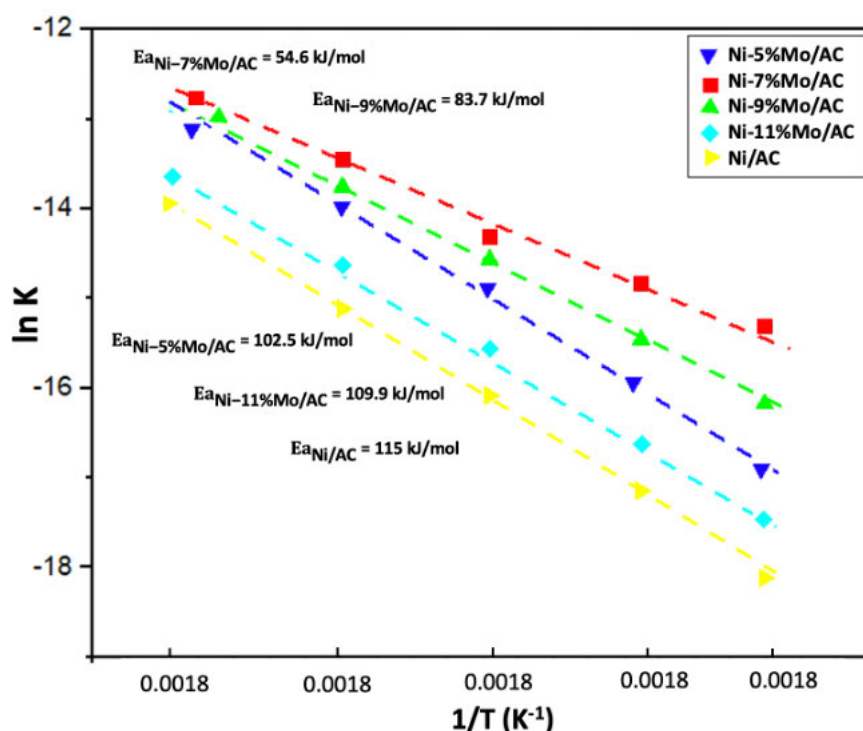


Figure 3-9. Arrhenius plots (T from 250 to 650 °C) and corresponding activation energy (E_a) over Ni/AC and Ni-Mo/AC catalysts.

3.3.2.2 Effect of Reaction Temperature

Figure 3.10 illustrates how CO_2 is converted over Ni/AC and Ni-Mo/AC catalysts under atmospheric pressure as a function of reaction temperature. Figure 3.10a shows that CO_2 conversion over a Ni/AC catalyst increased initially before decreasing as the reaction temperature rose. However, in Figure 3.10b, CO_2 conversion over Ni-5%Mo/AC catalysts mainly remained stable, maintaining nearly 80% at temperatures below 350 °C and progressively declining at temperatures over 350 °C.

Figure 3.10b illustrates the effect of reaction temperature on the selectivity of CH_4 over Ni/AC and Ni-7%Mo/AC catalysts at atmospheric pressure. Figure 3.10b demonstrates that the CH_4 selectivity of all the catalysts tended to increase at first and subsequently decrease as the reaction temperature increased. The activation energy for the reaction may be relatively high due to the stability of the CO_2 molecule. Consequently, an increase in temperature can provide the thermal energy necessary to overcome this activation barrier and thus accelerate the rate of reaction (Wang and Gong 2011a). Due to the highly exothermic nature of the methanation reaction, high temperatures are not favourable from a thermodynamic perspective (Yu *et al.*

2011). All catalysts' CH₄ selectivity reached its maximum at 350 °C, and the Ni-7%Mo/AC catalyst had the highest results with 92% at that temperature and atmospheric pressure.

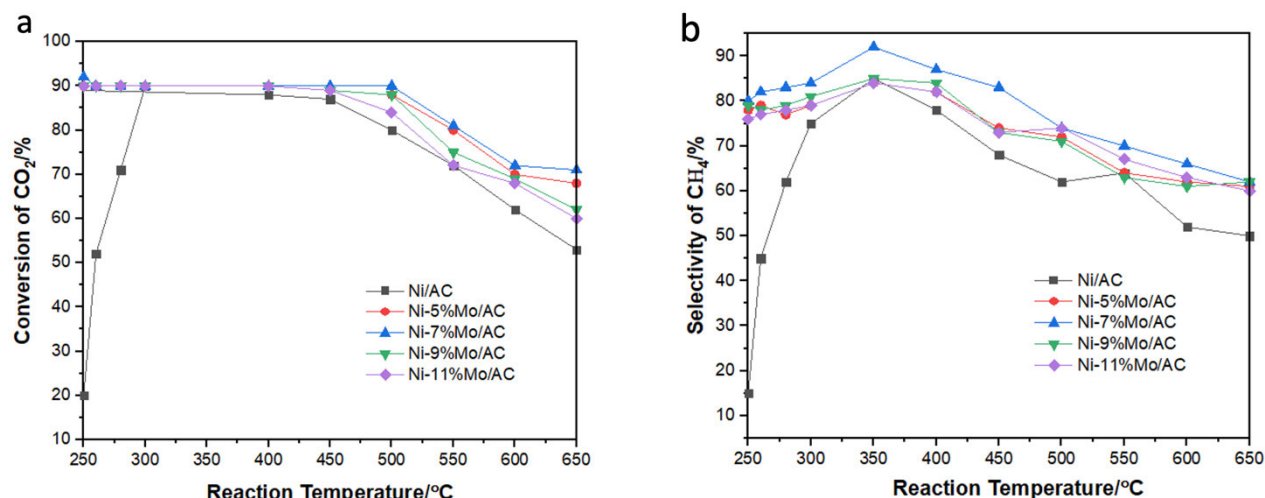


Figure 3-10. The effect of reaction conditions on the activity of Ni/AC and Ni-Mo/AC catalysts: (a) CO₂ conversion over the catalysts; (b) CH₄ selectivity over the catalysts.

3.3.2.3 Stability Test

Under atmospheric pressure, the catalytic stability of Ni-7%Mo/AC catalyst was studied at 350 °C for 100 h. For comparison, the Ni/AC catalyst was also studied under the same conditions, and the results are shown in Figure 3.11. During the stability test, the CO₂ conversion on Ni/AC and Ni-7%Mo/AC catalysts was about 90%. CH₄ selectivity over Ni-7%Mo/AC catalyst dropped more slowly from 83 to 79% in the first 50 h and remained at 79% in the following 50 h. The Ni/AC catalyst also displayed no discernible reduction during the stability test and maintained about 72%. Thus, both Ni-7%Mo/AC and Ni/AC catalysts showed excellent catalytic stability under the reaction conditions, with the Ni-7%Mo/AC catalyst exhibiting higher activity.

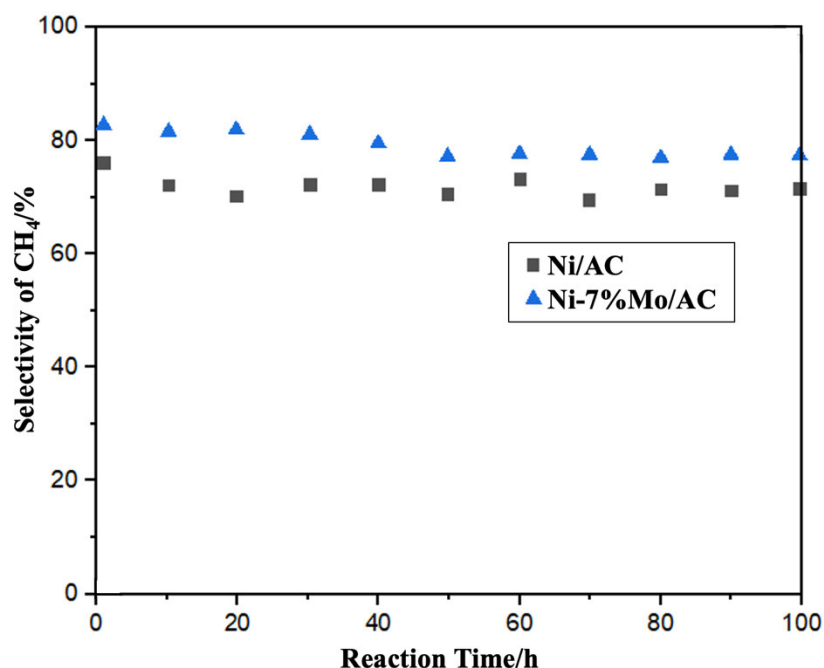


Figure 3-11. Stability test of Ni-7%Mo/AC and Ni/AC catalysts for CO₂ methanation.

3.3.2.4 Heat and Mass Transfer Limitation of the Catalysts

CO₂ methanation is known to be a highly exothermic reaction that would raise the temperature of the reactor. The deactivation of the catalyst is primarily caused by the formation of coke and the sintering of the active metal due to the high temperature. Therefore, the heat resistance performance of the catalysts at high temperatures after calcination is crucial for the industry. According to recent studies, the heat resistance of nickel-based catalysts can be significantly improved by the addition of MoO₃ (Zhang *et al.* 2014c).

Aksoylu, Mısırlı and Önsan (1998) discovered that MoO₃ species and active Ni sites synergize to alter the surface areas of metal and specific activity. In order to investigate the Ni/AC and Ni-Mo/AC catalysts' activity, they were first calcined for 2 hr at 700 °C and then cooled down to 350 °C. These tests were performed at 350 °C while the catalysts were under atmospheric pressure.

Table 3-5. Test for Heat and Mass Transfer Limitation with Ni/AC and Ni-Mo/AC catalysts.

Catalysts	Calcination (Before)		Calcination (After)	
	XCO ₂ (%)	CH ₄ (%)	XO ₂ (%)	SCH ₄ (%)
Ni/AC	68	66	59	55
Ni-5%Mo/AC	67	82	80	81
Ni-7%Mo/AC	69	83	78	83

Ni-9%Mo/AC	42	82	75	82
Ni-11%Mo/AC	39	76	60	76
Parameters: $n(\text{H}_2):n(\text{CO}_2):n(\text{N}_2) = 36:9:10$, 0.5 g catalyst, 12000 ml h ⁻¹ g ⁻¹ ; 350 °C; 1 atmosphere pressure.				
XCO ₂ = CO ₂ conversion, SCH ₄ = CH ₄ selectivity				

It could be observed in Table 3.5 that the heat resistance of the Ni/AC catalyst was significantly improved by the addition of MoO₃. The XCO₂ and SCH₄ of the Ni/AC catalyst decreased from 68% and 66% to 59% and 55%, respectively, after calcination. The XCO₂ and SCH₄ of the Ni-Mo/AC catalysts essentially did not decrease after calcination. Thus, it can be said that the Ni/AC catalyst's heat resistance can be considerably increased by adding MoO₃.

3.4 Conclusion

This study synthesized a series of activated carbon-supported Ni and Mo catalysts via wetness incipient impregnation with varying metal contents, analyzed by several methods (N₂-physisorption, TEM, XPS, XRD, and SEM - EDX), and tested for CO₂ methanation.

In a fixed-bed reactor, the effect of Mo content on the catalyst's ability to convert CO₂ and select CH₄ was examined. With CO₂ conversion and CH₄ selectivity ranging from 11 % to 92 % and 7 % to 80 %, respectively, adding Mo to a Ni/AC catalyst at a low temperature of 250 °C would increase its catalytic activity. The Ni-7%Mo/AC catalyst demonstrated superior activity. The catalytic activity of Ni-Mo/AC catalysts initially increased but decreased as Mo concentration increased. With a 4:1 molar ratio of H₂ to CO₂ at 1.0 atm and 12000 ml h⁻¹ g⁻¹, the Ni-7%Mo/AC catalyst displayed the best activity, converting CO₂ at a rate of 92% and selecting CH₄ with 80% selectivity.

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CHAPTER 4

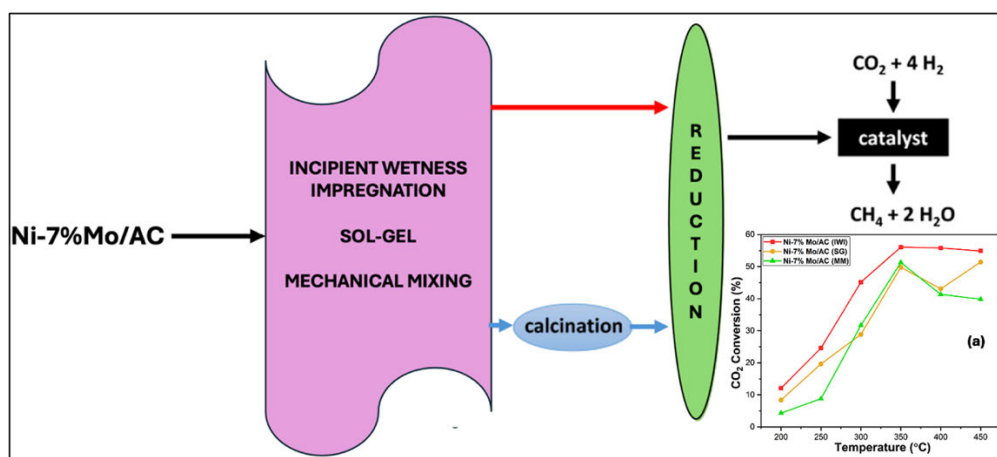
Evaluation of Mo-promoted Ni/AC catalysts in CO₂ methanation: Effect of different synthesis method

Abstract

This chapter explores the synthesis and evaluation of Ni-7%Mo/AC catalysts synthesized via three distinct methods: incipient wetness impregnation (IWI), sol-gel (SG), and mechanical mixing (MM), for CO₂ methanation. The catalysts were tested under operating conditions ($T = 200\text{--}450\text{ }^{\circ}\text{C}$, $P = 1\text{ atm}$, $\text{H}_2/\text{CO}_2 = 4/1$, $\text{WHSV} = 3600\text{ mL}^{-1}\text{h}^{-1}\text{g}^{-1}$). Characterization techniques, including X-ray diffraction (XRD), scanning electron microscopy (SEM-EDS), Fourier-transform infrared spectroscopy (FTIR), and N₂ adsorption-desorption isotherms, were employed to analyze their structural and morphological properties. Among the methods, the IWI catalyst exhibited the best performance, achieving 56% CO₂ conversion and >95% CH₄ selectivity at 350 °C, compared to 51.4% for the SG catalyst at 450 °C and 51.2% for the MM catalyst at 350 °C. The enhanced catalytic activity of the IWI catalyst is attributed to the uniform dispersion of Ni and Mo on the activated carbon (AC) support and improved crystallinity of the active phases. The chapter highlights the significant influence of synthesis methods on the catalytic performance and structural properties of Ni-7%Mo/AC catalysts in CO₂ methanation.

Keywords: CO₂ methanation, Ni-Mo catalyst, stability, activity, CO₂ conversion, CH₄ selectivity, Synthesis method

Graphical Abstract



4.1 Introduction

In recent years, there has been a significant rise in public awareness regarding the impact of greenhouse gas emissions on global warming (Li *et al.* 2021b). Various strategies have been

proposed for the removal of carbon dioxide (CO₂) from the atmosphere, including carbon capture and storage. Among these, the reduction of CO₂ using renewable hydrogen, stands out as a sustainable approach, as it converts CO₂ into a renewable and environmentally friendly carbon source, enabling the production of valuable fuels or chemicals. One particularly promising technology for CO₂ recycling is the production of methane (CH₄) through catalytic hydrogenation reactions, where CH₄ serves as a useful by-product of CO₂ conversion (Yamasaki 2003; Dhillon and von Wuehlisch 2013).

There have been reports of very active and selective catalysts for CO₂ hydrogenation process producing CH₄, including transition metals such as Ru (Janke *et al.* 2014), Rh (Sharma *et al.* 2011; Karelovic and Ruiz 2013b), Pd (Park and McFarland 2009; Kim, Lee and Park 2010), Co (Zhou *et al.* 2013) and Ni, (da Silva *et al.* 2012; Aziz *et al.* 2014). Nickel-based catalysts are among the most promising options due to their high selectivity for CH₄ and cost-effectiveness in the hydrogenation of CO₂ to synthetic natural gas (SNG) (Rostrup-Nielsen, Pedersen and Sehested 2007; Stangeland *et al.* 2018). However, their stability can be compromised by deactivation resulting from sintering and carbon deposition (Feng *et al.* 2019). Several factors, including the synthesis method (Ashok, Ang and Kawi 2017; Kim *et al.* 2020), the type of support material (Ferreira and Branco 2019; Liang *et al.* 2019; Riani *et al.* 2023) and the nickel (Ni) loading (Aziz *et al.* 2015c; Zhang *et al.* 2019d), play a critical role in determining the performance of Ni-based catalysts. These properties influence catalyst stability, the activation of hydrogen (H₂) and CO₂, as well as the reaction intermediates that eventually lead to CH₄ formation. Notably, Ni loading has a significant impact on Ni dispersion (particle size), which in turn affects the interactions between Ni and the support material (Aziz *et al.* 2015c; Zhang *et al.* 2019d).

In their study, Zhang *et al.* (2019d) examined how varying Ni loadings (from 0 to 50 wt%) influenced the catalytic performance of Ni/Al₂O₃ catalysts, linking these findings to the catalysts' physicochemical properties. The research revealed that higher Ni loadings led to the agglomeration of Ni particles, which in turn reduced the extent of Ni's strong interaction with alumina thus lowering the degree of NiO reduction. The catalyst with 25 wt% Ni exhibited the highest methanation activity. A similar trend was observed on a silica oxide (SiO₂) support, where the optimal methanation activity was achieved at 10 wt% Ni (Aziz *et al.* 2015c). Catalysts with smaller Ni particles and moderate Ni loadings exhibited strong interactions with the support, resulting in high catalytic activity and selective CH₄ formation without CO

production. In contrast, higher Ni loadings promoted the formation of larger Ni particles, leading to CO production (Garbarino *et al.* 2014). These studies highlight that an optimal Ni concentration is essential for achieving the best catalytic performance, balancing metal dispersion and support interaction.

Furthermore, the dispersion of Ni, its reducibility, and the overall properties of the catalyst are significantly affected by the nature of the support material. Recent studies have increasingly focused on activated carbon (AC) as a catalyst support due to its low energy requirement for regeneration, large surface area, and ability to be surface-functionalized (Samanta *et al.* 2012; Vargas, Giraldo and Moreno-Piraján 2012; Wickramaratne and Jaroniec 2013; El Gamal *et al.* 2018; Akpasi and Isa 2022; Hussin *et al.* 2022; Sahoo 2022). Their findings demonstrated that AC is an effective adsorbent for CO₂ under ambient conditions (Samanta *et al.* 2012; Vargas, Giraldo and Moreno-Piraján 2012; Wickramaratne and Jaroniec 2013; Akpasi and Isa 2022; Hussin *et al.* 2022; Sahoo 2022). For example, Vargas, Giraldo and Moreno-Piraján (2012) investigated CO₂ adsorption at 273 K (-0.15°C) using three types of AC monoliths derived from African palm shells, and their results showed that the carbon monoliths could adsorb up to 5.8 mmol CO₂ g⁻¹ at 1 bar and 273 K (-0.15°C). Similarly, Wickramaratne and Jaroniec (2013) found that AC spheres exhibited exceptional CO₂ uptake, achieving 8.9 mmol/g at 0°C and 4.55 mmol/g at 25 °C under atmospheric pressure. In another study by Li *et al.* (2016c), AC derived from pine cone shells demonstrated a CO₂ adsorption capacity of 7.63 mmol/g at 0°C under 1 bar pressure and 2.35 mmol/g under 0.15 bar pressure.

The adsorption of CO₂ onto the support and the dispersion of metal can be enhanced by the properties of AC, including its high pore volume, narrow pore size distribution, and large surface area. However, catalyst deactivation can occur due to coke deposition on Ni/AC, which is often caused by the presence of larger Ni particles. To mitigate this issue, the catalyst can be enhanced with suitable promoters that improve its selectivity, stability, and catalytic activity. Molybdenum (Mo) has shown distinctive redox properties (Mo⁴⁺/Mo⁶⁺) and key characteristics that facilitate oxygen transfer and prevent coke formation during the methanation process (Akpasi *et al.* 2024). Recent studies have highlighted the superior catalytic performance of MoO₃ as a promoter (Zhang *et al.* 2013c; Méndez-Mateos *et al.* 2020; Fan and Tahir 2021; Akpasi *et al.* 2024). The primary role of MoO₃ is to increase catalytic activity and selectivity at lower temperatures by enhancing oxygen vacancies and active metallic Ni sites. This not

only boosts CO₂ adsorption but also prevents carbon deposition, leading to improved overall catalytic performance (Fan and Tahir 2021).

In our previous study, we reported on AC catalysts promoted by 7 wt.% Mo with a 13 wt.% Ni, which demonstrated enhanced activity in the CO₂ methanation reaction (13 wt.% Ni) (Akpasi *et al.* 2024). This improvement can be attributed to the increase in basic sites, particularly medium basic sites (Pan *et al.* 2014; Zhang *et al.* 2022). These studies indicate that a complex interplay of factors influences the performance of the Ni-AC catalyst with Mo as a promoter. The observed behaviour is partly due to the dispersion of Ni and Mo, their interactions with each other, and the AC support. Additionally, the amount of Mo added, and the method used to deposit or incorporate it into the AC support are critical considerations. Several techniques have been employed to distribute both the metal active phase and the promoter, including soft-template co-precipitation (Atzori *et al.* 2018), incipient wetness impregnation (Atzori *et al.* 2018; Kim *et al.* 2020), wet impregnation (Ding *et al.* 2016; Kamonsuangkasem *et al.* 2017; Wu *et al.* 2020b), and one-pot synthesis (Nie *et al.* 2017; Biset-Peiró *et al.* 2019). The choice of method can significantly affect the final dispersion of the catalyst and, consequently, its efficiency. Thus, gaining a comprehensive understanding of the relationship between Ni loading and dispersion (particle size), Ni's interaction with the promoter and support, and the resulting catalytic activity is crucial for the development of stable, active, and selective Ni-based catalysts.

Building on the findings from the existing literature, this study aimed to develop highly dispersed Ni-7%Mo/AC catalysts by employing a range of catalyst synthesis methods, including sol-gel (SG), incipient wetness impregnation (IWI), and mechanical mixing (MM). The primary objective is to investigate the variations in the interactions between Ni and Mo and to correlate these interactions with the catalytic performance in CO₂ methanation as well as the fabrication techniques used. To achieve this aim, the catalysts were extensively characterized using N₂-physisorption, Fourier-transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), and scanning electron microscopy (SEM) coupled with energy-dispersive X-ray spectroscopy (EDS), enabling a comprehensive analysis of their structural properties in relation to catalytic activity. Additionally, the CO₂ hydrogenation reaction was performed over a temperature range of 200 - 450 °C with extended reaction times to evaluate the stability of the synthesized catalysts.

4.2 Experimental

4.2.1 Catalysts Preparation

During the catalyst preparation, commercial AC (Merck, 99.8 % purity) was purchased and used as a support. Metal salts of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Merck, 99.99 %) and $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ (Merck, 99.99 %) were used as precursor material for Ni and Mo respectively. Citric acid monohydrate (Merck, 99.5 %) was used as a gelling/complexing agent. The reagents were used as is unless otherwise stated.

To investigate the influence of synthesis method on the production of CH_4 via the methanation reaction, Ni-Mo/AC catalyst was used. For all samples, Ni and Mo loading were set to 13 and 7 wt%, respectively. The impregnation strategies are detailed as follows:

Ni-Mo/AC (IWI) catalyst – Ni-Mo based AC catalysts were synthesized via incipient wetness impregnation using $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (99% pure, Merck) as the nickel precursor, $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ as a precursor to molybdenum and activated carbon as the support. The AC was titrated with de-ionized water to find the pore volume. Then, a specific amount of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ was dissolved in distilled water, which corresponds to the pore volume of the AC support. After impregnation, the sample was dried at 100 °C for 10 h to remove residual water. It was then calcined in air at 500 °C for 1 h, with a heating rate of 2°C/min, as illustrated in Figure 4.1. Following calcination, the sample was crushed and sieved to obtain catalyst particles with sizes ranging from 50 to 212 μm . The catalysts were denoted as Ni- x Mo/M, where x indicated the wt.% of molybdenum.

Ni-Mo/AC (SG) catalyst – A series of mesoporous nickel (13 wt%) - molybdenum (7 wt%) - activated carbon (denoted as Ni-7wt.%Mo/AC) catalysts were prepared by a sol-gel method. 3.46g of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 8.50g of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ were dissolved in 15 mL of distilled water by continuous stirring at room temperature. Then citric acid was added to the resultant solution, according to CA/(Ni+Mo) molar ratio of 1.0. The mixture was stirred for 1 hr at room temperature. The formation of homogenous gel was observed in a period of 6 h and the gel was dried at 80 °C overnight. The resultant gel was then crushed and calcined at 500 °C for 4 h with the heating rate of 2 °C/min.

Ni-Mo/AC (MM) catalyst – 13 wt%-Ni-AC sample was prepared by mechanical mixing. A stoichiometric amount of the commercial AC, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ were mixed together, grinded in a mortar until homogenous sample was obtained and then calcined at 500 °C for 4h. The three catalyst synthesis steps are demonstrated in Figure 4.1.

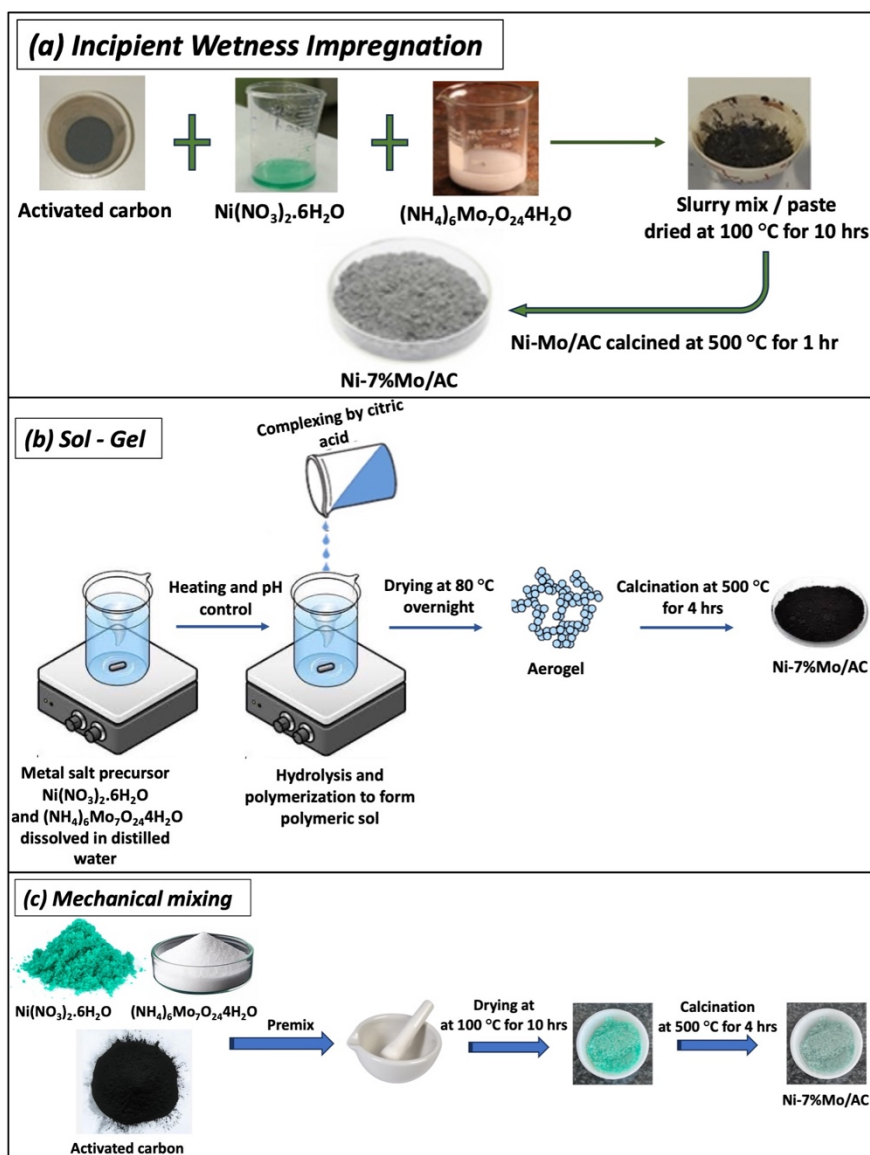


Figure 4-1. Preparation of Ni-7%Mo/AC catalysts via three different synthesis method.

4.2.2 Physico-Chemical Characterization

The fresh catalyst was analyzed using X-ray diffraction (XRD) with Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$) on a Siemens D5000 diffractometer. A scanning step size of $0.01^\circ \text{ s}^{-1}$ was used to scan the 2θ range from 10° to 90° . Phase identification was conducted using the ICDD-JCPDS database.

The Micromeritics ASAP 2020 apparatus was employed to measure the N₂ adsorption/desorption isotherms of the samples at -196 °C. Prior to analysis, each sample was outgassed under vacuum at 150 °C for eight hours. The Barrett-Joyner-Halenda (BJH) method was used to analyze the N₂ adsorption data, providing information on total pore volume, average pore diameters, and pore size distributions.

Microscopic analyses were conducted using a ZEISS SUPRA 40VP field emission scanning electron microscope (FE-SEM). This apparatus includes a solid-state backscattered electron (BSE) detector, a high-sensitivity secondary electron detector known as "InLens," and an energy dispersive X-ray spectrometer (EDS) "INCA Energie 450 × 3" from OXFORD for chemical analysis. After carbon coating, the samples, which were mounted directly on high-purity conductive double-sided adhesive carbon tabs, were imaged.

Functional groups were identified using a Nicolet 6700 spectrometer equipped with the appropriate cell. The samples, pressed into disks, were activated in a hydrogen stream at 500 °C for 1 h. Following activation, the catalysts were sequentially stabilized at 150 °C, 200 °C, 250 °C, and 300 °C, and background spectra were recorded under flowing argon. The samples were then exposed to a reaction gas mixture (4% CO₂:16% H₂:80% Ar) for 1 h. FTIR spectra were obtained by averaging 50 scans with a resolution of 4 cm⁻¹.

4.2.3 Catalyst Evaluation

The gas-phase hydrogenation of CO₂ to CH₄ was performed in a continuous-flow fixed-bed quartz reactor with an internal diameter of 8.5 mm, operating under standard atmospheric pressure. The reaction temperature was monitored with a thermocouple inserted into the catalyst bed. Each run utilized approximately 0.5 g of catalyst pellets (40 to 60 mesh), which were reduced *in situ* with a continuous flow of pure H₂ at 50 mL/min. The temperature was gradually increased to 450 °C (heating rate = 5 °C/min) from room temperature and held for 2 h before cooling to 200 °C. Following reduction, the catalyst was exposed to a gas mixture of CO₂, H₂, and N₂ with a molar ratio of CO₂:H₂:N₂ = 1:4:5. The reaction was conducted at a weight hourly space velocity (WHSV) of 3600 mL⁻¹h⁻¹g⁻¹ at atmospheric pressure. Catalytic activity was evaluated at temperatures of 200 °C, 250 °C, 300 °C, 350 °C, 400 °C, and 450 °C. For each temperature, an average value was calculated from three measurements of CO, CO₂, and CH₄ taken after 1 h on stream, once the catalytic system stabilized. To prevent water from

interfering with the analysis, the effluent gases were passed through a cold trap. Due to the low water levels in the trap, no significant gas absorption occurred. The evolved gases were analyzed using a Shimadzu GC-2016 online gas analyzer equipped with a thermal conductivity detector (TCD). During catalytic testing, carbon balances consistently ranged between 97% and 99%, ensuring accurate and reliable measurements. For stability testing, the optimal catalyst was subjected to identical pre-treatment and gas conditions at 350 °C for 50 h.

The CO₂ conversion (X_{CO_2}) and CH₄ selectivity (S_{CH_4}) were calculated as follows:

$$X_{CO_2} (\%) = \left(1 - \frac{CO_{2out}}{CO_{2in}}\right) \times 100 \quad (4.1)$$

$$S_{CH_4} (\%) = \left(\frac{CH_{4out}}{CH_{4out} + CO_{out}}\right) \times 100 \quad (4.2)$$

Where the percentages of CH₄, CO, and CO₂ identified by GC analysis are CO_{2 out}, CH_{4 out}, and CO_{out}, respectively.

For each catalyst, at least two repeated tests were conducted under identical conditions to assess intermediate precision. The results indicated that conversion values for all samples varied within ±5%, while selectivity measurements were within ±1%.

4.3 Results and Discussion

4.3.1 XRD – Phase Identification

The XRD patterns of the AC, Ni-7%Mo/AC (IWI), Ni-7%Mo/AC (SG) and Ni-7%Mo/AC (MM) catalysts are shown in Figure 4.2. The two broad peaks observed in the XRD patterns of the AC support are located at approximately 26.6° and 43.8°, respectively. These peaks correspond to the (002) and (100) planes of graphite in AC (Arie *et al.* 2016). These two diffraction peaks represent the amorphous, disordered structure of AC. This disordered structure leads to a high porosity of carbon materials, which is confirmed by SEM analysis in Figure (4.2a), as AC typically consists of randomly layered graphite planes (Shi *et al.* 2012).

After the addition of the metals (Ni and Mo), distinct diffraction peaks of cubic NiO at 2θ of 33.9°, 37.2°, 43.7° and 62.8° (JCPDS 96-901-2317) can be seen in all the synthesized catalysts, as shown in the graph (Chouke *et al.* ; Wardani *et al.* 2019; Taeño *et al.* 2021; Lin *et al.* 2022). On the other hand, it was clear that the synthesized Ni-7%Mo/AC catalysts using different

methods exhibited different intensities of NiO diffraction peaks. This indicates that the dispersion and grain size of NiO on the AC support could be significantly affected by the Ni salt precursor and the synthesis method (Wen *et al.* 2021). Ni-7%Mo/AC (IWI) catalysts exhibit sharper and stronger peak intensities of the NiO phase than Ni-7%Mo/AC (SG) and Ni-7%Mo/AC (MM) catalysts. This indicates that the NiO crystallinity was higher in the Ni-7%Mo/AC (IWI) catalyst. This could, therefore, lead to larger NiO particle sizes.

The Ni-7%Mo/AC (MM) catalyst exhibited the smallest particle size among all prepared catalysts. This was demonstrated by a decrease in peak intensity, which indicates a broader distribution of diffracted X-rays across a wider angular range (Ingham 2015). Furthermore, it was observed that all three synthesized catalysts exhibited visible NiMo₂ peaks at 19.9° corresponding to the (001) reflective planes (JCPDS 96-152-2821). Moreover, all the Ni-7%Mo/AC catalysts that were synthesized were found to have distinct diffraction peaks indicative of monoclinic molybdenum oxycarbide (MoOC) at $2\theta = 14.3^\circ$; these peaks can be ascribed to the reflecting planes (JCPDS 95-155-7341). It was also found that all the catalysts prepared had visible peaks of cubic MO₄ at 38.6°. These peaks were identified as (111) reflecting planes (JCPDS 96-153-4908).

Similarly, Ni-7%Mo/AC catalysts prepared by the IWI, SG and MM methods showed the peaks of the MoO₈ phase. These results demonstrate that both the three preparation methods contributed to introducing Mo species of MoO₁₂ and MoO₈. These results align with the findings of Hamdi *et al.* (2023), who reported that the successful impregnation of NiO and MoO significantly reduced the amorphous structure of AC.

