Solvent-Free Knoevenagel Condensation Over Supported Mixed Metal Oxides Catalysts

By

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DECLARATION

I, **Nokubonga Prudence Makhanya**, declare that:

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PREFACE

The experimental work described in this thesis was carried out at the Durban University of Technology, Department of Chemistry and University of KwaZulu-Natal, School of Chemistry and Physics under the supervision of Dr. Sooboo Singh.

These studies represent original work by the author and have not otherwise been submitted in any form for any degree or diploma to any tertiary institution. Where use has been made of the work of others, it is duly acknowledged in the text.

DEDICATION

This dissertation is dedicated to my late father, Ziphathe Petrus Makhanya, my late brothers, Lungile and Mthokozisi Cyril Makhanya, my late sister, Fezile Goodness Makhanya and my late grand-parents, My mother, Mrs Bawelile Hironica Makhanya, my four brothers, my sons Mfuneko Bonke and Scoco Ziyanda Makhanya who kept me going.

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ABSTRACT

Knoevenagel condensation reaction is a useful protocol for the formation of C=C bond in organic synthesis. This protocol is extensively utilized by synthetic chemist to generate dynamic intermediates or end-products such as perfumes, polymers, pharmaceuticals and calcium antagonists. The reaction is catalyzed by bases such as ammonia, primary and secondary amines, quaternary ammonium salts, Lewis acids, catalysts containing acid-base sites, which are carried out under homogeneous conditions. This necessitates the use of organic solvent which generate the large volumes of solvent waste. From green chemistry perspective, solvent free heterogeneous catalysts have received considerable attention. Since, these heterogeneous catalysts not only avoid the use of organic solvents but also suppress side reactions such as self-condensation and oligomerisation leading in better selectivity and product yield. In recent years, therefore, the use of heterogeneous catalyst, their recovery and reusability are in demand in industry. The use of cobalt, iridium and platinum hydroxyapatites, MgO/ZrO_2, MgO/HMCM-22, β and Y zeolites, has earlier been reported in the literature, and used as heterogeneous catalysts for the Knoevenagel condensation of aldehydes and esters. Based on these evidences, we envisioned that MgO and VMgO could also be used as heterogeneous catalysts for this reaction.

Magnesium oxide was synthesized from three precursors, viz. magnesium nitrate, magnesium carbonate and magnesium acetate. Magnesium oxide prepared from magnesium nitrate precursor was found to be the optimum giving an 81 % product yield. Vanadium-magnesium oxide catalysts with different vanadium loadings; 1.5, 3.5 and 5.5 wt. %, were synthesized by wet impregnation of magnesium oxide with aqueous ammonium metavanadate solution. The synthesized catalysts were characterized by ICP-AES, FTIR, Powder XRD, SEM-EDX and TEM. The Knoevenagel condensation reactions between benzaldehyde and ethyl cyanoacetate were carried out in a 100 mL two-necked round bottom flask equipped with a reflux condenser, magnetic stirrer and a $CaCl_2$ guard tube. An equimolar quantity (10 mmol) of substrates and 0.05g of catalyst were added to the flask and heated at 60 °C, stirred vigorously for the required time. The yields were determined using GC-FID equipped with a capillary column.

Elemental composition of the catalysts (vanadium and MgO) was determined by ICP-AES. IR spectra of MgO showed that magnesium oxide was the only phase present in the catalysts prepared from different precursors. The 1.5 and 5.5 wt. % VMgO showed weak bands attributed to pyrovanadate and orthovanadate phases present in small quantities. The phases manifested more with the increase in the vanadium concentration (3.5 and 5.5 wt. % VMgO). The diffraction patterns of all the catalysts showed the existence of MgO and magnesium orthovanadate. The morphology of the catalysts with increasing vanadium was more affected by precursor treatment rather than chemical differences. Electron microscopy showed that the VMgO surface is only sparingly covered with vanadium and MgO showed stacked with large rounded particles. Good to excellent yields were obtained for the MgO catalysts: MgO(1) – 68 %, MgO(2) 65 %, MgO(3) – 72 %, MgO(P) – 73 % and MgO(DP) – 82 %. Excellent yields were obtained for the VMgO catalysts: 1.5VMgO – 83 %, 3.5VMgO – 91 % and 5.5VMgO – 97 %. The 5.5VMgO catalyst was found to be the optimum catalyst and was further tested for it activity using different aldehyde substrates. Excellent yields of the products were obtained for benzaldehyde – 97 %, nitrobenzaldehyde – 94 %, bromobenzaldehyde – 96 %, chlorobenzaldehyde – 93 % and methoxybenzaldehyde – 95%.

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LIST OF ABBREVIATIONS

% - percent

°C - degrees Celsius

Å - angstrom

BET - Brunner Teller Emmett

BTEAC - benzyltriethylammonium chloride

cm - centimeter

DBSA - dodecylbenzene sulfonic acid

EDX - energy dispersive X-ray spectroscopy

EM - electron microscopy

FID - flame ionization detector

FAP - flouroapatite

g - gram

GC - gas chromatography

HAp - hydroxyapatite

HTMAB - hexadecyltrimethylammonium bromide

ICP-AES - inductively coupled plasma – atomic emission spectroscopy

IR - Infrared

K - Kelvin

ml - millilitre

mmol - millimole

M - molar

MW - microwave

µmol - microlitre

kPa - kilo-Pascal

ODH - oxidative dehydrogenation

PXRD - powder X-Ray diffraction

s - second

SEM - scanning electron microscopy

Tmax - maximum temperature

TEBA - triethylbenzylammonium chloride

TPD - temperature programmed desorption
TLC - thin layer chromatography
µmol - micro mole
viz. - namely
VMgO - vanadium magnesium oxide
wt.% - weight percent
TEBA - triethylbenzylammonium chloride

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CHAPTER 1

INTRODUCTION AND LITERATURE REVIEW

1.1 Catalysis

Catalysis is a phenomenon acknowledged from very archaic times, though not so its theory or characteristics. Nowadays, it executes a vital role in the processing of the vast majority of chemical products utilized by our society [1]. The available data on the starch conversion to sugars in the presence of acids, hydrogen peroxide decomposition in alkaline and H_2O solutions in the presence of metals and combustion of hydrogen over platinum, outlined by a Swedish scientist, Jöns Jakob Berzelius (1779-1848), led to him proposing the term *catalysis* in 1835 [2]. Berzelius inscribed that via the term catalysis he referred to "the property of exerting on other bodies an action which is very different from chemical affinity. By means of this action, they produce decomposition in bodies, and form new compounds into the composition of which they do not enter" [1].

This concept was instantly criticized by Liebeg, as the theory was placing catalysis outside of other chemical disciplines [2]. On the other hand, Ostwald, one of the founding fathers of chemical thermodynamics established thermodynamics into the physical chemical definition of a catalyst [3] and subsequently defined a catalyst as a "compound that increases the rate of a chemical reaction, but not consumed by the reaction". This definition permits the probability that miniature quantities of the catalyst are dissipated in the reaction or that the catalytic activity steadily declines [2].

From these statements, the relationship allying chemical kinetics and catalysis is apparently clear and accordingly, catalysis is the kinetic process. However, there are numerous drawbacks in catalysis that are not directly associated to kinetics, such as mechanisms of catalytic reactions, elementary reactions, surface reactivity, reactants adsorption on solid surfaces, structure and synthesis of solid materials and catalytic engineering. An important issue in catalysis is the selectivity towards a particular reaction [2]. The diagram portrayed below (Figure 1.1) shows an effect of the catalyst on a reaction where A + B are the reactants and C + D are the products.

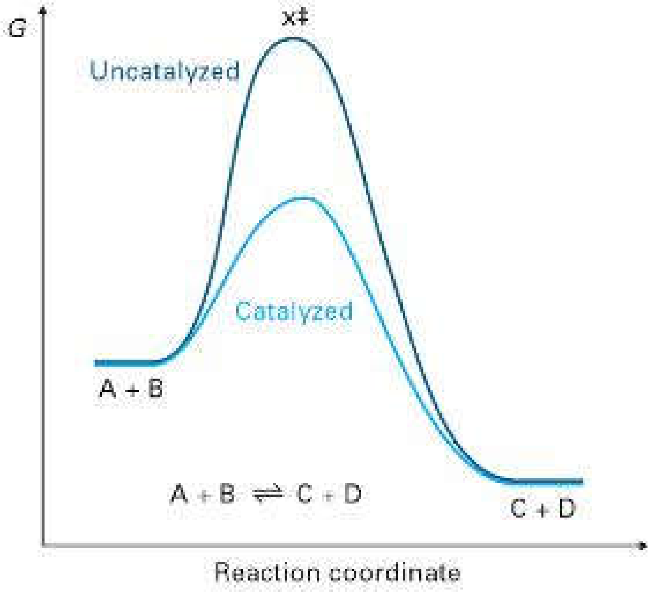


Figure 1.1: Effect of a catalyst on a reaction [4].

“A catalyst is ordinarily classified as a material that accelerates a chemical reaction. This declaration is, however, an over condensed definition. Although the catalyst is described as a substance that increases the rate of a reaction without itself being consumed, these statements may be also broadened by considering that a catalyst primarily impacts changes in the route to equilibrium of a reaction, which further counsel that only the reaction kinetics are affected and the thermodynamics remain unaffected” [5, 6].

Catalysis plays a pivotal role in life, to our contemporary lifestyles and to industrial applications. Numerous organic reactions are activated by diverse enzymes through various functionalities and assuring the life sustainability. Our lives are affected by the industrial catalysis which benchmarks and directs the economy. Catalysis has turn out to be a fundamental to world-wide issues concerning our environment, energy and resources [7]. Heterogeneous catalysis involves catalysts which are most utilized in industry. The heterogeneous catalysis modification from homogeneous, by catalyst supporting or establishing the auxiliary solid catalysts, is the chemical industry undeviating development.