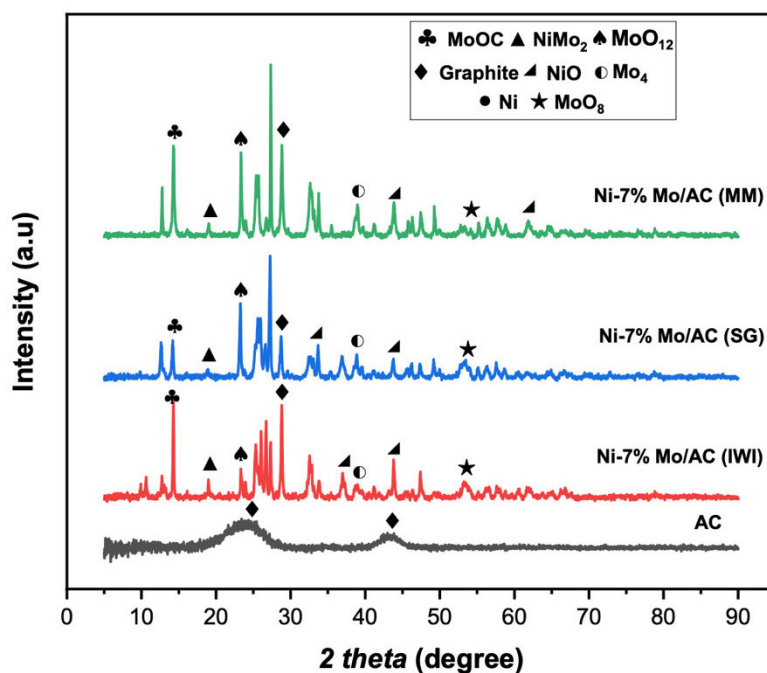


Figure 4-2. XRD patterns of AC, Ni-7%Mo/AC (IWI), Ni-7%Mo/AC (SG), and Ni-7%Mo/AC catalysts.

4.3.2 Structural and Morphological Properties

Scanning electron microscopy and energy dispersive spectroscopy (SEM-EDS) images of the catalysts are shown in Figure 4.3(a)–(d). The smooth surfaces and the irregularly shaped spheres with porous framework that make up the AC support can be seen in Figure 4.3(a) (Ordoñez Regil *et al.* 2022). This type of amorphous material is commonly found in AC and other adsorbents or catalytic supports (Wang and Yang 2007; Azman *et al.* 2021; Wang *et al.* 2022a). In addition, the SEM image of the AC revealed cavities ranging from 10 to 50 μm in width, consistent with the morphological characteristics reported in previous studies on AC (Lalhmunsiana *et al.* 2017). The Ni-7%Mo/AC (IWI) catalyst can be seen in an SEM image in Figure 4.3(b). When the pristine AC was combined with Ni and Mo, the morphology of the catalyst changed. A previous study has shown that the addition of the metals Ni and Mo causes a significant change in the surface morphology of AC (Azman *et al.* 2021). The synthesis method also had an impact on the shape and elemental distribution of the synthesised Ni-7%Mo/AC catalyst, as revealed by SEM examination. The catalysts prepared with SG and IWI were characterised by thick-porous network structures and regularly shaped particles. The two primary reaction steps in SG synthesis were hydrolysis and condensation, as described in the literature (Landau 2008). The preparation environment significantly influenced the condensation process, leading to the formation of diverse morphologies, such as single

monodisperse particles or three-dimensional networks (Singh *et al.* 2014). The presence of amorphous carbon in the catalysts prepared with SG was attributed to the decomposition of citric acid during the synthesis process (Bao *et al.* 2009). Rough, aggregated, and irregular spherical shapes with particle sizes larger than 1 μm can be seen in Figure (4d). Insufficient dispersion or contact forces between Ni, Mo and AC particles are the cause of these changes.

The EDS analysis revealed that the predominant elements in the structures of AC are C and O. Since carbon makes up more than 90% of the elements and is the main component of the support material, its most intense peak was to be expected. Carbon (91.80%) and oxygen (8.20%) are therefore confirmed by the elemental chemical composition determined by EDS. According to the EDS mapping of the synthesised catalysts, the catalysts prepared by different methods contained different amounts of Ni and Mo (Figure 4.3). The colour variations observed in Figure 2(b)-(d) correspond to the different Ni and Mo concentrations in the prepared Ni-7%Mo/AC (IWI), Ni-7%Mo/AC (SG) and Ni-7%Mo/AC (MM) catalysts, respectively. In contrast to the Ni-7%Mo/AC catalyst prepared by the SG and MM methods, the Ni-7%Mo/AC (IWI) catalyst exhibited a uniform distribution of Ni and Mo over different regions of the AC-supported surface, with no apparent agglomeration or segregation. The presence of NiMo alloy was confirmed by the uniform distribution on the Ni-7%Mo/AC (IWI) catalyst (Wang *et al.* 2013b).

Compared to the other two methods, the catalyst produced using the IWI method displayed bright spots in the distribution pattern of Ni and Mo, indicating a higher concentration of these elements, as shown in Figure (4.3b) - (4.3d). In contrast, the sol-gel (SG) method utilized solid citric acid (CA) powder for the preparation of Ni-7%Mo/AC catalysts. The CA powder was evenly dispersed in the mixture through stirring, ensuring uniform distribution of Ni and Mo throughout the catalyst. This approach resulted in a more porous structure, as depicted in Figure (4.3c). Compared to the Ni-7%Mo/AC catalysts synthesized by IWI and MM, the EDS analysis in Table 4.1 reveals that the Ni-7%Mo/AC (SG) catalyst exhibited a higher carbon content and lower Ni content. Additionally, the Ni-7%Mo/AC (IWI) catalyst showed the highest concentration of Mo. These findings clearly demonstrate that both Ni and Mo were effectively incorporated into the activated carbon support as nanoparticles. The detailed elemental composition of the Ni-7%Mo/AC (IWI), Ni-7%Mo/AC (SG), and Ni-7%Mo/AC (MM) catalysts, as determined by EDX, is presented in Table 4.1.

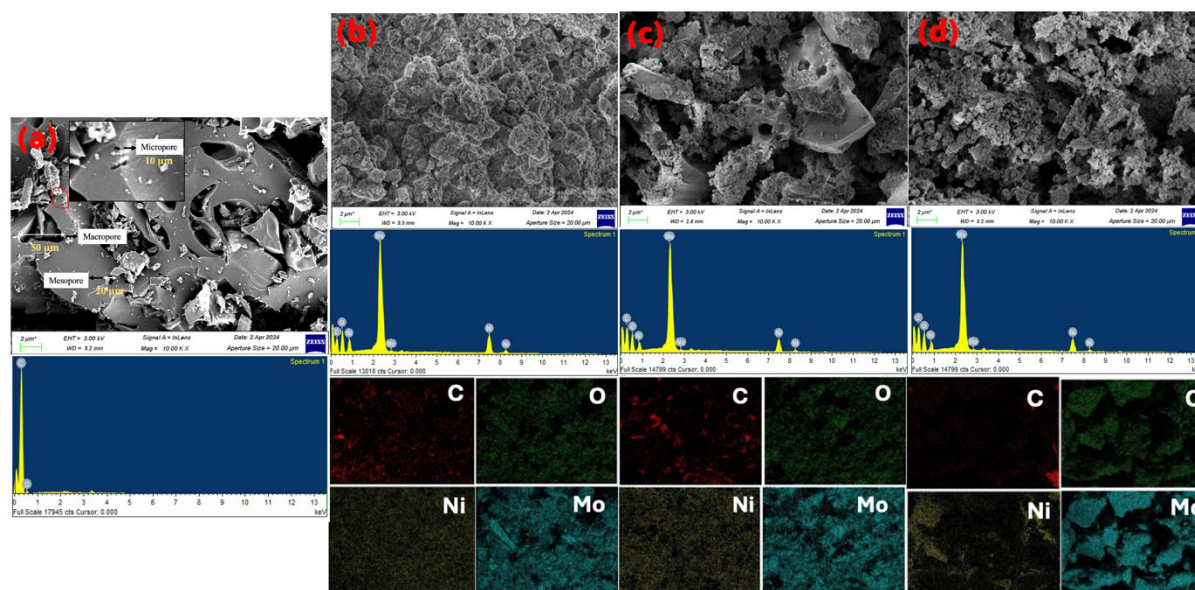


Figure 4-3. SEM images and EDS elemental mapping images of (a) AC, (b) Ni-7%Mo/AC (IWI), (c) Ni-7%Mo/AC (SG), and (d) Ni-7%Mo/AC (MM).

Table 4-1. The elemental composition (%) of the catalysts.

Catalysts	Elemental Composition (%)			
	Carbon (C)	Oxygen (O)	Nickel (Ni)	Molybdenum (Mo)
AC	91.80	8.20	-	-
Ni-7%Mo/AC (IWI)	28.17	24.67	12.69	34.48
Ni-7%Mo/AC (SG)	40.04	21.50	8.17	30.29
Ni-7%Mo/AC (MM)	16.05	30.00	19.07	34.89

4.3.3 N₂ Adsorption/Desorption Analysis

Figure 4.4 illustrates the N₂ adsorption-desorption isotherms and the pore distribution of AC and Ni-7%Mo/AC catalysts. It was seen that AC and Ni-7%Mo/AC catalysts fabricated via the IWI, SG, and MM approach had non-comparable N₂ adsorption-desorption isotherms. The N₂ adsorption-desorption analysis indicated that the synthesis methods influenced the pore structure and surface area of the catalysts, as shown in Figure 4.4(a). According to the IUPAC classification in Figure 4.4, the adsorption-desorption isotherms of two catalysts samples synthesized via IWI and SG methods were found to be of type II, with a turning point at $P/P_0 = 0.8$. Figure 4(a) shows type I and type IV N₂ adsorption-desorption isotherms for AC and Ni-7%Mo/AC (MM) catalysts. However, as P/P_0 increases, the isotherm of AC demonstrates that the adsorbed volume increases. The Ni-7%Mo/AC catalysts prepared by the MM method showed a broader hysteresis loop of 0.2 to 1 at the relative partial pressure (P/P_0), indicating the presence of a significant mesoporous framework.

Moreover, the adsorption and desorption branches of all the catalysts indicate that macro-mesoporous structures remained largely unchanged after the incorporation of metals (Ni and Mo) using the IWI, SG, and MM methods (Valencia and Klimova 2013; Wu *et al.* 2020a). There was a continuous increase in the adsorbed volume as the relative pressure increased. The specific surface area and total pore volume of the catalysts were determined based on this characterization (Table 4.2).

Table 4-2. Textural properties of the AC and Ni-7%Mo/AC catalysts prepared with different methods.

Catalysts	S_{BET} (m^2/g)	V_{total} (cm^3g^{-1})	Avg pore dia. (nm)	Volume @ STP (cm^3g^{-1})
AC	756.70	0.995	2.218	252.08
Ni-7%Mo/AC (IWI)	141.92	0.996	2.832	47.00
Ni-7%Mo/AC (SG)	119.10	0.996	3.028	38.94
Ni-7%Mo/AC (MM)	16.59	0.994	7.443	5.13

It was observed that the deposition of metals on the catalyst support leads to a reduction in the surface areas of the catalysts. During catalyst preparation, the metal species predominantly penetrate the pores of the AC support, obstructing the pores and causing a subsequent reduction in surface area (Bian *et al.* 2016). The specific surface area and pore volume of the catalyst prepared by the IWI method were much higher than the others, and the lowest values were obtained for the catalyst prepared by MM, which is due to the lowest volume adsorbed at STP. However, the catalysts prepared using the MM method have more mesopores, as can be seen in Figure. (4.4a) and (4.4b). The average pore size of Ni-7%Mo/AC (IWI) is 2.83 nm, resulting in a larger surface area ($141.92 \text{ m}^2/\text{g}$) and volume ($0.996 \text{ cm}^3/\text{g}$) than Ni-7%Mo/AC (SG) ($119.10 \text{ m}^2/\text{g}$ and $0.996 \text{ cm}^3/\text{g}$) and Ni-7%Mo/AC (MM) ($16.59 \text{ m}^2/\text{g}$ and $0.994 \text{ cm}^3/\text{g}$). The reduction in surface area of Ni-7%Mo/AC (SG) was due to the decomposition of citric acid (CA) that occurred during fabrication.

Studies have shown that the addition of citric acid leads to a reduction in the specific BET surface area and an increase in the average pore diameter (Sikhwivhilu, Pillai and Hillie 2011). This is mainly due to the dispersed citrate's possible penetration into the pores of the Ni-7%Mo/AC (SG) catalysts. CA can also promote the agglomeration of active metal particles, reducing the specific BET surface area. Studies have shown that during the synthesis of Ni-7%Mo/AC catalysts using the IWI method, the interaction between Ni and Mo can significantly affect the catalyst's surface area (Aksoylu, Mısırlı and Önsan 1998; Xu *et al.* 2023; Akpasi *et al.* 2024). A similar phenomenon was observed for the Ni-7%Mo/AC catalysts prepared using

the SG method, which promoted stronger interactions between the Ni metal and the support, resulting in a slightly larger surface area compared to the catalysts synthesized by the MM method. Figure (4.4b) and (4.4c) illustrate the pore size distribution of all the catalysts following the incorporation of metal species (Ni and Co), revealing the formation of larger mesoporous structures and a reduction in microporous structures. Additionally, a decrease in the BET surface area was noted for the synthesized catalysts.

As shown in Figure 4.4(b) and 4.4(c), the active components occupy the mesoporous channel of the supports between 1 and 50 nm. This is consistent with the pore size distribution of the support and the Ni-7%Mo/AC catalysts. Based on these findings, the active components may penetrate the AC support. This is in agreement with the results of Wei *et al.* (2012) and shows significant agreement with the pore pattern illustrated in Figure 4.4(b) and 4.4(c).

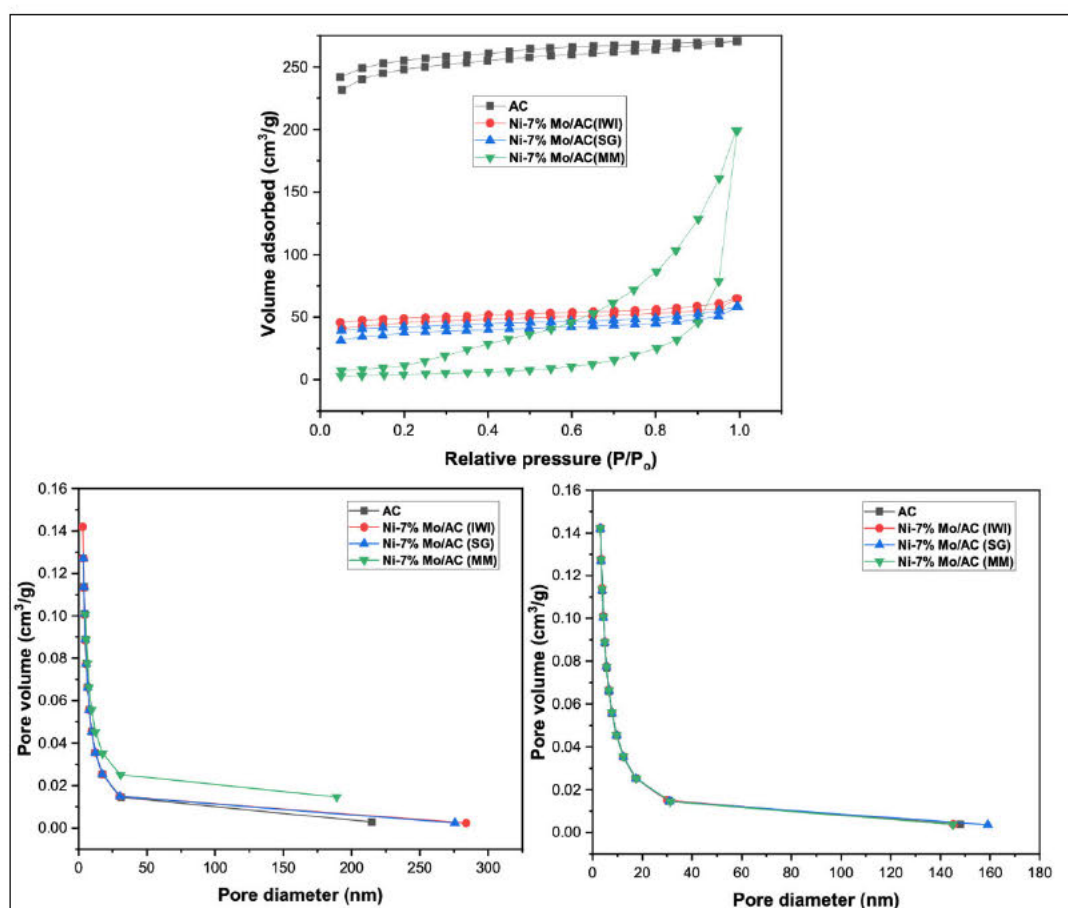


Figure 4-4. (a) N₂ adsorption-desorption isotherm; (b) BJH pore size distribution for adsorption, and (c) desorption of AC, Ni-7%Mo/AC (IWI), Ni-7%Mo/AC (SG), and Ni-7%Mo/AC catalysts.

4.3.4 FTIR – Identification of Functional Groups

Figure 4.5 shows FT-IR spectra of AC and the catalysts synthesized by different methods: Ni-7%Mo/AC (MM), Ni-7%Mo/AC (SG), and Ni-7%Mo/AC (IWI). The FTIR spectra were acquired in the wave number region between 500 – 4000 cm^{-1} . The formation of major peaks in the FT-IR spectra of AC catalysts is ambiguously missing. After catalyst calcination at 500°C, it is believed that expected oxygen-containing functional groups are thermally decomposed off at that temperature. This finding is similar to what has been reported elsewhere (Jiang *et al.* 2014). In all the supported catalysts, the presence of a broad peak between 437 and 594 cm^{-1} shows the hydroxyl group (OH^{-1}) presence, and the appearance of the bands at 874 cm^{-1} indicates the presence of weakly crystallised NiMoO_4 (Ouchabi *et al.* 2021). The peaks at 1671 cm^{-1} in the spectrum of the Ni-7%Mo/AC (SG) catalyst are attributed to the symmetry deformation vibrational modes of H-O in H_2O molecules (Hanif *et al.* 2021).

As can be seen from the Ni-7%Mo/AC (SG) spectrum, a peak has appeared at 1084 cm^{-1} , which represents the asymmetric stretching mode of the Si-O group in the SiO_4 tetrahedral structure. The FTIR spectrum of Ni-7%Mo/AC (MM) shows that the absorption band extending from 874 to 947 cm^{-1} indicates different types of Mo-O bonds, including Mo^{6+} , Mo^{5+} and particularly Mo^{4+} (Reddy *et al.* 2008). The peak at 594 cm^{-1} associated with Mo^{-4} and Mo^{-8} can be interpreted as an O-Mo-O mode. The Ni-7%Mo/AC (MM) catalyst exhibited a broader peak at about 926 cm^{-1} compared to the Ni-7%Mo/AC (SG) catalyst. In addition, the peak of MoO_3 shifted from 926 cm^{-1} to 868 cm^{-1} , indicating that AC promoted the development of active Mo sites.

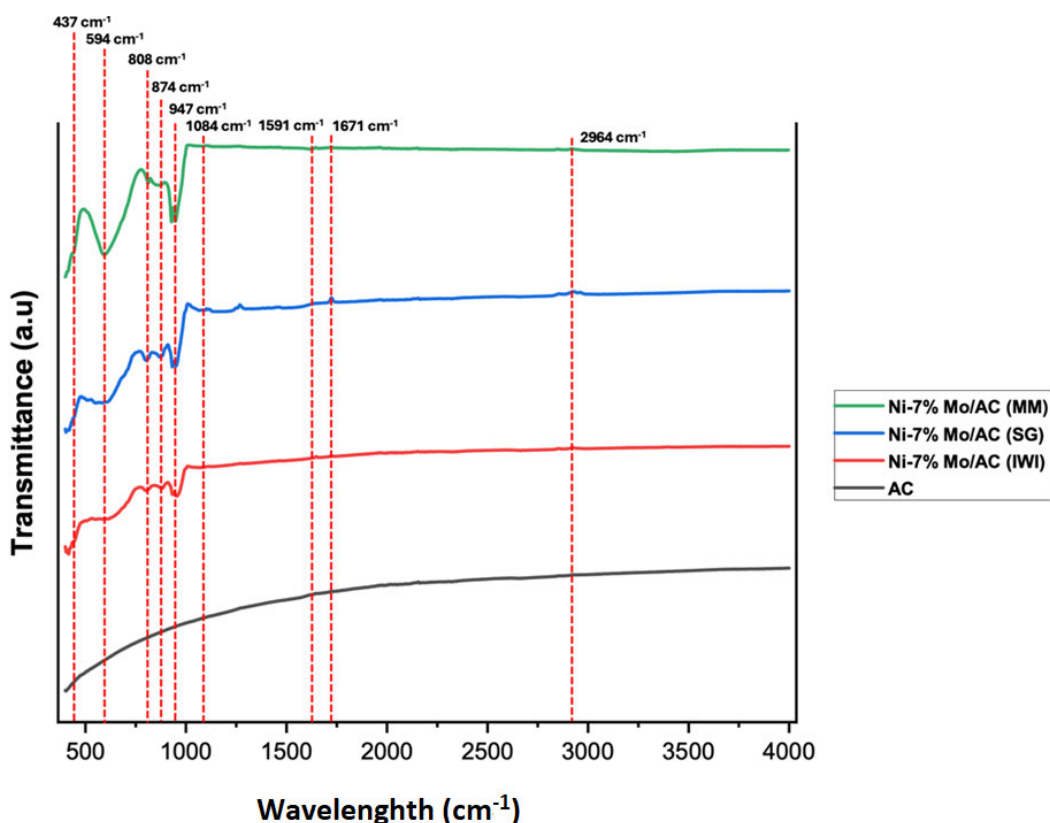


Figure 4-5. The FTIR spectra of the Ni-7%Mo/AC (MM), Ni-7%Mo/AC (SG), Ni-7%Mo/AC (IWI), and AC catalysts.

4.4 Activity and Selectivity of Ni-7%Mo/AC Catalyst in CO₂ Methanation

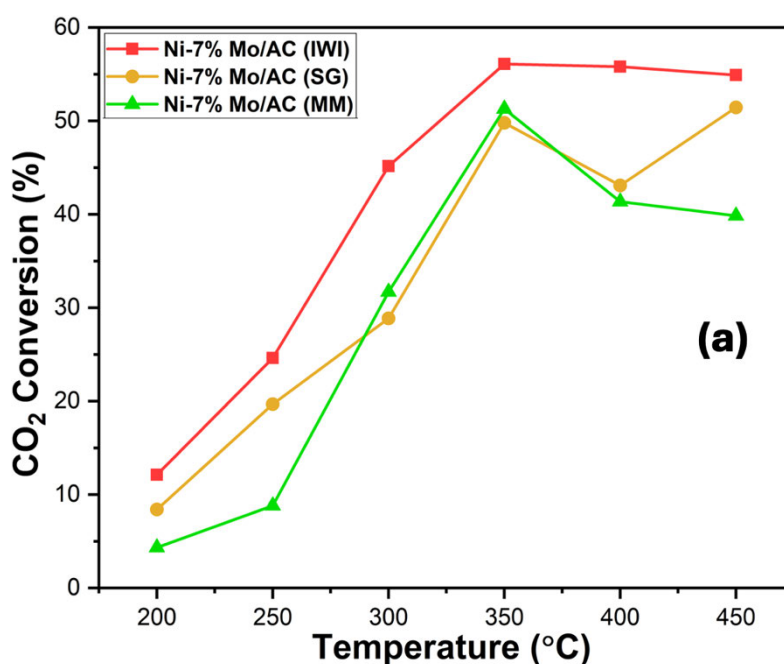
The catalytic performance of Ni-7%Mo/AC catalysts for CO₂ hydrogenation to CH₄, prepared using different synthesis methods, was evaluated across a temperature range of 200 to 450 °C. Prior to testing, all catalysts were reduced with H₂ gas at 400 °C. The main products of the CO₂ methanation reaction were CH₄, H₂O, and small amounts of CO. CO₂ conversion and CH₄ selectivity for each catalyst are shown in Figure 4.6. As depicted, the catalytic performance followed the trend: Ni-7%Mo/AC (IWI) > Ni-7%Mo/AC (MM) > Ni-7%Mo/AC (SG). The catalytic activities were thoroughly analyzed from three key perspectives: the influence of reaction temperature, catalyst performance, and stability.

4.4.1 Influence of Catalyst Temperature

The catalytic performance of Ni-7%Mo/AC catalysts for CO₂ hydrogenation to CH₄, prepared using different synthesis methods, was evaluated across a temperature range of 200 to 450 °C. Figure 4.6 illustrates the CO₂ conversion percentages and CH₄ selectivity as a function of reaction temperature for the various Ni-7%Mo/AC catalysts. Figure 4.6(a) shows that the Ni-7%Mo/AC (IWI) catalyst achieved a maximum CO₂ conversion of 56.1 % at 350°C, while the

Ni-7%Mo/AC (MM) catalyst reached a slightly lower maximum conversion of 51.2 % at the same temperature. In contrast, the CO₂ conversion for the Ni-7%Mo/AC (SG) catalyst increased progressively with temperature, peaking at 51.4 % at 450 °C. An increase in reaction temperature beyond the optimal point led to a decline in CO₂ conversion due to the thermodynamic equilibrium of the exothermic CO₂ methanation reaction, which favours the water-gas shift reaction (reverse Sabatier reaction) at higher temperatures. Additionally, elevated temperatures promote the reverse water-gas shift reaction, leading to increased CO production and a corresponding decrease in CH₄ selectivity. As shown in Table 4.3, the catalytic performance of the Ni-7%Mo/AC (IWI) catalyst is comparable to, or even exceeds, that of catalysts reported in the literature. Studies have demonstrated that the most efficient catalyst is one that achieves the highest CO₂ conversion at the lowest possible temperature (Liu *et al.* 2013; Zhen *et al.* 2015). Therefore, catalysts with superior low-temperature performance are considered the most effective for CO₂ methanation.

During the CO₂ methanation reaction (4.3), the primary byproduct is CO, which is formed through the partial reduction of CO₂ via the reverse water-gas shift (WGS) reaction (4.4).



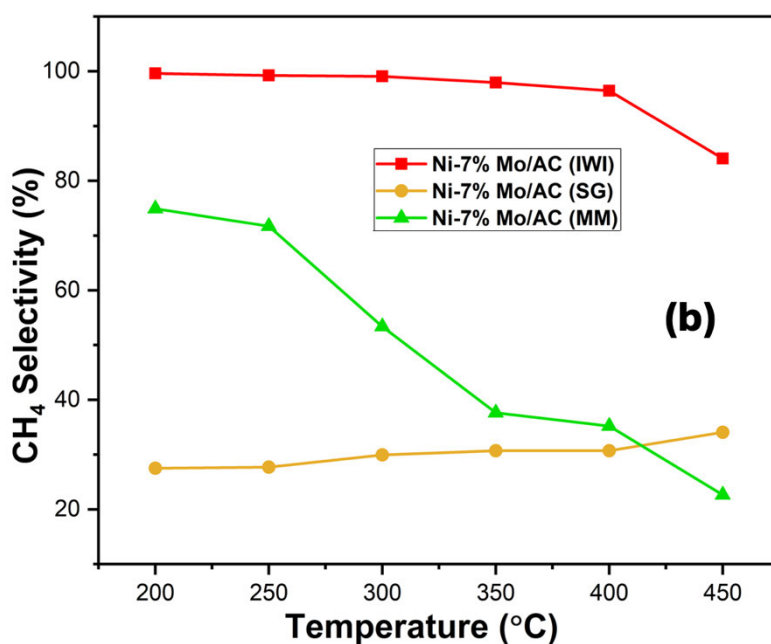


Figure 4-6. CO₂ methanation activity as: (a) CO₂ conversion and (b) CH₄ selectivity against reaction temperature over Ni-7%Mo/AC catalysts. Reaction conditions: W = 0.5g; H₂/CO₂ = 4; reaction temperature = 200 - 450 °C; WHSV = 3600 mL⁻¹h⁻¹g⁻¹; reduction temperature.

Table 4-3. Overview of Ni-based catalysts for CO₂ methanation.

Catalysts	Preparation methods	Active metal content wt%	Catalytic performance					Stability Test Time (h ⁻¹)	Ref.
			T (°C)	WHSV (mL g ⁻¹ h ⁻¹)	P (bar)	X _{CO2} (%)	S _{CH4} (%)		
Ni/Sm ₂ O ₃ -CeO ₂	MASG	10	350	25,000	1	44.9	100	20	(Siakavelas <i>et al.</i> 2021)
Ni/MgO-CeO ₂	MASG	10	350	25,000	1	43.2	100	20	(Siakavelas <i>et al.</i> 2021)
Ni/ZrO ₂	IWI	15	450	-	1	20	89	-	(Hu and Urakawa 2018)
Ni-K/ZrO ₂	IWI	15	450	-	1	50	98	-	(Hu and Urakawa 2018)
Ni-La/ZrO ₂	IWI	15	450	-	1	35	99	-	(Hu and Urakawa 2018)
Ni-TiO ₂	DP	15	260	2400	1	96	99	81	(Liu <i>et al.</i> 2013)
Ni-La/SiC	IP	15	250	12,000	1	39.6	99.6	70	(Zhi <i>et al.</i> 2011)
Ni@MIL-101	WII	10	320	4650	1	56.4	91.6	10	(Mihet <i>et al.</i> 2019)
Ni/Y ₂ O ₃	SCS	15	300	10,000	1	35.8	71	200	(Italiano <i>et al.</i> 2020)
Ni-7%Mo/AC (MM)	MM	13	350	3600	1	51.2	74.9	-	This work
Ni-7%Mo/AC (SG)	SG	13	450	3600	1	51.4	34	-	This work

<i>Ni-7%Mo/AC (IWI)</i>	<i>IWI</i>	13	350	3600	1	56	>95	50	<i>This work</i>

IWI – Incipient wetness impregnation, SCS – Solution combustion synthesis, WII – Wetness incipient impregnation, MM – Mechanical mixing, SG – Sol gel, IP – Impregnation precipitation, DP – Deposition precipitation, MASG – Microwave assisted sol gel.

To comprehensively evaluate the catalytic performance, CH₄ selectivity must be assessed for each catalyst as displayed in Figure (4.6b). For the Ni-7%Mo/AC (SG) sample, CH₄ selectivity remained limited to approximately 27 - 34% across all test temperatures. In contrast, the Ni-7%Mo/AC (MM) catalyst showed a gradual decline in CH₄ selectivity, starting from 74% at 200 °C and decreasing almost linearly to 22% at 450 °C. The Ni-7%Mo/AC (IWI) catalyst exhibited a markedly different behaviour, maintaining nearly 100% CH₄ selectivity up to 400 °C before dropping to 22% at 450 °C, a decrease attributed to reaction thermodynamics limiting CH₄ formation at higher temperatures. The CH₄ production performance of the Ni-7%Mo/AC (IWI) catalyst matched or even surpassed the results reported in other CO₂ methanation studies using conventional Ni-based catalytic systems (Italiano et al., 2020, Hu and Urakawa, 2018). These findings confirm that both catalytic activity and selectivity for CH₄ are influenced by the catalyst composition and preparation method. The detailed methanation experiment results are presented in Table 4.4.

Table 4-4. Catalytic activity and selectivity of the various catalysts: CO₂ conversion and CH₄ selectivity across a temperature range of 200 °C to 450 °C.

Catalyst Performance	Catalyst	Reaction Temperature (°C)					
		200	250	300	350	400	450
CO ₂ Conversion (%)	Ni-7%Mo/AC (IWI)	12.11	24.62	45.15	56.09	55.81	54.90
	Ni-7%Mo/AC (MM)	4.33	8.82	31.70	51.20	41.36	39.85
	Ni-7%Mo/AC (SG)	8.40	19.68	28.85	49.79	43.09	51.44
CH ₄ selectivity (%)	Ni-7%Mo/AC (IWI)	99.62	99.25	99.06	97.94	96.44	84.08
	Ni-7%Mo/AC (MM)	74.90	71.72	53.37	37.64	35.20	22.65
	Ni-7%Mo/AC (SG)	27.52	27.71	29.96	30.71	30.72	34.08

4.5 CO₂ Methanation using Ni-7%Mo/AC (IWI) Catalyst: Stability Test

The stability of the Ni-7%Mo/AC (IWI) catalyst, identified as the best-performing sample, was assessed by subjecting it to continuous on-stream testing under reaction conditions (3600 mL h⁻¹ g⁻¹, 350 °C) for 50 h. The results, shown in Figure 4.7, indicate that CO₂ conversion remained relatively stable at approximately 40% throughout the entire 50 h period. Furthermore, CH₄ selectivity remained consistently high, with values around 97.8% during the test duration. This result is consistent with previous studies, which have reported that Ni-based

catalysts can sustain excellent methanation activity over reaction times of nearly 100 h, maintaining high CH₄ selectivity of approximately 100% (Kosaka *et al.* 2020).

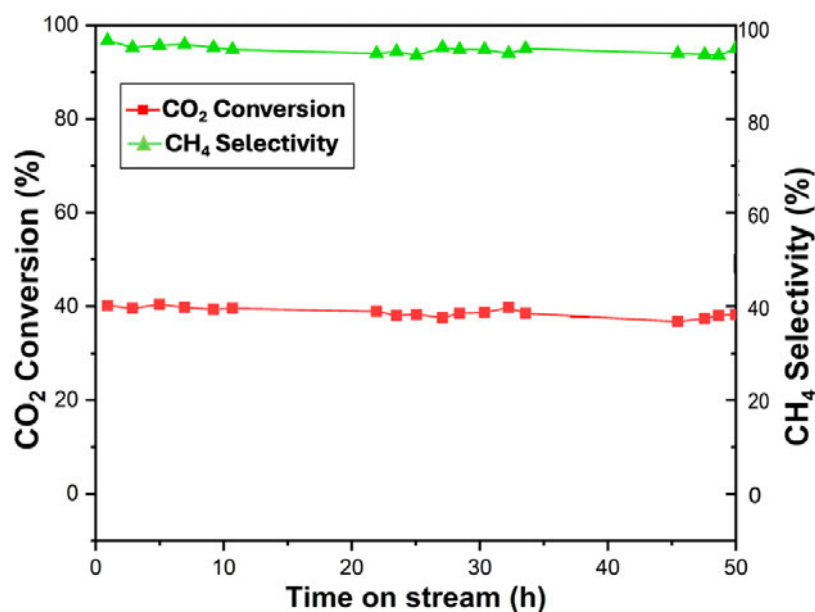


Figure 4-7. Stability profiles of Ni-7%Mo/AC. Reaction conditions: W = 0.5g; H₂/CO₂ = 4; reaction temperature = 350 °C; WHSV = 3600 mL⁻¹h⁻¹g⁻¹; reduction temperature = 400 °C/2 h.

The characterization and catalytic activity results clearly show that the preparation method significantly influences the catalytic performance of the AC-supported samples, with these variations attributed to the physical structure and interactions between the active phases.

4.6 Conclusion

In this study, Ni-7%Mo/AC catalysts were synthesized using three distinct methods: incipient wetness impregnation (IWI), sol-gel (SG), and mechanical mixing (MM), to investigate their performance in CO₂ methanation. It was found that the synthesis method significantly influenced the catalytic activity, with the IWI method yielding the highest CO₂ conversion (56%) and (>95%) CH₄ selectivity at 350 °C. In contrast, the SG and MM catalysts reached lower maximum CO₂ conversions, with the SG catalyst achieving 51.4% at 450°C and the MM catalyst reaching 51.2% at 350°C, respectively. The CO₂ conversions was ranked as: Ni-7%Mo/AC (IWI) > Ni-7%Mo/AC (SG) > Ni-7%Mo/AC (MM).

Characterization techniques revealed that the superior performance of the IWI catalyst could be attributed to its enhanced structural and morphological properties. X-ray diffraction (XRD) confirmed the presence of well-crystallized NiO and MoO₃ phases, and scanning electron

microscopy (SEM-EDS) showed uniform dispersion of Ni and Mo on the AC support for the IWI catalyst. Nitrogen adsorption-desorption analysis indicated that the IWI method produced a catalyst with a larger surface area (141.92 m²/g) and a mesoporous structure conducive to better reactant diffusion. Fourier-transform infrared spectroscopy (FTIR) identified key functional groups, confirming the interaction of metal oxides with the AC support.

The IWI-prepared catalyst demonstrated exceptional catalytic stability, maintaining around 97.8% CH₄ selectivity after 50 h of continuous reaction. This stability is attributed to the optimized interactions between Ni and Mo, which significantly reduced sintering and carbon deposition: two prevalent challenges commonly encountered with Ni-based catalysts in CO₂ methanation. In conclusion, the Ni-7%Mo/AC catalysts synthesized through the IWI method demonstrate significant potential for application in other thermodynamically controlled exothermic reactions, where metal activity is required at lower reaction temperatures.