The 20th century chemical industry might not have evolved to current status on the essence of stoichiometric and non-catalytic reactions only. Commonly, the reactions can be measured with the fundamental support of reactants concentration, temperature, contact time and pressure. Increasing the pressure as well as temperature will allow stoichiometric experiments to progress at a rational production rate. However, the conditions in which the reactors can be carefully sustained are progressively becoming costly and strenuous to create. Additionally, at hand, thermodynamic restrictions in which the products can be produced, such as the transformation of nitrogen and hydrogen into NH_3 is virtually not possible beyond 600 °C. Nonetheless, high temperatures are required to disintegrate the N-N bond in nitrogen. Devoid of catalysts, the common numerous reactions in chemical industries would be impossible and other measures would not be cost-effective. A catalyst facilitates reactions, permitting them to be conducted in the most suitable thermodynamic system, at low pressures as well as at lower temperatures. In such way, proficient catalyst, in cooperation with total plant design and optimized reactor, are essential aspects in minimizing both the operation costs and investment of a chemical processes [8]. Catalytic process is the most applied in the chemical industry; therefore, a sequential and economic importance of catalysis is extensive. Eighty percent and more of the modern industrial developments initiated since the year 1980 in the biochemical, chemical industries, petrochemical, in the protection of the environment and manufacturing of polymers, employ catalysts. More than fifteen global companies are specializing in innumerable catalysts production utilized in various industrial divisions. In 2008, revenue in catalysts global market approximated to stand at around 13-109 US dollars [9].

1.2 Classification of catalysis

Catalysis is distinguished into two main categories; that is, heterogeneous and homogeneous catalysis. These categories are systematized according to the phases implicated in process. In heterogeneous catalysis, the substrates are in a dissimilar phase from the catalyst. Homogeneous reactions utilize catalysts in the similar phase as substrates. An addition to that, biocatalysis is a third category of catalysis which exists and is also referred to as enzyme catalysis.

1.2.1 Biocatalysis

The colloidal size of protein molecules are enzymes that are considered to be in between the macroscopic heterogeneous and molecular homogeneous catalyst. The enzymes are the type carbon-based molecules that generally possess a metal centre. Reactions with extremely high selectivities can be catalyzed by enzymes under favourable conditions [10]. For the moment, considering the enzyme as bulky protein is sufficient, for the fact that the structure of which outcome in a specific shape active site. The enzyme catalase catalyzes the decomposition of H_2O_2 into H_2O and O_2 at an extremely high rate of 10^7 hydrogen peroxide molecules per second [11].

$$2H_2O_2 \xrightarrow{catalase} H_2O + O_2$$

Enzymes usually contest the shape of the substrates they ascribe to, or the state of transition of the reaction catalyzed. Enzymes are highly proficient catalysts that represent a great foundation of motivation for designing technical catalysts.

1.2.2 Homogeneous catalysis

Homogeneous catalysis is the type of catalysis where the substrates, catalysts and the products exists in a similar phase, generally the liquid phase. Salts, bases, soluble acids, organometallic compounds, Fe, Rh, and Co carbonyls are the catalysts generally involved. The solvent that is used to dissolve the catalyst can itself be substrate or the product. When substrates with catalyst exhibits a common physical phase, the reaction is said to be homogeneously catalyzed [11, 12]. Homogeneous catalysis advantages such as the utilization of virtually all the molecules of the catalyst in the catalytic act, the higher selectivity obtained in some reactions, the easier regulation of the temperature for highly exothermic reactions and the higher selectivity attained due to that it is possible to operate at milder conditions. However, it also has some disadvantages which include high-cost methods of separation and of catalyst corrosion (employing solvents or acid catalysts), and catalyst recovery, catalyst contamination possibility to the products; the presence of gas-liquid mass-transfer restrictions under circumstances where one of the substrate is a gas such as O_2 or H_2.

1.2.3 Heterogeneous catalysis

Heterogeneous catalysis is the type of catalysis that involves the systems where substrates, the catalyst, and products exhibit dissimilar phases. Substrates and products are generally in a gas or liquid phase and a catalyst is a solid. The catalyst surface is characterized by the presence of the "active site". The catalysts in this system can be either inorganic solids, for example sulfides, metal oxides and chlorides, or organic materials such as the enzymes, ion exchangers as well as hydroperoxides. In a heterogeneous reaction the adsorption of reactants from a liquid phase onto a solid surface, surface reaction of species adsorbed, and products desorption in liquid phase. Alternatively, catalyst's presence affords a series of elementary steps essential to achieve the anticipated chemical reaction from that in its absence. When the catalytic path energy barriers are less than non-catalytic path, significant improvements in the rate of reaction can be understood by catalyst usage [9]. Heterogeneous catalysts are typically more tolerant of extreme operational conditions than their homogeneous analogues. Some of the advantages of heterogeneous catalysis include separation processes of catalysts from reactants and products are much easier, problems of corrosion and liquid waste treatments are eliminated whereas the disadvantages include strenuousness in temperature control for very exothermic reaction, limitations in mass transfer of products and reactants high mechanical resistance and as well as erosion resistance requirements for the catalysts [12].

Even though there are variances in the information of different types of catalysis, a handier and undisputed beneficial partnership amongst the distinct communities constituting biocatalysis heterogeneous as well as homogeneous should be intensely sustained and reinforced. A statement by David Parker (ICI) during the 21st Irvine Lectures on 24 April 1998 at the University of St. Andrews, it ought be stated in this association, explicitly, that, "at the molecular level, there is little to distinguish between homogeneous and heterogeneous catalysis, but there are clear distinctions at the industrial level" [9].

1.3 Catalytic reactions

Chemical thermodynamics and chemical kinetics are areas that are central to the understanding of catalysis. Chemical kinetics forms the quantitative framework of catalysis, whilst the qualitative framework is provided by reaction mechanisms [13]. Catalytic reaction kinetics forms the basis for the definitions of activity, selectivity and stability. The activity of a catalyst is given by the reaction rate, or reaction rate constant for the conversion of reactants to products. The selectivity of a catalyst is a measure of the ability of the catalyst to direct the conversion to the desired product [13]. Since a catalyst accelerates the rate of a chemical reaction; it indicates that the reaction must be able to occur without a catalyst. It is also important that the chemical equilibrium reached remains unchanged with the application of a catalyst [14].

In a catalyzed reaction, reactants are transported to the catalyst and are then adsorbed onto the surface of the catalyst. These adsorbed reactants interact with each other to form the product. This product is then desorbed from the catalyst surface and transported away from the catalyst. Activation energy for the catalyzed reaction must be lower than the uncatalyzed reaction for these steps to occur. This is graphically illustrated in Figure 1.2 [14, 15].

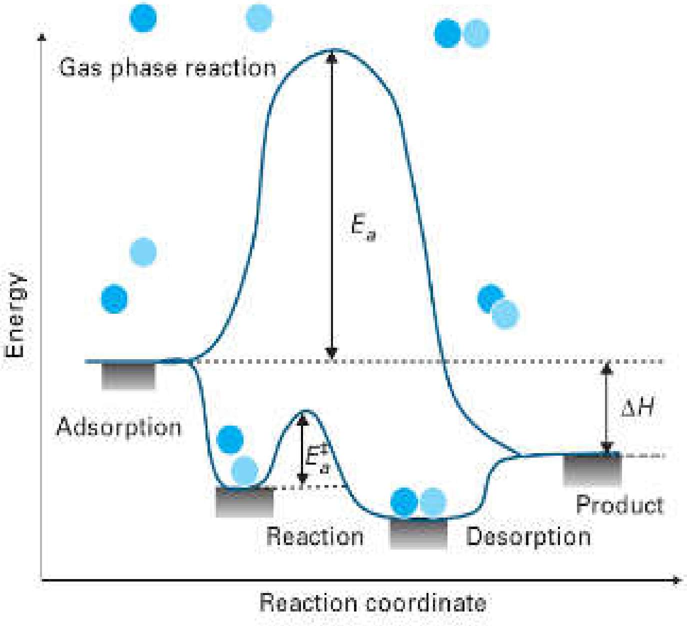


Figure 1.2: Potential energy diagram of a heterogeneous catalytic reaction [11].

In catalytic reactions, only small quantity of the catalyst is generally required which usually do not initiate the reaction and remains unchanged chemically throughout the reaction. It is specific in its action, but does not affect the equilibrium state in a reversible reaction and its activity is increased by the presence of promoters. On the other hand, it can be poisoned by the presence of a certain substance [16].

1.3.1 Types of catalytic materials

Various types of catalytic material exist ranging from solid materials to biological enzymes, from gas phase molecules to liquid coatings on surfaces. Metals and many types of metal oxides are used. Metals are attractive as catalysts due to their high surface energy making them highly active; however, selectivity to the desired product must also be considered. Many metal catalysts are placed on a support, such as alumina or silica, since these metal catalysts are thermally unstable in the high surface area form that they must be used in. Catalysts can be in a powder form, or as pellets with various pore sizes. The shape or physical form of the catalyst used depends on the process to be used for. The most common methods of making catalysts are impregnation, slurry precipitation, co-precipitation, fusion, physical mixing, wash coating and pelleting. Pelleting is used to make the macroscopic form of the catalyst that is utilized in the six industrial plants (chemical, petrochemical, oil-refining, pharmaceutical, fuel-energetic industries and environment protection). The method chosen to make the catalyst depends on the individual synthesis and the properties desired in the catalyst [6].

1.3.2 Solid catalysts

A solid catalyst comprises of three main components, viz. the catalytic agent, support /carrier and promoters or inhibitors.

1.3.2.1 Catalytic agent

Catalytic agents are components in a catalyst that are catalytically active. These components play a role by generating the "active sites" which participate in chemical reaction. These active sites concentration is proportional to the catalyst activity. Although the concentration of the active sites is influenced by the amount of catalytically active component, however, it is not always directly proportional. Active sites availability depends primarily on the distribution of catalytic agent. Dispersion is defined as "ratio of total number of exposed atoms/molecules of catalytic agent available for reaction to total number of atoms/molecules of catalytic agent present in the catalyst sample". Catalytic agents can be predominately classified into metallic conductors such as Fe, Pt and Ag, semiconductors such as ZnO and NiO and insulators such as MgO , Al_2O_3, and SiO_2 [17].

1.3.2.2 Support or carrier

Support or carrier is a material that furnishes larger surface area for the dispersion of smaller quantity of catalytically active agent. In particular, this is significant when the high-cost metals, including palladium, ruthenium, platinum and/or silver are employed as active agents. Supports provide the catalysts its mechanical resistance, physical texture, shape and definite activity predominantly for bifunctional catalysts. The support might be unreactive or cooperate with the active component. The surface structure of the active agent may result in the changes due to this interaction and thereby affects the activity and selectivity of the catalyst. The support may contribute to the reaction processes and may also present the ability to adsorb the reactants [18]. Catalyst supports, are compounds present in the highest quantity in the composite material which play multiple roles in the catalyst. The main role of the support is decrease the quantity of the high-cost active species, increase the mechanical resistance of the catalyst composite, generate a poly functional catalyst by presenting new active sites, escalates the heat exchange volume of the catalyst composite, stabilize species of metal oxide in coordination state and valence dissimilar from unsupported oxide, stabilize metal components with a small particle size [12].

1.3.2.3 Promoters

Generally, promoters are classified as substances that are added during synthesis of the catalysts in order to enhance the selectivity, improve the activity, and stabilize catalytic agents. The promoters are present in smaller quantities and by themselves have minute or no activity. The promoters are chemical or physical in nature contingent on the way they enhance the performance of a catalyst [18, 19]. Physical promoters are also compounds or elements added in smaller quantities that aid to stabilize the composite material surface area or increase the composite material's mechanical resistance. The active species selectivity and activity is altered by chemical promoters.

1.3.3 Supported catalysts

The catalyst components are utilized in heterogeneous catalysis which includes the active species comprises of one and/or more compounds that either impart to each one with its individual novel functional properties, or correlate amongst themselves generating synergetic effects on interfaces. Catalyst support is the material, generally a solid with a high surface area, to which a catalyst is attached. The activity of heterogeneous catalysts and nanomaterial-based catalysts transpires at the surface atoms. Therefore, prominent effort is formulated to increase the surface area of a catalyst by disseminating it over the support. The support may be unreactive or may participate in the catalytic reactions. Different kinds of typical supports include those of alumina, carbon, magnesia and silica. Supported catalysts are concocted by the active metal deposition onto the support materials. The key motive of utilizing a support is to attain an optimum dispersion of the catalytically active component and also to stabilize it against sintering [20].

The most commonly used catalyst in industry is the supported metal and metal oxide catalyst, making it an important component of heterogeneous catalysis [21]. Such catalysts play a major role in society and the economy [22]. The commercial applications that utilize these catalysts include oil refining, chemicals manufacture and environmental catalysis. These applications encompass reactions such as oxidation, (de)-hydrogenation, condensation and isomerization [22, 23]. Synthesizing supported catalysts must produce a catalyst with higher selectivity, stability and activity. To achieve such features, an active metal phase must be highly dispersed throughout the support, resulting in a large specific surface area and maximum specific activity. The catalyst support can disperse the metal and maximize thermal stability and consequently, the catalyst life [24]. Supported metal catalysts are discussed in more detail in the subsections to follow.

Some of the reasons for supporting catalysts are because the support can act as a thermal stabilizer, where it stabilizes the catalyst against agglomeration and coalescing, act as a component enhancing selectivity (the support causes resistance to by-product formation) or poison resistance, decrease the density of the catalyst and allow for the diluting of costly ingredients with less costly ingredients and resist breakage and minimize pressure drop, achieved by supports such as saddles and rings [25]. The attachment to the support can have the following beneficial effects, viz. the support can not only be an inert backbone but also promote selectivity by leading to the preferred orientations of the substrate at the catalytic site, the supported metal catalyst can have different chemical properties to the non-supported metal catalyst, using a multidentate ligand as a support for a metal catalyst can alter the stereochemistry around the metal ion, the position of the equilibrium between metal ions and their surrounding ligands may be altered by supporting the metal catalyst and catalytically active structures that are normally unstable can be stabilized with the use of a support. It is clearly seen that the attachment of the support to the metal catalyst produces a united catalyst that can possess the advantage of being highly selective [26]. This further supports the use of supported catalysts for this study.

The two main classes of supports include organic polymers and inorganic supports. Polymers that function as supports are polystyrene, polypropylene, polyacrylates and polyvinyl chlorides. Such supports possess advantages such as easy functionalization, chemical inertness, and a wide range of physical properties. However, these polymers have poor mechanical properties and heat transfer abilities. Inorganic supports, on the other hand, possess the quality that organic polymers lack. Silica (SiO_2), alumina (Al_2O_3), glasses, clays and zeolites are among the inorganic supports that have been used. Other supports include titania (TiO_2), zirconia (ZrO_2), chromia (Cr_2O_3) and other metal oxides. Inorganic supports tend to be mainly metal oxides and contain hydroxyl groups which affect their attachment [27].

1.4 Green chemistry

In the recent years, green catalytic processes have been frequently practiced. This sustainable technology approach necessitates a paradigm shift from traditional concepts of process largely on chemical yield, to one that assigns economic value to eliminate waste at source, avoid the usage of hazardous or toxic substances, target products with high yields, high energy efficiency and high selectivities. The concept of Green chemistry was initiated by the USA and Europe In the 1990's due to world-wide demand of energy based on fossil fuel and diminishing natural resources and with elevated awareness to taking care of the earth. This initiation has been implemented by chemical industry as a whole. The main target is to design and use methods and products that utilize, generate less or no toxic substances leading to low environmental impact. Addition to this, employing "prevention rather than cure" strategy, since prevention is promoted over waste remediation. Fundamental goals of "Green Chemistry were summarised as follows waste prevention instead of treatment, where possible, choice of synthetic routes using non-toxic alternatives, atom efficient synthetic methods design, design of new products that preserve functionality while reducing toxicity, auxiliary reagents and solvents minimal use, design of processes with minimal energy requirements, preferable use of renewable raw materials, stoichiometric reagents replacement with catalytic cycles, new products with biodegradable capabilities design, monitoring methods and development of real-time online process analysis design processes that minimise possibility of accidents and choice of feedstock" [5].

The prime goal of green chemistry is consequent development and utilization of more environmentally benign methods in manufacturing valuable organic and inorganic products. This goal has been implemented in application of catalysis in chemical syntheses. With stringent environmental regulations and worldwide awareness to more environmentally friendly and greener options, an appalling necessity exists to investigate these methods more broadly. The swing towards a world-wide commitment in decreasing the carbon emissions results in more favorable green synthetic procedures [5]. The major advantages of catalysis are the attainment of favorable reaction conditions with chemical processes that are environmentally benign and reduced energy consumption. Through the catalytic route, increased rates of reaction and selectivities are more economically feasible. Enhancing the selectivities of the desired product can be achieved by tailoring and tweaking the catalysts. These dynamics suggest that little waste is produced, and that is a desired effect, consequential to a lower E factor, "the mass ratio of waste and by-products to desired products", and a lesser energy consumption with higher product yields. An analysis by Cavani [28], indicates the extent to which the greener methods have been implemented and current trends in research towards integrations of the greener options.

1.5 The Knoevenagel condensation reaction

Generally, condensation reactions are any group of chemical (organic) reaction in which two moieties combine, usually in the presence of a catalyst, to form larger molecules with the loss of water or other simple molecules. Self- condensation is the combination of two identical molecules. Compounds that are essential intermediate compounds combine in organic synthesis forming larger molecules; among them are ketones, alkynes (acetylenes), aldehydes and esters. Generally, the catalysts utilized in condensation reactions incorporate bases, acids, complex metal ions and the cyanide ion [29].

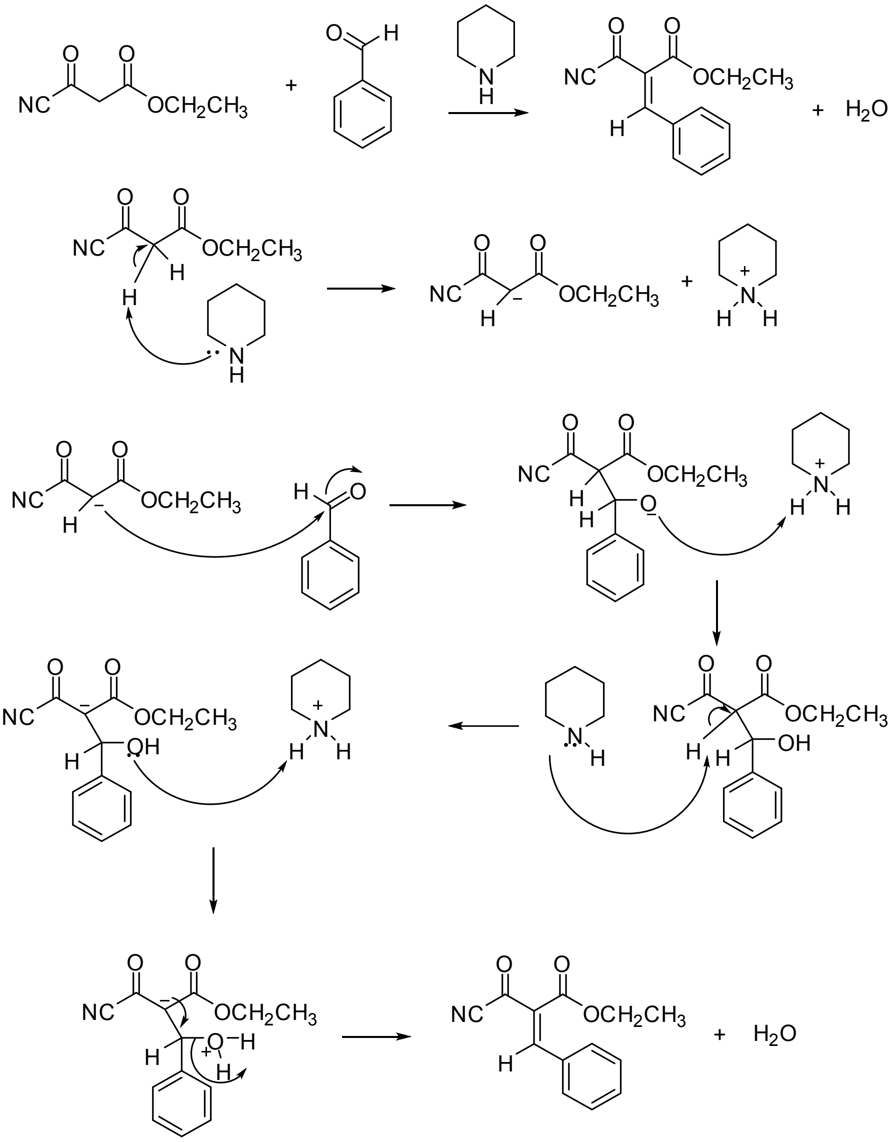
Due to the necessity for more environmentally benign production technology, this has led to application of heterogeneous catalysis in the fine chemical industries. This is aided by the availability of contemporary techniques of investigating and designing the specific active site on catalyst surfaces and the accessibility of novel catalytic materials. In the production of fine chemicals, important steps of bulky and complex molecules such as C–C forming reactions such as Knoevenagel condensations and/or Michael additions. Knoevenagel condensation is one of the most effective and extensively applied methods for C–C formation in organic synthesis. It has innumerable applications in fine chemical synthesis, carbocyclic, hetero Diels–Alder reactions and heterocyclic compounds of biological significance. In recent years, due to their redox and acid-base properties, metal oxides comprise the leading family of catalyst in heterogeneous catalysis [30].