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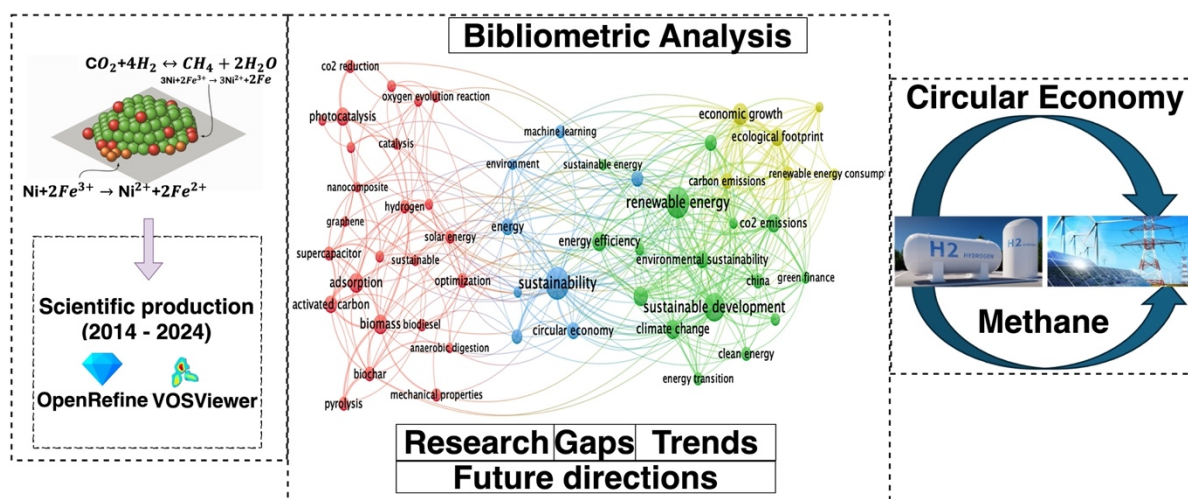
CO₂ Methanation: A Bibliometric Analysis and Review of Activated Carbon-Based Materials (2014 – 2024)

Abstract

*This chapter highlights the significant potential of activated carbon (AC)-based materials in environmental remediation and energy production, particularly in converting CO₂ and H₂ into CH₄ and H₂O using transition metal-based catalysts. It emphasizes the role of porous AC in waste reduction and resource utilization, examining various applications of CO₂ and evaluating environmental impacts. The chapter explores commercialization opportunities and specifically investigates CO₂ methanation using AC-based materials. Using bibliometric analyses of 4196 articles from the Web of Science database, the chapter identifies a growing research interest in porous AC-related CO₂ methanation from 2014 to 2024. The top three journals in this field are **Environment Development and Sustainability**, **Biomass Conversion and Biorefinery**, and **Journal of Environment Science and Pollution**. However, there is limited inter-institutional collaboration in this field, suggesting room for development towards commercializing sustainable CH₄ production pathways. CH₄ is highlighted as a crucial intermediate in industrial processes, and research directions are identified through co-occurring author keywords analysis. The chapter suggests the need for a comprehensive approach integrating AC materials into carbon-neutral energy processes while addressing the potential adverse effects of activated carbon nanoparticles (ACNPs) on biological and environmental factors. Ultimately, it clarifies the potential uses and commercialization prospects for porous AC materials, especially in conjunction with carbon capture and utilization technologies, promoting sustainable practices in energy production and environmental management.*

Keywords: CO₂ methanation, scientometrics, activated carbon, bibliometric analysis, methane.

Graphical Abstract



5.1 Introduction

The emission of CO₂ poses a significant challenge for both society and industry, prompting substantial efforts to mitigate its production and release into the atmosphere. The current focus is on promoting processes that involve underground storage and capture of CO₂ (Wilson, Johnson and Keith 2003). However, converting CO₂ into high-value molecules is increasingly recognized as a crucial approach for regulating atmospheric emissions in the future (Chen *et al.* 2022b). Many scientists argue that low temperature methanation could potentially reduce reliance on underground CO₂ storage (Schaaf *et al.* 2014; Ma *et al.* 2018; Strobel *et al.* 2020). This process requires hydrogen, obtainable through water electrolysis or from industries with surplus hydrogen production. Electricity needed for these processes can come from "green" sources like biomass, wind, or solar energy. In addition to converting CO₂ into a high-value molecule, this conversion process offers the advantage of transforming hydrogen (H₂) into a more easily usable energy source, exemplified by the production of CH₄. Furthermore, the produced CH₄ can substitute natural gas (SNG) in the chemical and petrochemical sectors, thereby lowering natural gas consumption. Ecologically and environmentally, converting CO₂ and H₂ into CH₄ presents a viable alternative.

The CO₂ methanation reaction ($4\text{H}_2 + \text{CO}_2 \rightarrow \text{CH}_4 + 2\text{H}_2\text{O}$, $\Delta H_{298\text{ K}} = -164\text{ kJ/mol}$) remains highly advantageous thermodynamically, significantly outpacing other reactions that produce hydrocarbons or alcohols (Inui and Takeguchi 1991). Known as the Sabatier reaction, it holds promise for industrial implementation, contingent upon hydrogen sourced from renewables. CO₂ methanation is not only a pivotal catalytic process of academic interest but also shows potential for commercial applications (Lunde and Kester 1974; Tomsett *et al.* 1986; Ravindranathan Thampi, Kiwi and Grätzel 1987). With dwindling interest in large-scale SNG production from coal gasification byproducts (Alstrup 1995), CO₂ methanation finds utility in industries like fuel cells and ammonia (NH₃) synthesis, removing trace CO from H₂-rich streams and preventing catalyst poisoning (Galletti *et al.* 2010). Furthermore, the Sabatier reaction holds potential applications in human space colonization on Mars, as acknowledged by the National Aeronautics and Space Administration (NASA) (Lunde and Kester 1974). Moreover, NASA explores the Sabatier reaction for potential applications in future manned missions to Mars, converting Martian CO₂ into CH₄ and H₂O for propellant and life support systems facilitated by transporting hydrogen from Earth (Hu *et al.* 2007). Effective catalysts are crucial for achieving high selectivity and conversion rates in these processes (Bermúdez,

Arenillas and Menéndez 2011; Goula *et al.* 2017; Abdulrasheed *et al.* 2020; Osazuwa and Abidin 2020). Carbon-based catalysts, particularly porous activated carbon (AC), have emerged as promising candidates for CO₂ methanation due to their unique properties. AC has an exceptional adsorption capacity as a support, with a large specific surface area, a rich pore structure and cost efficiency (Zhang *et al.* 2014). These attributes enhance catalytic stability, supported by efficient combustion for recycling metal-supported carbon carriers. Moreover, the surface functional groups, pore structure, and surface area of AC play pivotal roles in enhancing the CO₂ methanation reaction.

In this context, Wei and Jinlong (2011) provided an extensive overview of CO₂ methanation, focusing on porous supports. Their article highlights recent advancements in catalytic materials, novel reactors, and the underlying reaction mechanisms. They emphasized how the catalytic properties of active metal sites can be influenced by interactions between the metal and its support. Similarly, Jwa *et al.* (2013) investigated the hydrogenation of carbon oxides (CO₂ and CO) into CH₄ using Ni/ β -zeolite catalysts, emphasizing the importance of enhancing CO₂ delivery to the catalyst surface to improve methanation efficiency. Numerous studies have explored nickel catalysts supported on materials such as porous alumina (Xu *et al.* 2012) or MCM41 (Du *et al.* 2007; Zhang *et al.* 2013) catalysts. These investigations consistently demonstrate that the porous structure of these supports enhances nickel dispersion and prevents the sintering of nickel species. AC, known for its substantial surface area, surface functionalization, and low regeneration energy requirements, has received significant research interest. AC has proven effective as an adsorbent for CO₂ under ambient conditions (Samanta *et al.* 2012; Vargas, Giraldo and Moreno-Piraján 2012; Wickramaratne and Jaroniec 2013). For example, Vargas, Giraldo and Moreno-Piraján (2012), impregnated African palm shell-derived AC monoliths and found they could adsorb up to 5.8 mmol CO₂ per gram at 273 K and 1 bar. Wickramaratne *et al.* (2013) reported AC spheres achieving high CO₂ uptakes of 8.9 mmol/g at 0°C and 4.55 mmol/g at 25°C under atmospheric pressure. Additionally, studies by Li *et al.* (2016) showed that pinecone shell-based AC exhibited notable CO₂ adsorption capacities, achieving 7.63 mmol/g at 0°C under 1 bar and 2.35 mmol/g under 0.15 bar pressure. Previous work by our team Akpasi *et al.* (2024) employed mesoporous AC-supported bimetallic Ni-Mo catalysts to investigate CO₂ methanation, highlighting AC's capability to adsorb CO₂ effectively. The composition and structure of the catalyst, including specific surface area and pore characteristics, significantly influence its catalytic performance. Supported nickel catalysts with high dispersion on AC, known for their developed pore

structures and large specific surface area ($>1000 \text{ m}^2/\text{g}$), exhibit promising catalytic properties. AC serves as an effective support for modifying surface properties to enhance nickel catalyst activity for CO_2 hydrogenation, positioning it favourably despite the current absence of reported porous AC-related CO_2 methanation studies.

A bibliometric review, sometimes referred to as science mapping or scientometrics, involves the analysis and visualization of different bibliometric networks based on the outputs of academic literature in a given scientific field using text and data mining techniques (Van Eck and Waltman 2014; Akinwekomi, Bamisaye and Bodunrin 2024). According to Pritchard (1969) original definition, this analysis uses statistical techniques and mathematical applications. Citations are fundamental to the dynamics of scientific and technological progress, creating connections between researchers, their ideas, publications, and institutions (Mingers and Leydesdorff 2015). Garfield (2006) first proposed the concept of the Science Citation Index. Since then, bibliometrics has been used to evaluate research performance and allocate research funding at various levels, from individuals and groups to institutions and universities (Bornmann and Leydesdorff 2014). For a detailed overview of the history of scientometrics and bibliometrics, readers are referred to these studies (Hood and Wilson 2001; Garfield 2009; Smith 2012; Mingers and Leydesdorff 2015). A bibliometric review can overcome the subjectivity often seen in narrative and systematic reviews (Hussein and Zayed 2021) as well as in peer reviews, which is a significant advantage (Bornmann and Leydesdorff 2014). Additionally, bibliometric mapping helps professionals deepen their understanding of a particular field (Chang, Huang and Lin 2015), provides a comprehensive visual reference platform for new researchers, and aids in understanding the evolutionary and historical changes in a research area (Heersmink *et al.* 2011). Fields such as microbial fuel cells (Khudzari *et al.* 2018), library and information science (Chang, Huang and Lin 2015), medicine (Kokol, Blažun Vošner and Završnik 2021), computational intelligence (Van Eck and Waltman 2007), materials engineering (Akinwekomi, Bamisaye and Bodunrin 2024) and conversion technologies for CO_2 (Xing *et al.* 2020) have all benefited from bibliometric analyses.

Furthermore, researchers can visualize collaborations and networks within specific domains by analyzing co-authorship patterns, affiliations, and collaboration networks (Chang, Huang and Lin 2015). This data is invaluable for fostering interdisciplinary collaborations, gaining deeper insights into scientific community dynamics, and facilitating the assessment of journal quality,

research reputation, and discipline, among other factors. Bibliometric analysis also provides evidence-based insights that assist policymakers and funding agencies in resource allocation, promoting multidisciplinary research, and supporting strategic objectives (Saravanan *et al.* 2022). Institutions can use bibliometric analysis to evaluate research initiatives, assess research productivity, benchmark against peers, impact, and global visibility, and monitor overall research performance. Despite extensive investigations into AC-based materials and dedicated sections on CO₂ commercialization, environmental pollution, remediation, and energy, there remains a significant gap in comprehensive records focusing on research trends, the productivity of active institutions and authors over time, and specific contributions of AC-based materials to CO₂ methanation. This gap highlights the need for a unified framework that integrates bibliometric trends to evaluate commercialization potential and outline the environmental impacts of incorporating AC-based materials into CO₂ methanation. This paper aims to fill this void by conducting a meticulous analysis that not only evaluates individual components but also integrates them into a cohesive narrative. One objective is to provide a comprehensive and up-to-date understanding of the broader context surrounding AC-based materials. This compilation addresses existing research gaps and lays the groundwork for identifying future research and application opportunities. The methodology employed in this study utilizes VOSviewer and OpenRefine software for data analysis, highlighting emerging research areas. Ultimately, this evaluation serves as a guiding marker, synthesizing scholarly inputs to illustrate progress, challenges, and forthcoming pathways in the production of CH₄ using porous AC catalysts.

5.2 Review Gap

Despite extensive studies of AC based materials and their role in CO₂ commercialization, pollution control, environmental remediation and energy production, there is a surprising lack of comprehensive records tracing research trends, the productivity of leading authors and institutions over time, and the specific contributions of AC-based materials in CO₂ methanation, including their applications in energy and fuel production and environmental remediation. This gap highlights the need for a coherent framework that integrates bibliometric trends to assess the commercialization prospects and outline the environmental impact of the use of AC-based materials in CO₂ methanation. This research aims to fill this gap by providing a comprehensive analysis that not only examines each component separately but also integrates them into a coherent narrative and provides an up-to-date understanding of the broader context

around AC-based materials. This synthesis fills gaps in current knowledge and lays the foundation for future research directions and applications.

Table 5.1 provides a detailed overview of relevant research on porous AC materials for environmental remediation, greenhouse gas mitigation and CO₂ and CH₄ utilization. VOSviewer and OpenRefine were used in the analysis to highlight key research areas. This evaluation serves as a roadmap that integrates academic contributions to highlight progress, challenges and future directions in the production of synthetic fuels using porous AC catalysts.

Table 5-1. An overview of published articles relevant to porous AC materials.

Title of Article	Highlights	Year	Ref.
Recent Progress in the Synthesis of Porous Carbon Materials	The study explored advancements in porous carbon synthesis, covering methods like templating, activation, and green synthesis, while highlighting their applications in energy storage, remediation, and catalysis.	2006	(Lee, Kim and Hyeon 2006)
Last Decade of Research on Activated Carbons as Catalytic Support in Chemical Processes	The study addresses recent advances in the use of activated carbon as a catalyst support, highlighting its tailored properties to improve catalyst performance and stability in applications such as hydrogenation, oxidation and coupling. It explored novel design strategies that address challenges such as catalyst deactivation and cost efficiency and highlighted the potential of activated carbon-supported catalysts for sustainable and efficient chemical processes.	2010	(Calvino-Casilda <i>et al.</i> 2010)
Porous Carbon-Supported Catalysts for Energy and Environmental Applications: A Short Review	The study investigated porous carbon-based catalysts and emphasized their high surface area, chemical stability and adaptable properties for applications in energy storage, environmental remediation and chemical synthesis. It also highlights the challenges and future research opportunities in this area and emphasizes the potential of these catalysts to tackle global energy and environmental problems.	2011	(Yang, Chiang and Burke 2011)
CO ₂ Methanation over Heterogeneous Catalysts: Recent Progress and Future Prospects	The article reviews recent advances in heterogeneous catalysts for CO ₂ methanation, focusing on various materials such as nickel-based catalysts with promoters, transition metal carbides, nitrides, borides and structured catalysts for improved performance. Challenges such as catalyst deactivation, energy efficiency and cost effectiveness were highlighted and the need for further research and development in this area was emphasized.	2015	(Aziz <i>et al.</i> 2015)
Porous Carbon: A Versatile Material for Catalysis	The study stressed porous carbon materials' unique properties, such as high surface area and tunable porosity, and their applications in energy conversion, remediation, and chemical synthesis, highlighting their potential as efficient, sustainable catalysts.	2017	(Matos, Bernardo and Fonseca 2017)
Recent Progresses in Constructing the Highly Efficient Ni Based Catalysts with Advanced Low-Temperature Activity toward CO ₂ Methanation	The study reviews recent progress in the development of efficient Ni-based catalysts for CO ₂ methanation, focusing on the use of promoters, support materials and innovative design strategies such as hierarchical structures, core-shell architectures and monatomic catalysts. It also highlighted challenges such as catalyst deactivation, energy efficiency and cost	2020	(Lv <i>et al.</i> 2020)

	effectiveness and emphasized the need for further research and development in this area.		
Promising Catalytic Systems for CO ₂ Hydrogenation into CH ₄ : A Review of Recent Studies	The review provided an overview of recent advances in catalytic systems for the hydrogenation of CO ₂ to CH ₄ , focussing on nickel-based catalysts with promoters, various support materials and innovative designs such as hierarchical structures, core-shell architectures and monatomic catalysts. Challenges such as catalyst deactivation, energy efficiency and cost-effectiveness were also discussed, emphasizing the need for further research and development.	2020	(Bacariza <i>et al.</i> 2020)
A Review of Recent Catalyst Advances in CO ₂ Methanation Processes	The review examined advancements in CO ₂ methanation catalysts, highlighting nickel-based catalysts and emerging materials such as metal carbides, nitrides, and borides.	2020	(Ashok <i>et al.</i> 2020)
Recent Trends in Developments of Active Metals and Heterogenous Materials for Catalytic CO ₂ Hydrogenation to Renewable Methane: A review	The study examined recent trends in catalysts for the hydrogenation of CO ₂ to CH ₄ , focussing on nickel-based, transition metal and heterogeneous materials such as zeolites and metal-organic frameworks. It highlighted challenges such as deactivation, efficiency and cost and emphasized the need for further research.	2021	(Fan and Tahir 2021)
<i>CO₂ Methanation: A bibliometric Analysis and Review of Activated Carbon-based Materials (2014 – 2024)</i>	<i>The study examines the use of porous AC in CO₂ methanation to convert CO₂ and H₂ into CH₄. It explores AC's role in carbon capture, environmental remediation, and sustainable energy, while conducting a bibliometric analysis of research trends and identifying commercialization challenges and prospects.</i>	2024	<i>Current Study</i>

5.3 Utility and Properties of Activated Carbon

5.3.1 Activated Carbon as Catalyst

Acids catalyse many reactions in fine chemical synthesis. Traditionally, these reactions are carried out in a homogeneous phase and the presence of strong inorganic acids. Acids such as sulphuric acid (H₂SO₄), nitric acid (HNO₃) or hydrochloric acid (HCL) often exhibit poor selectivity despite their fast kinetics and high conversion rates, which poses numerous challenges to the process. These substances also place high demands on the equipment as they are corrosive and aggressive. They also require post-treatment, which can be time-consuming, difficult and potentially harmful to the environment. AC is a very cost-efficient and environmentally friendly replacement for the various heterogeneous catalysts that have been developed and used as acid catalysts in fine chemical synthesis (Melero, Iglesias and Morales 2009).

Building on this shift towards more sustainable catalytic processes, Swalus *et al.* (2012) studied the low-temperature methanation of CO₂ using a Rh/γ-Al₂O₃ catalyst, with hydrogen supplied *in-situ* by a Ni/AC catalyst. The methanation process was significantly enhanced by the combined mechanical properties of the Rh/γ-Al₂O₃ and Ni/AC catalysts, with the effect being

particularly pronounced at a Ni content of 1 wt%. Compared to the performance of the individual catalysts, the mixed catalyst exhibited superior CH₄ production, a result attributed to the synergistic interaction between the two catalysts during methanation. Specifically, the 1 wt% Rh/ γ -Al₂O₃ catalyst efficiently adsorbed CO₂, while the 1 wt% Ni/AC catalyst demonstrated a high capacity for hydrogen adsorption and minimal CO₂ adsorption. This complementary behaviour of the two catalysts, when combined, led to an enhanced conversion of CO₂ and increased CH₄ formation, with CH₄ being the sole product in all cases. The improved catalytic performance was likely driven by the migration of activated hydrogen species from the Ni/AC catalyst to the Rh/ γ -Al₂O₃ catalyst, where the hydrogen reacted with adsorbed CO₂ species to produce CH₄. Additionally, this transfer of hydrogen helped maintain the rhodium particles in a reduced state, which is crucial for efficient CO₂ hydrogenation.

These findings highlight the importance of the production and modification methods of AC itself in determining its catalytic effectiveness. The two primary methods for producing AC, physical and chemical activation, each significantly impacts the final material's surface properties depending on the activation conditions and chemical agents used (González-García 2018). Physical activation involves two steps: First, the raw material is carbonized in the absence of oxygen in a process called pyrolysis, which is usually carried out at temperatures between 400 °C and 850 °C. The carbon resulting from the carbonization is then activated with oxidizing gases such as steam or CO₂ at temperatures between 600 °C and 1000 °C (Ioannidou and Zabaniotou 2007; Yahya, Al-Qodah and Ngah 2015). Chemical activation is a one or two-step process that starts with the impregnation of the precursor (biomass or the char resulting from the first carbonization step) with the chemical agent (oxidizing agent and dehydrating agent). The mixture is then heated at temperatures between 400 °C and 800 °C in an inert atmosphere (Ioannidou and Zabaniotou 2007; Yahya, Al-Qodah and Ngah 2015). The simultaneous use of chemical and physical activation is also possible. The type of precursor or feedstock used in the production of biomass-derived activated carbons (ACs) has a major impact on the characteristics and properties of the final carbon (Khan *et al.* 2015). ACs are incredibly adaptable materials with fascinatingly tunable properties that can be used to tailor surface chemistry and porous structure. Modification processes can be used to create materials with very different properties so that the physicochemical properties can be fine-tuned to achieve the desired catalytic performance. The presence of functional groups on the surface of AC is a key feature that is particularly important for these specialized catalytic processes. Since

certain of these groups can act as active sites, their use as acid catalysts depends on their nature, type and concentration (Matos, Bernardo and Fonseca 2017).

In this context, the chemical properties of ACs are largely determined by the surface's chemical heterogeneity, which is influenced by the presence of heteroatoms. Heteroatoms are atoms in the carbon structure that are not carbon, such as phosphorus, sulfur, hydrogen, nitrogen, and oxygen, which are not carbon (Snoeyink, Weber Jr and Mark Jr 1969; El-Sayed and Bandosz 2004). The composition and quantity of these elements are influenced by the characteristics of the starting material and the conditions under which they are introduced during the activation process. The acidic or basic properties of the AC surface are influenced by the delocalized electrons within the carbon structure and the surface functional groups formed by the presence of heteroatoms (Laszlo and Szűcs 2001).

Acidic Surfaces

The acidic nature of AC surfaces is closely associated with oxygen-containing surface groups (Otake and Jenkins 1993; Barton *et al.* 1997; Ania, Parra and Pis 2004). These groups, primarily located on the outer surface or at the edges of the basal planes, significantly influence the chemical properties of the carbon. The oxygen concentration on the surface significantly influences the adsorption capacity of the carbon, as these peripheral sites occupy the largest part of the adsorption surface (Menéndez *et al.* 1996; Szymański *et al.* 2002). Examples of oxygen-containing functionalities identified on the carbon surface are quinone, chromene, pyrone, carbonyl, phenol, lactone, carboxyl and ether groups (Figure 5.1). Carboxylic anhydride is another example of a carboxylic group (Van Den Brand *et al.* 2004; Rosillo-Lopez *et al.* 2015). The chemical properties of surface oxygen functional groups can be classified into three categories: acidic, basic, and neutral. Surface acidity is primarily attributed to functional groups such as carboxylic anhydrides, carboxylic acids, lactones, and phenolic hydroxyl groups (Chen and Wu 2004; Li 2012).

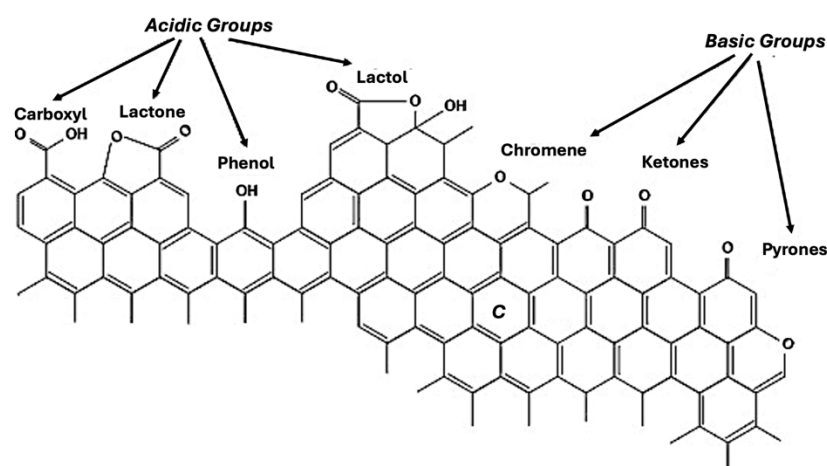


Figure 5-1. Surface functionalities of acidic and basic on a basal plane of carbon. Adapted from (Montes-Morán *et al.* 2004).

Oxygen-containing functional groups are formed when the carbon surface is oxidized. The most commonly employed methods for incorporating these acidic groups involve oxidation using gases or aqueous oxidants (Moreno-Castilla, López-Ramón and Carrasco-Marín 2000; Yin, Aroua and Daud 2007). In the gas-phase treatment, oxidants such as steam, CO₂, air, and oxygen can be used. Low-temperature gas-phase oxidations typically generate strong acidic groups, such as carboxylic groups, while high-temperature oxidations tend to produce a higher concentration of weaker acidic groups, like phenolic groups (Brezinsky 1986; Figueiredo *et al.* 1999). As opposed to gas-phase treatments, liquid-phase oxidations can contribute a greater quantity of oxygen to the carbon surface at a much lower temperature (Jaramillo, Álvarez and Gómez-Serrano 2010). HNO₃, or H₂SO₄ – H₂SO₄ acid mixture, are particularly effective oxidizing agents, introducing a significant number of oxygenated acidic functionalities, such as phenolic hydroxyl, carboxylic and lactone groups, onto the carbon surface (Yin, Aroua and Daud 2007; Santangelo *et al.* 2012). Studies have shown that gas-phase oxidation of AC primarily increases the concentration of hydroxyl and carbonyl surface groups. In contrast, liquid-phase oxidation, even at lower temperatures, can incorporate a greater amount of oxygen in the form of phenolic hydroxyl and carboxylic groups (Figueiredo *et al.* 1999; Plaza *et al.* 2013).

Basic Surfaces

The basicity of AC can be attributed to two main factors: (i) the resonating π -electrons in the aromatic carbon rings, which attract protons, and (ii) basic surface functionalities, such as nitrogen-containing groups, which can bind to protons (Bandos 2008; Shen and Fan 2013; Chen *et al.* 2022a). It has been hypothesised that the basicity of carbon can be influenced by

certain oxygen-containing surface functionalities, including pyrones (Boehm 2002), ketones (Shafeeyan *et al.* 2010) and chromenes (Jaramillo, Álvarez and Gómez-Serrano 2010) (Figure 5.2). The fundamental properties of ACs are primarily attributed to the delocalized π -electrons within the graphene layers (Montes-Morán *et al.* 2004; de Souza *et al.* 2018). Research has demonstrated that these π -electrons can function as Lewis bases (Pérez-Cadenas, Maldonado-Hodar and Moreno-Castilla 2003; Chen *et al.* 2021). Several studies have explored how the basal planes contribute to the basicity of carbon (Darmstadt and Roy 2003; Pérez-Cadenas, Maldonado-Hodar and Moreno-Castilla 2003). For instance, Leon y Leon *et al.* (y Leon *et al.* 1992) examined the surface basicity of two series of carbons and found that oxygen-free carbon sites can effectively adsorb protons from a solution. These sites are situated in regions abundant with π -electrons on the basal plane of the carbon crystallites. Consequently, the carbon structure itself is associated with Lewis-type basic sites (Boehm 1994).

It has been demonstrated that introducing nitrogen functional groups onto the carbon surface can significantly enhance the ability of AC to adsorb CO₂ (Maroto-Valer *et al.* 2008; Pevida *et al.* 2008; Plaza *et al.* 2008). Nitrogen-containing functionalities can be incorporated either by reacting with nitrogen-rich reagents (such as NH₃, HNO₃, or R-NH₂) or by activating the carbon with nitrogen-containing precursors (Mangun *et al.* 2001; Shen and Fan 2013). Figure 5.2 illustrates the potential structures of these nitrogen functionalities, which include amide, imide, lactam, pyrrolic, and pyridinic groups (Abe *et al.* 2000; Wood, O'Hayre and Pylypenko 2014). These nitrogen-containing groups typically exhibit properties that enhance interactions between acidic molecules and the carbon surface, such as covalent bonding, hydrogen bonding, and dipole-dipole interactions (Shen and Fan 2013).

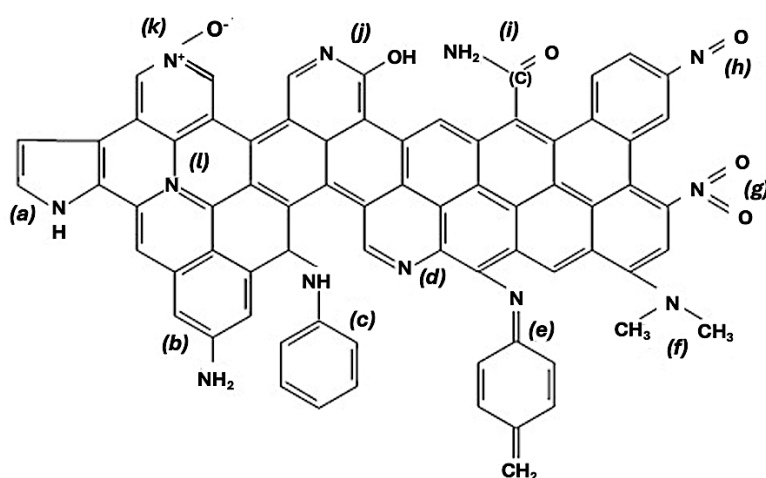


Figure 5-2. Various nitrogen-containing surface functional groups: (a) pyrrole, (b) primary amine, (c) secondary amine, (d) pyridine, (e) imine, (f) tertiary amine, (g) nitro, (h) nitroso, (i) amide, (j) pyridone, (k) pyridine-N-oxide, (l) quaternary nitrogen (Pietrzak 2009).

Several treatments can be carried out to obtain an oxidized carbon surface. The best known are the liquid phase treatments with acids (usually H_2SO_4 , HNO_3 or a combination of both); the gas treatments with hydrogen peroxide (H_2O_2), N_2 doped with O_2 , air or even NH_3 and N_2O , where additional heteroatoms can be added. Studies using X-ray photoelectron spectroscopy (XPS) and temperature-programmed desorption mass spectrometry (TPD/MS) can be used to identify and quantify surface functional groups and their relationship to catalytic activity.

Moreover, Matos *et al.* (2014) investigated the methoxylation of α -pinene using three HNO_3 -oxidized carbon materials: a commercial microporous carbon (NoritN), a xerogel carbon (CMN) and a meso-microporous AC from olive stones (CBN) as acid catalysts to generate α -terminal methyl ether as the main product of the reaction. The results showed that the surface chemistry of these catalysts was their most important component, although some influence of their textural properties was evident (Figure 5.3). As phosphate groups were added during the synthesis of the carbon, the olive stone-based carbon prepared by chemical activation with phosphoric acid (H_3PO_4) produced a biomass catalyst with improved properties for the reaction studied. The catalytic activity increased in the following order: NoritN < CMN < CBN, showing that the textural properties also have some influence. All catalysts showed good selectivity towards the α -terminal methyl ether.

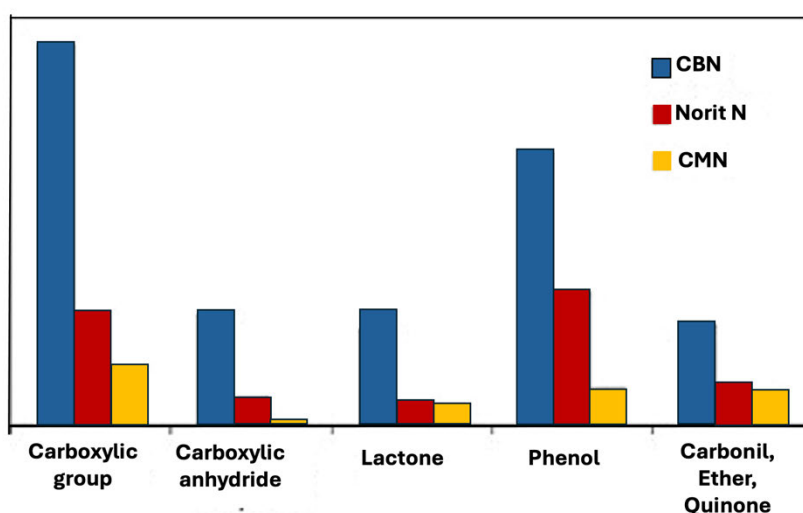


Figure 5-3. Comparative surface group oxygen content for CBN, Norit N, and CMN as determined by TPD. Adapted from (Matos *et al.* 2014).

Palm kernel shells, a low-grade by-product of the palm oil industry, were used as a raw material to produce another biomass-based carbon. After carbonization, the solid acid catalyst was produced by an intensive H_2SO_4 treatment. It was found that the produced solid acid was very active in cellobiose hydrolysis processes. The results showed a correlation between the catalytic activity and the amount of sulfonic groups on the surface. Higher turnover numbers

are the consequence of a mechanism of preferential sulfonation position on the surface, which was hypothesized and validated by quantitative XPS. Lower concentrations of sulfonic groups are located at sites with better access to the reactants. When carbons were used instead of resins with higher sulphur content, better results were obtained. The importance of additional functional groups present on the carbon surface in a synergistic effect can, therefore, be deduced from this result (do Couto Fraga *et al.* 2016).

The most acidic microporous carbon materials with sulphonic groups on the surface proved to be effective catalysts in the Friedlander reaction and a cost-effective substitute to produce quinolines with moderate selectivity and high conversions. Theoretical calculations also support the importance of the functional acid group. According to the calculation results, the intermediate product that is formed after binding to the surface is less flexible. The porosity and the specific surface area of the carbon materials are also important factors in these studies that probably contribute to selectivity (López-Sanz). The results shown in Table 5.2 highlight the importance of understanding the effects of nickel loading, CO₂ methanation, promoter influence and particle size on activated carbon nanoparticles (ACNPs).

Table 5-2. Catalytic performance of unpromoted and promoted Ni catalysts over activated carbon-based supports for various CO₂ methanation processes.

Catalysts	Ni (wt%)	Promoter	Synthesis method	Conditions/Performance				Ref.
				P (bar)	T (°C)	X _{CO2} (%)	S _{CH4} (%)	
Ni-Ca/AC	15	Ca	IWI	1	360	76	100	(Feng, Yang and Chu 2016)
Rh/γ-Al ₂ O ₃ + Ni/AC	1	Rh	IWI	2	125	50	100	(Swalus <i>et al.</i> 2012)
NiCe/AC _N	15	Ce	IWI	1	360	70	99	(Mateus <i>et al.</i> 2023)
Ni-Mo/AC	13	Mo	IWI	1	350	80	92	(Akpasi <i>et al.</i> 2024)
NiRe/C	50	Re	CPM	1	325	72	96	(Gonçalves <i>et al.</i> 2021)
NiMo/C	50	Mo	CPM	1	325	70	98	(Gonçalves <i>et al.</i> 2021)
Ni/C	50	-	CPM	1	330	83	99.7	(Gonçalves <i>et al.</i> 2021)
Ni/ACR–CeO ₂	15	CeO ₂	CPM	1	370	87.4	100	(Gonçalves <i>et al.</i> 2022)
Ni - ACR	15	-	CPM	1	450	76	97	(Gonçalves <i>et al.</i> 2022)
Ni/AC-ZrO ₂	15	ZrO ₂	IWI	1	430	76.4	98.5	(Quatorze <i>et al.</i> 2023)
Ni/AC550	10	-	IWI	1	330	75	97	(Wang <i>et al.</i> 2023)
Ni-Mg _{0.26} /		Mg	CI	1	450	90.1	99.22	(Li <i>et al.</i> 2019)

CSC								
Ni/CSC	-	-	CI	1	450	77.06	98.5	(Li <i>et al.</i> 2019)
Ni/CeZr	7	CeZr	IWI	1	350	85	100	(Le <i>et al.</i> 2017)
AC								

IWI – Incipient wetness impregnation; CI – Co-impregnation; ACN – AC from natural cork waste; ACR – reduced activated carbon; CSC – coconut shell carbon catalysts

Surface functional groups are crucial for both the conversion and the selectivity in the gas-phase reaction of cyclohexanol, in which benzene phenol cyclohexanone and cyclohexene can be formed (Figure 5.4). The oxidation process used for the same starting carbon was varied to produce different catalysts. The resulting materials were characterized to determine the amount and type of surface groups originating from the different oxidation processes. After HNO₃ treatment, it was found that the dehydration of cyclohexanol occurs mainly in the carboxylic acid groups. The highest concentration of phenolic groups and the best selectivity to cyclohexanone were found for carbons produced with oxygen or peroxide. A high phenol selectivity was achieved by treating the carbon with N₂O, but in this case, the involvement of the nitro groups in the reaction process should be taken into account (Silva *et al.* 1998).