The Knoevenagel condensation is the synthesis of the electrophilic olefins from the active methylene and carbonyl compounds, first reported in 1894. The establishment Knoevenagel condensation has a very long history and since then, numerous improvements have been made. The improvements made in recent years include utilizing microwave irradiation, Lewis acid catalysis, ionic-liquids, organo-base mediation and heterogeneous catalysts. Nonetheless, in many of these approaches somewhat harsh conditions are needed [31].

Knoevenagel condensation is widely employed in the synthesis of intermediate or end products for pharmaceuticals, perfumes, bioactive compounds, polymers and calcium antagonists. The reaction is often catalyzed “by bases such as ammonia, primary and secondary amines, quaternary ammonium salts, Lewis acids and acid-base sites, and commonly carried out under homogeneous conditions, which require organic solvent” [32]. The use of solvents results in large volumes of waste generated. From the viewpoint of sustainable environment, the aim is therefore to protect our environment in this overpopulated world of escalating demands by application of the cost-effective, novel, efficient, simple, high-yielding and environmental friendly methodologies. The solventless heterogeneous catalysts recognition is escalating. Since, these heterogeneous catalysts not only steer the utilization of organic solvent but also side reactions are suppressed such as oligomerization and self-condensation. This leads to improved selectivities and product yields. In recent years, employment of heterogeneous catalysts, the recyclability and recovery are very much sought after in industry [33]. The Knoevenagel condensation as mentioned earlier is a nucleophilic addition of the active hydrogen compound to a carbonyl group. Here, the ketone or aldehydes with activated methylene are converted to a substituted olefin employing an amine base catalyst. A catalyst deprotonates an activated methylene using the catalyst producing a resonance stabilized enolate. An intermediate (iminium ion) is formed when the catalyst reacts with the ketone or an aldehyde. The enolate then attacks the intermediate ion. The formed intermediate compound gets deprotonated by a base to form another enolate. The intermediate of the amine on the other hand is protonated. The intermediate of the amine base is then released by the ensued rearrangement which regenerates a catalyst and olefin final product is formed [34]. An efficient, novel and environmentally benign MgO/ZrO_2 catalyst for the Knoevenagel condensation was investigated by Gawande and co-workers [35]. The 15.85 wt. % MgO/ZrO_2 was synthesized by method of co-precipitation. The basic MgO/ZrO_2 catalyst activity was determined by employing different types of aromatic aldehydes. The active methylene reagents used were ethyl cyanoacetate and malononitrile. It was clearly displayed that MgO/ZrO_2 is a good catalyst due to high surface area on the mixed oxides and component effect. Recyclability studies were done on the same batch of the catalyst and observations showed that the MgO/ZrO_2 activity was somewhat reduced past the 5th cycle. This work offered an easier approach of aldehydes with active methylene in Knoevenagel condensation under solventless conditions, in the production of α-cyanocinnamates in good yield utilizing recycled MgO/ZrO_2.

On the same type of reaction with a different catalyst employed, Reddy *et al.* [36] studied the condensation of several aldehydes, aromatic, aliphatic and heterocyclic reacted with malononitrile. They were performed in a one-step liquid phase using a solid acid catalyst, sulphate-ion promoted ZrO_2. The catalyst accelerates the reaction under solventless conditions in modest temperatures furnishing excellent product yields. The catalysts was prepared by dissolving the fine powder of

$Zr(OH)_4$ into 1M H_2SO_4 solution, dried and calcined at 650 °C. The hydrolysis of a dilute aqueous NH_3 with a solution of aqueous $ZrOCl_2{\bullet}8H_2O$ was used to prepare $Zr(OH)_4$. The physicochemical properties of the catalyst were determined by PXRD, BET, TPD-NH_3 and Raman spectroscopy techniques. Significant changes were observed on the surface and bulk properties of ZrO_2. At ambient conditions, a metastable ZrO_2 phase (tetragonal) is stabilized by the impregnated sulfate-ions, enhancing the strength and total number of acidic sites.



Scheme 1.1: General mechanism of Knoevenagel condensation [33].

The sulfate-ion promoted ZrO_2 exhibited superior catalytic conversions for the Knoevenagel condensation of different aromatic, aliphatic and heterocyclic aldehydes with malononitrile. The noticeable significance is that this catalyst accelerates the reaction under solventless conditions and present better reusability capacity. This study established a plausible use for sulfate-ion promoted ZrO_2 catalyst for synthesis of organic molecules and transformation reactions.

The reaction of aromatic aldehydes and active methylene compounds to prepare arylidene compounds at room temperature by grinding the reactants using a mortar and pestle in the presence of triethylbenzylammonium chloride (TEBA) over phase-transfer catalyst was studied by Rong *et.al* [37]. The findings showed that the reaction was efficient and high yields were achieved. To extend the study, an investigation of the employment of different phase-transfer catalysts was conducted. The 4-dodecylbenzenesulfonic acid (DBSA), Hexadecyltrimethylammoinium bromide (HTMAB), and again triethylbenzylammonium chloride (TEBA) gave catalytic activity of 55, 70, 89 - 90 % yield, respectively. TEBA displayed the supreme catalytic effect (80 – 90 % yield). The reaction was examined by different types of aromatic aldehydes containing electron withdrawing such as –Cl and $–NO_2$ or electron donating groups such as $–N(CH_3)_2$ and $–OCH_3$ as substrates. The expected result attained for all the substrates tested were good to excellent yields, and the reactions completed within short reaction times. It also showed that the condensation of aldehydes bearing electron-withdrawing groups in the aromatic ring, with active methylene compounds, could be carried out in relatively shorter times with relatively higher yields compared to those bearing electron donating groups. For product identification, the physical information was used to compare the ^1H NMR and IR spectra with those in literature. The development of a green Knoevenagel condensation between different aldehydes and active methylene compounds in the presence of TEBA catalyst, employing a method of grinding was successfully developed. Compared with the definitive heating procedures, the foremost advantages of this method are better yield, moderate reaction condition, easier procedure and short reaction time.

The grinding method was further investigated by Muralidhar and Girija [38] who worked onto developing an auxiliary method, more exceptionally with the application of simple, novel, efficient, better yields, cost-effective and green methodologies. Grinding method with solvent-free reaction offers extra advantage, the reactions complete within minutes instead of long hours. This method offered faster rates of reaction coupled with economically viable methods of conducting reactions and without a need for employing special techniques like microwaves. The products were characterized by comparing their physical data with reference samples or by comparing their IR and NMR spectra. The reaction completed within two minutes achieved a yield of 98 %. Under the same reaction conditions, the amount of catalyst optimized got supreme yield in a lesser time. It was established that 1 mol % of catalyst is adequate in facilitating the reaction to achieve high yield as 98 % in two minutes. This material did not tailor the rate of reaction or product yield produced at more than 1 mol % or less. The reaction generality and the scope were extended by treating different aromatic aldehydes with malononitrile and ethyl cyanoacetate. Heteroaromatic aldehydes such as furfuraldehyde was also reacted with either malononitrile or ethyl cyanoacetate compound to achieve excellent yield. There was also no influence on the yields from the aromatic aldehydes products bearing electron withdrawing groups like the halogens, NO_2, or electron donating groups $–CH_3$, $–OCH_3$, –OH.

Solvent-free Knoevenagel condensation was also studied using the grindstone method by Pasha and Manjula [39] who described their work on the successful synthesis of arylmethylidenes from araldehydes and active methylene compounds catalyzed by catalytic amount of $LiOH{\bullet}H_2O$ under solventless conditions employing grindstone method. The products were identified with ^{1}H NMR, FTIR and LC-mass spectroscopy. The amount of the catalyst had a crucial effect on the Knoevenagel condensation. The 4-methoxybenzaldehyde was treated with ethyl cyanoacetate and lithium hydroxide to get ethyl-(E)-2-cyano-3-(4-methoxyphenyl)-2-propenoate. An 82% yield was obtained after grinding for ten minutes. Reducing the amount of the catalyst from 0.5, 0.25 and 0.1 mmol resulted in increasing reaction yields from 88, 92 and 98 % respectively. From this study it is clear that, the use of just 0.1 mmol lithium hydroxide at 26 °C in less than one minute under grindstone method is sufficient to facilitate the reaction. Higher amount of the catalyst did not increase the product yields. Therefore 0.1 mmol LiOH was chosen for further reactions. By using 0.1 mmol of LiOH as a catalyst in a solventless grindstone reaction, a study was conducted to investigate the Knoevenagel condensation of a series of araldehydes possessing electron withdrawing groups and electron donating groups with active methylene compounds. From the results, it is clear that excellent yields were achieved within one to five minutes. The reaction of benzaldehyde and ethyl cyanoacetate with different catalysts and solvents was carried out at 26 °C and found that, use of lithium hydroxide under solvent-free grindstone method gives the desired products with excellent yields.

Dumbre and co-workers [40] studied the Knoevenagel condensation of aromatic aldehydes with active methylene compounds employing a highly efficient and thermally decomposed Ni–Fe–HT under solventless conditions at 600 °C. The thermal decomposition of the catalysts was to establish a mesoporous metal oxide. The solid catalyst employed was attained by calcination of the Ni–Fe layered hydroxide (hydrotalcite-like). The synthetic approach applied here to attain Ni–Fe–HT catalyst was somewhat tailored from the general method of synthesizing layered hydroxide structures. The reaction product was isolated by the column chromatography and proven by its NMR spectra which compared well with that of authentic product. Hydrotalcite like structures usually form when metal precursors that are divalent and trivalent are hydrolyzed under basic conditions. The formation of their layered hydroxide resulted when nickel and iron nitrate are hydrolyzed. Mixed metal oxides are formed when the material is calcined at 600 ℃ forming their porous structures when the hydroxyl groups undergo dehydroxylation and condensation processes. Therefore, XRD of the calcined and dried material was done to ascertain the structural significant changes. The potential of the free ligand Ni–Fe material in solventless conditions was investigated with Ni–Fe–HT catalyzed condensation reaction between different aldehydes with active methylene compounds. A strong effect on the yield of product showed by the results is due to the various substituents present in both the substrates. The catalyst displayed a very high activity and selectivity and following high product yield in all cases. Aromatic aldehydes possessing electron withdrawing groups such as 4-nitro- and 4-chloro-benzaldehyde as well as aldehydes possessing electron-donating groups such as 4-methoxy, 3-methoxy, and 2-methoxy exhibited relatively high catalytic conversion and gave the desired products in good to excellent yields. Independent of its high conversion, the catalyst also exhibited excellent reusability with insignificant degradation in its conversion.

Mitra and co-workers [41] utilized microwave irradiation for enhancing Knoevenagel condensation reaction rate. The reaction between ethyl cyanoacetate and different aromatic aldehydes in the presence of ammonium acetate under solventless conditions was carried out. Knoevenagel condensation products with ethyl cyanoacetate have been utilized successfully in the synthesis of cyanocoumarins, marcaptopyrimidine as an intermediate for an antimetabolite, substrates for Guareschi reaction, and indanone derivatives for diterpene. For the aldehydes bearing two electron donating substituents in aromatic ring appear to decelerate the reaction rate due to slogging of aldehyde group. The unambiguous stereochemical assignment could not promptly be made based on single geometric isomers that were primary attained in all the cases.

Mogilaiah *et al.* [42] also reported the solventless Knoevenagel condensation on ethyl cyanoacetate and different aromatic aldehydes over NaF and LiCl under solventless conditions employing microwave assisted method. The compounds were synthesized and characterized using IR as well as ^{1}H NMR techniques. All the compounds were compared with the data of their known samples. NaF and LiCl catalysts results showed that both are suitable for the Knoevenagel condensation of aldehyde and ethyl cyanoacetate. Reason being, the attained yields employing both catalysts were found to be 92 - 99 %. The rates of reactions were very quick and completed in two minutes with excellent yields. The reaction process is efficient and environmental friendly. Further purification was unnecessary because the products attained were pure. Furthermore, using benzene as solvent was eluded. Therefore, Apparatus of Dean-Stark was also unnecessary for H_2O removal which eliminated the tiresome work-up. The same reactions were prolonged when executed at 140 - 150 ℃ (using an oil bath) which was the observed temperature after the microwave irradiation completed, the reactions were incomplete, even after twenty hours. The results thus attained showed the supreme performance of Knoevenagel reaction with microwave assisted in arid media. Furthermore, the reaction is facile, fairly general, efficient, and is devoid of side products. At ambient pressure the reaction proceeded efficiently with high yields in two minutes. The absence of LiCl resulted in the reaction not proceeding. The attracting features of this methodology are high purity products and its simplicity of the isolation procedure.

A sustainable approach of Knoevenagel condensation utilizing the microwave activation effect was investigated by Mallouk and co-workers [43]. The natural hydroxyapatite [$Ca_{10}(PO_4)_6(OH)_2$] (*p*-HAP) was used in solventless conditions. The porous calcium hydroxyapatites were also employed *viz*. *p*-HAP100, *p*-HAP300 and *p*-HAP800. They were synthesized by wet chemical method and thermally prepared at various temperatures; 100, 300 and 800 ℃, respectively. The reactions activated with *p*-HAP300 preceded efficiently and in short reaction times. Simple filtration was used to isolate the products and identified with the corresponding *E*-isomers. The conversions of electron-rich as well as electron-poor benzaldehydes to the corresponding alkenes showed good to excellent yields. This proved that the effect (electronic) was insignificant to the activity (89 - 98 %). From the first Knoevenagel condensation reaction, 46 % product yield was obtained. This however showed that benzaldehyde is light sensitive to the oxidation of air during the reaction. An 89 % yield was provided by employing N_2 or hydroquinone as antioxidant during the process. The utilization of microwave heating was pivotal to the push the reaction forward. The compounds were attained with 95 % yield when the experiments were conducted on 4-chloro- and 4-nitrobenzaldehyde under microwave activation. The poor yield (36 % and 28 %

respectively) were attained from conventional due to the production of side products that are dissimilar as attested by thin layer chromatography (TLC). Control experiments for all the reaction under the same conditions were conducted for the microwave effects in Knoevenagel condensation. For instance: 4-nitrobenzaldehyde and *p*-HAP300 were reacted in a preheated oil bath at 76 ℃ for 1 - 24 hours, under solventless conditions. The yield of product did not exceed 10 % (gas chromatography - mass spectrometry analysis), whereas under MW irradiation the same reaction resulted to a 96 % yield. This result clearly showed a significant unambiguous non-thermal microwave effect, which gave rise to the improvement of the catalyst's activity.

The exploitation of metal perchlorates in recent years has been reported. Their application as Lewis acids, the capability to coordinate 1, 3-bidentate substrates, their possibility to in promotion and reactivity in the Knoevenagel condensation in the presence of a perchlorate salt with β-diketones with aldehydes was investigated by Bartoli *et al.* [44]. To assess the reactivity of β-diketones, the reaction of acetoacetone with benzaldehyde in the presence of various catalytic systems was chosen, under solventless conditions at room temperature. In order to accomplish a conversion of 65 % of the desired product without by-products, a combination of 10 mol % $Mg(ClO_4)_2$ and 20 mol % $MgSO_4$ are one of the best obligatory conditions to be used. The formation of side products which was derived from the acetoacetone attack on the Knoevenagel adduct resulted due to temperature increase to 40 ℃, even after thirty hours. During the condensation reaction, the addition of $MgSO_4$ was necessary for H_2O molecules adsorption. The reaction was slow (55 % vs 65 % of conversion) when conducted in the presence of $Mg(ClO_4)_2$. The reaction over $Zn(ClO_4)_2 \bullet 6H_2O$ was ineffective compared to the other reactions, hence $Mg(ClO_4)_2$ was more effective than $Zn(ClO_4)_2 \bullet 6H_2O$. Knoevenagel condensation's reactivity is poor when employed on β-diketones, aliphatic and aromatic aldehydes. However, this approach is more suitable for the β-ketoesters reactivity systems.

A succession of Alkali-tailored metal oxides has been studied in order to understand the basicity and reactivity utilizing a solvent-free Knoevenagel condensation as a probe reaction. The investigation were conducted by Calvino-casilda *et al.* [45]. The hydrated and dehydrated, SiO_2 and Al_2O_3 metal oxides were synthesized by the alkali metal acetates impregnation. Hydrosulphurisation, decomposition of isopropanol and acetonylacetone cyclization were tested previously for the material's acid-base properties. Tailoring niobia support with alkali metal provides the catalysts (acid-base) that are highly selective in the process such as in the production of methanethiol. The silica and alumina impregnation with these alkali metals results in the generation of alkalinity. The matrices of the silica, alumina and niobia showed basic properties and most of their basic sites have the capability to abstract protons in the range $9 \leq pKa \leq 10.7$ and others are able to abstract protons with $10.7 \leq pKa \leq 13.3$. The basicity increase in the range $9 \leq pKa \leq 10.7$ and $10.7 \leq pKa \leq 13.3$ is due to the tailoring of the alumina and silica support with alkali metal species. Also, the increase in strong interaction of alkali metal-support was due to tailoring of niobia, reducing the existing basic cites ($9 \leq pKa \leq 10.7$). The catalyst showed sufficient basicity for proton abstraction. Thus, K/SiO_2 and K/Al_2O_3 are active and selective catalysts in this synthesis by the condensation of benzaldehyde and various substituted benzaldehydes with ethyl acetoacetate. Moreover, K/SiO_2 and K/Al_2O_3 showed more activity in this reaction compared to other solid basic catalysts as an alkali activated carbon, known as Cs-Norit.

The effect of V/P mole ratio of the catalyst in the Knoevenagel condensation reaction and the influence of substituent on the benzaldehyde in catalysis was investigated by Viswanadham *et al.* [46]. Keggin-type vanadium substituted phosphomolybdic with various mole ratios were prepared and characterized by XRD, FT-IR and RS. The acidity of the catalysts was confirmed utilizing NH_3-TPD. The relationship of the acidity of the catalysts was inversely proportional to the mole ratio. This relation was also confirmed by ^{31}P NMR analysis. Catalytic properties depend on the concentration of vanadium merged in PMA; hence the higher V/P mole ratio resulted in sophisticated catalytic activity. The PMA containing vanadium is competitive and showed superiority in Knoevenagel condensation under solventless conditions when compared with other catalytic systems, even employing solvents.

Zinc-exchanged Hβ and HY, thermally dealuminated Hβ, Hβ, HY zeolites were investigated in the liquid phase solventless Knoevenagel condensation [47]. The reaction between benzaldehyde with ethyl cyanoacetate was conducted. The imperative parameters that affect the yield on the reaction were considered. The parameters include the time, the catalyst loading, the temperature, and the type of catalyst. The Ethyl-2-cyano-3-phenyl acrylate achieved a yield that is considerably higher than the other catalysts. The reactions benzaldehyde/acetophenone with various active methylene groups was attempted. It was established that Znβ is a superior catalyst for Knoevenagel condensation. The Hβ zeolite was unfavorable for the production of the Knoevenagel product in the generation of Lewis acid sites during thermal dealumination. The benzaldehyde/acetophenone reacted with different active methylene groups. The chosen compounds included acetylacetone, acetoacetate, ethyl acetoacetate, diethyl malonate, methyl acetoacetate and malononitrile. The ethyl cyanoacetate showed to be a superior compound among all the chosen. The Knoevenagel product yield with benzaldehyde was higher than with acetophenone. This therefore confirmed the higher reactivity of benzaldehydes than the reactivity of ketones.