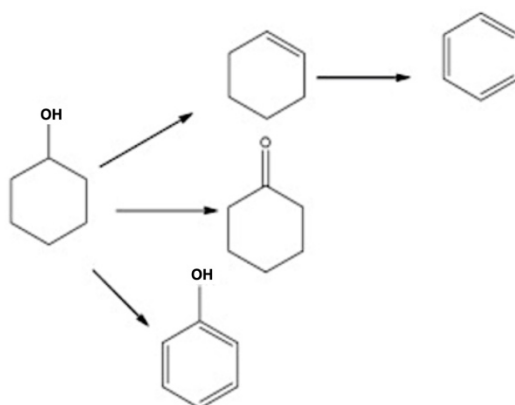


Figure 5-4. Schematic depicting the reaction pathway for converting cyclohexanol using carbon catalysts, as developed by (Silva *et al.* 1998).

Various commercially available AC products have also proven suitable as catalysts. Specifically, ACs produced using H₂SO₄ and HNO₃ have been identified as highly efficient and selective catalysts for N-heterocycle alkylation (Durán-Valle *et al.* 2012). The ionic liquid imidazolium, a high-value product with increasing demand, can be produced using this process (Figure 5.5). The most important property of carbon was its acidity, and the improved results of the reaction without solvent further emphasized the environmental friendliness of the catalyst.

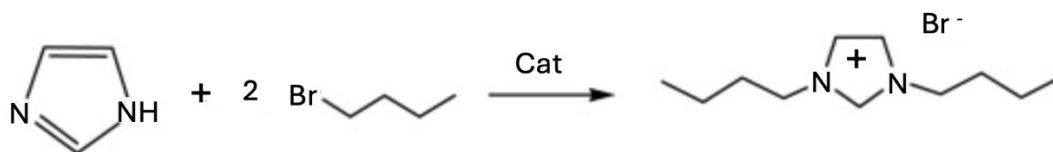


Figure 5-5. Reaction scheme illustrating the synthesis of N,N-di-n-butyl-imidazolium bromide. Adapted from (Durán-Valle *et al.* 2012).

The sol-gel method is the most widely used of the various processes for producing synthetic carbon. Using a basic catalyst, resorcinol is polycondensed with formaldehyde in a simple process, which is then dried and pyrolyzed in an inert atmosphere. A xerogel is produced by evaporating the solvent under normal, non-supercritical conditions (Lin and Ritter 1997). In addition to adjusting the synthesis conditions, surfactants can be used to fine-tune the distribution of porosity, which is one way to control the resulting nanostructure (Matos *et al.* 2006). It is also possible to modify the mesoporous carbons produced by this method and use them as catalysts (Machado *et al.* 2010). In the ring-opening reaction of epoxides by alcohols, mesoporous ACs showed high conversion and selectivity, which makes them effective catalysts (Figure 5.6). In addition, the catalyst can be regenerated to regain its original activity (Matos *et al.* 2012).

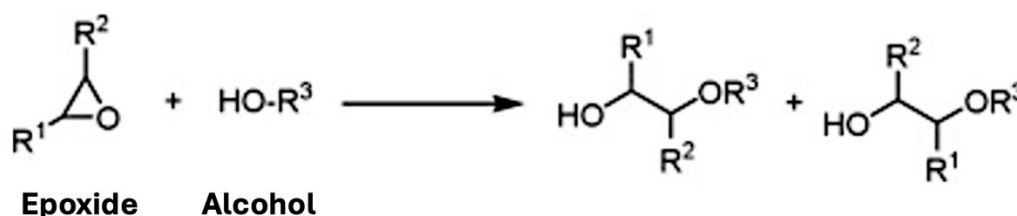


Figure 5-6. Epoxide and alcoholic reactions. Adapted from (Matos *et al.* 2012).

5.3.2 Activated Carbon as Support

In addition, metals, organocatalysts and organometallic catalysts can be supported by AC in a variety of processes (Kharisov and Kharissova 2014; Pérez-Mayoral, Calvino-Casilda and Soriano 2016). The ongoing effort to combine the advantages of solid supports and homogeneous catalysts with known active sites has led to the heterogenization of homogeneous active species, potentially improving selectivity even further. When palladium (Pd) catalysts are present, hydrogenation reactions can take place (Benavidez *et al.* 2014; Belskaya *et al.* 2016). Zea *et al.* (2004) synthesized and characterized PdAg/C and Pd/C catalysts using plasma

torch technology. According to the authors, the metal catalysts obtained were extremely highly dispersed, in some cases with a dispersion of over 50%. The high activity of these catalysts was demonstrated in two hydrogenation processes. When the Pd/C catalysts were compared with those prepared by conventional methods, they showed comparable or superior activity and selectivity for the isomerisation of 1-butene. The hydrogenation of acetylene by the PdAg/carbon supported catalysts was more selective than that of the PdAg/Al₂O₃, indicating the importance of the support in these systems.

Similarly, studies conducted on AC with Ni have also demonstrated its effectiveness as a support for catalysts, particularly in CO₂ methanation. A high surface area and improved dispersion of the metal particles on the support were key factors noted in various articles (Feng, Yang and Chu 2016; Gonçalves *et al.* 2022) and Wang *et al.* (2023) using AC. For instance, according to Feng, Yang and Chu (2016), AC provided a high surface area (940 m²/g) and a pore volume of 0.51 cm³/g when used as a support for Ni, resulting in significant catalytic performance. At 360 °C, with 68% CO₂ conversion and 65% CH₄ production, the catalyst Ni/AC synthesized by impregnation and containing 15 wt% of Ni was able to exhibit the maximum catalytic activity (Feng, Yang and Chu 2016). Gonçalves *et al.* (2022) also reported a Ni/AC catalyst with 15 wt% Ni that achieved 95% CH₄ selectivity and 72% CO₂ conversion at 425 °C. Additionally, Wang *et al.* (2023) investigated Ni catalysts supported on AC and prepared by impregnation of 10 wt% Ni and found that the catalyst provided 96% CH₄ selectivity and 69% CO₂ conversion at 340 °C.

Building upon the versatility of AC as a support material, Valente *et al.* (2001) investigated the oxidation of pinane with switch metal-acetylacetonate complexes immobilized on modified AC. The surface of the functionalized AC was effectively chemically anchored by copper and cobalt acetylacetonate complexes. Through *in situ* Schiff condensation between the complexes and the amine groups added to the carbon surface, a method for covalent binding of these organometallic complexes to AC supports was demonstrated in this work (Figure 5.7). The results showed that Schiff condensation could be performed well, giving these catalytic materials more durability against complicated leaching and yielding materials that would be very valuable for liquid-phase oxidations. In the oxidation of pinane at ambient temperature and atmospheric pressure, these catalysts were extremely selective and active towards 2-pinane hydroperoxide.

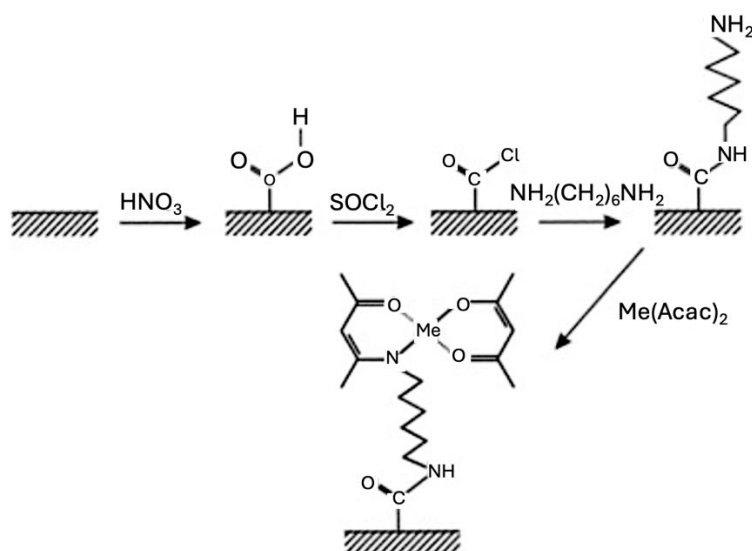


Figure 5-7. A schematic depiction of the acetylacetonate complex heterogenization process. Adapted from (Valente *et al.* 2001).

In another work, iron phthalocyanines, a homogeneous catalyst, were supported on AC to create heterogeneous catalysts (Valente *et al.* 2003). The surface of commercially available Norit carbon was modified by a series of chemical and thermal processes, including oxidation in the liquid and gas phases. At atmospheric pressure and room temperature, various catalysts were investigated for the oxidation of cis-pinane using *tert*-butyl hydroperoxide. The primary reaction product obtained was 2-pinane hydroperoxide, with a selectivity of 77% at 91% conversion. Additionally, minor products such as verbanol, pinocampheol, and 2-pinanol were also identified. An intriguing finding related to the carbon surface chemistry emerged: catalyst supports with either very high or very low oxygen content exhibited minimal activity, whereas supports with moderate oxygen content demonstrated a strong correlation between the presence of lactones and phenols and catalytic activity.

Heteropolyacids (HPAs) are renowned for their strong Brönsted acidity and are frequently employed as acid catalysts (Kozhevnikov 1998). However, HPAs typically have a low specific surface area (1–10 m²/g). To overcome this limitation, AC supports have been utilized to immobilize HPAs, thereby increasing their specific surface area and the number of accessible acid sites. In a recent study, glycerol was acetylated using dodecatungstophosphoric acid (PW) supported on AC (Ferreira *et al.* 2011). Catalysts were prepared by impregnation and heat treatment at 403 °C. The catalytic esterification of glycerol with acetic acid (3.5 - 6.5 wt%) was evaluated over various loadings of PW immobilized on AC, with the catalyst containing 4.9 wt% PW exhibiting the highest activity. Increasing the loading of heteropolyacid on the AC resulted in decreased catalytic activity, attributed to pore blockage within the porous AC

framework. The main reaction products observed were triacetin, diacetin, and monoacetin (Figure 5.8), with good selectivity towards diacetin achieved across all catalysts tested. Furthermore, the catalytic stability of the most active catalyst was assessed through successive batch runs, revealing a stabilization of catalytic performance after the third batch.

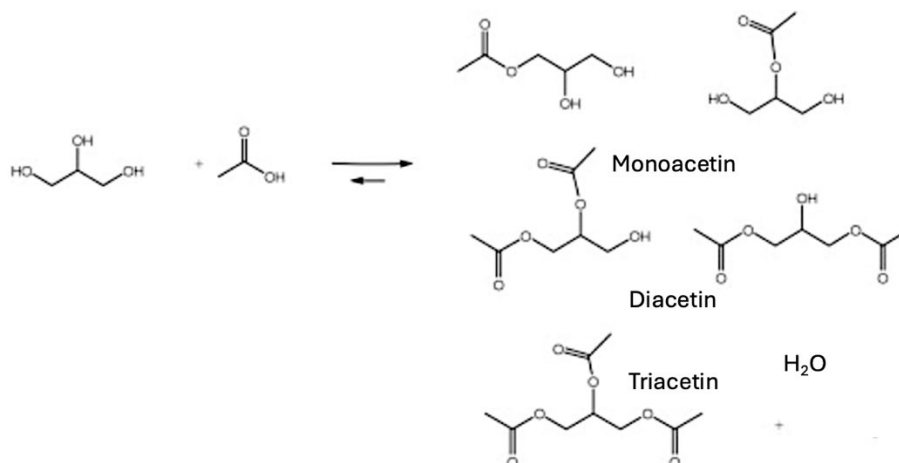


Figure 5-8. Glycerol Esterification with acetic acid. Adapted from (Ferreira *et al.* 2011).

5.4 Methods

Bibliometric analysis generates networks of citation links between authors, journals, and countries and includes analyses of co-authorship among authors and co-occurrence of keywords. This method utilizes the outputs of academic literature to map and understand the relationships and trends within a specific scientific research area (Van Eck and Waltman 2014).

5.4.1 Data Sourcing Strategy

The schematic flowchart in Figure 5.9 outlines the procedures used to complete the systematic review and bibliometric analysis for this study. The Web of Science (WOS) database was searched, and all articles published between 2014, and July 2024 were retrieved. The WOS is a renowned citation database that provides a current and retrospective index of journals, books and proceedings of multidisciplinary publications. Numerous studies have shown that WOS is suitable for bibliometric analysis (Tian *et al.* 2018). Therefore, the data for this study were restricted to articles published in WOS. The title, abstract and keyword fields in WOS were searched with specific keywords related to CO₂ methanation and CO₂ hydrogenation. The query string utilized was (Porous activated carbon) OR (Activated carbon-based porous materials) OR (Porous AC) OR (AC-based fibers) OR (activated carbon porous catalyst) OR (activated carbon-supported catalysts) OR (activated carbon mesoporous porous material) OR

(mesoporous AC) OR (Activated carbon supported catalysts) OR (Activated carbon-based catalytic materials) OR (Activated carbon fiber catalyst systems) OR (Activated carbon fiber-supported heterogenous catalysts) OR (Nanoscale activated carbon catalyst) OR (Nanostructured activated carbon fibers) OR (Nanofibrous activated carbon composites) OR (Activated carbon nanocomposites) OR (CO₂ valorization) OR (CO₂ methanation) OR (CO₂-CH₄ utilization) OR (CO₂ utilization) OR (greenhouse gas valorization) OR (sustainable energy) OR (synthesis gas generation) OR (synthesis gas production) OR (hydrogenation of CO₂ to CH₄) OR (carbon dioxide methanation) OR (CO₂ hydrogenation to methane) OR (methanation of CO₂) OR (methanation of carbon dioxide) OR (CO₂ recycling) OR (Carbon-neutral technologies) OR (Eco-friendly catalysts) OR (Renewable syngas production)) OR (Clean energy generation) OR (Sustainable catalysis) OR (Greenhouse gas conversion) OR (Carbon-neutral energy) (Topic) and Early Access (Document Types) and English (Languages) and Article (Document Types) and English (Languages). 4196 articles matching the search term were extracted from the database. The metadata for the selected literature was retrieved as of July 10, 2024. These search terms encompassed various aspects pertinent to CO₂ methanation, renewable energy, greenhouse gas (GHG) conversion, and the utilization of porous activated carbon catalysts in CH₄ and CO₂ applications. The comprehensive search approach was designed to ensure all relevant research publications were included.

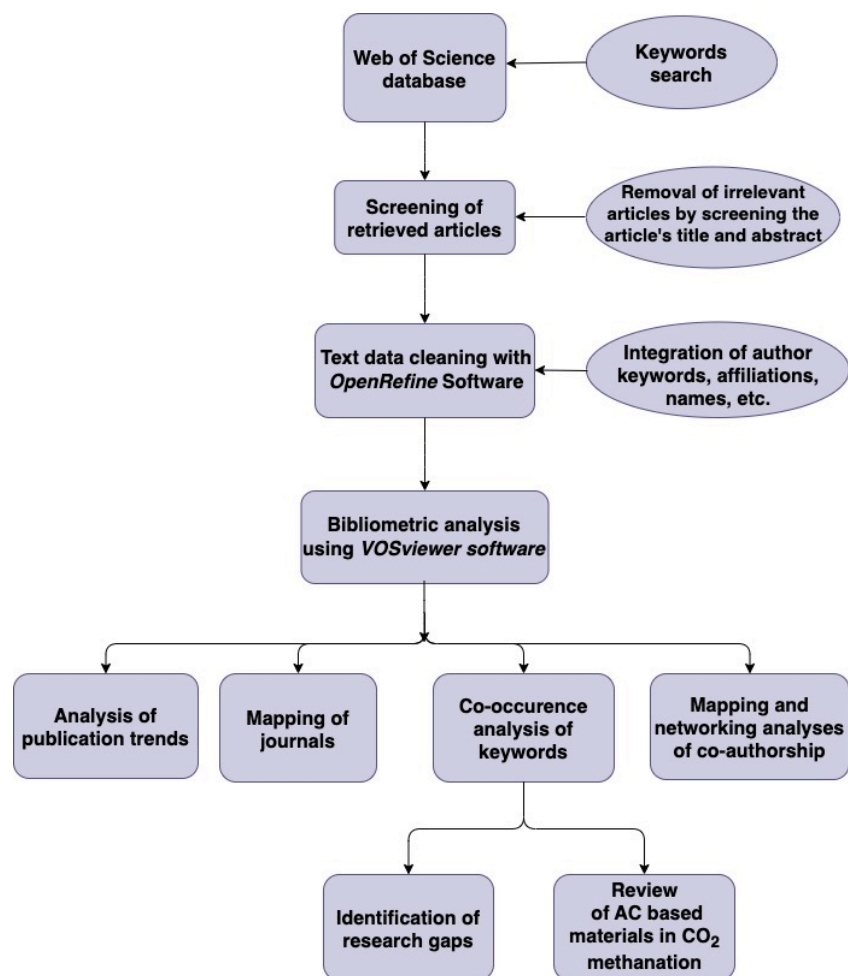


Figure 5-9. Flowchart depicting the process of bibliometric analysis.

5.4.2 Data Reconciliation and Text Cleaning

The titles, keywords, and abstracts of the 4196 retrieved articles were screened to identify and exclude any that were clearly unrelated. Since no irrelevant articles were found, all 4196 articles underwent further text cleansing and bibliometric analysis. The text cleansing process involved standardizing various author keywords to ensure consistency. For instance, keywords like “Ni-catalysts” and “nickel catalyst” were combined and treated as *ni catalyst*. Likewise, “bi-functional catalysts” and “Bifunctional catalysts” were combined as *bifunctional catalyst*. Additionally, author keywords such as (“power to gas” and “Power-to-Gas” were grouped as *power-to-gas*. Text cleaning was performed using the open-source software OpenRefine, version 3.4.1(OpenRefine 2022).

5.5 Bibliometric Analyses

Following data cleaning, the articles underwent analysis to determine the publication growth trend over time. Additionally, bibliometric analyses were conducted to scrutinize the co-occurrence of article keywords (i.e., author keywords), co-citations among articles and scientific journals, and co-authorship among countries. These analyses aimed to unveil primary research interests and directions, citation patterns, influential platforms for scientific papers, and scientific collaborations among institutions and countries. VOSviewer 1.6.17, an open-source, free science mapping software, was utilized for these analyses (Van Eck and Waltman 2010). VOSviewer employs a distance-based map, where the relationship between items is depicted by the length of the distance between them; a shorter distance signifies a stronger relationship. This visual representation facilitates the identification of clusters of related items (Van Eck and Waltman 2010). Each facet of the analyses (e.g., journal, country, author) is denoted by a node (e.g., circle or rectangle), with the size of the node indicating its influence and significance. For instance, the importance of an article can be assessed based on metrics such as the number of documents, citations, and average citations. Items sharing the same colour belong to the same cluster, suggesting they are frequently cited together in research on porous AC-related CO₂ methanation studies. Density visualization maps, such as those for journals, elucidate which journals have received a high number of citations or have published a larger number of articles (Van Eck and Waltman 2010).

5.6 Analysis and Discussion of Bibliometric Findings regarding Literature on Porous Activated Carbon-related CO₂ Methanation (2014 – 2024)

5.6.1 Scientific Publication Trend

Figure 5.10 illustrates the annual scientific publication trends for CO₂ methanation based on porous AC. According to the publication trend, significant research attention on porous AC – related CO₂ methanation began to gain traction in 2019, with 15 articles published. In 2020, 46 articles were published, which is twice the total publications from 2019. From 2021 to 2024, a cumulative total of 4,135 publications were indexed in the WOS database, indicating significant growth in this research area. As of May 2024, approximately 2,329 articles have been published. This trend suggests that the number of publications will continue to rise as more researchers focus on porous activated carbon – related CO₂ methanation, as evidenced by the increased output in 2024.

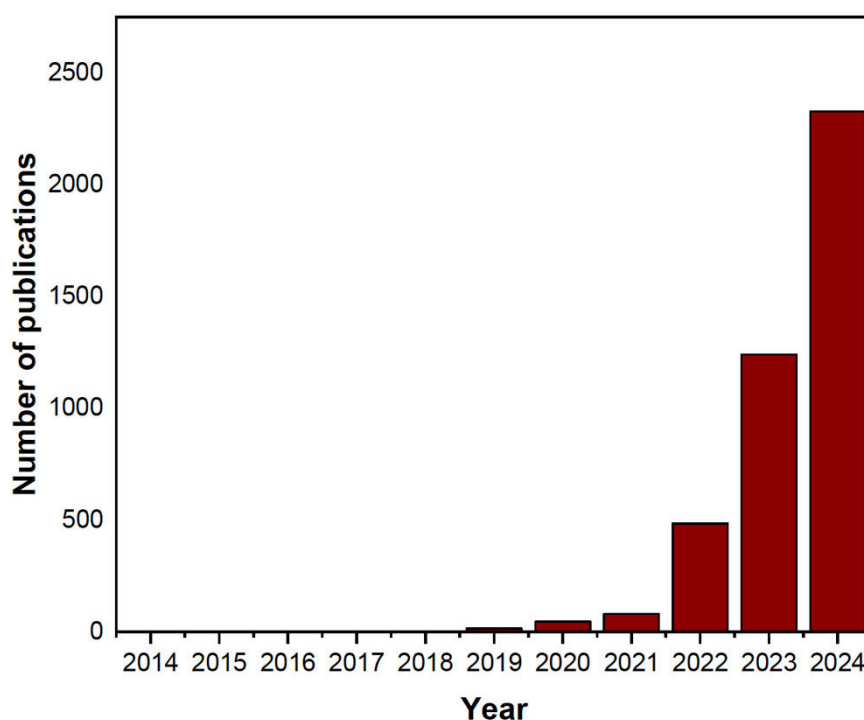


Figure 5-10. Annual scientific outputs on porous activated carbon-related CO₂ methanation.

5.6.2 Top Journals for Publishing Porous Activated Carbon-related CO₂ Methanation

Identifying the most reputable journals for publishing research on porous AC – related CO₂ methanation is crucial for both funders and researchers. Reputable journals ensure that information sources are reliable and current while also serving as vital channels for disseminating novel concepts and receiving recognition for their work. Publishing in a reputable journal has been demonstrated to boost article citation rates significantly (Tahamtan, Safipour Afshar and Ahamdzadeh 2016; Liskiewicz, Liskiewicz and Paczesny 2021). Figure 5.11 illustrates the article network map for porous AC – related CO₂ methanation studies within the top 20 research journals. The map was created by setting the minimum number of articles per journal to 5 and the minimum number of citations per journal to 10. It is important to note that there are no standardized criteria for creating this type of network map in the bibliometric literature. Nevertheless, we selected these criteria to facilitate the study of 151 distinct scientific journals.

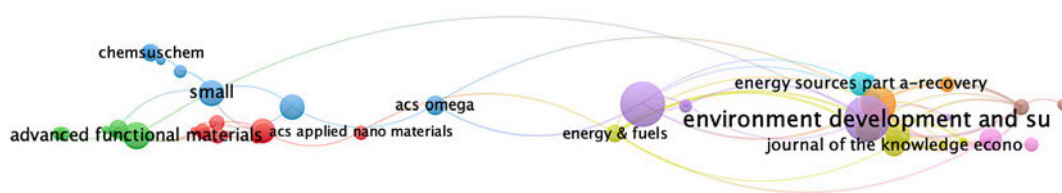


Figure 5-11. Network map highlighting key journals for publishing porous activated carbon-related CO₂ methanation.

Figure 5.11 shows the 46 journals that meet these criteria. Table 5.3 below lists the top 20 journals ranked by overall link strength, citations, and the number of articles published. The overall link strength is a key metric that measures the strength of connections between an item (e.g., journal, country) and other items being analyzed (Bornmann and Leydesdorff 2014).

Table 5-3. Top 20 bibliometrically analysed research journals.

S. No.	Journal	Cluster	Number of articles	Citations	Total link strength
1	Environment Development and Sustainability	5	274	458	60
2	Biomass Conversion and Biorefinery	5	259	579	11
3	Environment Science and Pollution	7	159	637	52
4	Advanced Functional Materials	2	92	42	9
5	Small	3	90	54	5
6	Energy and Environment	4	82	261	34
7	ACS Applied Materials & Interfaces	1	80	872	6
8	Natural Resource Forum	4	79	62	61
9	Energy Sources Part A – Recovery Utilization	6	70	776	10
10	Journal of the Knowledge Economy	4	64	95	12
11	ACS Omega	3	48	253	4
12	Industrial & Engineering Chemistry	1	47	165	1
13	Advanced Materials	2	44	58	8
14	Chemsuchem	3	41	97	2
15	Energy & Fuels	4	40	183	16
16	Clean Technologies & Environment	6	40	16	10
17	Angewandte chemie-international	1	37	95	2
18	Economic Research – Ekonomiska Istrazivanja	8	30	312	23
19	Advanced Energy Materials	1	30	116	4
20	Nano Research	1	29	39	4

Figure 5.12 represents nine clusters of journals, each marked by a different colour. Red denotes cluster 1 (11 journals), green cluster 2 (8 journals), blue cluster 3 (5 journals), yellow cluster 4

(6 journals), purple cluster 5 (5 journals), cyan cluster 6 (3 journals), orange cluster 7 (2 journals), brown cluster 8 (2 Journals), and pink cluster 9 (2 journals). Journals within the same cluster exhibit higher citation rates compared to those outside the cluster. The number of publications or citations a journal has is indicative of its influence, with this influence visually represented by the size of the node assigned to it. The strength of the link between the two journals is indicated by the length of the line connecting them, with shorter lines representing stronger links (Van Eck and Waltman 2010). *Environment Development and Sustainability* emerges as the most influential journal, boasting the highest total link strength (60), number of published articles (274), and number of citations (458). It publishes more articles than *Biomass Conversion and Biorefinery*, which ranks second with 259 articles and 579 citations. The next three leading journals are *Environment Science and Pollution*, *Advanced Functional Materials*, and the *Journal of Small*. These five journals combined account for 53.4 % of all papers on porous AC – related CO₂ methanation. While these journals are the most prolific in terms of the number of papers published, *Energy & Fuels* and *Clean Technologies & Environment* have each published 40 papers, together accumulating a total of 199 citations. Additionally, both *Economic Research – Ekonomiska Istrazivanja* and *Advanced Energy Materials* have published 30 papers, together amassing 155 citations. The *Angewandte chemie-international* has fewer published articles compared to *Chemsuchem*, the *Advanced Materials*, *Industrial & Engineering Chemistry*, *ACS Omega*, and the *Journal of the Knowledge Economy*. *Energy Sources Part A – Recovery Utilization Journal* and *ACS Applied Materials & Interfaces* have fewer articles but more citations than *Energy and Environment* and *Natural Resource Forum*. This strongly suggests that the research published in these journals is of high quality. Factors such as the novelty of the research, the reputation of the publishing journal, and the journal's publication model (subscription-based or open-access) also contribute significantly to high citation counts (Tahamtan, Safipour Afshar and Ahamdzadeh 2016; Liskiewicz, Liskiewicz and Paczesny 2021; Akinwekomi and Akhtar 2022).

5.6.3 Scientific Collaboration Networks

5.6.3.1 Co-Authorship Analysis of Researchers

Scientific cooperation among researchers facilitates access to costly and specialized research facilities, knowledge exchange, and technology transfer (Marsh and Reinoso 2006; Khudzari *et al.* 2018). Furthermore, it serves as a critical metric for evaluating universities (Bornmann and Leydesdorff 2014; Khudzari *et al.* 2018). Using the criteria "minimum number of

documents of an author = 3" and "minimum number of citations of an author = 6," a co-authorship cluster density map of authors is generated in VOSviewer. This map, illustrated in Figure 5.12, includes seventy-one authors out of the 19,239 researchers in the database. Table 2 displays the top 10 authors based on *total link strength* and other ranking attributes, while Figure 5.12 shows the co-authorship cluster density map of the top 71 connected researchers. These researchers are organized into ten clusters, denoted by different colours: red (*Cluster 1*; 11 researchers), green (*Cluster 2*; 10 researchers), blue (*Cluster 3*; 8 researchers), yellow (*Cluster 4*; 8 researchers), purple (*Cluster 5*; 8 researchers), cyan (*Cluster 6*; 7 researchers), orange (*Cluster 7*; 7 researchers), brown (*Cluster 8*; 4 researchers), pink (*Cluster 9*; 4 researchers), and light pink (*Cluster 10*; 4 researchers). Each cluster represents a collaborative group of scientists. A brighter node linked to a researcher indicates a stronger and more collaborative network. Apparently, the most influential researchers in each of these clusters are Adebayo Tomiwa Sunday (red; 14 articles; 13 collaborators), Al-faryan Mamdouh Abdulaziz (green; 9 articles; 6 collaborators), Ibrahim Ridwan Lanre (blue; 8 articles; 6 collaborators), Anwar Ahsan (yellow; 8 articles; 10 collaborators), Usman Mohammad (purple; 8 articles; 5 collaborators), Wang Ying (cyan; 8 articles; 1 collaborator), Pata Ugur Korkut (orange; 7 articles; 11 collaborators), Ahmed Zahoor (brown; 7 articles; 5 collaborators), Bekun Festus Victor (pink; 6 articles; 9 collaborators), and Radulescu Magdalena (peach; 6 articles; 7 collaborators). Among all these clusters, Adebayo Tomiwa Sunday emerges as the most prominent author, with research collaborators situated in *red, pink, green, brown* and *orange* clusters. The diversity of research collaboration could be influenced by various factors, including the presence of numerous foreign postgraduate students and visiting scholars, as well as substantial research funds (Khudzari *et al.* 2018).

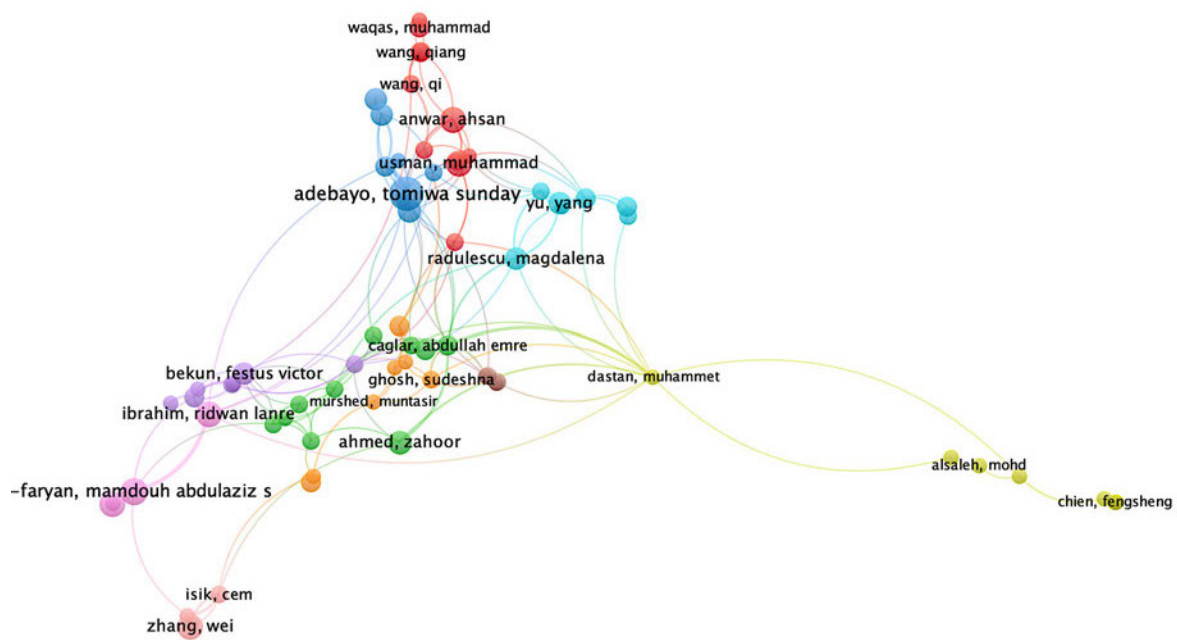


Figure 5-12. Co-authorship cluster map of authors based on publication volume.

Table 5-4. Analysis of co-authorship of authors.

S. No.	Author	Cluster	Citations	Number of articles	Institution/Country
1	Adebayo, Tomiwa Sunday	3	51	14	Cyprus International University, Nicosia, Cyprus
2	Al-faryan, Mamdouh abdulaziz	9	37	9	University of Portsmouth Faculty of Business and Law, Portsmouth, England
3	Ibrahim, Ridwan Lanre	9	25	8	University of Lagos, Lagos, Nigeria
4	Anwar, ahsan	1	118	8	Materials Science and Chemical Engineering Department, State University of New York, NY, USA
5	Usman, mohammad	1	11	8	King Fahd University of Petroleum & Minerals (KFUPM), Dhahran, Saudi Arabia
6	Wang, ying	9	55	8	Department of Physics, Harbin Institute of Technology, Harbin, China
7	Pata, ugur korkut	3	30	7	Faculty of Economics and Administrative Sciences, Department of Economics, Osmaniye Korkut Ata University, Osmaniye, Turkey
8	Ahmed, zahoor	2	22	7	Max Planck Institute for Dynamics of Complex Technical Systems, Magdeburg, Germany
9	Bekun, festus victor	5	10	6	Istanbul Gelişim University, Istanbul, Türkiye
10	Radulescu, magdalena	6	37	6	POLITEHNICA Bucharest National University of Science and Technology, Bucharest, Romania

The collaborative network of the top 10 most prolific authors is detailed in Table 5.4. Adebayo, Tomiwa Sunday (14 articles), Al-faryan, Mamdouh Abdulaziz (9 articles), Ibrahim, Ridwan Lanre (8 articles), Anwar, Ahsan (8 articles), and Usman, Mohammad (8 articles) emerge as the five most prolific authors. However, when considering citation counts, the rankings of these authors exhibit fluctuations. The top five authors by citation count are: Anwar, Ahsan (118 citations), Wang, Ying (55 citations), Adebayo, Tomiwa Sunday (51 citations), Al-faryan, Mamdouh Abdulaziz (37 citations), and Radulescu, Magdalena (37 citations). This new ranking emphasizes that the number of articles published by an author does not necessarily correlate with increased citation counts. Instead, high citation counts are more likely attributed to factors such as the quality of research work, novelty, the reputation of the publishing journal, and access type (subscription-based or open access) (Tahamtan, Safipour Afshar and Ahamdzadeh 2016; Liskiewicz, Liskiewicz and Paczesny 2021).

5.6.3.2 Analyses of International and Institutional Co-authorship

Table 5.5 illustrates the analysis of institutional co-authorship, generated by setting the "minimum number of documents of an institution" and "minimum number of citations of an institution" to 3 and 6, respectively. Only the top ten institutions are listed in Table 5.5, while 584 out of 4,707 institutions meet these criteria. Additionally, only 332 of the 4,707 institutions have collaborative relationships with other institutions, indicating a low level of inter-institutional collaboration. The Chinese Academy of Sciences (CAS) in China leads with the highest number of articles (135) and citations (472). The Lebanese American University (LAU), China, closely follows in terms of publication quantity. Despite LAU publishing more papers than UCAS, UCAS's citation count is over 79% higher. This suggests that UCAS's articles are likely of superior quality and published in highly regarded journals compared to those of LAU.

The significantly higher number of citations for UCAS compared to LAU, even though UCAS published fewer articles, can be attributed to several key factors. Firstly, UCAS probably publishes in higher-impact journals that have a wider readership and are more influential in the academic community. These high-impact journals tend to attract more citations due to their high profile. Secondly, UCAS could focus on research areas of greater global interest, such as cutting-edge fields like technology, environmental science or biomedical research, which tend to generate more citations due to their relevance and popularity. In addition, while LAU has a higher total link strength, indicating more collaborations, UCAS' association with the

prestigious Chinese Academy of Sciences gives it an advantage in terms of academic reputation and visibility. Research from prestigious institutions tends to be cited more frequently as these institutions are trusted, and their publications carry more weight. In addition, UCAS citations could also benefit from stronger international collaborative networks, as co-authored papers with prestigious institutions increase the likelihood of being cited more frequently. Language and accessibility could also play a role. If UCAS publishes more frequently in widely accessible languages such as English, its research could reach a wider global audience, which would further increase its citations. Finally, cultural differences in citation practises between different academic communities could also play a role. For example, UCAS research may be embedded in an academic environment where higher citation rates are important. Taken together, these factors suggest that the higher citation rate of UCAS is likely due to the higher quality, greater visibility and wider accessibility of its research compared to LAU rather than the mere quantity of publications.