Pillai and co-workers [33] conducted the solventless Knoevenagel condensation experiments of different aldehydes and esters. The chosen aldehydes included benzaldehyde, 1-naphthaldehyde, 4-bromobenzaldehyde, 4-methoxhybenzaldehyde and esters included ethyl acetoacetate, ethyl cyanoacetate and diethyl malonoester. The cobalt hydroxyapatite (CoHAp) catalyst was synthesized and utilized on the reactions. The yields attained in the range of 35 - 96 %. From the results, CoHAp showed to be superior over FAp and other different heterogeneous catalysts. Each experiment was done three times by varying the catalyst amount in order to investigate the role and the effect of the catalyst. Similar reaction was conducted under the same conditions devoid of catalyst and the Knoevenagel product did not form within the required time (five minutes). The recyclability studies were conducted and the catalyst can be reused three times. Therefore, CoHAp can substitute the current homogeneous and many heterogeneous catalysts.

Pillai *et.al* [32] further studied the same reaction using different catalysts, reported the Knoevenagel condensation on different aldehydes: benzaldehyde, 4-methoxybenzaldehyde and 1-naphthaldehyde and esters: ethyl cyanoacetate, ethyl acetoacetate and diethyl malonoester under solventless condition over iridium hydroxyapatite (IrHAp) and Platinum hydroxyapatite (PtHAp) as a catalyst. Each reaction experiment was conducted out twice by changing the catalyst amounts as 0.05 and 0.10 g. The reaction with 0.05 and 0.10 g over IrHAp, 62 and 95 % of product yields were achieved respectively. Similarly, the experiment was conducted in the presence of 0.05 over 0.10 g of PtHAp, 65 and 91 % product yields were attained respectively. In general, the reactions catalyzed by IrHAp gave somewhat higher yields than reactions catalyzed by PtHAp. Overall, both catalyzed reactions by IrHAp and PtHAp were very proficient and gave excellent yields. It was observed that IrHAp and PtHAp catalyst was found to be better than other heterogeneous catalyst in the sense that it required a meagre quantity to provide a maximum yield.

The experiments on the use of FAp individually by water activated by H_2O, BTEAC together with FAp in the Knoevenagel condensation was conducted by Sebti *et al.* [48]. The reaction was between an aldehyde with activated methylene compound at room temperature under solventless conditions. Co-precipitation method used to prepare the FAp. Vacuum distillation employed for product isolation and ^1H NMR and FTIR techniques were used for product identification. Similar approach applied for the activated FAp with H_2O and BTEAC reactions. H_2O addition at the end of the reaction benefitted the reaction system. The yield of 98 % was attained for the FAp alone. In preparation of alkenes, the attained results were improved after the H_2O addition to FAp. Thus, after 15 minutes of reaction, the yields went from 25 to 98 %. This showed that the activation of the FAp is due to the addition of H_2O under solventless media. Adding BTEAC in the reaction led to an increase on FAp catalytic activity. The high yields of 93 - 98 % were attained within short reaction times. The addition of both H_2O and BTEAC simultaneously resulted to a superior activation for FAp. Under such conditions, the alkenes were attained in short reaction times with 96 to 98 % yields. Even over ammonium salts, H_2O was observed to play an essential role. The results attained in the reaction of FAp with BTEAC, with or without H_2O revealed increase rates of reaction in the H_2O presence.

Further investigations on HAp in the Knoevenagel condensation also activated by H_2O, BTEAC and both on their alkaline properties, Sebti *et al.* [49]. Here, various HAp materials were synthesized by differing Ca/P mol ratios and characterized by different physical methods. The synthesis of hydroxyapatite was in the experiments conducted with $CaNO_3$ and NH_3PO_4 with NH_3. The products were purified under vacuum and identified by ^1H NMR, ^{13}C NMR and IR techniques. It was observed that the Knoevenagel condensation got promoted by HAp alone. The rates of reaction were slow. However, prolonging the reaction, over 80 % yields were attained. The HAp possessed alkaline properties and from the results, a significant application of this catalyst to solid/liquid heterogeneous synthesis. A noticeable increase in yields also seen when introducing the BTEAC in the reaction. HAp are activated significantly in the alkene synthesis and the rates of reaction were drastically increased, hence over 90 % yields were achieved in short reaction times. The superiority on HAp activation with H_2O and NH_3 added simultaneously was clearly manifested. The method is versatile because the reaction rates were improved for the synthesis of alkene with short times. However, suggestions arose that the reaction may be further improved if the amount of BTEAC is increased and the simultaneous introduction of H_2O and BTEAC are best conditions to actually promote the Knoevenagel condensation.

A microreactor was tested employing Cs-exchanged NaX catalyst with NaA membrane in the Knoevenagel condensation under solventless conditions by Lau and co-wokers [50]. The substrates were benzaldehyde and ethyl acetoacetate. Major Knoevenagel products, 2-acetyl-3-phenylacrylic acid ethyl ester led to the formation of side product and poor selectivity. This was the result of laminar flow and the bulky products which were slowly diffused in the microchannel. Thin film of CsNaX for replacement of the powder catalyst increased the selectivity from 55 % to 78 %. The conversion was also doubled to 60 % from 25 % when the height-to-width ratio was increased. The removal of H_2O by product in microreactor assisted the reaction. Although the reactions of benzaldehyde and ethyl cyanoacetate, ethyl acetoacetate and diethylmalonate had the high conversions, the improvement got reduced with the increasing difficulty of reaction. The deposition of a hybrid NaA membrane-CsNaX film resulted in the high selectivity on 2-acetyl-3-phenylacrylic acid ethyl ester were attained. The SEM revealed that the morphology of the zeolite was deposited uniformly in the channel. The Cs ion exchanged successfully with a ratio of 0.63 Cs/ (Cs + Na) by XPS analysis. The sensitive bands at 745 cm^{-1}, 929 cm^{-1} and 1078 cm^{-1} displayed structure of the NaX and Cs-exchanged NaX films. The cesium ion-exchanged shifted the intensities or the locations of the IR bands.

Lai *et al.* [51], investigated Cs-exchanged NaX material prepared from NaX powder in order to test the membrane reactor performance for the Knoevenagel condensation reaction. An 85 % yield was attained from the microreactor membrane. A catalyst showed some agglomeration of zeolite in the SEM analysis. The catalyst displayed the morphology that is identical to NaX zeolite. Rough spherical shape with poor facets appeared on each crystal of zeolite. The diffraction pattern characteristics of the NaX zeolite were displayed from the calcined NaX powder. The intensities diminished diffraction lines due to ion exchange with the CsCl. Additionally, the surface area was slightly reduced from 430 to 400 m^2/g after Cs exchange.

Zhou and Sun [52] investigated Knoevenagel condensation reaction of one aromatic aldehyde and active methylene compounds using ethylenediammonium diacetate as a recyclable catalyst at room temperature in solvent-free condition. Melting points were recorded on a Thiele tube in open capillary tubes. The product identification was done by physical data and spectra comparison the attained products with the reported ones reported. The reaction between benzaldehyde with ethyl cyanoacetate was conducted in order to study the effect of catalyst loading. A 20 mol % was the optimum loading for ethylenediammonium diacetate. The catalyst amount was decreased to 10 mol % from 20 mol % in relation to substrates; an 87 % yield was not reduced instead longer reaction time required for reaction completion. However, 30 mol % of the catalyst 89 % yield did not change in the same time required. Furthermore, the effects of catalyst loading on the condensation of benzaldehyde and malononitrile were examined. In contrast to the condensation of benzaldehyde and ethyl cyanoacetate, the condensation of benzaldehyde and malononitrile could be completed in a short time with only 1 mol % of ethylenediammonium diacetate (96 %). With the results obtained, Knoevenagel condensation of ethyl cyanoacetate and malononitrile with different aromatic aldehydes was investigated. Aromatic aldehydes with electron-withdrawing or electron-donating substituents could react very well with ethyl cyanoacetate and malononitrile in a short time, and good to excellent yields were achieved. It should also be mentioned when reaction of 4-chlorobenzaldehyde with malononitrile was carried out in the absence of catalyst for a long period of time (2 hours) under solvent-free conditions at 65 ℃, the yield of product was poor (15 %). These results indicate that EDDA is an efficient catalyst. This followed by investigation on the reusability of EDDA. The recovered catalyst may be recycled for about four extra runs in successive reactions without significant reduction of the yields, indicating that EDDA is recyclable.

1.6 The VMgO catalyst

Elkhalifa and Friedrich [53] established the VMgO catalysts, with different vanadium concentrations, in the *n*-octane activation. The selectivity and activity of the catalyst were affected by the concentration of vanadium of textural and chemical properties. The VMgO catalyst with a 15 wt. % V_2O_5 loading had the highest selectivity to 1-octene and styrene. From another investigation, [54] it was demonstrated that the production of products such as octenes, ethylbenzene, styrene and to a smaller amount xylene over VMgO catalysts produced most and some cracking products under partial oxidation of *n*-octane. The presiding isomers of octene were found to be 2-octenes. The minor compounds were 4-octenes, implying that activation of *n*-octane was favored at C_2 and C_3 and vice versa at C_4. A presiding isomer over 15 wt. % vanadium supported on MgO was 1-Octene. The 50 wt. % vanadium supported on MgO presiding isomer was found to be 3- octane and 1-octene was the minor product. The 50 wt. % vanadium supported on MgO had the lowest aromatics correspondingly to highest activity to octenes. In the formation of 1-octene and styrene, 15 wt. % vanadium supported on MgO exhibited supreme results compared to the catalysts.

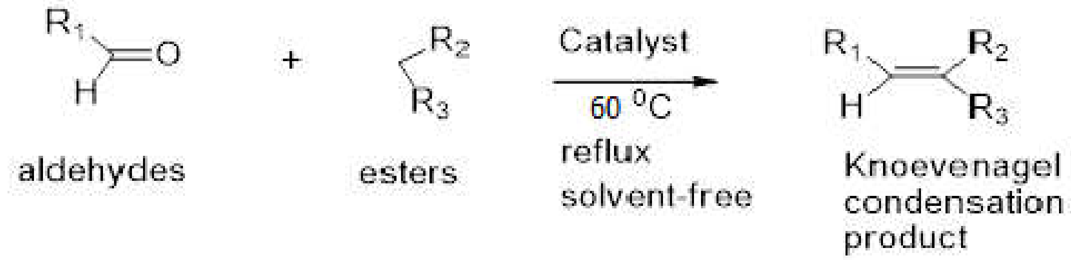
The effect of VMgO catalyst on the conversion and selectivity profiles in the reactor when diluted and also when combined with voids was established by Friedrich and co-workers [55]. The hexenes and the cracked products, namely propane, propene, butane, isomers of butane from the report in the literature were expected to be shorter through the reactor that is empty than the *n*-hexane on alkane reactions on gas phase. The diffraction peaks revealed Mg-orthovanadate presence in the VMgO catalyst. The VMgO diffractions were also showed. The IR bands were broader and implying that the catalyst was not fully crystallized. The IR spectrum of VMgO catalyst showed that orthovanadate phase was formed when vanadium was incorporated. Elemental analysis revealed the presence of 23 wt. % of V_2O_5 supported on 77 wt. % MgO elements. SEM of the surface of the catalyst showed expected round edges and EDX showed a 40 wt. % of V_2O_5 supported on 60 wt. % MgO in the catalyst. The products attained from a non-catalytic and the catalytic *n*-hexane oxidations were similar. The products attained from the reactor glass were also similar. Therefore it was concluded that the VMgO catalyst is a suitable catalyst for these reactions only because the catalytic conversions were higher at temperature up to 400 °C over MgO rather than its absence.

Kinetic studies were conducted on various hydrocarbons *viz*. *n*-butane, 1-butene, 2-butenes and as well as butadiene for selective ODH reactions [56]. In addition to this, the study of the intermediate addition method for the primary and secondary steps in oxidative dehydrogenation of *n*-butane was investigated. The catalyst, 30 wt. % V_2O_5 supported on MgO was synthesized by impregnation of MgO with a solution of NH_4VO_3. The ODH results on the hydrocarbons revealed that the 30VMgO activity is reduced in the 2-butenes>1-butene > *n*-butane ≫butadiene order. The high activation energy resulted to the reactivity differences between *n*-butane and butenes. At higher temperatures, the reactivity is reduced and leads to consumption of *n*-butane. Additionally, at higher temperatures, oxidation of butadiene proceeded at lower rates of reaction. The conversions of butenes to butadiene, having 65 % selectivity and only 5 % of the butenes are isomerized. The relative significance of primary and secondary approach and the reactions rate was elucidated by the employment of the product intermediate addition method. The results were evaluated and the network reaction analysis on oxidation dehydrogenation of *n*-butane catalyzed by 30VMgO revealed that butadiene and oxides of carbon are produced along with betenes from *n*-butane. These oxides are formed via deep oxidation steps and consecutive dehydrogenation of butenes. From directly *n*-butane, over 67 % of carbon dioxide and 70 % of carbon monoxide attained at 10

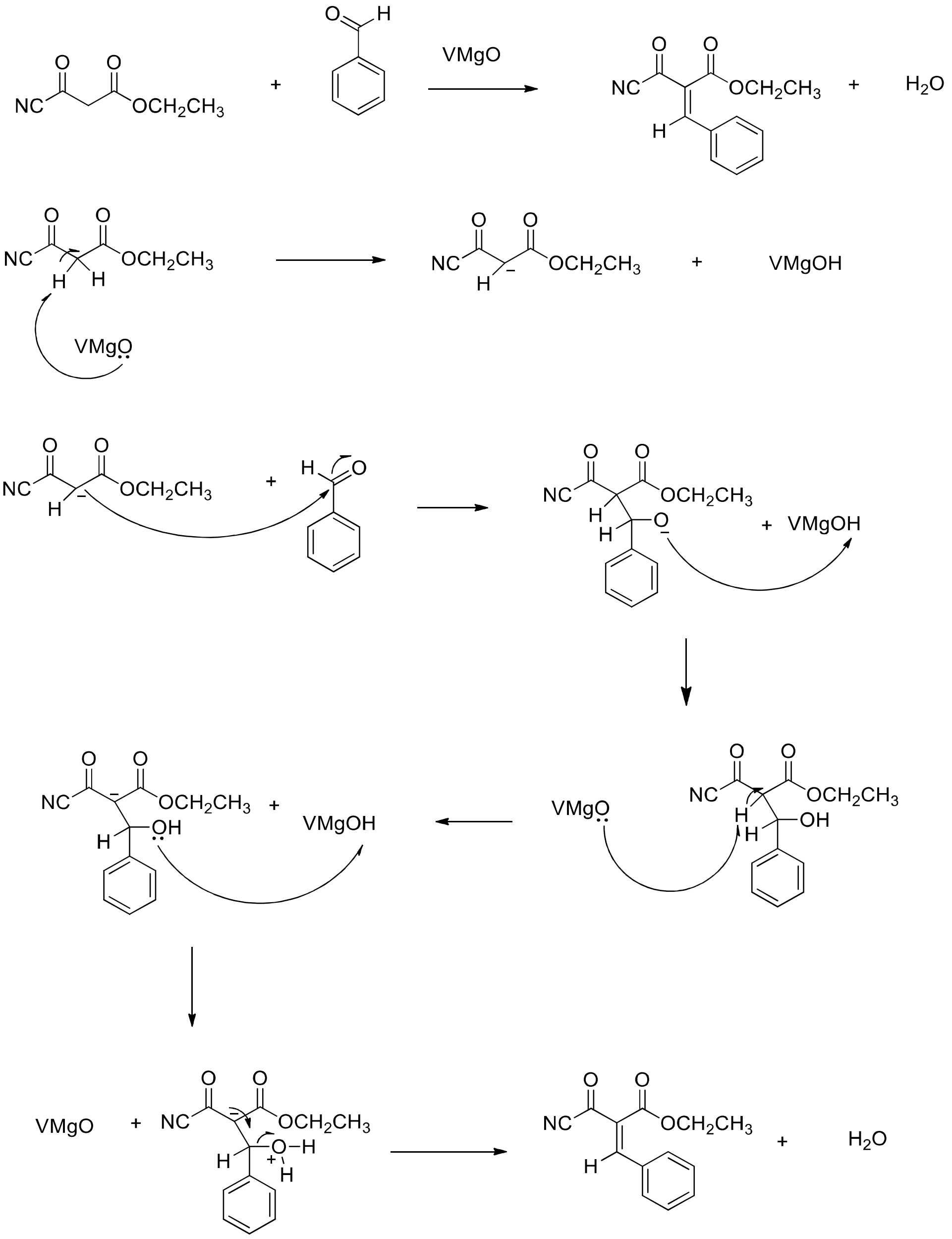
% conversion are produced. From the observation of the experiment, the increase in the partial pressure in analysis of butane, butadiene and CO had insignificant effect in the consumption rate of butane. The results attained preliminary under anaerobic conditions, provided an insight to alternative future applications of the 30VMgO in fluid bed reactors.

Physico-chemical properties of the V-Mg-O systems, clarifying the significance of preparation methods on their catalytic properties was further studied by Nieto *et al.* [57]. They also conducted studies on the oxidation dehydrogenation activity and selectivity of *n*-butane. This was done to actually gain an insight whether catalytic properties could be improved by using nitrous oxide than utilizing molecular O_2 as an oxidant. The results were attained from the extent of agreement between continuous flow and pulsed-reactant processes. The possible ODH mechanism of *n*-butane was also established. The VMgO catalysts were synthesized by variations of the wet-impregnation (utilizing $NH_4VO_{3\ (aq)}$) or organically based methanolic vanadyl acetylacetonate solutions. Results attained from the catalyst characterization techniques revealed that magnesium-orthovanadate ($Mg_3V_2O_8$) appeared to have poor crystallinity. The other magnesium vanadates presence was unclear. The isotopic exchange of O_2 experiments indicated that an R_2 process: [$^{18}O_2 + 2^{16}O^{2-}{}_{(s)} \rightarrow (^{18}O^{18}O^{16}O^{16}O)^{4-}{}_{(s)} \rightarrow 2^{18}O^{2-}{}_{(s)} + {}^{16}O_{2\ (g)}$] at temperatures higher than 1023 K. The R_0-type [$^{18}O_{2(g)}\ {}^{16}O_{2(g)} \rightarrow 2^{16}O^{18}O_{(g)}$] showed lower activity for the isotopic homophase at 823 K. The behavior observed that in oxidative dehydrogenation of *n*-butane with oxygen and nitrous oxide depends on the concentration of vanadium but independent on preparation methods. However, the *n*-butane conversion was found to be higher when utilizing nitrous oxide. The pulse experiments revealed that the surfaces that are prereduced are ineffective in the formation of olefins. Selective catalysts are formed with the surface that is preoxidized.

Solventless organic synthesis in recent years has received increased recognition due to escalating global demands and concerns over chemical waste and the resources of the future, in particular, from the green chemistry perspectives. Therefore, taking such facts into consideration and based on these evidences, we envisioned that VMgO supported catalyst could also be extended as a heterogeneous catalyst for the solvent- free Knoevenagel condensation. The results reported in the literature, confirmed the necessity of VMgO catalyst for the proposed Knoevenagel condensation of this study shown in Scheme 2 and the possible mechanism of the Knoevenagel condensation reaction of a carbonyl compound and an active methylene shown in Scheme 3.



Scheme 1.2: Knoevenagel condensation reaction [32, 33].



Scheme 1.3: Possible mechanism of Knoevenagel condensation between benzaldehyde and ethyl cyanoacetate over VMgO catalysts.