Table 5-1. Analyses of institutional co-authorship.

S. No	Institution	Country	Number of published articles	Total link strength	Citations
1	Chinese Academy of Sciences	China	135	48	472
2	Lebanese American University	Lebanon	58	192	144
3	King Saudi University	Saudi Arabia	57	34	99
4	University of Chinese Academy of Sciences	China	46	17	258
5	Xi'an Jiaotong University	China	45	32	107
6	Beijing Institute Technology	China	38	42	137
7	Tsinghua University	China	35	13	142
8	University of Science & Technology	China	35	8	176
9	Zhejiang University	China	33	12	102
10	Sichuan University	China	32	9	122

Furthermore, as noted in Table 5.5, all the listed institutes exhibit relatively low *total link strengths*, meaning that while institutions like LAU may have more collaborative efforts, these collaborations do not always translate into higher citation counts. UCAS, though with lower collaboration rates, capitalizes on its prestigious affiliations and research impact. Notably, China hosts more than half of the top institutions listed, highlighting the growing dominance of Chinese institutions in publishing high-impact research. This emphasizes the need for enhanced inter-institutional and global collaboration, as strengthening such networks can further advance knowledge and increase citation visibility.

In addition to inter-institutional collaboration, international research collaborations are another crucial avenue for enhancing technology transfer and information sharing. Figure 5.13 displays the density map of countries with the most publications. To produce this figure in VOSviewer, the “minimum number of documents of a country” is set to 3, while the “minimum number of citations of a country” is set to 6. From the data retrieved from the Web of Science database, it is evident that all porous activated carbon-related CO₂ methanation articles are associated with 124 countries. However, only 71 countries meet this threshold, as depicted in Figure 5.13. Notably, Palestine (*Link 1, Research articles 4; Citations 8*) and New Zealand (*Link 1, Research articles 13; Citations 72*) have the least number of co-authorships with other nations. The most prominent nodes are attributed to China (1462 articles), followed by India (802 articles), and then the USA (354 articles). The brightness of a node corresponds to the density or number of articles published by the respective country.

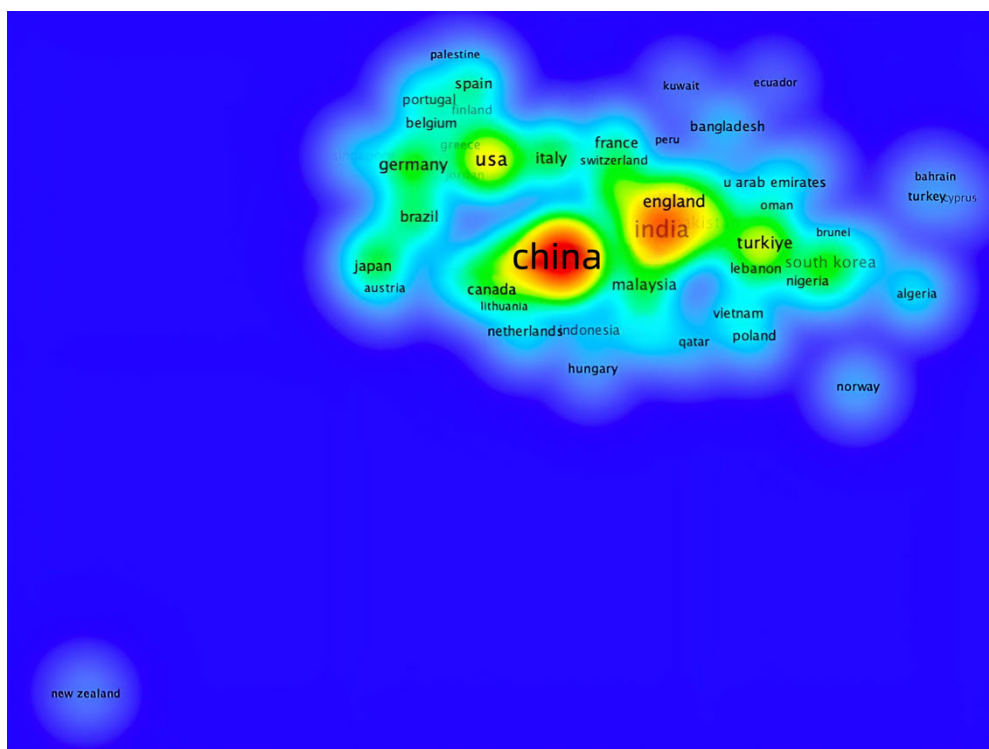


Figure 5-13. Co-authorship density map of countries based on scientific publications.

This international collaboration is well-established and emphasizes the interconnectivity of all countries in research. Table 5.6 further summarizes the statistics regarding the ten most prolific countries, highlighting their contributions to global scientific output and reinforcing the importance of continued cross-border partnerships.

Table 5-2. Top ten countries leading research in porous AC-related CO₂ methanation.

S.No	Country	Number of Articles	Citations
1	China	1462	4316
2	India	802	2223
3	USA	354	1152
4	Turkey	224	324
5	Pakistan	223	981
6	England	213	705
7	Saudi Arabia	199	577
8	Germany	165	505
9	Iran	152	426
10	Australia	145	734

China leads with the highest number of publications (1,462) and citation counts (4,316). During the reviewed period, China's publication output exceeded that of the next four countries in the rankings: India, the USA, Turkey, and Pakistan, demonstrating the country's dominance in porous AC-related CO₂ methanation research.

5.7 Analysis of Citations for Influential Articles on Porous AC-related CO₂ Methanation

Figure 5.14 illustrates the citation analysis of the most influential articles on porous AC-related CO₂ methanation, highlighting the outcomes of examining the most influential publications in this field. Out of the 19,239 articles, 183 meet the minimum criterion of 6 citations per document. However, Figure 5.14 focuses solely on the top 71. Notably, while the initial articles in this field were published before 2020 (Grabow and Mavrikakis 2011; Grabowski *et al.* 2011), the top five most frequently cited articles emerged after 2021 (Adebayo and Kirikkaleli 2021; Anwar *et al.* 2021; Balsalobre-Lorente *et al.* 2022; Balsalobre-Lorente *et al.* 2023; Zheng *et al.* 2023). This deviation from the norm is somewhat unusual; typically, pioneering research articles boast the highest citation counts as they continue to be referenced by newer articles. The most frequently cited articles in the expansive field of porous AC-related CO₂ methanation studies are those authored by Anwar *et al.* (2021) and Adebayo and Kirikkaleli (2021), regarded as pioneering publications on this subject. Together, these two articles amass over 169 citations.

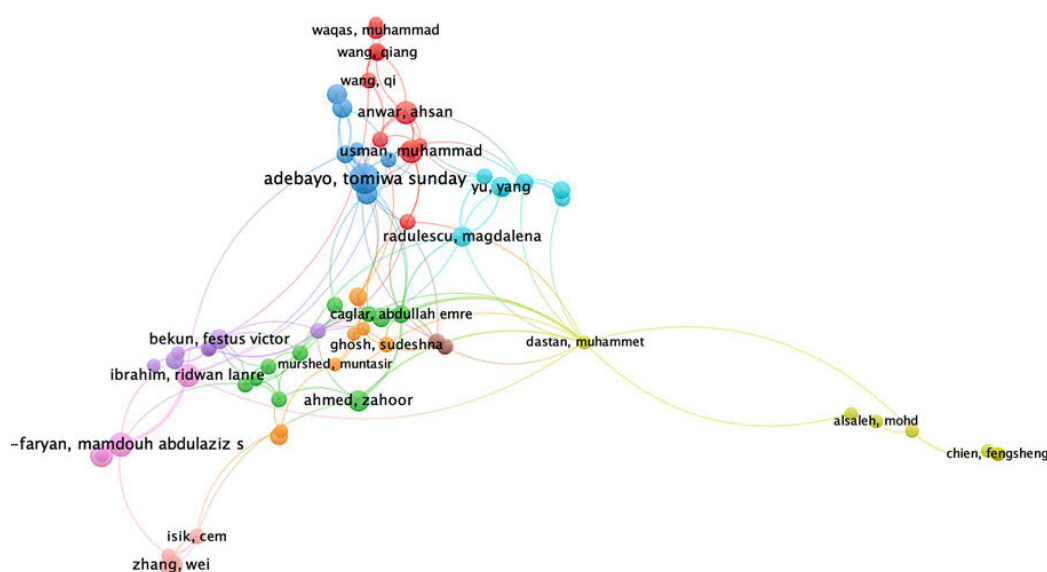


Figure 5-14. Network map of highly cited articles on porous AC-related CO₂ methanation.

The most-cited article in the subfield of porous AC-related CO₂ methanation is Anwar *et al.* (2021), boasting 118 citations. Following closely are Adebayo and Kirikkaleli (2021), with 51 citations and Balsalobre-Lorente *et al.* (2018), with 49 citations. The top five most cited articles are rounded out by Shah *et al.* (2023) with 41 citations and Al-faryan *et al.* (2023) with 37 citations. Table 5.7 contains additional details regarding these highly cited articles and the publication outlets.

Table 5-3. Top 20 influential articles on porous AC-related CO₂ methanation.

S. No	First author and year	Article Title
1	Anwar (2021)	The moderating role of renewable and non-renewable energy in environment-income nexus for ASEAN countries: Evidence from Method of Moments Quantile Regression
2	Adebayo (2021)	Impact of renewable energy consumption, globalization, and technological innovation on environmental degradation in Japan: application of wavelet tools
3	Balsalobre (2022)	Influence of growth and urbanization on CO ₂ emissions: The moderating effect of foreign direct investment on energy use in BRICS
4	Shah (2023)	Tourism, urbanization and natural resources rents matter for environmental sustainability: The leading role of AI and ICT on sustainable development goals in the digital era
5	Al-faryan (2023)	Do renewable energy, urbanisation, and natural resources enhance environmental quality in China? Evidence from novel bootstrap Fourier Granger causality in quantiles
6	Ibrahim (2021)	Non-renewable and renewable energy consumption, trade openness, and environmental quality in G-7 countries: the conditional role of technological progress
7	Zhang (2018)	Additive manufacturing of metallic components–process, structure and properties
8	Wang (2012)	Recent Advances in the Synthesis and Application of Layered Double Hydroxide (LDH) Nanosheets

9	Pata (2018)	Renewable energy consumption, urbanization, financial development, income and CO2 emissions in Turkey: testing EKC hypothesis with structural breaks
10	Ahmed (2020)	Moving towards a sustainable environment: the dynamic linkage between natural resources, human capital, urbanization, economic growth, and ecological footprint in China
11	Zhang (2019)	Over 16% efficiency organic photovoltaic cells enabled by a chlorinated acceptor with increased open-circuit voltages
12	Bekun (2019)	Toward a sustainable environment: Nexus between CO2 emissions, resource rent, renewable and non-renewable energy in 16-EU countries
13	Radulescu (2022)	Examining the role of nuclear and renewable energy in reducing carbon footprint: does the role of technological innovation really create some difference?
14	Nassani (2017)	Community-based ecotourism management for sustainable development of marine protected areas in Malaysia
15	Yu (2017)	Perovskites in catalysis and electrocatalysis
16	Liu (2021)	EKC and carbon footprint of cross-border waste transfer: Evidence from 134 countries
17	Zaman (2017)	Dynamic linkages between tourism transportation expenditures, carbon dioxide emission, energy consumption and growth factors: evidence from the transition economies
18	Zhang (2017)	Toward safe lithium metal anode in rechargeable batteries: a review
19	Calgar (2021)	Investigating the EKC hypothesis with renewable energy consumption, human capital, globalization and trade openness for China: evidence from augmented ARDL approach with a structural break
20	Eweade (2024)	Japan energy mix and economic growth nexus: Focus on natural gas consumption

5.8 Co-occurrence Network Analysis of Author Keywords

A co-occurrence network serves as a valuable tool for identifying significant research areas and potential future research directions (Hussein and Zayed 2021). The co-occurrence network map of author keywords was created in VOSviewer by setting the minimal number of occurrences of a keyword to 20. Out of a total of 12,597 keywords, 55 meet this criterion. In Figure 5.15, every circular node symbolizes a keyword, and the node's size correlates directly with the frequency of appearance of the keyword across articles. The relatedness of any two keywords is quantified by their distance; closer distances indicate stronger links. Additionally, keywords within the same cluster share the same colour, suggesting that they are more likely to occur together than those in separate clusters (Heersmink *et al.* 2011).

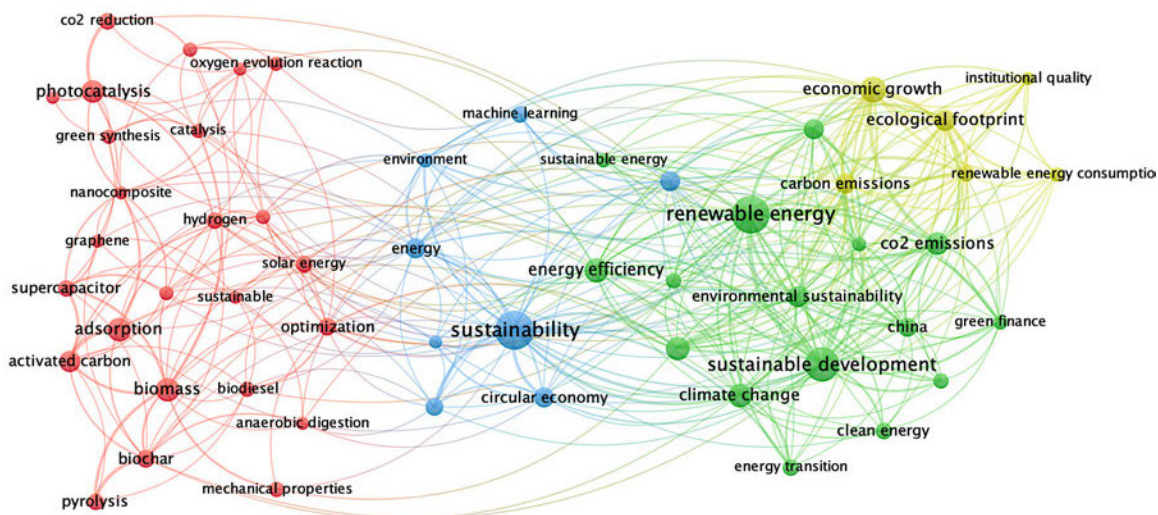


Figure 5-15. Co-occurrence network visualization of author keywords.

All 55 keywords are organized into four clusters. *Cluster 1*, highlighted in red and comprising 25 keywords, is the largest. The most prominent keywords in this cluster are "*adsorption*" and "*biomass*," each occurring 63 times. Additionally, "*adsorption*" is linked 9 times, while "*biomass*" is linked 14 times with other keywords. Other keywords in this cluster include *anaerobic digestion*, *biochar*, *biodiesel*, *graphene*, *carbon dioxide*, etc. *Cluster 2*, depicted in green and containing 16 keywords, is notable for the prevalence of "*Renewable energy*" (162 occurrences, with 30 links). This suggests that there is a gradual shift from fossil fuels to renewable energy. Hence, other keywords co-occurring in this cluster with "*Renewable energy*" include *energy transition*, *energy efficiency*, *green innovation*, *clean energy*, *carbon emission*, *environmental quality*, *energy consumption*, *CO₂ emissions*, *climate change*, *sustainable energy*, etc. All these keywords share a strong correlation with "*CO₂ methanation*." For example, CO₂ methanation, depending on the catalyst employed, is an exothermic catalytic reaction typically conducted within the temperature range of 150°C to 550°C (Ashok *et al.* 2020). Moreover, CO₂ methanation plays a crucial role in the context of renewable energy integration, energy efficiency improvement, carbon emission reduction, and overall sustainability, making it a significant area of research and development in the field of clean and sustainable energy technologies.

Cluster 3, depicted in blue, encompasses 8 keywords. Notable among these are *sustainability* (176 occurrences, 32 links), *circular economy* (46 occurrences, 14 links), *energy* (46 occurrences, 23 links), *environment* (22 occurrences, 16 links), *life cycle assessment* (36

occurrences, 14 links), machine learning (30 occurrences, 6 links), recycling (21 occurrences, 11 links), and sustainable development goals (45 occurrences, 17 links).

Cluster 4, represented in yellow, consists of 6 keywords, including carbon emissions, economic growth, institutional quality, renewable energy consumption, “ecological footprint”, and technological innovation. “Economic growth” stands out as the most frequently used keyword, with 78 mentions and 22 links. These keywords reflect the ongoing discourse on the economic and environmental impact of renewable energy, with a focus on how sustainable development is influenced by factors such as carbon emissions and institutional quality. This group emphasizes research that examines the relationship between environmental sustainability and economic development.

The current research trends in the fields of environmental sciences, renewable energies and sustainability are reflected in the keywords of the four clusters illustrated in Figure 5.14. The *"red cluster"* focuses on the development and application of innovative materials, including activated carbon, graphene and nanocomposites, for applications such as adsorption, oxygen evolution reactions, photocatalysis and CO₂ reduction. These results point to a research trend that aims to develop advanced materials for renewable energy technologies and environmental remediation. The *"blue cluster"* includes keywords such as solar energy, hydrogen and optimization, which indicate a focus on improving the efficiency and sustainability of a variety of energy systems. The *"green cluster"* is centred on the intersection of renewable energy and sustainable development, which includes topics such as clean energy, climate change and energy transition. This cluster emphasizes the link between the deployment of renewable energy and the achievement of broader sustainable development goals. The *"yellow cluster"* includes keywords related to the economic and environmental dimensions of renewable energy, emphasizing economic growth, ecological footprint and carbon emissions. This group refers to research that examines the relationship between environmental sustainability and economic development. Ultimately, the compilation of these keywords demonstrates a multidisciplinary approach to research that addresses the complex challenges of environmental protection, renewable energy and sustainability.

In addition to these clusters, CO₂ methanation is emerging as an evolving field, as shown by the articles retrieved from the WOS database. Technological innovations such as direct CO₂ electrolysis, advanced catalyst developments, and process intensification are complemented by ongoing efforts in digitization and automation, aimed at enhancing the efficiency and reliability

of methanation processes. Alongside the technological advances, there is an emerging discourse on institutional quality, which explores how governance structures, regulatory frameworks, and institutional practices influence the adoption and success of CO₂ methanation technologies (Salman *et al.* 2019; Haldar and Sethi 2021; Yang *et al.* 2022). Strengthening institutional quality through improved transparency, accountability, and governance can significantly impact the implementation of CO₂ methanation projects, ensuring they are not only economically viable but also socially and environmentally sustainable. This broader perspective highlights the importance of robust institutional frameworks in supporting the transition to cleaner energy technologies and addressing climate change. Hence, the occurrence of keywords such as institutional quality fewer than twenty times suggests they represent potential future research directions.

5.9 Study Limitations

The study under consideration shares limitations commonly observed in similar reviews and bibliometric analyses. A primary constraint is the reliance on data sourced solely from one database, Web of Science. This approach inherently excludes articles not indexed in Web of Science from the scope of the study. While efforts were made to use comprehensive keywords covering a majority of relevant publications, there is a possibility that some articles were missed due to mismatches or variations in search terms. Additionally, the study's data collection was limited to articles published between 2014 and 2024, thereby excluding documents published before or after this timeframe. However, this focused timeframe allows for a detailed analysis within the selected period. Future researchers can mitigate these limitations by considering publications from other citation index databases, such as Dimensions or Web of Science, provided by Clarivate Analytics. These databases may offer a broader perspective and enhance document retrieval. These limitations are typical in bibliometric research and are not unique to this study. Future studies can improve upon these constraints by utilizing multiple databases and employing a wider array of keywords to achieve more comprehensive document retrieval and analysis.

5.10 The Potential of Porous Activated Carbon Catalysts for CO₂ Methanation

Porous AC-based catalysts have emerged as promising options for enhancing the efficiency of CO₂ methanation and related energy processes. These catalysts offer distinct advantages, such as improved stability, resistance to carbon deposition, and enhanced catalytic activity (Jüntgen

1986). Their large surface area provides numerous active sites for catalytic reactions and efficient adsorption of reactants, thereby boosting catalytic performance and utilization. The porous architecture promotes a high surface-to-volume ratio, facilitating easier access to active sites and enhancing the mass transfer of reactants and products (Hwang *et al.* 2020). The interconnected porous network of AC catalysts minimizes diffusion limitations, allowing for faster gas diffusion and ensuring better contact between reactants and active sites. This improves reaction kinetics and overall catalytic efficiency in CO₂ methanation (Luque *et al.* 2024). Moreover, the efficient heat dissipation capability of porous AC reduces the risk of catalyst deactivation or sintering, thereby extending catalyst lifespan and enhancing methanation efficiency. Porous AC catalysts also demonstrate improved resistance to coking, a common challenge in CO₂ methanation, by inhibiting the accumulation of carbon species and facilitating their desorption (Lv *et al.* 2020). These characteristics preserve catalyst selectivity and effectiveness. Additionally, the regenerability of porous AC catalysts enables effective cleaning of clogged pores, restoring surface access and active sites, which contributes to consistent and sustainable catalytic performance over time (Alivand *et al.* 2020; Tian *et al.* 2020). Overall, porous AC catalysts hold significant promise for enhancing CO₂ methanation efficiency. Their attributes, including large surface area, thermal stability, improved mass transport, resistance to carbon deposition, and regenerability make them valuable catalysts for improving activity, selectivity, and stability in catalytic processes (Jüntgen 1986; Calvino-Casilda *et al.* 2010). Leveraging these benefits, researchers can advance the development of effective and economically feasible methods for sustainable CH₄ synthesis and GHG utilization through CO₂ methanation.

5.11 Challenges Inhibiting Activated Carbon Catalysts

Catalyst deactivation poses a significant challenge in the CO₂ methanation process, gradually diminishing catalytic activity through mechanisms such as sintering, poisoning, and carbon deposition. Carbon deposition, resulting from carbon species adhering to the catalyst surface, leads to the formation of coke, which reduces the catalyst's active surface area and hampers reactant access to active sites, thereby impairing CO₂ methanation conversion and selectivity (Shah *et al.* 2019; Yelwa *et al.* 2023). Strategies to mitigate catalyst deactivation include developing coke-resistant catalysts, optimizing reaction conditions, and employing catalyst regeneration methods (Guharoy *et al.* 2021; Zhang *et al.* 2023). During CO₂ methanation, high carbon activity and a low hydrogen-to-carbon ratio in the feed gas exacerbate carbon

deposition, where reactant gases thermally decompose, forming amorphous and graphitic carbon species on the catalyst surface (Pattiya 2018; Palmer 2021). These carbon deposits diminish reactant conversion and product selectivity by altering reaction kinetics and obstructing active sites. Designing catalysts and modifying surfaces to promote the formation of more reactive surface species and prevent coke formation are two strategies to mitigate carbon deposition (Song *et al.* 2018; Wang *et al.* 2020).

Thermal stability is critical in CO₂ methanation due to the operation at relatively low temperatures (200-400 °C), where catalysts may suffer from phase changes, sintering, or agglomeration at higher temperatures (>400 °C), resulting in loss of catalytic activity and surface area (Alrafi *et al.* 2020; Ashok *et al.* 2020). Furthermore, thermal cycling during startup and shutdown activities can contribute to catalyst deactivation. Enhancing thermal stability involves developing robust catalyst supports, advanced formulations, and implementing thermal management strategies (Arakawa *et al.* 2001). Achieving the desired H₂-to-CO₂ ratio for CH₄ production in CO₂ methanation requires precise control over reaction conditions, catalyst composition, and operational parameters to optimize selectivity for downstream applications in chemical synthesis and energy production (Currie 2019; Zhuang 2022). Balancing methane reforming and reverse water-gas shift processes is crucial for controlling product selectivity. Ongoing research focuses on developing novel catalyst materials, such as metal alloys or bimetallic catalysts, to improve stability, selectivity, and catalytic activity in CO₂ methanation.

5.12 Applications and Commercialization Prospects

CH₄ serves as a crucial intermediate in numerous industrial processes and can be sustainably produced through CO₂ methanation (Younas *et al.* 2016; Lee *et al.* 2021). This process offers an environmentally and economically viable alternative to traditional fossil fuel-based methods by utilizing H₂ and CO₂ as feedstocks for CH₄ production (Varvoutis *et al.* 2022). By harnessing these feedstocks, the process not only generates energy but also mitigates negative environmental impacts, addressing both financial and ecological concerns simultaneously. Integration with Carbon Capture and Utilization (CCU) technologies allows CO₂ emissions from diverse sources, such as power plants or industrial facilities, to be captured and converted into CH₄ thereby contributing to GHG reduction and achieving carbon neutrality (Mikulčić *et al.* 2019; Sabri *et al.* 2021).

Table 5.8 summarizes the applications of CO₂ and its potential for industrialization, highlighting the current state of technological readiness. Processes like FT synthesis enable the efficient and clean conversion of CO₂ into liquid hydrocarbon fuels, which can serve as energy sources for fuel cells, gas turbines, and transportation. Furthermore, coupling CO₂ methanation with renewable energy sources like wind or solar power presents opportunities for developing a more sustainable energy ecosystem, prompting further exploration in this field.

The CO₂ methanation market shows significant promise. It offers a compelling alternative to traditional carbon-intensive practices and GHG emissions as the demand for sustainable technologies continues to grow.

Table 5-4. CO₂ prospects and existing sector applications. Adapted from (Valluri, Claremboux and Kawatra 2022).

CO ₂ utilization techniques			
Applications	Sector	Impact	Readiness (1–10)
High urea, ammonia, chemicals (oxalic and formic acid) and fertiliser production are included. Production of carbonates, processing of biodiesel, production of olefins and polymers are components of fuels, which include CH ₄ , ethanol, diethyl ether, methanol and synthesis gas.	Fuels and Chemicals	High	5–6
Enhanced Oil Recovery (EOR): CO ₂ is used for a variety of purposes, including producing acid during well stimulation, removing hydrogen sulphide from natural gas, maintaining pressure in depleted reservoirs and improving oil flow in gas lift systems.	Oil and gas	High	10
Operating cycle of fluid (in power): CO ₂ is used for acid gas removal, dry ice cleaning for equipment maintenance, enhanced oil recovery, carbon capture, fire suppression and cooling functions in power generation.	Power	Medium	3–4
Materials/concrete construction; neutralisation of bauxite residues (red mud); In addition to material and waste treatment, CO ₂ is used in the carbonation of minerals for a variety of purposes. It is used for geological sequestration, waste disposal, ocean alkalinity enhancement, carbon storage and soil improvement.	Mineral carbonation	Medium	7–8
To reduce emissions from steel production and produce bio-based polymers, CO ₂ is used in iron and steel production, rare earth extraction, dewatering of acid drainage, carbonisation of steel and the use of CCS. CO ₂ is also employed as a raw material in chemical synthesis, helps in metal casting and treats water to control pH. It is also used in EOR, experimental carbonisation of minerals and other industrial processes.	Materials processing/chemical industries	Medium	6–8
The functions of CO ₂ in food processing are varied. It is used to reduce the acidity of drinks, to modify packaging for a longer shelf life, to cool food and to act as a leavening agent in baking. In food production, it is also used in extraction, pH control, controlled ripening and fermentation. In addition, it enables precise temperature control and reduces the growth of microorganisms at certain stages of food processing	Food	High	10
Energy requirements for generating CO ₂ -based chemicals			
Overall equation	Reagent/ chemical	Energy (mJ/kg)	
$6CO_2 + 8H_2O \rightarrow 2C_3H_7OH + 9O_2$	Propanol	29.53	
$3CO_2 + 4H_2O \rightarrow C_3H_7OH + 4.5O_2$			
$2CO_2 + 2H_2O \rightarrow 2HCOOH + O_2$	Formic acid	5.51	
$2CO_2 + H_2O \rightarrow 2CO + O_2 + H_2O$	Carbon monoxide	9.19	
$2CO_2 \rightarrow C_2O_4^{2-}$	Oxalate	2.68	
$2CO_2 + 3H_2O \rightarrow C_2H_5OH + 3O_2$	Ethanol	28.70	
$2CO_2 + 2H_2O \rightarrow C_2H_4 + 3O_2$	Ethylene	41.29	

$2CO_2 + 4H_2O \rightarrow 3O_2 + 2CH_3OH$	Methanol	21.17
$CO_2 + 2H_2O \rightarrow 1.5O_2 + CH_3OH$		
$CO_2 + 2H_2O \rightarrow 2O_2 + CH_4$	Methane	51.15

5.13 Environmental Consequences

Catalysts based on porous AC have emerged as transformative materials offering significant environmental benefits. For instance, they play a pivotal role in the catalytic process of CO₂ methanation, facilitating the conversion of CO₂ and H₂ into valuable CH₄ (Swalus *et al.* 2012). Porous AC materials are recognized for their ability to contribute to climate change mitigation, aligning with global shifts towards cleaner energy. The growth of the Direct Air Capture (DAC) industry, powered by renewable energy sources, emphasizes the potential of AC catalysts in advancing environmental sustainability through concerted multidimensional efforts. Activated carbon nanoparticles (ACNPs) find extensive use across various industrial sectors, including engineering, synthesis, manufacturing, and medicine, owing to their perceived low toxicity and versatility. They are often proposed as ideal negative controls in studies evaluating the impacts of exposure to other nanoparticles like fullerenes and polystyrene NPs. However, uncertainties remain regarding the potential adverse effects of ACNPs, with current literature predominantly focusing on their implications for human health (Jeirani, Niu and Soltan 2017; Yadav *et al.* 2021). Notably, despite their small size, ACNPs have been shown to penetrate the blood-brain barrier, raising concerns about potential neurotoxicity (Yang *et al.* 2010; Vinod and Jena 2021). Extensive assessments have documented impacts on multiple physiological systems in various cell and animal models, encompassing the heart, skin, lungs, liver, immune system, reproductive system, kidneys, and nervous system (Valente *et al.* 2001).

While human health impacts have been extensively studied, less attention has been given to the interactions of ACNPs with biological entities, non-target organisms, and both inorganic and organic substances in the environment. A comprehensive understanding of their toxicity is crucial for expanding research beyond human health concerns to encompass broader environmental interactions and non-target species. Such a holistic approach will enable informed decisions regarding the industrial and medical applications of ACNPs. Figure 5.15 illustrates various types of ACNPs, including hollow, mesoporous, covalently or non-covalently bound variants, among others (Zheng *et al.* 2020). It explores their targets, such as small compounds, peptides, and antibodies, as well as applications spanning biorecognition agents, medical devices, molecular imaging, and textiles. Discussions encompass environmental conditions and mechanisms like concentrations of silanol groups, agglomeration, interactions, degradability, toxicology mechanisms, bioaccumulation,

inflammation, cytotoxicity, pH, substance exposure duration, and temperature (Lazlo and Szűs 2001).

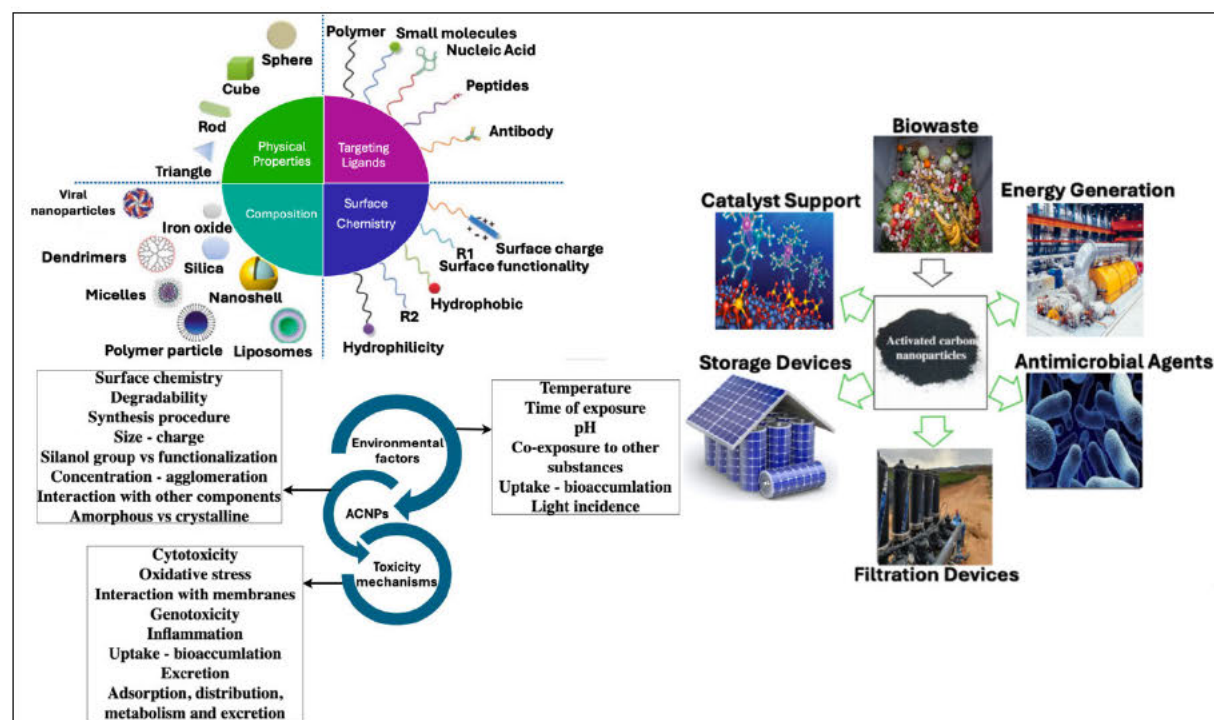


Figure 5-16. Types of ACNPs for (A) delivering active drugs and biological agents (B), Main applications of ACNPs (C), Parameters affecting toxicity mechanisms in ACNPs. (Lakshmi, Avti and Hegde 2018; Saxena *et al.* 2020).

5.14 Conclusion and Future Outlooks

In conclusion, this article offers a comprehensive analysis of activated carbon catalysts, encompassing their applications, environmental considerations, and prospects for commercialization. It presents diverse perspectives on the utilization and advancement of activated carbon materials, drawing from an extensive review of literature spanning 2014 to 2024. The study emphasizes the key role of activated carbon in carbon-neutral energy processes and environmental applications while addressing challenges encountered by porous activated carbon based on a detailed analysis of 4196 published articles. Significantly, the research identifies areas necessitating further collaboration and acknowledges leading contributors in the field, such as the Chinese Academy of Sciences and Anwar Ahsan. Through literature evaluation and keyword co-occurrence analysis, the study elucidates the strengths and limitations of porous activated carbon, highlighting its potential in environmental remediation and energy generation. This investigation lays a foundation for advancing sustainable practices in carbon-neutral technology and energy production, employing advanced data mapping techniques. In summary, the interdisciplinary nature of activated carbon research and its

transformative impact on fostering a sustainable and eco-friendly future are elaborated, positioning activated carbon materials at the forefront of innovative solutions for global environmental challenges.

Building on this foundation, the research findings of this study have significant implications for the future of catalytic technologies, particularly in the use of porous AC catalysts for CO₂ methanation processes. The findings reinforce previous research by demonstrating that the porous nature of AC enhances catalytic performance through improved reactant adsorption and increased surface area for reactions. Moreover, the study confirms the advantages of AC catalysts in reducing carbon deposition and enhancing the sustainability of methanation processes. However, it also highlights areas where existing findings may be challenged, especially regarding the practical application of these catalysts outside laboratory settings. The study suggests that further exploration of institutional and policy factors is necessary to promote the real-world adoption of these technologies. Therefore, future research should focus on improving the scalability and long-term stability of these catalysts while aligning technical advancements with supportive government policies to enable broader industrial use.

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CHAPTER 6

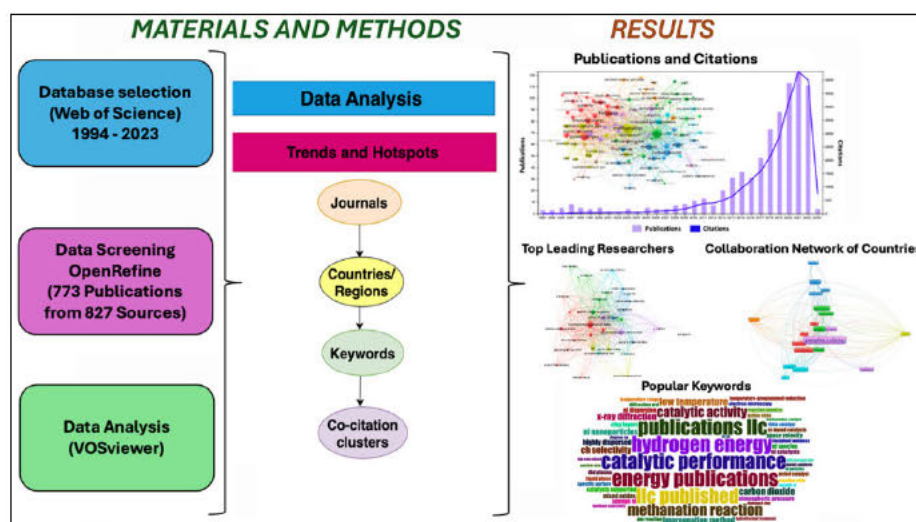
Molybdenum-Promoted Nickel Catalysts for CO₂ Methanation: A Critical Review and Informetric Perspective

Abstract

In this chapter, the role of molybdenum in nickel-based catalysts for enhanced catalytic CO₂ methanation was investigated through an informetric analysis. Contemporary studies in the field of informetrics were thoroughly explored using VOSviewer and RStudio software to evaluate the CO₂ methanation reaction. The data search was conducted using the keyword “CO₂ methanation” within the Web of Science (WoS) database, covering the period from 1994 to 2023. The analysis identified the most referenced journals, prominent keywords, highly cited articles, and patterns of collaboration by co-authorship from the 773 most cited publications. Additionally, several analytical tools were employed, including Sankey diagrams, word cloud analysis, co-occurrence network maps, and keyword visualization maps, to depict the global landscape of CO₂ methanation research. The chapter highlighted numerous gaps and future prospects for enhancing molybdenum-catalyzed CO₂ methanation using nickel-based catalysts. Frequently used keywords in the WoS search results include CO₂ methanation, methane, CO methanation, molybdenum, CO₂, synthetic natural gas, catalyst, and nickel catalyst. Among the journals analyzed, the Journal of Energy and Fuels featured the most publications, while China, the United States, Germany, Japan, Spain, and France emerged as the leading countries in terms of publication and citation counts. The chapter concludes by discussing the technical challenges identified and offering recommendations for future research in the development of molybdenum-based catalytic systems.

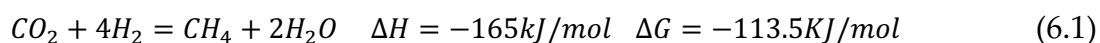
Keywords: CO₂ methanation, nickel, molybdenum, MO₃, informetric analysis, hydrogen

Graphical Abstract



6.1 Introduction

In the past century, rapid industrialization has disrupted the carbon cycle and caused a significant increase in greenhouse gas (GHG) emissions. The increase in the production of renewable energy sources has not yet been able to compensate for the adverse effects on the climate and the ecosystems of our planet (Gielen *et al.* 2019; Mardani *et al.* 2019). Even though hydrogen (H₂) production technology via water electrolysis has advanced, hopes have been raised for its use as a green fuel that does not emit any carbon dioxide (CO₂) when combusted (Yentekakis and Dong 2020). However, its transportation and storage still need to be improved compared to conventional energy carriers, like natural gas (Ren *et al.* 2017). In the preceding decade, researchers have concentrated on developing catalysts that can use this surplus renewable hydrogen to hydrogenate CO₂ from industrial exhaust gases. Therefore, H₂ can be converted into a resourceful energy carrier, synthetic natural gas (SNG) or methane (CH₄), with a substantially greater energy density while forming a closed carbon cycle (Thema, Bauer and Sterner 2019). The Sabatier reaction, commonly known as the complete hydrogenation of CO₂ into CH₄, is an exothermic reaction defined by the following equation:



The CO₂ methanation process has received significant attention for its potential in hydrogen storage and CO₂ reduction (Shen *et al.* 2020; Zheng *et al.* 2021). As a highly exothermic reaction, it is most efficient under low-temperature conditions (Jo *et al.* 2022). However, at high temperatures (>500 °C), catalyst deactivation processes such as sintering are accelerated, and carbon monoxide (CO) production as a by-product increases (Schmider, Maier and Deutschmann 2021). Elevated pressures favour the reaction by shifting the equilibrium towards CH₄ production, owing to the reduction in the number of gas molecules involved. Consequently, a primary goal in this field is to conduct methanation at relatively low temperatures to enhance catalyst durability and CH₄ selectivity (Ashok *et al.* 2020; Hu *et al.* 2021a). At lower temperatures, the CO₂-to-CH₄ conversion is kinetically challenging because the reaction requires the transfer of eight electrons from hydrogen to the carbon atom in CO₂. This process involves a significant energy barrier that is difficult to overcome without adequate thermal energy, making the reaction less favourable under low-temperature conditions (Thampi, Kiwi and Graetzel 1987). This makes the development of efficient, stable, and low-temperature catalysts essential. Transition metal carbides, including those of Ti, Mo, and V, have emerged as promising candidates for CO₂ conversion into CH₄, methanol (CH₃OH), CO,

and other hydrocarbons (Gao *et al.* 2016a; Liu *et al.* 2016b; Posada-Perez *et al.* 2016; Han *et al.* 2019; Reddy *et al.* 2019). Among these, molybdenum (Mo) stands out as a versatile catalyst for reactions such as CO₂ methanation, syngas conversion, hydrogen evolution, and hydrodesulfurization (Dhar *et al.* 2003; Zaman and Smith 2012). Mo's effectiveness stems from its ability to activate CO₂ through dual functionalities: H₂ dissociation and C=O bond scission. Computational studies further confirm the strong CO₂ adsorption and activation capabilities of Mo carbide surfaces, making them highly suitable for CO₂ methanation applications (Kunkel, Vines and Illas 2016, 2017; Liu *et al.* 2017; Kunkel *et al.* 2018).

Although research on the role of Mo in Ni-based catalysts for CO₂ methanation is not new, the number of published articles is rapidly increasing. Therefore, it is crucial to summarize the expanding body of knowledge in this field and stay informed about new developments. Consequently, a limited number of review studies (Saito and Anderson 1980; Chen, Choi and Thompson 2015; Xu *et al.* 2015; Chen, Choi and Thompson 2016) have been published to provide concise summaries of the key findings on the function of Mo in Ni-based catalysts for CO₂ methanation. While Saito and Anderson (Saito and Anderson 1981) investigated the performance of several Mo compounds, including oxides, sulfides, metals, carbides, and nitrides, for the methanation of CO₂, Xu *et al.* (2014) focused on synthesizing molybdenum carbide (Mo₂C) catalysts for CO₂ hydrogenation through thermal carburization of Mo oxide precursors in mixtures of H₂ and hydrocarbons. A study by Chen, Choi and Thompson (2015) explored the use of (Mo₂C) supported metal catalysts in liquid-phase reactions. The study reveals that Mo₂C itself serves as both a co-catalyst and a support for CO₂ hydrogenation, exhibiting activity at temperatures as low as 135 °C. At this temperature, CH₃OH is the primary product. However, increasing the reaction temperature to 200 °C leads to the production of a broader range of products, including CH₃OH, C₂H₅OH (ethanol), and C²⁺ hydrocarbons (Chen, Choi and Thompson 2015). However, there is a notable lack of data-driven informetric studies dedicated to assessing, investigating, and visualizing the global literature on CO₂ methanation. This study addresses a critical gap in the literature by presenting novel insights into the catalytic performance of Mo as a promoter for CO₂ methanation, with a particular emphasis on its reaction mechanisms and unique contributions to catalyst efficiency.

Despite the fact that many reviews (Aziz *et al.* 2015a; Su *et al.* 2016; Younas *et al.* 2016; Frontera *et al.* 2017; Sreedhar *et al.* 2019; Wang *et al.* 2022b) have been published on CO₂ methanation, there are few detailed studies on the role of Mo in Ni-based catalysts for CO₂

methanation. The informetric analysis of this study is more extensive. It shows the development of this topic more comprehensively than previously published reviews (Aziz *et al.* 2015a; Frontera *et al.* 2017; Sreedhar *et al.* 2019), examining the number of publications in this field. Driven by these factors, the contribution of Mo to Ni-based catalysts for CO₂ methanation was highlighted. In addition, a brief informetric evaluation of the research area has been provided. Table 6.1 outlines the most notable CO₂ methanation-related findings in the search results. Although previous articles on this topic have deliberately covered various trending topics, this article provides an in-depth analysis of the current state of the informetric study and recent advances in Mo-based catalysts for CO₂ methanation to produce CH₄. Web of Science (WoS), now recognized as the most reliable search source, was utilized to summarize the topic's search results, and informetric tests were performed using the obtained data.

Table 6-1. A list of the articles in the field with the most citations and limitations.

Refs.	Highlights of the Articles	Limitations	Year
(Bogdanov <i>et al.</i> 2021)	The economic viability and technical feasibility of 100% renewable energy systems including the transport, heat, power, and desalination sectors were highlighted.	The model used is computationally intensive but may oversimplify real-world energy systems. It lacks comprehensive integration of sector coupling, Power-to-X technologies, water scarcity, biofuels, regional differences, and the effects of storage technologies. It assumes high electrification and ongoing energy demand growth in developing nations, which may not match real trends. Moreover, the study overlooks technologies such as fossil CCS and nuclear power in the energy transition.	2021
(Lebrouhi <i>et al.</i> 2022)	A review was presented and analyzed of scientific and technological advancements in hydrogen production, purification, compression, transport, and utilization. Also discussed were the strategies and roadmaps developed in recent years by various nations regarding the production of hydrogen at a large scale.	The study emphasizes technical aspects of hydrogen but overlooks broader geopolitical and economic factors like government policies, market dynamics, and international cooperation. It also neglects the impact of storage technologies, the role of fossil CCS and nuclear power in energy transition, and regional variations in energy demand and resources. Assumptions about rising energy demand and high electrification in developing countries may not align with actual trends.	2022
(Grim <i>et al.</i> 2020)	An evaluation and characterization of the top technical drawbacks to applying renewable electricity for CO₂ reduction (CO₂R) across five distinct conversion techniques (indirect thermochemical, direct non-thermal plasma, indirect bioelectrochemical, direct bioelectrochemical, and direct electrochemical) were conducted under state-of-the-art technology conditions. Based on an analysis of the five pathways for CO₂R, indirect routes (bioelectrochemical and thermochemical) offer the most technically feasible opportunities for CO₂ utilization in the near future. These routes represent immediate deployment pathways for	The study primarily examines the technical and economic aspects of CO₂ utilization technologies but overlooks broader environmental, social, and policy implications of widespread adoption. It focuses on specific CO₂ utilization pathways without fully assessing overall sustainability. Moreover, the study assumes ongoing reductions in renewable electricity costs, which might not occur as projected, and it doesn't fully consider regional resource availability and infrastructure constraints that could affect feasibility.	2020

producing products with high values and comparatively high volumes.

(Staff ell <i>et al.</i> 2019)	An extensive update on the state of the art of fuel cells and hydrogen for transportation, industrial heating, power generation, and storage was provided, encompassing infrastructure requirements, technologies, government policies, and economics. According to the review, significant improvements are still required for hydrogen to truly compete in terms of costs and performance.	The study on "The role of hydrogen and fuel cells in the global energy system" overlooks several critical factors. It does not address the costs and challenges of storing and transporting hydrogen, especially on a large scale and over long distances. Additionally, the study does not examine the feasibility of producing hydrogen from non-renewable sources like fossil fuels, nor does it comprehensively assess the infrastructure needs for industrial applications. Furthermore, the economic viability of hydrogen and fuel cells including production, transport, utilization costs, and potential economic benefits is not thoroughly investigated.	2019
(Bui <i>et al.</i> 2018)	A multiscale perspective is presented in this paper on CO₂ capture, transportation, utilization, and storage in terms of global to molecular scales. The authors identified and articulated the critical research challenges that can be usefully addressed over the next two decades in all areas.	The study provides a comprehensive review of CO₂ capture technologies but lacks an in-depth analysis of the specific limitations and challenges hindering their large-scale deployment. Additionally, it does not offer a comparative assessment of CO₂ capture with other mitigation options.	2018
(Tee <i>et al.</i> 2017)	The water-splitting processes of thermolysis, electrolysis, photolysis, and biolysis were compiled. The highlights included solar-driven water electrolysis with integrated photovoltaics and photonic and electrically driven water splitting. It is anticipated that photocatalytic water splitting, which produces hydrogen at a low cost and with minimal environmental impact under favourable operating conditions, will be crucial to the development of the hydrogen economy.	While these studies focused on a comprehensive overview of recent advances in energy-driven water splitting, they do not fully consider the practical, economic, environmental and systemic challenges that need to be overcome for large-scale deployment and commercialization of these technologies.	2017
(Youn as <i>et al.</i> 2016)	Extensive research is currently being conducted to provide researchers with an in-depth review of CO₂ methanation in terms of recent advances in the catalytic materials, reaction mechanism, and the innovative combination of the active metal phase with its synergy. Electrochemical and thermochemical routes of CO₂ methanation have been highlighted, but thermochemical routes have received the most attention. As a result of CH₄'s high selectivity, the thermochemical route appears to be the more promising of the two methods for producing an energy carrier.	Although the study provides a thorough examination of recent developments in catalytic CO₂ methanation, it does not adequately address the practical, economic, environmental and systemic barriers that must be overcome to commercialize and deploy these technologies on a large scale.	2016
(Thrä n <i>et al.</i> 2015)	New and improved concepts and technologies for biomethane, biogas, solid biofuels, and liquid were discussed. Also highlighted were their market implementation's regulatory framework and price signals from electricity markets.	While the study emphasizes the importance of gas storage capacity and feed management for flexible biogas production, it does not address the impact of long-term weather patterns and seasonal fluctuations on the availability of bioenergy.	2015
[This review]	<i>Informetric studies on CO₂ methanation, recent advances in the role of molybdenum as a promoter in nickel-based catalysts, its basicity, oxygen vacancies, regeneration, challenges, durability, suggestions, and future prospects.</i>	<i>One limitation of the informetric analyses in this study is that we confined literature retrieval to a single database (Web of Science). It's possible that certain significant articles were not indexed in this database. Future research would benefit from incorporating articles from multiple databases to ensure a more comprehensive analysis. Additionally, our data only includes articles published in</i>	2023

English, which may exclude relevant research published in other languages. Furthermore, our analysis did not extend to other academic sources such as encyclopedias, books, and conference proceedings. These considerations highlight areas for improvement and expansion in future studies.

Using the VOSviewer software to analyze the literature on CO₂ methanation from 1994 to 2023, this work fills a significant gap by employing informetric visualization approaches and text-extraction methodologies (Van Eck and Waltman 2010). This study aims to achieve the following primary objectives: (i) analyze the trend in scientific publications on CO₂ methanation; (ii) identify networks of leading research journals, countries and prevalent keywords used in publications in this field; (iii) summarize current findings on the role of Mo as a promoter in Ni-based CO₂ methanation catalysts. Additionally, the information gathered will support the establishment of future research paths and initiatives to encourage further study in this area. This study will also act as a model for assessing informetrics within the specialized CO₂ methanation domain. The structure of this work is delineated as follows: Section 6.2 elucidates the article retrieval process and informetric analyses. Section 6.3 presents the findings from the informetric exploration of CO₂ methanation literature. In Section 6.4, recent advancements in the role of Mo in Ni-based catalysts for CO₂ methanation are succinctly reviewed. Section 6.5 discusses the basicity and oxygen vacancies of Mo when used as a promoter, while Section 6.6 presents the conclusions and outlines future research trajectories. By providing a comprehensive visual roadmap of ongoing work in this field, fostering research collaboration, and identifying potential future research topics, this study offers immense value to researchers.

6.2 Methods

An informetric analysis systematically examines many journal publications in a specific field of study. This research type generates the most up-to-date information possible. It provides insights into bibliographic linkages, co-authorship networks, co-citation analysis, scientific movements, and insights into developing new fields. This study examines the most cited articles, the most popular search terms, the development of published works overtime, and the relationship between co-authors using Rstudio and VOSviewer software. It is an assessment of the literature using data analytics to show the links in quantitative terms between articles related to a particular scientific topic or field by analyzing how often other published articles have also

cited them, relating specifically to the same subject or field. The method of search and approach included screening and evaluating the results of the most referenced journals, prominent countries, and articles with the most citations.

6.2.1 Data Sourcing Strategy

A comprehensive search of the WoS database identified all articles published between 1994 and 2023. As an internationally recognized citation database, WoS provides a robust index of books, journals, and conference proceedings across various disciplines, making it highly suitable for informetric and bibliometric analysis (Tian *et al.* 2018; Akpasi *et al.* 2024). For this study, the dataset was restricted to articles published in WoS. Specific keywords related to CO₂ methanation were used to search the title, keyword, and abstract fields. A total of 773 articles matching the search criteria were extracted, and the metadata for the selected literature was obtained as of September 18, 2023.

6.2.2 Data Reconciliation and Text Cleaning

The keywords, titles, and abstracts of the retrieved articles were carefully reviewed to pinpoint and remove any irrelevant entries. As no irrelevant articles were identified, all 773 articles underwent further text cleaning and bibliometric analysis. The text cleaning process involved standardizing various author keywords to ensure consistency across the dataset. For instance, terms like “synthetic natural gas” and “substitute natural gas” were unified under the abbreviation “sng”, while “bi-metallic catalysts” and “Bimetallic catalysts” were consolidated as bimetallic catalyst. Similarly, keywords such as “power to x” and “Power-to-Gas” were grouped under the power-to-gas category. This standardization was conducted using the open-source software OpenRefine (version 3.4.1) (OpenRefine 2022), ensuring uniformity and reliability in the analysis.

6.2.3 Informetric Analyses

After data cleaning, the articles were analyzed to determine publishing trends over time. Informetric studies were conducted to examine the co-occurrence of article keywords (author keywords), co-citations among scientific journals and articles, and co-authorship networks between countries. These analyses aimed to identify key research areas, citation patterns, leading scientific publication platforms, and international collaborations. The investigations utilized the open-source science mapping software VOSviewer (version 1.6.17) (Van Eck and Waltman 2010). VOSviewer utilizes a distance-based mapping approach, where the proximity

between two elements reflects the strength of their relationship, with shorter distances indicating a stronger association. This visual depiction simplifies the identification of clusters of related elements. Each aspect of the analysis (e.g., country, journal) is represented by a node (rectangle or circle), with the node size reflecting its importance and influence. For example, the importance of an article can be evaluated using metrics such as publication count, citation frequency, and average citations. Items sharing the same colour belong to the same cluster, signifying frequent co-referencing in CO₂ methanation research. Density visualization maps further highlight journals with higher publication outputs or citation counts, providing a clear overview of influential contributors in the field (Van Eck and Waltman 2010).

6.3 Analysis and Discussion of Informetric Findings Regarding Literature on CO₂ Methanation

6.3.1 Scientific Publication Trend on CO₂ methanation from 1994 to 2023

The fact that there are numerous publications on the CO₂ methanation process should not be surprising, as it is an essential focus in fuel, energy, and environmental research. The terms found related to CO₂ methanation with the most frequent occurrence on average are shown in Figure 6.1. The yellow, red, blue, purple, green, and cyan clumps are the most significant clusters (where the density display is centred). The following list shows the frequency (links strength) of the most pertinent keyword: methanation 181 (167), CO₂ methanation 164 (123), power-to-gas 79 (77), carbon-dioxide 57 (56), nickel 39 (37), hydrogen 34 (34), methane 29 (29), synthetic natural gas 30 (28), nickel catalyst 27 (24), and energy storage 25 (24). These terms within the figure revealed that the investigation into the CO₂ methanation reaction had been adequately conducted. In light of its tremendous potential for energy production, a great deal of effort has been (and is still being) put into generating synthetic natural gas.

network map in the bibliometric literature (Hussein and Zayed 2021). Nevertheless, we selected these criteria to facilitate the study of 151 distinct scientific journals.

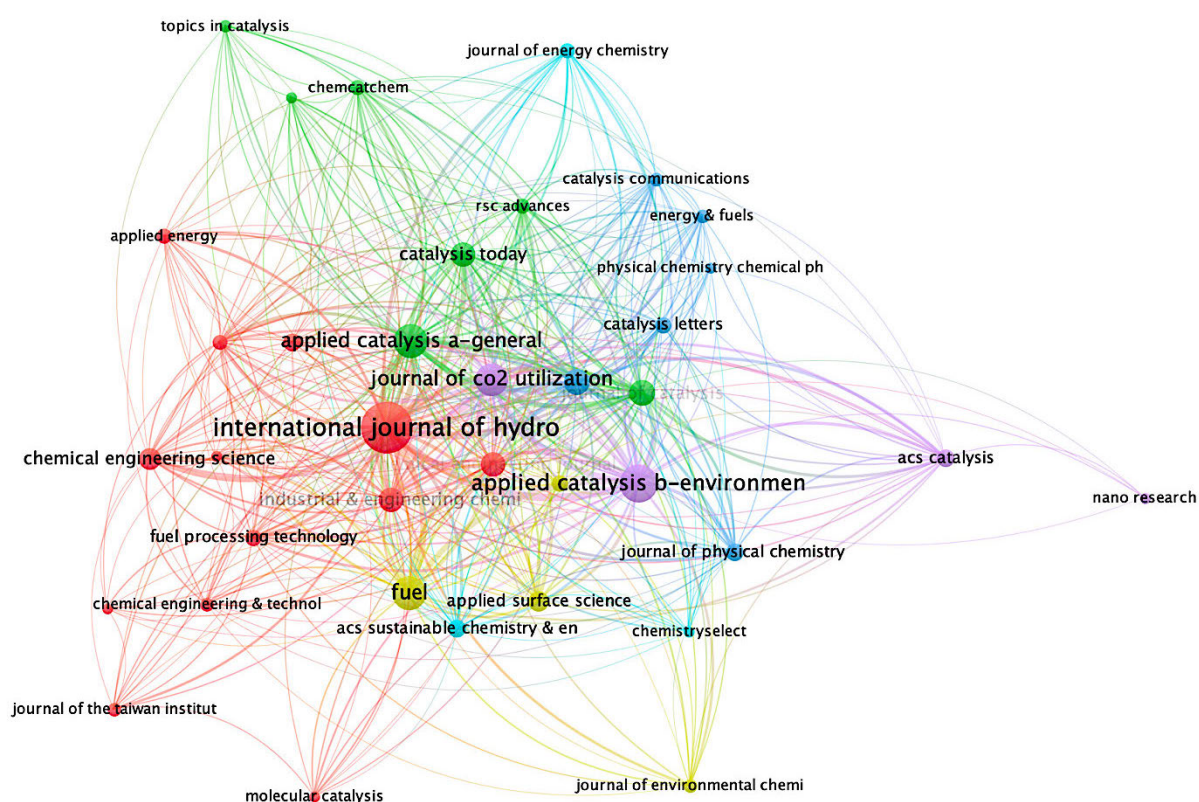


Figure 6-2. Network map of the leading research journals for the publication of CO₂ methanation work.

Figure 6.2 shows the 37 journals that meet these criteria. Table 6.2 below lists the top 20 journals ranked by overall link strength, citations, and the number of articles published. The overall link strength is a key metric that measures the strength of connections between an item (e.g., journal, country) and other items being analyzed (Van Eck and Waltman 2010).

Table 6-1. Top 20 bibliometrically analysed research journals.

S. No.	Journal	Cluster	Number of articles	Citations	Total link strength
1	International Journal of Hydrogen Energy	1	91	4,199	1048
2	Applied Catalysis B - Environmental	5	51	4,278	792
3	Applied Catalysis A - General	2	41	2,982	599
4	Fuel	4	41	1,132	538
5	Journal of CO ₂ Utilization	5	37	1,790	3,337
6	Journal of Catalysis	2	23	2,805	2,411
7	Catalysis Science & Technology	3	23	1,317	2,892
8	Chemical Engineering Journal	1	22	846	3,571
9	Catalysis Today	2	21	1,145	2,886
10	Industrial & Engineering Chemistry Research	1	21	613	4,089

11	Chemical Engineering Science	1	17	516	2,372
12	Applied Surface Science	4	14	755	1,903
13	ACS Catalysis	5	11	1,080	1,436
14	Journal of Physical Chemistry	3	11	716	1,592
15	ACS Sustainable Chemistry & Engineering	6	11	508	2,028
16	Energy Conversion and Management	1	11	453	957
17	Fuel Processing Technology	1	9	458	1,146
18	Catalysis Letters	3	9	343	1,382
19	ACS Applied Materials & Interfaces	4	9	404	1,946
20	Journal of Industrial & Engineering	1	8	643	588

Figure 6.2 represents six clusters of journals, each marked by a different colour. Red denotes cluster 1 (13 journals), green cluster 2 (7 journals), blue cluster 3 (6 journals), yellow cluster 4 (4 journals), purple cluster 5 (4 journals), and cyan cluster 6 (3 journals). Journals within the same cluster exhibit higher citation rates compared to those outside the cluster. The number of publications or citations a journal has is indicative of its influence, with this influence visually represented by the size of the node assigned to it. The strength of the link between the two journals is indicated by the length of the line connecting them, with shorter lines representing stronger links (Van Eck and Waltman 2010). *International Journal of Hydrogen Energy* emerges as the most influential journal, boasting the highest total link strength (1,048), number of published articles (91), and number of citations (4,199). It publishes more articles than *Applied Catalysis B: Environmental*, which ranks second with 51 articles and 4,278 citations. The next three leading journals are *Applied Catalysis A: General*, *Fuel*, and the *Journal of CO₂ Utilization*. These five journals combined account for 54% of all papers on CO₂ methanation. While these journals are the most prolific in terms of the number of papers published, the *Journal of Catalysis* and *Catalysis Science & Technology* have each published 23 papers, together accumulating a total of 4,122 citations. Additionally, both *Catalysis Today* and *Industrial & Engineering Chemistry Research* have published 21 papers, together amassing 1,758 citations. *ACS Catalysis* has fewer published articles but more citations than *Chemical Engineering Science*, *Applied Surface Science*, and *Journal of Physical Chemistry*. The *Journal of Industrial & Engineering* also has fewer articles but more citations than *ACS Sustainable Chemistry & Engineering*, *Energy Conversion and Management*, *Fuel Processing Technology*, *Catalysis Letters*, and *ACS Applied Materials & Interfaces*. This strongly suggests that the research published in these journals is of high quality. Factors such as the novelty of the research, the reputation of the publishing journal, and the journal's publication model (subscription-based or open-access) also contribute significantly to high citation counts (Tahamtan, Safipour Afshar and Ahamdzadeh 2016; Liskiewicz, Liskiewicz and Paczesny 2021; Akinwekomi and Akhtar 2022).

Figure 6.3 displays the density map of countries with the most publications. To produce this figure in VOSviewer, the “minimum number of documents of a country” is set to 5, while the “minimum number of citations of a country” is set to 10. From the data retrieved from the WOS database, it is evident that all CO₂ methanation articles are associated with 61 countries. However, only 30 countries meet this threshold, as depicted in Figure 4.3. Notably, Russia (*Links 11, Research articles 13; Citations 218*) and Canada (*Links 12, Research articles 6; Citations 85*) have the least number of co-authorships with other nations. The most prominent nodes are attributed to China (310 articles), followed by the United States (78 articles), and then Germany (67 articles). The brightness of a node corresponds to the density or number of articles published by the respective country.

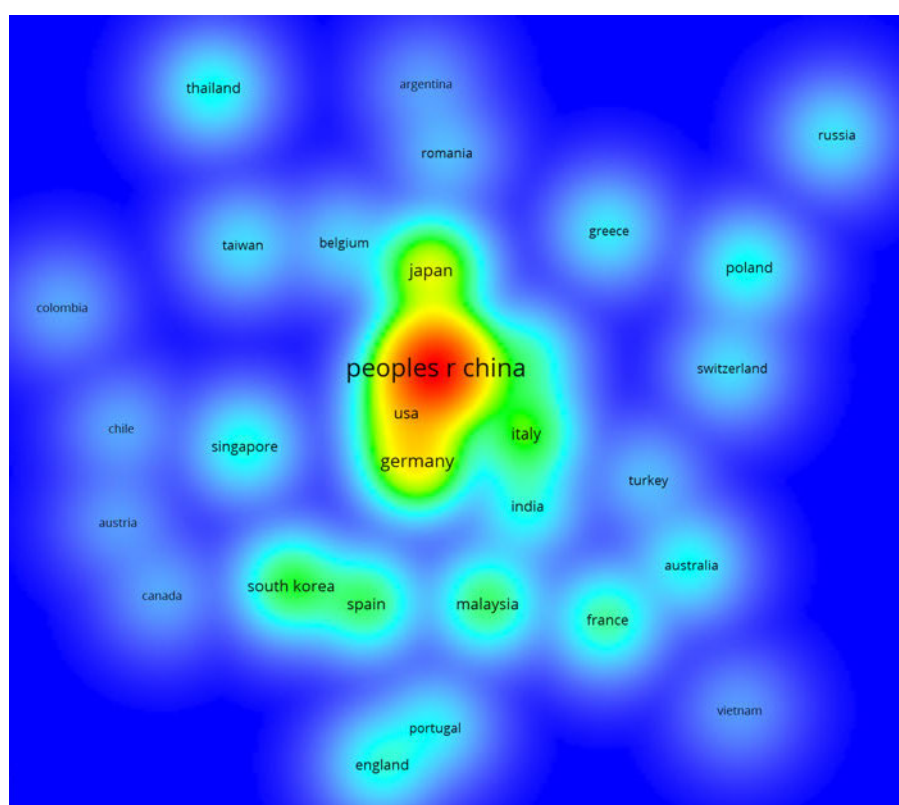


Figure 6-3. Co-authorship density map of countries based on scientific publications.

International collaboration is well-established, evident from the interconnectivity of all countries. Table 6.3 summarizes the statistics regarding the ten most prolific countries.

Table 6-2. Top ten countries leading research in CO₂ methanation.

S.No	Country	Number of Articles	Citations
1	China	310	13,735
2	USA	78	2,988
3	Germany	67	2,927
4	Japan	48	3,548

5	Spain	40	1,717
6	France	37	1,610
7	Italy	32	1,597
8	England	32	1,223
9	India	26	1,793
10	South Korea	25	1,169

China leads with the highest number of publications (310) and citation counts (13,735). During the reviewed period, China's publication output exceeded that of the next four countries in the rankings: the United States, Germany, Japan, and Spain. Network collaboration was developed in Figure 6.4 to represent research collaborations and potential cross-country synergies. With Singapore and Norway as their primary allies, China has the most significant overall strength. Spain, Brazil, and Argentina are three nations in another cluster that frequently collaborate because they are the closest to one another and have nearly identical strength intensities.

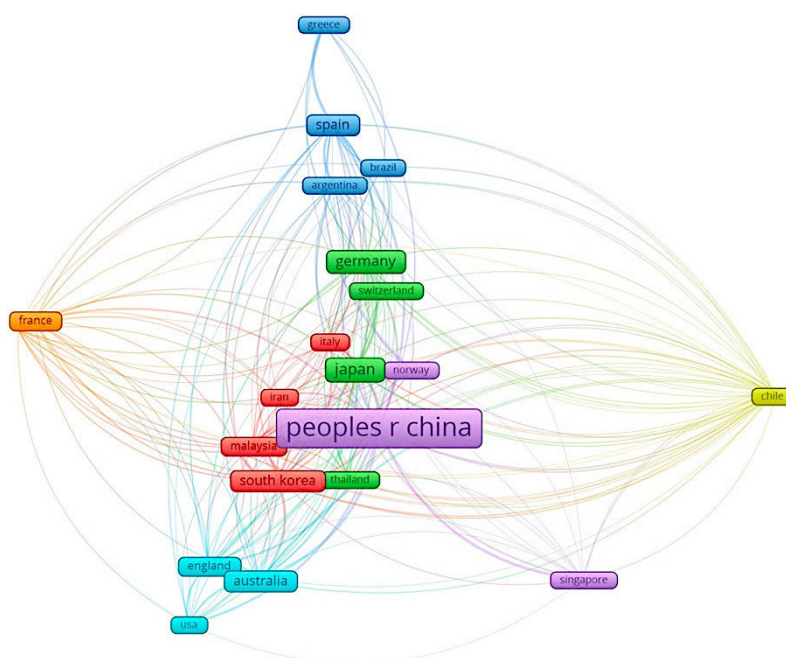


Figure 6-4. Collaboration networks of countries extracted from the Web of Science databases.

Data from the Web of Science literature was employed to determine the connection strength and frequency of CO₂ methanation-related keywords. Figure 6.5 shows a word nexus with the keywords most significant in CO₂ methanation. The significance of each word illustrates its importance, occurrence in the literature, and applicability to the subject. *Catalytic performance*, *hydrogen energy*, *methanation reaction*, *low temperature*, *reaction kinetics*, *nickel*, *carbon dioxide*, *particle size*, and *methane selectivity* are significant catchphrases to reminisce about. Extensive research has been done on nickel-based catalysts, mixed oxides, and the removal of CO from H₂-rich streams; however, there is work on other topics not covered here, including the use of additional supports such as SiO₂, TiO₂, and CeO₂, the mechanism of CO₂

The terms with the most robust overall connections are *CO₂ methanation*, *density-functional theory*, *carbon deposition*, and *hydrogenation*. These words are all the cluster's keywords that are most closely related to one another. The interconnected clusters display the contrasting traits of various CO₂ methanation research subjects. On the other hand, *bimetals*, *reduction*, *syngas*, *CO methanation*, *Ni/Al₂O₃*, and *molybdenum* were discovered on the periphery, suggesting lower interactivity and frequency compared to other clumps. The analysis above indicates that molybdenum is one of the current new trend topics because of its yellow colour. Despite recent developments, more research needs to be done on using molybdenum catalysts. Therefore, it is crucial to investigate and evaluate the possibility of using molybdenum as a catalyst promoter for CO₂ methanation.

6.3.2 Limitations of Informetric Analysis

One limitation of the informetric analyses in this study is that we confined literature retrieval to a single database (Web of Science). It's possible that certain significant articles were not indexed in this database. Future research would benefit from incorporating articles from multiple databases to ensure a more comprehensive analysis. Additionally, our data only includes articles published in English, which may exclude relevant research published in other languages. Furthermore, our analysis did not extend to other academic sources such as encyclopedias, books, and conference proceedings. These considerations highlight areas for improvement and expansion in future studies.

6.4 Recent Advances in the Role of Molybdenum in Nickel-Based Catalysts

6.4.1 Catalytic Performance and Functional Attributes of Molybdenum as a Promoter in CO₂ Methanation

To understand the physical and chemical properties of Mo compounds, Spevack and McIntyre (1992) investigates the reduction of MoO₃ under a nitrogen atmosphere across a temperature range of 350–730 °C. The reduction process occurs in distinct stages, involving the gradual loss of oxygen from MoO₃ and the formation of reduced species such as MoO₂ and intermediate oxidation states (Mo(IV) and Mo(V)). Significant reduction begins around 500 °C, with complete reduction to MoO₂ confirmed at this temperature through Raman and XPS analyses. Additionally, it was found that the orthorhombic crystal structure of MoO₃ is more stable than the monoclinic structure, making it less likely to reduce to MoO₂ during methanation. This stability is attributed to the higher coordination number of Mo atoms in the orthorhombic

structure, which reduces their reactivity toward oxygen. Figure 6.7 illustrates the most common crystal phases of MoO_3 .

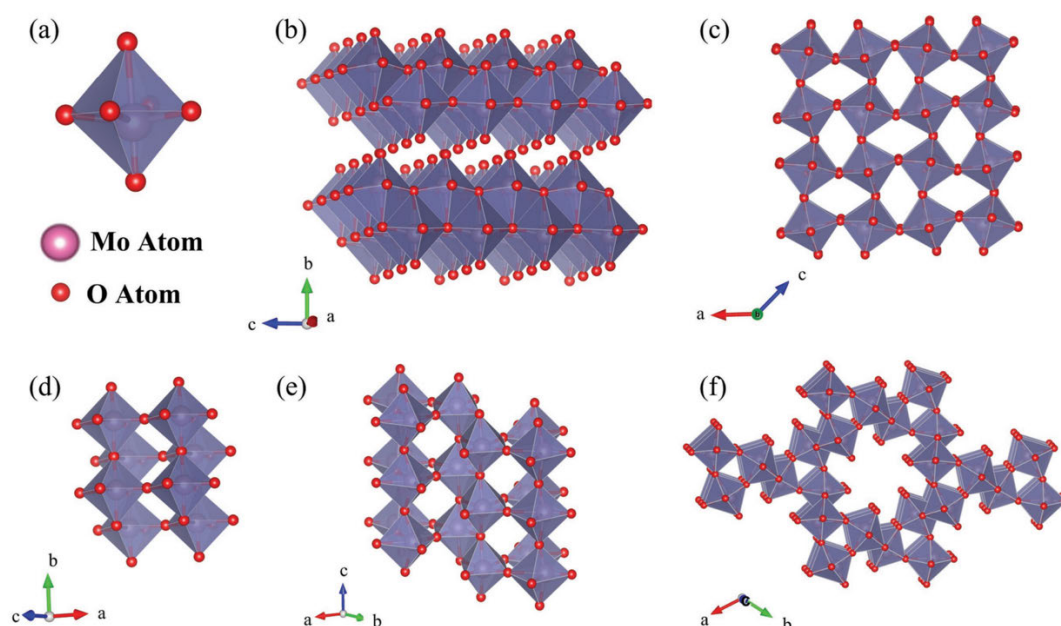


Figure 6-7. a) MoO_6 octahedra present in the thermodynamically stable MoO_3 material, made up of oxygen and molybdenum atoms. Lattice parameters adapted from ref. (Chithambararaj and Bose 2011; De Castro *et al.* 2017). b) Orthorhombic α - MoO_3 that is thermodynamically stable and composed of the layered structure held together by van der Waals' forces. Lattice parameters adapted from ref. (Chithambararaj and Bose 2011; De Castro *et al.* 2017). c) Metastable monoclinic β - MoO_3 . Lattice parameters adapted from (Chen *et al.* 2010; De Castro *et al.* 2017). d) ϵ - MoO_3 , also referred to as MoO_3 -II. Lattice parameters adapted from ref. (Parise, McCarron III and Sleight 1987; De Castro *et al.* 2017). e) Metastable h- MoO_3 . Lattice parameters adapted from ref. (Chen *et al.* 2010; De Castro *et al.* 2017). f) The c-axis tunnel structure of the h- MoO_3 unit cell. Lattice parameters adapted from ref. (Chen *et al.* 2010; De Castro *et al.* 2017).

Furthermore, it was discovered that the surface area and pore size of MoO_3 have a significant impact on its activity for methanation. Hence, a higher surface area and pore size provide more sites for the adsorption of reactants and products, which can increase the rate of the reaction. Also, the oxygen vacancy concentration on the surface of MoO_3 is important for its methanation activity. Oxygen vacancies create active sites on the surface of the catalyst, which can facilitate the activation of the reactants. In another study, Zheng *et al.* (2019) investigated the effects of Mo oxide composition (MoO_3 , Mo_5O_{18} ,), and (Mo_2C) and particle size on the catalytic activity of zeolite-supported Mo oxide catalysts for CO_2 methanation. They found that the catalytic activity increased with decreasing particle size and increasing Mo oxide content. The study attributed the improved catalytic activity to the increased surface area and reduced metal-support interaction (MSI) of smaller Mo oxide particles. They also found that the presence of Mo_5O_{18} was beneficial for the catalytic activity, as it provided a more active site

for CO₂ adsorption. In addition to the chemical properties of the Mo oxide, the study revealed that the physical properties of the zeolite support played a role in the catalytic activity. Also, zeolites with larger pore sizes were more active for CO₂ methanation, as they allowed for better access of the reactants to the catalyst surface. Based on these findings, it can be concluded that adding MoO₃ positively affects the methanation of CO₂. The chemical and physical properties of Mo compounds can affect their catalytic activity for CO₂ methanation. Mo sulfide is the active phase for carbon CO₂ methanation, and its properties can be affected by the type of Mo compound used, the preparation method, and the calcination temperature. Mo oxides are generally more reactive than Mo sulfides (Baloglou *et al.* 2018), but they are also more prone to deactivation (Cheng and Notestein 2022).

The surface area of the Mo compound is also important for its catalytic activity. A higher surface area provides more sites for the adsorption of CO₂ and H₂, which are the reactants in the methanation reaction (Wei and Jinlong 2011). The acidity of the Mo compound can also affect its catalytic activity. A more acidic Mo compound can more effectively dissociate CO₂ and H₂, which is beneficial for the methanation reaction (Zhou *et al.* 2021). Also, the type of Mo oxide present on the catalyst surface can affect the strength of the adsorption of CO₂. For example, MoO₃ is a stronger adsorbent of CO₂ than MoO₂. This can lead to higher rates of CO₂ dissociation and, consequently, higher rates of CO₂ methanation. Mo oxides can act as promoters by providing active sites for the dissociative adsorption of CO₂. Figure 6.8 shows the result of the TPR analysis employed to evaluate the reducibility of Ni-Mo bimetallic nitride catalysts (Zhao *et al.* 2023). The TPR profile shows peaks between 200–450 °C, which can be assigned to reducing surface oxides. The Mo₂N sample is a higher-temperature H₂-consuming peak at 436.3 °C, assigned to reducing octahedral Mo species (Mo⁶⁺ - Mo⁴⁺). The 600–800 °C temperature ranges belong to the deep reduction of the Mo⁴⁺ phase. Additionally, compared with the Mo₂N sample, a significant decline in the reduction temperature of Mo species is obtained by adding Ni species over Ni_xMo_yN catalysts, especially in Ni₂Mo₃N. Therefore, this indicates that the Mo species in Ni₂Mo₃N is more easily reduced, which is consistent with the XPS results. In general, the reducing ability of the NiMo species has been changed because of the electron transfer from Ni to Mo, demonstrating the close interaction between the bimetallic species.

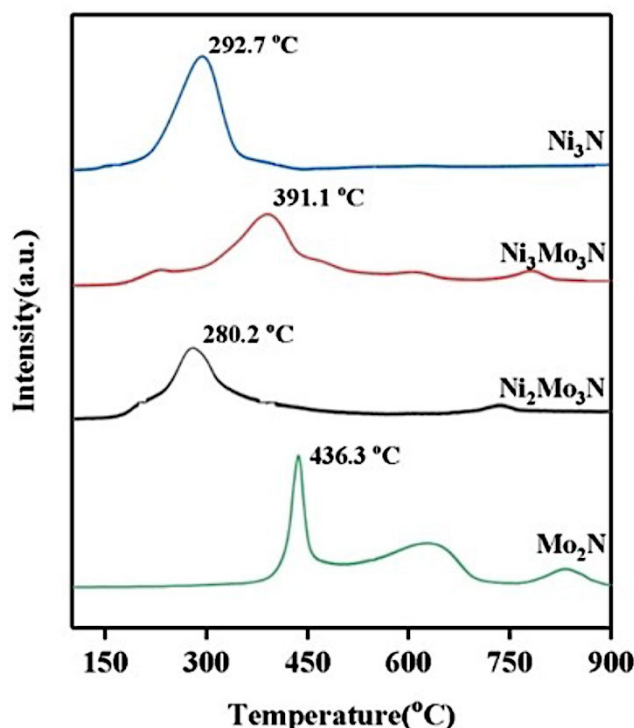


Figure 6-8. H₂-TPR profiles of Mo₂N, Ni₂Mo₃N, Ni₃Mo₃N, and Ni₃N samples. Adapted from (Zhao *et al.*).

Furthermore, combining Mo with various elements such as zirconia (Zr), strontium (Sr), ruthenium (Ru), rhodium (Rh), manganese (Mn), lanthanum (La), iron (Fe), copper (Cu), cobalt (Co), cerium (Ce), alkali metals (e.g., potassium (K), cesium (Cs)), and palladium (Pd) enhances its catalytic properties for CO₂ methanation (Ramsay 1891; Conkling and Mocella 1985; Krebs 2006; Kuo 2024). Supports like Zr and Ce improve oxygen vacancy formation and CO₂ activation (Liu *et al.* 2018; Singh *et al.* 2024), while alkali metals and La enhance basicity, promoting intermediate formation (Ahmad *et al.* 2021). Transition metals such as Fe, Co, and Cu synergize with Mo to boost hydrogen activation and stabilize active sites (Breysse *et al.* 2002; Fang *et al.* 2023), while noble metals like Ru, Rh, and Pd improve hydrogen dissociation and CO₂ reduction (Avanesian, Gusmão and Christopher 2016; Mori *et al.* 2021). These combinations enhance catalyst stability, activity, and resistance to sintering or carbon deposition, making them highly effective for sustainable CO₂ conversion in industrial applications. Together, these findings highlight the role of Mo and its synergies with other elements in optimizing catalytic efficiency and durability for CO₂ methanation.

6.4.2 Contribution of Molybdenum as a Catalyst Promoter for CO₂ Methanation

Mo plays a critical role in enhancing catalytic performance for CO₂ methanation, particularly when combined with Ni-based catalysts. Several studies have demonstrated how Mo's unique

properties improve catalyst activity, stability, and efficiency. Research on γ -alumina-supported Ni-Mo carbides highlights that carburization of molybdenum species increases the basicity of the catalyst, significantly enhancing CO₂ adsorption and methanation activity (Al-Saleh and Çeliker 1987; Aksoylu, Mısırlı and Önsan 1998; Zhang *et al.* 2013; Kharaji, Shariati and Ostadi 2014; Yao *et al.* 2017; Li *et al.* 2019). Similarly, studies on nickel-based MCM-41 catalysts show that MoO₃ enhances interactions between Ni and the support, increasing resistance to sintering and maintaining high catalytic performance at elevated temperatures, which indirectly boosts CO₂ methanation efficiency (Zhang *et al.* 2014; Guo *et al.* 2018; Yang *et al.* 2020; Zhang, Chen and Liu 2021).

Further insights come from investigations of MoO_x-La₂O₃-Ni composites, which indicate that MoO_x facilitates the reverse water-gas shift reaction and improves Ni's catalytic activity, further contributing to CO₂ methanation (Li *et al.* 2019). Chemisorption studies also reveal that Mo increases the number of active sites for CO₂ methanation when combined with Ni, although Mo alone exhibits negligible activity (Al-Saleh and Çeliker 1987). The interaction between Mo and Ni on Al₂O₃ supports, as demonstrated in studies on Ni-Mo/Al₂O₃ catalysts, promotes better dispersion of Ni particles, enhancing methanation activity. At lower Mo loadings, Mo acts as a matrix diluent, improving Ni particle distribution, while the electronic interactions between MoO_x species and nickel significantly influence catalytic behaviour (Aksoylu, Mısırlı and Önsan 1998). Research on Ni-Mo/Al₂O₃ catalysts for the RWGS reaction emphasizes that Mo enhances catalytic activity by introducing electron-deficient Mo species and NiMoO₄ phases, which contribute to efficient CO₂ conversion (Kharaji, Shariati and Ostadi 2014). Additionally, a study on Mo-doped Ni catalysts for solid oxide fuel cells (SOFCs) applications demonstrates that Mo improves coke resistance and stability, ensuring sustained activity during reforming processes. While not specific to CO₂ methanation, these findings underline the broader catalytic benefits of Mo in Nickel-based systems (Bkour *et al.* 2020). A review on Mo oxides further highlights their ability to create and manipulate oxygen vacancies, which are critical for enhancing catalytic efficiency in CO₂ methanation. The versatile oxidation states of Mo (+6 and +4) enable the optimization of these oxygen vacancies, further improving catalytic performance (De Castro *et al.* 2017).

Together, these findings highlight the importance of Mo's properties, such as enhancing basicity, improving metal-support interactions, resisting sintering, and creating active sites in driving efficient CO₂ methanation processes. These insights pave the way for optimizing Mo-

promoted Ni catalysts for sustainable energy applications. Mo's unique structural and electronic properties contribute to better Ni dispersion, enhanced stability, and improved methanation activity, solidifying its position as a valuable promoter in CO₂ methanation catalysts.

In recent years, much work has been done on the development of methanation catalysts with high thermal stability and high activity at low temperatures. Several metal promoters have been proven to facilitate CO₂ methanation reactions, such as Mo, Zr, Sr, Ru, Rh, Mg, La, Fe, Cu, Co, Ce, Ca, Ba, Li, K, Rb, Cs, Zr, and Pd. Mo is a well-established support because of its redox properties and diverse oxidation states, including Mo(0), Mo(II), Mo(III), Mo(IV), Mo(V), and Mo(VI), which allows it to participate in a wide range of redox reactions.

In this context, Mo typically acts in a specific oxidation state, varying based on the chemical reaction conditions and the specific catalyst system. The oxidation state of Mo in a catalyst can significantly impact its performance, as it influences the ability of the catalyst to interact with reactants and facilitate chemical reactions. For example, in the oxidation of alcohols to aldehydes or ketones, Mo is often used as a promoter in the +6 oxidation state, as it can form strong bonds with oxygen-containing molecules and facilitate the transfer of oxygen atoms (Jiang *et al.* 2021). On the other hand, Mo in the +4 oxidation state is often used as a promoter in the hydrogenation of organic molecules, as it can facilitate the activation of hydrogen molecules and promote their addition to organic substrates (Piera and Bäckvall 2008). Furthermore, Mo can react with oxygen to form Mo oxide species, such as MoO₃ (De Castro *et al.* 2017). This reaction can proceed via several intermediate steps, such as forming MoO₂ and MoO, before reaching the final oxide product.

Similarly, Mo can undergo reduction reactions, such as reducing Mo oxide to elemental Mo. This reaction typically requires a reducing agent, such as hydrogen or carbon monoxide. It proceeds via the formation of intermediate Mo species, including MoO₂ and MoO, before the final reduction to elemental Mo. Due to its low cost, high activity, and availability, Ni has been the most commonly used transition metal catalyst for producing CH₄ for a very long time (Sharifianjazi *et al.* 2022; Wang *et al.* 2022). The performance and stability of Ni-based catalysts are often hampered by sintering and carbon deposition at high temperatures during CO₂ methanation (Al-Fatesh *et al.* 2023; Kaydouh *et al.* 2024). A popular method to counter some of these drawbacks of Ni-based catalysts is to use a second metal (e.g., Mo, Fe, Co or Ru) as a dopant to create appropriate bimetallic CO₂ methanation catalysts. These second

metals can act as supports with large surface area or extra positive characteristics like high basicity and a disproportionately large number of oxygen vacancies. Moreover, recent publications have demonstrated that the addition of molybdenum trioxide (MoO_3) could enhance the interaction between metal nickel and the support in the way of Ni–Mo alloy, which can inhibit the catalyst sintering (Rajeswari *et al.* 2001; Damian and Omanovic 2006; Yagi *et al.* 2007; Bian *et al.* 2016). Therefore, MoO_3 can be adopted to inhibit the aggregation of nickel particles. In addition, rare earth elements, such as samarium oxide (Sm_2O_3), can modulate the growth of NiO in nickel-based catalysts, controlling the active components' microstructure and enhancing CO_2 methanation at low temperatures by increasing surface oxygen vacancies and stabilizing active phases (El-Salamony *et al.* 2023b). While rare earth promoters effectively reduce carbon deposition and sintering (El-Salamony *et al.* 2023a), Mo-based promoters provide additional advantages, such as enhanced electron transfer, improved hydrogen activation, and superior resistance to sintering (Younas *et al.* 2016). MoO_3 's ability to closely interact with Ni ensures better dispersion of active sites and high CH_4 selectivity (>95%), making it a versatile and scalable option for CO_2 methanation applications.

For instance, Bkour *et al.* (2020) introduced a small amount of Mo atoms into a Ni/YSZ catalyst for the partial oxidation reaction of gasoline. They found that a Ni-Mo/YSZ catalyst displays a high reforming activity and stability with an isooctane conversion of 90 % and H_2 yield of 76 % with less degree of coking and sintering as compared to a Ni/YSZ catalyst. Additionally, their research raises the possibility that an active site connected to the high coke resistance of Ni-Mo/YSZ catalysts may be well-dispersed Mo=O species over a Ni surface. Furthermore, when Ni and Mo were loaded on the catalyst, electrons on the surface of adjacent metal atoms were affected due to the high electronegativity of fluoride, which is used as a modified carrier. The electron exchange between Ni and Mo affects the performance of the catalyst by modifying the electronic properties of the catalyst, which can affect its catalytic activity and stability. Malaibari *et al.* (2015) demonstrated that the synergistic effect between Mo and Ni is due to electron transfer from MoO_x species to Ni, increasing the electron density of metallic Ni. Promoting a 15 wt.% Ni/ Al_2O_3 catalyst with small amounts of Mo (0.1 and 0.5 wt.%) for propane oxidative steam reforming at 450 °C significantly enhanced activity, stability, and resistance to coking. The 0.1 wt.% Mo-promoted catalyst showed higher propane conversion, improved H_2 yields, and superior deactivation resistance. Characterization revealed that Mo's

electronic effects and increased oxygen mobility on the catalyst surface enhanced carbon gasification, preventing coking and improving overall performance.

Significant efforts have been made to improve the essential features that affect the functionality of Mo, including shape, particle size, and size distribution. Hu *et al.* (2021) investigated how the mechanical properties of Mo powder are affected by particle size. They discovered that reducing the particle size of Mo powder from micrometer (μm) to nanometer (nm) scale improved its hardness and strength and decreased its ductility and toughness. Therefore, the optimal particle size of Mo powder should be selected based on the desired properties for the intended application. Rathore, Salve and Dabhade (2015) investigated the influence of particle size distribution on the sintering behaviour and microstructure of Mo powders. The authors found that a narrow particle size distribution led to a more homogeneous microstructure and enhanced densification during sintering, resulting in improved mechanical properties. Lee *et al.* (2014) investigates the effect of oxygen concentration on the mechanical properties of Mo powder during sintering, revealing that low-oxygen Mo (oxygen content ≤ 100 ppm) exhibited a Vickers hardness of 220 HV and an average grain size of 6 μm , compared to commercial-grade Mo (oxygen content ~ 350 ppm) with a hardness of 185 HV and grain size of 14 μm , highlighting the role of reduced oxygen in enhancing hardness and suppressing grain growth.

In an early study, Aksoylu, Mısırlı and Önsan (1998) demonstrates that adding Mo (4.0 wt.%) to Ni/Al₂O₃ catalysts (10.0 wt.% Ni) enhances CO₂ methanation activity by increasing Ni dispersion, promoting electron transfer, and stabilizing active sites, achieving a CO₂ conversion of 17.2%, a CH₄ production rate of 464 mmol/g/s, and a CH₄ selectivity of 98% at 523 K. The study also found that the interaction between Ni and Mo depends on the relative amounts of the two metals. For example, the maximum CH₄ production rate was observed for catalysts with a Ni/Mo ratio of 3:1. This suggests that Mo can act as a promoter for Ni during CO₂ methanation. On the other hand, Kharaji, Shariati and Ostadi (2014) reported that incorporating Ni (10 wt.%) into Mo/Al₂O₃ (10 wt.% Mo) significantly enhances catalytic activity, achieving a CO₂ conversion of 35%, a CH₄ selectivity of 4.7% at 873 K, with a CO₂/H₂ ratio of 1:3 and a GHSV of 30,000 mL/g/h, due to the formation of the NiMoO₄ phase, which facilitates electron transfer and improves hydrogen activation. The differences in reported selectivity in the two studies of CO₂ reduction on Ni-Mo catalysts may be due to different catalyst compositions and structures. Therefore, understanding how the structure and property of the

Ni-Mo catalyst affect the activity and selectivity of CO₂ reduction helps to achieve desirable selectivity by fine tuning the structure of the catalysts.

Gonçalves *et al.* (2021) investigated the CO₂ methanation properties of three commercially available Ni-based electrocatalysts: Ni/C, NiMo/C, and NiRe/C. The study highlights that the monometallic Ni/C catalyst demonstrated exceptional performance, achieving an 83% CO₂ conversion and 99.7% CH₄ selectivity at 400 °C, with stable activity maintained over 90 hours of TOS. In comparison, the bimetallic NiMo/C and NiRe/C catalysts exhibited lower CO₂ conversions of 70% and 74%, respectively, at 400 °C, with the NiMo/C catalyst showing the least stability, experiencing a 25% decrease in CO₂ conversion and a 13% drop in selectivity over 90 hours. Mo was identified as a suitable promoter due to its ability to enhance electron transfer, facilitate hydrogen activation, and improve the dispersion of active sites. However, the NiMo/C catalyst's stability was limited compared to Ni/C and NiRe/C, which maintained their activity and selectivity throughout the 90-hour TOS testing. XPS analysis of the Ni 2p^{3/2} spectra revealed the presence of two distinct phases for all catalysts in their as-received state, highlighting the structural differences influencing their performance (Figure 6-9).

The XPS analysis provided detailed insights into the electronic and structural properties of the catalysts. The lower energy component at 852.7 eV was attributed to Ni⁰ in metallic Ni species, while components at 853.9 eV and 855.8 eV corresponded to Ni²⁺ in the nickel oxide phase. Satellite peaks at 861.1 eV and 863.6 eV further confirmed the presence of Ni²⁺ (Biesinger *et al.* 2009). Based on Figure 9a–c, the combination of three main components at approximately 852.7, 853.9, and 855.8 eV indicated a thin layer of Ni oxide, primarily Ni²⁺, on metallic Ni, consistent with nanoscale oxidation layers commonly observed in Ni compounds (Biesinger *et al.* 2009; Owens-Baird *et al.* 2019; Owens-Baird *et al.* 2020). In the Mo 3d spectra for NiMo/C (Figure 9d), two distinct components were observed: Mo(IV) oxide (Mo⁴⁺) with a doublet at 229.3 eV and 232.4 eV, and Mo(VI) oxide (Mo⁶⁺) at 232.4 eV and 235.5 eV (Choudhary *et al.* 2022). These features demonstrate that Mo species act as electron promoters in NiMo/C, enhancing the electronic density of active Ni species and increasing the interaction between Ni and MoC, thereby improving the catalytic performance of NiMo/C for CO₂ methanation.

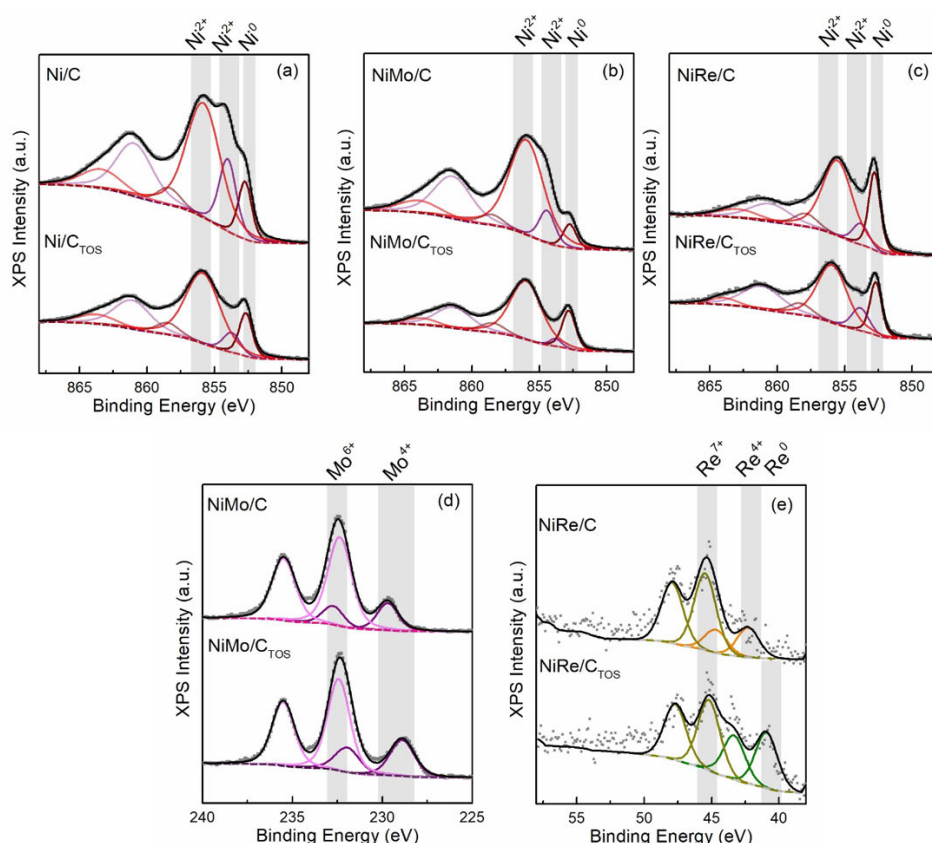


Figure 6-9. High-resolution XPS data obtained from as-received and TOS-tested (a) Ni/C (b) NiMo/C (c) NiRe/C (d) NiMo/C and (e) NiRe/C. Adapted from (Gonçalves *et al.* 2021).

In a different study, Saconsint *et al.* (2022) found that the Ni-Mo/MgO catalyst with 30% Ni exhibited excellent activity in CO₂ methanation. This was attributed to the catalyst's high surface area (127.4 m²/g), the nickel particles' small size (below 7 nm), and the excellent metal dispersion. Moreover, it can be deduced that the Ni content of the catalyst causes the metal particles to be tiny, which increases the active surface area and improves the dispersion and catalytic activity of the active nanoparticles. The experimental results also showed that adding a third component, such as Co or Fe, to the Ni-Mo/MgO catalyst did not improve the catalytic activity. Regarding CO₂ methanation, the Ni-Mo/MgO catalyst had the highest activity with 86.4% CH₄ conversion and 95.6% CO₂ conversion. The Ni-Mo/MgO catalyst was also deactivated only slightly over 3 hours. Mo has stabilizing capabilities in catalytic processes due to its significant metallic dispersion and potential to impede the catalyst's carbon deposition-induced deactivation. Mo is often used as a catalyst in chemical reactions because it increases the reaction rate and selectivity. One of the reasons for its effectiveness as a catalyst is its ability to disperse as small metallic particles on the surface of the support material. This high degree of dispersion can increase the number of available active sites for a reaction, improving the catalyst's overall performance. Mo has also been demonstrated to prevent the

deactivation of the catalyst due to carbon deposition. Carbon deposition occurs when hydrocarbons in the feedstock react with the catalyst and form carbonaceous deposits on its surface. These deposits can block the catalyst's active sites and reduce its effectiveness. However, Mo has been found to inhibit the formation of these deposits and, therefore, increase the catalyst's stability and longevity. Table 6-4 illustrate the effect of Mo on coke formation in Ni-based catalysts during CO₂ methanation.

Table 6-3. Effect of molybdenum on coke formation in nickel-based catalysts for CO₂ methanation.

Catalyst	Mo Loading (wt%)	Coke Formation/Reduction	Observations	Ref.
Ni-Mo/Al ₂ O ₃	4	Significantly reduced coke formation	Enhanced stability due to interaction between Ni and MoOx species	(Aksoylu, Mısırlı and Önsan 1998)
Ni-Mo/MgO	5	Lower coke formation compared to Ni-only	Electron transfer from Mo to Ni mitigates carbon deposition	(Saconsint <i>et al.</i> 2022)
NiMo/C	0.1–0.5	Up to 25% less carbon deposition	Reduced deactivation by coking	(Gonçalves <i>et al.</i> 2021)
Ni-MoO ₃ /MCM-41	5	20% reduction in coking	Enhanced BET surface area and basicity due to MoO ₃	(Zhang <i>et al.</i> 2014)
Ni-Mo-La ₂ O ₃ /SiO ₂	7	Maintained low coke formation at 350 °C	Prolonged operation with enhanced metal dispersion	(Li <i>et al.</i> 2019)
Mo–Ni/Al ₂ O ₃	8	Improved resistance to coke in H ₂ S environments	Stabilized active sites under sulfur-rich conditions	(Méndez-Mateos <i>et al.</i> 2020)

Additionally, Saito and Anderson (1981) investigated the catalytic performance of various Mo compounds for CO₂ methanation. Their study synthesized and evaluated Mo oxides, sulfides, carbides, and several supported catalysts under conditions of 350 °C and 1 atm. Among the tested materials, Mo₂C achieved a specific rate of 43.8 μmol/g/min with a CH₄ selectivity of 100% at 350 °C and 1 atm, while MoO₃ showed negligible activity; Mo₂C also demonstrated strong water-gas shift activity. These findings highlights the superior stability and water-gas shift activity of Mo compounds compared to traditional catalysts such as Ni and Fe.

Similarly, Al-Saleh and Çeliker (1987) conducted a detailed investigation into the chemisorption of CO, CO₂, H₂, and CH₄ on Ni-Mo/Al₂O₃ catalysts. The study involved preparing a series of catalysts with varying Ni and Mo loadings and measuring the gas uptake of each gas at room temperature (298 K). The results revealed that the CO adsorption isotherms for all three catalysts were of type I, indicative of dissociative CO adsorption. For the Ni and Mo catalysts, the CO(ads)/H(ads) ratio was approximately 1, suggesting linear CO adsorption

on the catalyst surface. In contrast, the Ni-Mo catalyst exhibited a CO(ads)/H(ads) ratio of about 2, implying that each active site adsorbed two CO molecules.

The Ni-Mo catalyst demonstrated the highest H₂ uptake, followed by the Ni catalyst, and then the Mo catalyst, highlighting the synergistic effect of combining Ni and Mo. CH₄ uptake across the three catalysts was generally low, indicating weak adsorption of CH₄ on the catalyst surface. However, the CH₄ uptake increased in the order of Ni < Ni-Mo < Mo, reflecting the influence of Mo in enhancing CH₄ adsorption. These findings emphasize the significant role of Mo in improving the adsorption properties and overall performance of Ni-based catalysts for CO₂ methanation. The number of active sites determined by hydrogen chemisorption was well defined for a nickel catalyst consisting mainly of Ni particles. The number of active sites increased with the addition of Mo, which is consistent with the results of the CO adsorption experiments. Table 6-5 presents an overview of recent developments in applying Mo as a promoter catalyst for CO₂ methanation. Mo has proven to be a viable additive component due to its stabilizing properties resulting from its significant metallic dispersion and its ability to prevent catalyst deactivation caused by carbon deposition. In addition, adding a range of doped metals will enhance the performance of supported Mo as a catalyst for producing CH₄.

Table 6-5. Literature on the catalytic performance of molybdenum-promoted catalyst for CO₂ methanation.

Catalyst	Ni content (wt.%)	Mo content (wt.%)	Metal Loading (%)	Synthesis method	Reaction Conditions				CO ₂ conversion (%)	CH ₄ selectivity (%)	CH ₄ yield (%)	Refs.
					Temperature (°C)	Pressure (atm)	H ₂ : CO ₂	GHSV/h ⁻¹				
Ni/MoO _x - La ₂ O ₃ /SiO ₂	6	1	nd	Impregnation	250 - 500	1	4:1	15 000	75	100	75	(Li <i>et al.</i> 2019)
Ni-Mo-MCM-41	10	1 - 7	nd	Impregnation	280	1	3:1	12 000	100	80	80	(Zhang <i>et al.</i> 2014)
MoO ₂ /Al ₂ O ₃	nd	nd	nd	Impregnation	300 - 400	1	4:1	1,530	90	95	86	(Frontera <i>et al.</i> 2017)
MoO ₂ /TiO ₂	nd	nd	nd	Sol-gel	300 - 400	1	4:1	nd	88	94	83	(Frontera <i>et al.</i> 2017)
Ni-Mo/Al ₂ O ₃	10	10	10	Solvent impregnation	250 - 500	1	4:1	20,000	5.3	10	0.53	(Yao <i>et al.</i> 2017)
Ni-Mo ₂ C/Al ₂ O ₃	10	10	10	Solvent impregnation	250 - 500		4:1	20,000	13.8	98.1	13.5	(Yao <i>et al.</i> 2017)
MoS ₂	-	0	5	Hydrothermal synthesis	220 - 330	20	3:1	nd	nd	20	20	(Pacholik <i>et al.</i> 2021)
Mo ₂ C/Al ₂ O ₃	10	10	10	Solvent impregnation	250 - 500	1	4:1	20,000	26.5	8.4	2.3	(Yao <i>et al.</i> 2017)
Co-Mo ₂ C	nd	7.5	7.5	Incipient wetness impregnation	250 - 500	1	4:1	nd	9.5	51.3	4.9	(Porosoff <i>et al.</i> 2014)
Mo ₂ C	nd	7.5	1	Incipient wetness impregnation	300 - 500	1	4:1	nd	8.7	14.5	1.3	(Porosoff <i>et al.</i> 2014)
Ni-Mo/Al ₂ O ₃	0 - 15	0 - 15	5	Impregnation	250	1	2:1	nd	17.2	97	nd	(Aksoylu, Mısırlı and Önsan 1998)

nd: no data

Li *et al.* (2019) developed Ni/MoO_x-La₂O₃/SiO₂ by reducing LaNi_{1-x}Mo_xO₃/SiO₂ with a perovskite structure in which Ni, nickel nanoparticles (NPs), molybdenum oxide (MoO_x), and lanthanum oxide (La₂O₃) are in close proximity, and this proximity was maintained throughout the CO₂ methanation reaction. The authors focused on the development of a nanocomposite catalyst for the storage of hydrogen in CH₄ by CO₂ methanation. At temperatures below 350 °C, the catalyst utilized in this work demonstrated high activity for CO₂ methanation, with a CO₂ conversion of 75%, a CH₄ yield of 75%, and a CH₄ selectivity of 100%. The catalyst also demonstrated excellent stability, with no significant loss of activity after 100 hours of operation. It is, therefore, evident that the addition of Mo enhanced the low-temperature activity and sintering resistance of Ni NPs. Compared to Zhang *et al.* (2014), which emphasized the influence of MoO₃ on the heat resistance of Ni-based MCM-41 methanation catalysts. According to the study, the catalyst's ability to withstand heat was improved by the addition of MoO₃, which also increased its BET surface area (553 m²/g) and pore volume (0.34 cm³/g) in comparison to the catalyst's absence of MoO₃. At 250 °C, the catalyst containing MoO₃ demonstrated a CO₂ conversion of 100%, a CH₄ yield of 80%, and a CH₄ selectivity of 80%, all of which are greater results than those mentioned in Li *et al.* (2019)'s study. The main cause of the Ni-Mo/MCM catalysts' increased activity at a low temperature of 250 °C was due to electron transfer from MoO₃ to the metal nickel.

A comparison of Ni-Mo catalysts with recently reported Sr-promoted Ni catalysts highlights distinct advantages and performance metrics. Ni-Mo/Al₂O₃ catalysts have demonstrated enhanced stability, low-temperature activity, and improved hydrogen activation due to electron transfer between Mo and Ni. For instance, Mo-based catalysts like Ni-Mo/MCM-41 achieve 100% CO₂ conversion and 80% CH₄ yield at 250 °C, attributed to MoO₃'s effect on heat resistance and dispersion (Zhang *et al.* 2014). Conversely, Sr-promoted Ni catalysts, such as 5Ni₄Sr/10ZrO₂+Al₂O₃, achieve high CO₂ conversion (84.3%) and CH₄ yield (75.9%) at 400 °C, supported by Sr-induced strong basic sites and enhanced Ni dispersion (Abahussain *et al.* 2024). While Sr catalysts excel in basic site optimization, Ni-Mo catalysts offer superior performance at lower temperatures, highlighting their potential for energy-efficient CO₂ methanation.

In another study by Yao *et al.* (2017), CO₂ methanation with hydrogen (H₂) to generate CH₄ was investigated. The γ -alumina-supported Mo and Ni-Mo catalysts were either reduced or carburized for application in CO₂ methanation. At 300°C, the CO₂ conversions for the reduced

Ni-Mo/Al₂O₃ catalyst and the Ni-Mo₂C/Al₂O₃ catalyst were 5.3% and 13.8%, respectively, with a comparable selectivity in CH₄ of 10.0% and 98.1%. For the decreased Ni-Mo/Al₂O₃ and Ni-Mo₂C/Al₂O₃ catalysts, the CH₄ yield was 0.53 and 13.5%, respectively. Therefore, adding Ni enhanced the extent of Mo-species' carburization, resulting in higher catalytic activity and selectivity for the catalytic CO₂ methanation reaction. Carburization often increases the basicity of materials and, hence, their surface CO₂ absorption. The presence of Ni also enhanced the synthesis of the Mo₂C species, significantly lowering oxy-carbide formation. Carburization greatly enhanced CO₂ absorption, hence enhancing CO₂ methanation catalytic activity. Despite this, the carburized catalysts included a significant amount of oxycarbide species, indicating incomplete carburization. Even though the results are highly promising and demonstrate that Ni-Mo carbide catalysts can be utilized successfully for CO₂ methanation, the carburization process must be optimized.

6.4.3 Basicity and Oxygen Vacancies of Molybdenum as a Promoter

In CO₂ methanation, material parameters such as oxygen storage capacity and basic properties significantly impact catalytic performance, coke inhibition, and behaviour. Due to its redox properties and exceptional oxygen storage capacity, Mo has been identified as a suitable promoter for CO₂ methanation, reducing the probability of carbon deposition. Mo has exceptional oxygen retention capabilities, particularly at high temperatures. This is because Mo forms a stable oxide layer on its surface when exposed to oxygen, which protects it from further oxidation (De Castro *et al.* 2017). This oxide layer is also self-healing, meaning that if it is damaged or removed, it will reform on the surface of the Mo (Dong and Li 2022). This property makes Mo valuable in high-temperature applications, such as aerospace and defence industries, where it can withstand extreme temperatures and remain stable over long periods (Lemberg and Ritchie 2012). However, the oxygen vacancies in Mo-based catalysts can significantly affect their basicity (Hatta *et al.* 2022).

The basicity of a catalyst is related to its ability to accept protons. Oxygen vacancies in Mo-based catalysts can create Lewis basic sites interacting with acidic species, such as proton donors. These interactions can facilitate the reaction between the acidic species and the substrate, increasing the catalytic activity of the catalyst. On the other hand, the basicity of a catalyst can also be affected by the presence of different chemical species in the catalyst, such as metal oxides or support materials. For example, the acidity of the support material can

influence the basicity of Mo-based catalysts supported on Al_2O_3 . The interaction between the Mo-based catalyst and the support material can create acid-base pairs, which can affect the overall basicity of the catalyst. Qiu *et al.* (2023) investigated the catalytic performance of $\text{Fe}_2(\text{MoO}_4)_3$, including its enriched surface oxygen vacancies. This study synthesized $\text{Fe}_2(\text{MoO}_4)_3$ via the hydrothermal and calcined methods. The study found that the catalysts with abundant surface oxygen vacancies exhibited good catalytic performance and acted as electron transfer centres and mediators for the redox cycle. The oxygen vacancies and $\text{Fe}^{2+}/\text{Fe}^{3+}$ shuttle formed $^1\text{O}_2$, h^+ , and O_2 via unique pathways in the UV-vis + PDS + FMO-6 photoFenton system. Many oxygen vacancies are strongly related to the high CO_2 adsorption capacity and the easily broken C-O bond in an environment with reduced H_2 levels. Wang *et al.* (2015) reported that a high oxygen vacancy concentration is the active site for activating and converting carbon oxides. As a result of oxygen vacancies acting as mobile reactive sites, CO_2 molecules are adsorbed onto them. Oxygen fills the vacancies upon breaking the C-O bond, and carbon hydrogenates into CH_4 . Sub-stoichiometric CeO_{2-x} helps to increase the yield and selectivity of CH_4 significantly.

In addition, Mo can generate oxygen vacancies in CO_2 methanation. According to research, Mo sub-oxide has abundant surface oxygen vacancies and redox ability that promote CO_2 hydrogenation to the CH_3OH (Kuwahara *et al.* 2021). Hydrogen atoms can reduce Mo oxide to produce oxygen vacancies (Kuwahara *et al.* 2021). The hydrogen treatment can also generate oxygen vacancies (Tsai *et al.* 2016). The role of oxygen vacancies in CO_2 methanation has been studied using various catalysts, including Ni/ ZrO_2 doped with Ca (Everett *et al.* 2020). The carbon vacancies created by the α -MoC phase also facilitate the CO_2 adsorption (Zhao *et al.* 2021). Oxygen vacancies in Mo-based catalysts can also play an essential role in their basicity. When oxygen atoms are removed from the catalyst's surface, the oxygen vacancies can be filled with different species. Depending on the nature of the species that fill these vacancies, the basicity of the catalyst can be affected. For example, if the oxygen vacancies are filled with hydroxyl groups (OH^-), the catalyst will have basic properties. On the other hand, if the oxygen vacancies are filled with protons (H^+), the catalyst will have acidic properties. The basicity of Mo-based catalysts can also be affected by other elements in the catalyst, such as alkali or alkaline earth metals. The basicity of Mo-based catalysts is essential in various catalytic reactions, including the hydrogenation of CO_2 and the conversion of CH_4 to higher hydrocarbons. The basicity can affect the reaction mechanism and the selectivity of the

catalyst. Therefore, understanding the basicity of Mo-based catalysts is essential for optimizing their performance in various catalytic applications.

6.4.4 Electronic Structure of Mo-Based Catalysts

The electronic structure of Mo-based catalysts is a critical determinant of their catalytic behaviour, influenced by interactions between Mo and ligands such as C, N, P, or S. These interactions, along with the geometric arrangement of Mo and its ligands on the catalyst surface, significantly affect the electronic properties and catalytic performance. The catalytic behaviour of Mo bound to C, N, P, or S may be attributed to changes in the electronic structure of the Mo surface induced by the ligands and the geometric arrangement of Mo and the ligands at the catalyst surface. These changes suggest that both electronic and geometric factors play a critical role in influencing the impact of ligands on Mo's catalytic activity (Liu and Rodriguez 2003; Kitchin *et al.* 2005).

Tables 6 and 7 summarize the primary geometric and electronic characteristics of Mo-based catalysts. The literature highlights the density-of-states (DOS) of MoS₂, Mo₂C, Mo₂N, and MoP (Tan and Harris 1998; Kitchin *et al.* 2005; Zaman and Smith 2008; Chen *et al.* 2010; Wei *et al.* 2010), demonstrating that Mo 3d orbitals hybridize with the s and p orbitals of the ligand in the presence of the ligand. These hybridizations influence the adsorption energies of various adsorbates by shifting the surface Mo d-band centre to lower energies compared to Mo (001). Additionally, Table 6 reveals that the surface Mo-Mo distances are altered, accompanied by significant charge transfer from the metal to the ligand. These modifications collectively impact the catalytic behaviour of Mo-based materials. Furthermore, the catalytic activity of transition metal carbides and nitrides is comparable to that of noble metals, a phenomenon attributed to the combination of valence *sp* electrons with the metal *spd* bands, as demonstrated by Oyama (1992). These findings highlight the interplay between geometric and electronic properties in driving the catalytic performance of Mo-based systems.

Table 6-6: Crystallographic and lattice parameters of Mo-based catalysts.

Catalyst	Unit cell	Space group	Point position			Ref.
			Mo atomic position	Ligand (P/S/C/N/B) Atomic position	Lattice parameter (Å)	
Mo ₂ B ₅	Hexagonal	(166)-R-3m	(0, 0, 0.0761)	(0,0, 0.3315); (0,0, 0.1850)	a = 3.0097; b = 20.9259	(Shein and Ivanovskii 2006)
MoB ₂	Rombohedral	(191)-P6/mmm	(0, 0, 0)	(0.333, 0.667, 0.5)	a = 3.0012; b = 3.3304	(Shein and Ivanovskii 2006)
γ-Mo ₂ N	fcc	(225) – Fm $\bar{3}$ m	(0, 0, 0)	(0.5, 0.5, 0.5)	a = 4.1613	(Bull <i>et al.</i> 2006)
δ-MoN	Hexagonal	(186)-P6 ₃ mc	(0, 0, 0.6195); (0.489, 0.511, 0.560)	(0.333, 0.667, 0.794); (0.148, 0.852, 0.264)	a 3 = b = 5.7402; c = 5.6203	(Bull <i>et al.</i> 2004)
β-Mo ₂ C	Hexagonal	(164) – D _{3d} ³ – P $\bar{3}$ m1	(0.333, 0.667, z); (0.667, 0.333, -z) [z = 0.25]	(0, 0, 0)	a = 3.002	(Parthé and Sadogopan 1963)
α-Mo ₂ C	Orthorombic	(60)-P _{bcn}	(0.25, 0.125, 0.083)	(0.5, 0.375, 0.25)	a = 4.724; b = 5.199; c = 6.004	(Wang, Yan and Chen 2009)
MoS ₂	Hexagonal	(194)-P6 ₃ /mmc	(0.333, 0.667, 0.25); (0.667, 0.333, 0.75)	(0.333, 0.667, 0.62); (0.667, 0.333, 0.12); (0.667, 0.333, -0.62); (0.333, 0.667, -0.12)	a = b = 3.18; c = 12.60	(Zaman and Smith 2012)
MoP	AHexagonal	(187)-P ₆ m2	(0,0,0)	(0.667, 0.333, 0.50)	a = b = 3.235; c = 3.165	(Zaman and Smith 2012)
Mo	bcc	(229)-Im-3m	(0,0,0)	-	a = 3.147	(Zaman and Smith 2012)

Liu and Rodriguez (2003) investigated the impact of C, N, and P ligands on the stability and activity of Mo-based catalysts. Their study focused on catalysts with an equivalent ligand-to-Mo atom ratio (C/Mo = N/Mo = P/Mo = 1) by examining the γ-MoC (001), δ-MoN (001), and MoP (001) surfaces, all of which possess hexagonal symmetry. Mo-terminated surfaces were selected to allow for direct comparison with the Mo (001) surface (1). On the Mo (001) surface, calculations revealed that Mo atoms interact strongly with subsurface Mo atoms but are more weakly bound to other surface Mo neighbours. This is reflected in a surface Mo-Mo bond distance of 3.165 Å, compared to the subsurface Mo-Mo bond distance of 2.646 Å (Table 6-7). Interestingly, the γ-MoC (001) and δ-MoN (001) surfaces showed decreased surface Mo-Mo distances, while the MoP (001) surface exhibited an increased Mo-Mo distance relative to Mo (001). In all cases, strong interactions were observed between surface Mo atoms and subsurface ligand atoms.

Table 6-7: Bond length and charge distribution on Mo-based catalyst surfaces.

	Mulliken charge		Bond distance	
	q_{X-Sub} (e)	$q_{Mo-surf}$ (e)	$d(Mo_{surf}-X_{sub})$ (Å)	$d(Mo_{surf}-Mo_{surf})$ (Å)
Mo ₆ S ₈ ^b	-0.20	0.27	2.66	2.46
MoS ₂ (1010) ^b	-0.07	0.19	2.73	3.20
Mo(001)	-0.051	0.040	2.646	3.165
MoP(001)	-0.077(-0.128 ^a)	0.045(0.048 ^a)	2.379(2.45 ^a)	3.235(3.19 ^a)
δ-MoN(001)	-0.910	0.19	2.132	2.875
γ-MoC(001)	-1.079	0.27	2.118	3.046

^aOn Mo₆P₃ cluster (Zaman and Smith 2008).

^bLiu P. et al.,(Liu *et al.* 2010).

Note: “d” and “q” represent the bond length and Mulliken charge, respectively; Mo_{surf} and X_{sub} stand for a Mo atom in the surface and a ligand atom “X” in the subsurface, respectively; “X” corresponds to C in the case of γ-MoC(001), N in the case of δ-MoN(001), P in the case of MoP(001), and Mo in the case of Mo(001).

Mulliken (1955) charge analysis indicated significant electron transfer from Mo to the non-metal components in MoC and MoN. The direction of charge transfer from Mo to the C/N ligands aligns with theoretical and experimental findings reported by Chen, Eng Jr and Kelty (1998). For MoP, the charge transfer was much smaller compared to Mo (001). Zaman and Smith (2008) observed higher charge transfer to P for a Mo₆P₃ cluster compared to Liu and Rodriguez (2003), but both studies agreed that the charge transfer in phosphides is considerably lower than that in carbides and nitrides. This difference was attributed to the lower electronegativity of 3p group elements (e.g., P and S) compared to 2p group elements (e.g., C and N).

Liu and Rodriguez (2003) also evaluated the relative stability of the surface structures by calculating the formation energy $E_f = E[MoX(001)] - E(Mo) - E(X)$, where E represents the total energy of the bulk compound, and X denotes C, N, or P. The E_f was normalized by the number of atoms in the supercell, including both Mo and ligand atoms. Their calculations showed that the Mo (001) surface becomes more stable upon forming carbides, nitrides, and phosphides, with the MoP (001) surface emerging as the most stable among the systems considered. Figure 6-10 illustrates the relative stability of Mo-based catalysts with different ligands, emphasizing the significant influence of ligand choice on catalyst properties.

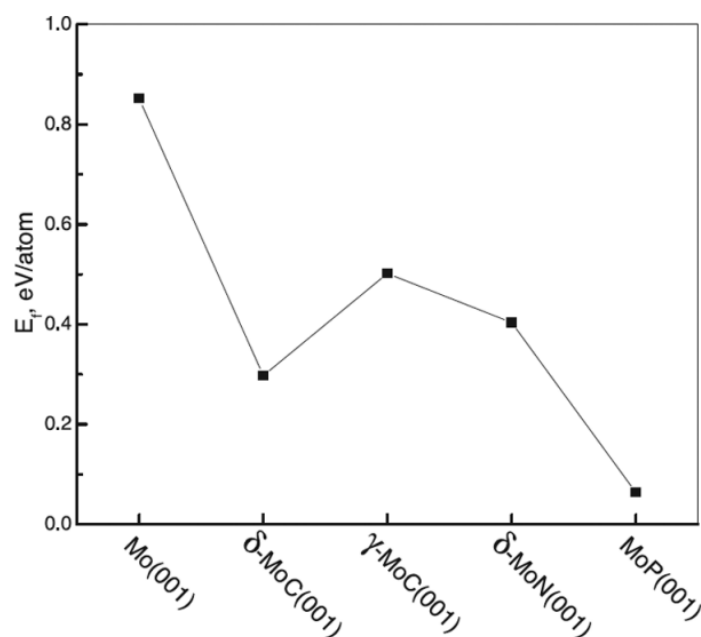


Figure 6-10. Calculated formation energy (E_f , see text for definition) of Mo(001), γ -MoC(001), δ -MoN(001), and MoP(001) surfaces. E_f is normalized by the number of Mo and X (C, N, or P) atoms. Reprinted with permission from (Liu and Rodriguez 2003). Copyright © 2003 Springer.

In addition to stability, Liu and Rodriguez (2004) investigated the surface properties of α -Mo₂C (001), where the Mo-to-C atom ratio is 2. The study identified two distinct types of Mo-Mo bond distances on the surface. At the hcp site, where a C atom is located beneath the Mo atom, the Mo-Mo distance increased to 3.14 Å, compared to the 2.75 Å observed for the Mo (110) surface. Conversely, at the fcc site, where no subsurface C atom is present, the Mo-Mo distance decreased to 2.89 Å. Furthermore, the surface charge of Mo varied with the number of neighbouring C atoms but remained positive relative to the Mo (110) surface. With one neighbouring C atom, the Mo charge was 0.19e more positive than on the Mo (110) surface, and with two neighbouring C atoms, the charge increased by 0.33e. These findings suggest significant charge transfer from the Mo atom to the C atom, further emphasizing the impact of Mo-C interactions on both the stability and surface properties of α -Mo₂C. Together, these studies underline how ligand choice and Mo-C interactions dictate the structural and electronic characteristics of Mo-based catalysts.

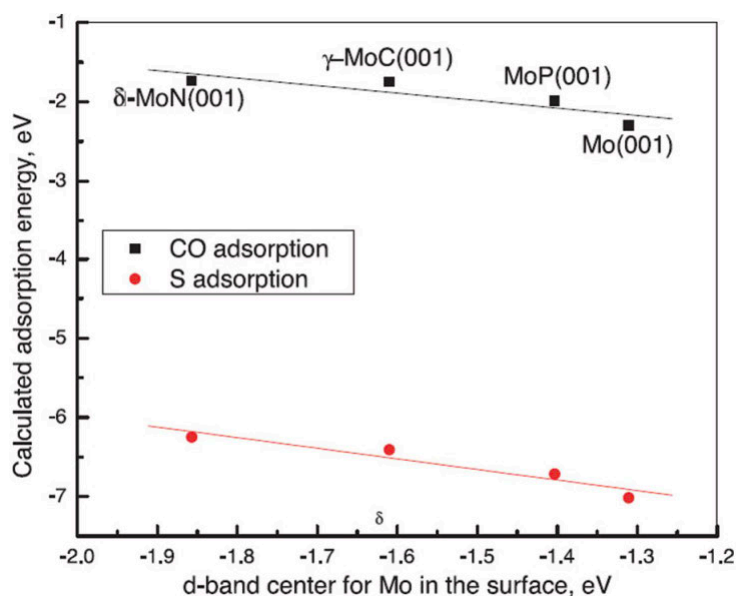


Figure 6-11. Calculated adsorption energy of CO(g) and S(l) as a function of the d-band centre for Mo on clean surfaces of Mo(001), γ -MoC(001), δ -MoN(001), and MoP(001). The d-band centres are relative to the Fermi energy. Reprinted with permission from (Liu and Rodriguez 2003). Copyright © 2003 Springer (colour figure available online).

This charge transfer and interaction between Mo and ligands, such as C, N, O, and P, significantly influence the electronic properties of Mo-based catalysts. The addition of these ligands induces hybridization between the Mo 4d band and the s and p bands of the ligands. This hybridization broadens the DOS and simultaneously lowers the d-band centre of the catalysts. The shift in the d-band centre is crucial as it modulates the adsorption strength of adsorbates, directly affecting the interaction between the catalyst surface and adsorbed species. Liu and Rodriguez (2003) further demonstrated that an increase in the d-band centre energy corresponds to a decrease in the adsorption energies of CO and S on Mo-based catalyst surfaces (Figure 6.11). These findings collectively highlight the importance of electronic structure tuning and ligand interactions in optimizing the stability, catalytic activity, and selectivity of Mo-based catalysts.

6.5 Conclusion and Future Outlooks

This study highlights the pivotal role of Mo as a promoter in Ni-based catalysts for CO₂ methanation. Mo's ability to enhance basicity and create oxygen vacancies is instrumental in improving catalytic performance. Additionally, Mo significantly stabilizes catalytic systems by preventing sintering and facilitating electron transfer in bimetallic configurations. Its dual functionality in H₂ dissociation and CO₂ activation positions it as a critical component for achieving efficient low temperature methanation. These findings establish Mo as a key element

in advancing sustainable catalytic technologies and addressing global energy and environmental challenges.

Through a detailed informetric investigation, contemporary research trends on Mo-promoted Ni-based catalysts in CO₂ methanation were analyzed using VOSviewer and RStudio. This analysis included keyword co-occurrence, citation networks, and collaboration patterns, revealing key publications, prominent journals, and leading countries like China, the United States, and Germany. Commonly used keywords such as "CO₂ methanation," "methane," and "nickel catalyst" highlighted the primary focus areas, while less frequent terms like "reaction kinetics," "space velocity," and "nickel nanoparticles" indicate gaps and opportunities for future exploration. These insights provide valuable guidance for directing future research.

The review further highlights Mo's exceptional properties, such as its oxidation-reduction capabilities (Mo⁴⁺/Mo⁶⁺), high carbon oxide adsorption, and resistance to carbon deposition. These attributes make MoO₃ an effective promoter, addressing challenges like instability, metal sintering, and carbon deposition in CO₂ methanation. Key parameters such as optimal metal dispersion, preparation methods, calcination temperature, and active site selection are critical for improving catalyst performance and ensuring long-term stability.

Despite these advancements, several challenges persist. The high temperatures required for CO₂ methanation often lead to undesirable side reactions, such as the Boudouard reaction, CO methanation, and the reverse water-gas shift reaction. Mitigating these side reactions while optimizing catalyst design remains a critical research priority. Additionally, advancements in low-temperature CO₂ methanation processes are essential for improving efficiency and sustainability.

This study emphasizes the need for interdisciplinary collaboration between academia and industry to develop cost-effective, energy-efficient materials and stable catalytic systems. Future research leveraging advanced techniques such as in-situ spectroscopy, X-ray absorption spectroscopy, and computational modelling can deepen the understanding of Mo's role in Ni-based catalysts during CO₂ methanation. Such efforts will expand the scientific knowledge base and enable practical applications that contribute to global Sustainable Development Goals.

To address the challenges and unlock the full potential of Mo based catalysts for industrial CO₂ methanation, the following research directions are proposed:

- Future studies should focus on the influence of Mo oxidation states and their transitions during methanation. Research should also explore the synergistic effects between Mo and other transition metals to design bimetallic catalysts with enhanced activity and stability.
- Developing strategies to enhance oxygen vacancy concentrations without compromising catalyst stability is critical. The impact of these vacancies on reaction kinetics and methane selectivity under industrial-scale conditions should be thoroughly examined.
- Investigating the long-term stability of Mo-based catalysts under operational conditions will be vital. Identifying mechanisms of deactivation, such as sintering and coking, and developing effective regeneration techniques will ensure sustained catalyst performance.
- Efforts should prioritize scalable, cost-effective synthesis methods for Mo-promoted catalysts. Incorporating renewable feedstocks in catalyst production can improve sustainability while maintaining performance consistency in large-scale applications.
- Tailoring Mo-based catalysts for specific applications like power-to-gas systems and CO₂ utilization in waste-to-energy processes is essential. Performance evaluation under realistic conditions, including variable pressures, temperatures, and feed compositions, will bridge laboratory findings with industrial needs.
- Research should assess the compatibility of Mo-based catalysts with advanced technologies like plasma-assisted or photothermal CO₂ methanation. The integration of hybrid systems combining chemical and electrochemical reduction methods offers opportunities for enhancing overall efficiency.

These directions aim to establish Mo-based catalysts as pivotal contributors to sustainable energy transitions. Addressing existing challenges while leveraging emerging technologies will position these catalysts as key players in advancing CO₂ methanation for industrial and environmental applications.

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Conclusion and Recommendation

This chapter presents the major findings obtained in this work based on the following specific objectives: (i) Investigate the effect of Ni and Mo metal loading in the catalyst system in CO₂ methanation, (ii) Evaluate optimal Mo concentrations for maximizing CO₂ conversion and CH₄ selectivity in Ni-Mo/AC catalysts, (iii) Synthesize catalyst systems using incipient wetness impregnation (IWI), sol-gel (SG), and mechanical mixing (MM) and study how the catalyst preparation method affects the catalyst activity, (iv) Review advancements in AC-based materials for CO₂ methanation (2014-2024) and their sustainable energy potential (v) Conduct an informetric analysis on the role of Mo in enhancing Ni-based catalysts for CO₂ methanation.

7.1 Overall Results and Conclusion

The novelty of the work presented in this thesis focused on the development of a tunable mesoporous activated carbon (AC)-supported bimetallic Ni–Mo catalysts for effective conversion of CO₂ to CH₄. The extent to which the above objectives are met, and their main findings are summarised below:

A tunable mesoporous Ni–Mo catalysts with Ni wt.% of 13 was successfully synthesized and modified with varying concentrations (5–11 wt.%) of molybdenum (Mo) as a promoter. Comprehensive characterisation techniques (XRD, FTIR, SEM, EDS, BET, XPS) were employed to analyse the catalysts and reveal changes in properties such as crystallinity, surface area, pore volume, particle size, and acidity. The introduction of Mo as a promoter notably influenced the catalysts' crystallinity, structure, and chemical state.

- I. Modifying Ni/AC catalysts with Mo influenced the catalysts' physicochemical properties and catalytic performance. The presence of Mo affected characteristics such as crystallinity, surface area, and catalytic activity, ultimately impacting the selectivity toward CH₄. A moderate concentration of metal (>7 wt%) led to decreased surface area, pore volume, and crystallinity. The 7 wt% Mo-doped Ni/AC catalyst was identified as optimal, with a 131.7% increase in pore size relative to pure AC, enhancing CO₂ conversion efficiency. This catalyst also exhibited a superior balance of surface area and catalytic activity for CH₄ production, indicating that controlled metal doping can improve catalytic outcomes while minimizing deactivation from coke formation. These

findings suggest that the Ni-7% Mo/AC catalyst has strong potential for sustainable methane production from CO₂, making it a viable option for clean energy applications.

- II. The evaluation of Mo's impact on enhancing CO₂ methanation activity in Ni-based AC catalysts reveals that an optimal Mo concentration of 7 wt% maximizes CO₂ conversion and CH₄ selectivity. Through BET surface area analysis, X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS), it was observed that Mo additions improve the dispersion and electronic properties of Ni, enhancing both catalytic activity and stability. The electron transfer from MoO₃ to nickel facilitates CO₂ conversion by lowering the activation energy, with the Ni-7%Mo/AC catalyst achieving a notably low activation energy of 54.6 kJ/mol compared to 115 kJ/mol for Ni/AC. This makes the Ni-7%Mo/AC catalyst highly effective at low temperatures, achieving 92% CO₂ conversion and 80% CH₄ selectivity at 250 °C. Additionally, Mo's presence inhibits nickel particle aggregation, leading to sustained catalytic activity and improved thermal resistance compared to Mo-free Ni/AC catalysts. In a 100-hour stability test, Ni-7%Mo/AC demonstrated minimal activity loss, with CH₄ selectivity remaining at approximately 79%, indicating Mo's role in promoting long-term catalytic resilience by reducing sintering and coking risks. These findings highlight Ni-7%Mo/AC as an optimal catalyst for CO₂ methanation, combining high activity, stability, and efficient electron dynamics.
- III. The synthesis of Ni-7%Mo/AC catalysts through three distinct methods: incipient wetness impregnation (IWI), sol-gel (SG), and mechanical mixing (MM) for CO₂ methanation produced catalysts with unique structural properties that significantly influenced their catalytic performance. The IWI catalyst exhibited superior performance, achieving the highest CO₂ conversion of 56% and >95% CH₄ selectivity at 350 °C. This enhanced activity is attributed to the IWI method's promotion of better Ni and Mo dispersion and interaction, which improved the catalytic structure. Characterization results showed that the IWI catalyst had a larger surface area (141.92 m²/g), more uniform Ni and Mo dispersion, and stronger metal-support interactions than those prepared via SG and MM. These features contributed to its superior stability and effectiveness. The SG and MM catalysts, while showing promising activity, achieved lower CO₂ conversion rates (51.4% at 450 °C and 51.2% at 350 °C, respectively). Despite these differences, each method demonstrated advantages and

limitations in catalyst properties, influencing activity and selectivity. The study emphasize that the preparation method is crucial in optimizing catalyst performance for CO₂ methanation applications, with the IWI method standing out as the most effective for achieving high CO₂ conversion and CH₄ selectivity. These findings offer valuable insights for developing efficient catalysts in sustainable CO₂ utilization.

- IV. The analysis of advancements in AC-based materials for CO₂ methanation between 2014 and 2024 highlights substantial progress in using porous AC for sustainable energy applications. Key findings indicate that AC-supported catalysts, especially those integrated with transition metals like Ni and Mo, exhibit high efficiency in converting CO₂ to CH₄, leveraging AC's large surface area, pore structure, and stability. The analysis also highlights AC's cost-effectiveness and environmental benefits, making it a promising material for CCU technologies. However, challenges remain in scaling these systems for industrial application, particularly in enhancing catalyst stability and reducing energy requirements for regeneration. The bibliometric analysis reveals a surge in publications on AC-based methanation, with increased research interest aligning with global sustainability goals. Collaborative networks and research trends point toward further integration of AC in green chemistry and renewable energy frameworks, as well as growing interdisciplinary approaches among institutions. The study concludes that AC materials hold potential for broad-scale CCU applications, with future work needed on optimizing catalyst formulations, improving lifecycle efficiency, and assessing environmental impacts of AC-derived nanoparticles. The study provides a foundation for advancing sustainable CH₄ production, supporting carbon-neutral initiatives in energy production and environmental management.
- V. The informetric analysis conducted on the role of Mo in enhancing Ni-based catalysts for CO₂ methanation provides valuable insights into recent advancements in this field. Mo's incorporation into Ni-based catalysts shows a substantial improvement in CO₂ methanation performance due to its unique ability to create active sites and enhance catalyst stability. Key findings indicate that Mo promotes Ni's activity by increasing oxygen vacancies and influencing electronic properties, which are vital for enhancing CO₂ adsorption and catalytic reactions. Additionally, Mo's redox properties (Mo⁴⁺/Mo⁶⁺) support coke resistance, mitigating common issues like sintering and carbon deposition that affect catalyst longevity. The bibliometric analysis underscored

Mo's increasing prominence as a catalyst promoter in recent literature, with significant research contributions from countries like China and the USA. Prominent keywords such as "CO₂ methanation" and "synthetic natural gas" suggest a focus on sustainable energy applications, emphasizing Mo's role in environmentally friendly catalyst systems. However, research gaps exist in areas like reaction kinetics and space velocity, and future research could further explore these areas to enhance Ni-Mo catalyst efficacy. This study highlights the need for ongoing research in developing low temperature methanation processes and stable, cost-effective catalyst systems. Future work should focus on optimizing Mo content, refining preparation methods, and enhancing catalyst reusability for large-scale applications. Additionally, advanced in-situ characterization techniques, like X-ray absorption spectroscopy, could deepen the understanding of Mo's role in Ni-based systems, driving progress toward sustainable energy solutions.

7.2 Implications:

The findings from this study have several implications:

- I. The incorporation of Mo into the Ni catalyst system boosts CO₂ methanation by enhancing CO₂ conversion and CH₄ selectivity. Mo improves metal dispersion and stability on activated carbon, reducing carbon deposits and enabling effective performance at lower temperatures. This approach optimizes CO₂ methanation, advancing cleaner energy through efficient carbon conversion.
- II. The optimal Mo concentration not only enhances methane yield but also supports the stability of the catalyst under high-temperature conditions, reducing sintering and carbon deposition. This strategy provides a pathway to more efficient utilization of CO₂, addressing environmental challenges by potentially contributing to renewable energy storage solutions through methanation.
- III. By employing incipient wetness impregnation (IWI), sol-gel (SG), and mechanical mixing (MM), significant variations in catalytic performance highlight that careful selection of catalyst synthesis methods is crucial for designing efficient systems that maximize CO₂ utilization, thereby supporting sustainable carbon capture and conversion technologies.

- IV. Leveraging the unique porous structure and adsorptive properties of activated carbon (AC), recent advancements in AC-based materials, particularly for CO₂ methanation, highlight their transformative potential as a promising sustainable energy technology. These developments mark a significant step toward commercially viable carbon capture and utilization systems, addressing global energy needs and contributing to a circular carbon economy.
- V. Through systematically mapping research trends, co-authorship networks, and keyword occurrences, the informetric analysis emphasizes Mo's utility in creating more efficient CO₂ methanation catalysts with significant implications for sustainable energy applications.

Conclusively, this research provides valuable insights into the synthesis and application of a tunable mesoporous Ni-Mo/AC catalyst for effective CO₂ methanation to CH₄. The incorporation of an optimal 7 wt.% Mo enhances Ni dispersion and stability, achieving high CO₂ conversion and CH₄ selectivity while minimizing coke formation, thus promoting long-term catalyst efficiency. The choice of incipient wetness impregnation (IWI) as a synthesis method notably improves metal dispersion and interaction, further boosting the catalyst's performance. The AC-supported structure not only offers cost-effectiveness but also facilitates efficient CO₂ adsorption and conversion, positioning these catalysts as promising for scalable carbon capture and utilization. The research highlights Mo's critical function as a promoter in Ni-based systems, highlighting future directions in optimizing Mo concentrations, refining synthesis methods, and utilizing advanced characterization techniques to further develop sustainable methanation catalysts for clean energy applications.

7.3 Recommendations and Future Work Considerations:

Based on the milestones and findings of this research, the following recommendations and considerations are essential for advancing the optimization of CO₂ methanation over Ni-Mo/AC catalysts and enhancing their application in sustainable CH₄ production:

- I. Further investigate the effects of different metal concentrations and combinations on catalyst performance, selectivity, and stability. Evaluate the potential of other transition metals for doping.

- II. Focus on developing strategies to minimise coke formation and enhance catalyst regeneration processes, including catalyst surface modification, reaction conditions optimisation, and the use of additives or promoters.
- III. Investigate opportunities for process intensification, such as reactor design optimisation, catalyst bed configuration, and process integration, to improve conversion efficiency and selectivity.
- IV. Investigate the factors affecting catalyst regeneration (reaction, temperature, time, and WHSV) and determine the optimal regeneration conditions based on the initial parameters to which the spent catalysts were exposed.
- V. Explore other catalyst materials and structures beyond AC support to enhance catalytic performance and selectivity in CO₂ to CH₄ conversion processes.

These recommendations and future work considerations seek to enhance the understanding and application of catalysts for CO₂ conversion to CH₄, optimize methanation process conditions at moderate temperatures, and support the advancement of sustainable, clean energy solutions.

Appendix

1a. Co-authorship Network Analysis in terms of Countries

 **Verify selected countries**

Selected	Country	Documents	Citations	Total link strength
☒	iran	25	1169	432
☒	spain	32	1597	428
☒	greece	14	1367	357
☒	portugal	14	899	349
☒	england	19	784	338
☒	belgium	10	948	316
☒	malaysia	32	1223	302
☒	thailand	18	402	253
☒	india	18	645	228
☒	australia	17	609	219
☒	poland	18	590	205
☒	switzerland	12	803	203
☒	taiwan	12	343	136
☒	romania	8	267	100
☒	vietnam	5	160	99
☒	colombia	6	216	91
☒	turkey	8	287	81
☒	chile	6	178	79
☒	austria	5	119	68
☒	argentina	5	167	67
☒	ruissia	13	218	60
☒	canada	6	85	24

1b. Occurrences and Link Strength of Keywords

 **Verify selected keywords**

Selected	Keyword	Occurrences	Total link strength
☒	co2 hydrogenation	1221	1483
☒	methanol	384	722
☒	carbon dioxide	326	668
☒	co2 methanation	602	623
☒	hydrogenation	283	588
☒	methanol synthesis	345	523
☒	methanation	274	490
☒	heterogeneous catalysis	175	326
☐	co2	151	313
☒	nickel	140	298
☒	density functional theory	127	237
☒	copper	90	210
☒	formic acid	114	194
☒	oxygen vacancy	94	174
☒	methane	80	169
☒	catalysis	92	164
☒	reaction mechanism	87	164
☒	dft	78	155
☒	hydrogen	70	149
☒	power-to-gas	92	147
☒	ruthenium	64	147
☒	ceria	54	140

1c. Co-authorship Network Analysis in terms of Authors

Selected	Author	Documents	Citations	Total link strength ▼
☒	yan, binhang	23	2760	17
☒	zhu, minghui	28	1105	17
☒	li, feng	27	911	16
☒	wang, peng	21	574	16
☒	liu, qing	40	1238	10
☒	yang, bo	26	686	10
☒	ma, xinbin	26	562	5
☒	coperet, christophe	25	1128	4
☒	tada, shohei	31	1485	4
☒	zeng, hua chun	20	716	4
☒	zhan, guowu	22	931	4
☒	kawi, sibudjing	27	1231	3
☒	li, zhenhua	24	1298	2
☒	garbarino, gabriella	20	749	1
☒	hensen, emiel j. m.	27	1506	1
☒	ozin, geoffrey a.	25	1428	1
☒	fan, maohong	22	1393	0
☒	garcia, hermenegildo	20	694	0
☒	hong, xinlin	22	1120	0
☒	konya, zoltan	21	332	0
☒	liu, bing	20	1238	0
☒	rezaei. mehran	24	1088	0

1d. Co-authorship Network Analysis in terms of Authors

Selected	Author	Documents	Citations	Total link strength ▼
☒	song, chunshan	64	3719	1396
☒	guo, xinwen	55	3166	1286
☒	sun, yuhan	44	3651	979
☒	gao, peng	38	3290	974
☒	wang, hui	38	2947	798
☒	witoon, thongthai	32	1651	778
☒	limtrakul, jumras	29	1704	730
☒	sun, jian	30	1779	712
☒	liu, chang-jun	28	2657	662
☒	chareonpanich, metta	29	1539	635
☒	rui, ning	28	2165	611
☒	tsubaki, noritatsu	41	1085	552
☒	yang, guohui	33	1111	550
☒	rodriguez, jose a.	41	3237	529
☒	xu, jing	27	1021	503
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1e. Co-authorship Network Analysis in terms of Journals



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