1.7 Motivation of the study, aims and objectives

This research is focused on heterogeneous catalysis with solvent-free Knoevenagel condensation with various aldehydes and esters as reactants. From this research we hope to study catalysis in detail on commercial applications, looking at numerous applications of catalysts in a small scale laboratory synthesis and also its use in industrial production of chemicals. Catalysts containing d-block metals are of immense importance to the chemical industry since they provide more cost effective syntheses and give high specificity of reactions rather than producing mixed products. The search for new catalysts is one of the major driving forces behind catalyst research. Current research also includes the development of environmentally friendly catalysts. The aims and objectives of this study include the following:

- To synthesize MgO supports using different precursors and to synthesize VMgO catalysts by wet impregnation.
- To characterize all the catalysts using various physico-chemical techniques such inductively coupled plasma optic emission spectroscopy (ICP-OES), X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), and infrared spectroscopy (IR).
- To test all the catalysts for the Knoevenagel condensation reaction.

CHAPTER 2

EXPERIMENTAL

2.1 Materials

Table 2.1 Materials used in the study.

Reagent / chemicals	Molar mass (g/mole)	Supplier	Purity (%)
$Mg(NO_3)_2•6H_2O$	256.4	Sigma Aldrich	98
$Mg(CH_3COO)_2•4H_2O$	214.4	Sigma Aldrich	≥99
$MgCO_3$	84.31	Sigma Aldrich	99.5
NH_4VO_3	157.3	Sigma Aldrich	99
HNO_3	63.0	Sigma Aldrich	55
HCl	36.5	Sigma Aldrich	47.0 – 49.0
C_6H_5CHO	106.1	Sigma Aldrich	99
$C_5H_7NO_2$	113.1	Sigma Aldrich	≥98
Na_2CO_3	105.9	Sigma Aldrich	≥99
$C_7H_5NO_3$	151.1	Sigma Aldrich	98
C_7H_5ClO	140.8	Sigma Aldrich	97
C_7H_5BrO	185.0	Sigma Aldrich	99
$C_8H_8O_2$	136.2	Sigma Aldrich	98

2.2 Catalyst preparation

The wet impregnation and deposition precipitation techniques were selected based on their effortlessness, simplicity on scale up and applicability to an industrial context. Wet impregnation encompasses the utilization of an excess solution with respect to the support pore volume. A mixture is left to age for a certain time (1-2 hours) under stirring, filtered and dried and calcined. The metal precursor concentration on the support depends on the solution concentration, pore volume of support or the type of adsorbing sites at the surface of the catalyst, hence encountering the interaction of precursor-support. The ammonium metavanadate precursor was chosen because of availability and cost. Deposition precipitation method involves the precipitation of the metal carbonate or hydroxide on powder support particles by the reaction of a base with the metal precursor. Metal distribution on support is affected by the nucleation rate and the growth of particles inside the pores. Ideally, faster nucleation and growth is unwanted since it produces large crystallites and in homogeneous distribution. Thus, an essential requirement for this preparation method becomes an efficient mixing in conjunction with a slow tallying of an alkali solution.

2.2.1 Synthesis of magnesium oxide from precursors

The MgO supports were prepared from the precursors; namely, magnesium carbonate, magnesium acetate tetrahydrate and magnesium nitrate hexahydrate by the calcination method. Calcination process causes the decomposition of the metal precursor which produces an oxide and generates gaseous products such as H_2O and CO_2. This heat treatment allows for the removal of these gases as well as anions and cations introduced in the preparation steps. The temperature (500 °C) chosen to calcine the catalyst is one that is higher than the temperature of the reaction. In addition, the heat treatment process is carried out in an oxidizing atmosphere. Not only can the process of calcination decompose the catalyst, it can also cause sintering of the precursor or the formed oxide and the possibility of a reaction between the formed oxide and the support occurring.

2.2.1.1 Synthesis of MgO from $MgCO_3$

The appropriate amount, 40 g of magnesium carbonate was calcined using the muffle furnace. The furnace was set at 200 °C, ramped at 20 °C until it reached 500 °C for 12 hours, yielding white fine magnesium oxide. The magnesium oxide attained was named as MgO(1).

2.2.1.2 Synthesis of MgO from $Mg(CH_3COO)_2 \cdot 4H_2O$

The appropriate amount, about 35 g magnesium acetate tetrahydrate was calcined using the muffle furnace. The furnace was set at 200 °C, ramped at 20 °C until it reached 500 °C for 12 hours, yielding light-grey magnesium oxide. The magnesium oxide obtained was designated as MgO(2).

2.2.1.3 Synthesis of MgO from $Mg(NO_3)_2{\cdot}6H_2O$

The appropriate amount, about 100 g of magnesium nitrate hexahydrate was calcined using the muffle furnace. The furnace was set at 200 °C, ramped at 20 °C until it reached 500 °C for 12 hours, yielding white magnesium oxide. The magnesium oxide obtained was designated as MgO(3).

2.2.2 Preparation of MgO by deposition precipitation method

The appropriate amount of $Mg(NO_3)_2{\bullet}6H_2O$ was dissolved in 50 mL of deionized water and precipitated with Na_2CO_3 by adjusting pH to ~8-10. The solution was then left to stand for 48 hours to allow the precipitate to settle. The settled precipitate formed at the bottom without disturbing. The solution layer was decanted using the bulb pipette. The precipitate was dried overnight at 110 °C and then calcined at 500 °C for 4 hours, ramping the temperature at 20 °C in a static air furnace and the magnesium oxide obtained was designated as MgO(DP).

2.2.3 Preparation of MgO by precipitation method

The appropriate amount of $Mg(NO_3)_2{\cdot}6H_2O$ was dissolved in in 50 mL of deionized water and precipitated with Na_2CO_3 by adjusting to pH ~8 - 10. The solution was filtered using filter disc (150 mm, 84 g/m^2, BOECO Germany), the precipitate was washed three times with deionised water, overnight dried at 110 °C and then calcined at 500 °C for 4 hours, ramping the temperature at 20 °C in a static air furnace and the magnesium oxide obtained was designated as MgO(P).

2.2.4 Synthesis of vanadium magnesium oxide (VMgO)

Vanadium magnesium oxide catalysts with varied amount of vanadium (1.5, 3.5 and 5.5 wt. %) were prepared using the MgO synthesized by deposition precipitation and commercially purchased ammonium metavanadate by wet impregnation. Proper amount of magnesium oxide in the catalysts 1.5, 3.5, and 5.5VMgO were 9.4554, 5.3632 and 3.4541 g of MgO; respectively, to a well-stirred ammonium metavanadate solution. Continuous stirring of the suspension under thermal heating resulted in a paste. The paste was dried overnight at 120 °C. The product attained was grinded with mortar and pestle and calcined at 500 °C for 4 hours, ramping the temperature at 20 °C in a static air furnace. The calcined catalysts were pale-yellow in colour. The catalysts were labelled according to the notation shown in Table 2.2.

Table 2.2 Labels and compositions of catalysts

Catalyst	Theoretical mass of V (wt. %)	Theoretical mass of MgO (wt. %)
MgO(1)	0	100
MgO(2)	0	100
MgO(3)	0	100
MgO(DP)	0	100
MgO(P)	0	100
1.5VMgO	1.5	98.5
3.5VMgO	3.5	96.5
5.5VMgO	5.5	94.5

2.3 Catalyst characterization

The techniques used in the characterization of freshly synthesized catalysts were powder X-ray diffraction (XRD), inductively coupled plasma-atomic emission spectroscopy (ICP-AES), scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS) and Fourier Transform Infrared spectroscopy (FTIR).

2.3.1 Inductively Coupled Plasma-Atomic Emission Spectroscopy

Inductively coupled plasma-atomic emission spectroscopy (ICP-AES) was used in the determination of composition of elements present in the catalysts. Generally, mineral acids such as nitric, sulphuric, hydrofluoric, hydrobromic, hydrochloric, phosphoric, perchloric and boric perchloric acid are used in dissolving the catalysts. Materials that were hard to digest were subjected to thermal heat treatment. The dissolved catalyst was diluted with deionized water bringing the concentration into an appropriate range. The samples were nebulized by argon gas flow and carried into the plasma of the instrument. Ionization of the samples occurred in the plasma and a solid-state detector was utilized to ascertain the wavelengths and intensities. The vanadium loading of each catalyst was verified by ICP-AES analysis using the ICPE-900 Shimadzu plasma atomic emission spectrometer. The appropriate concentration range of standards was prepared having the essential elements. The samples were digested with nominal quantity of aqua regia ($3HCl:HNO_3$). The calibration was done using 0, 3, 5 and 10 mg/L standards of vanadium that were prepared by ammonium metavanadate and sodium carbonate.

2.3.2 Powder X-ray diffraction

Powder X-ray diffraction (XRD) is a fundamental technique for the structural characterization of condensed materials. It provides invaluable evidence for bulk structures in various dimensions and chemical phase composition and yields information that allows for the identification of the crystalline phases within the catalysts. The crystalline materials with the domains which are greater than 3-5 nm are detected. The information is obtained by means of lattice structural parameters. An insight into the particle size is also obtained from the XRD data. This technique is attractive for catalyst characterization since the information obtained from the analysis is clear and can sometimes be obtained under reaction conditions. However, such information is obtained for large crystalline particles only; hence either too small or amorphous particles will not be detected. Powder X-ray diffraction (PXRD) patterns were recorded at room temperature on a Bruker D8 Advance diffractometer equipped with an Anton Paar XRK 900 reaction chamber, a TCU 750 temperature control unit. A Cu Kα radiation source was used with $\lambda = 1.5406$ Å. The range covered was between 2θ angles of 15° and 90°.

2.3.3 Scanning electron microscopy and energy dispersive spectroscopy

Scanning electron microscopy (SEM) is the most widely used type of microscopy to study the surface topography of a catalyst. The image is formed by focused electron beam that scans over the surface area of specimen. The focused beam of electron forms the image over the specimen surface area. The signals with different energies, photons, x-rays, the backscattered, auger and secondary electrons are generated by a finely focused electron beam which is scanned across. Secondary and backscattered electrons are very important in SEM because they are used to form images on the cathode-ray tube. The secondary electrons are produced when the electron beam interacts with the samples and the standard SEM detects the backscattered electrons [58].

In energy dispersive x-ray spectroscopy (EDS), the electrons generate the X-rays and these electrons are analyzed quantitatively and qualitatively by an energy dispersive detector. The X-ray characteristics emit along with backscattered and secondary electrons as high energy electrons strike the catalyst surface whose wavelength depends on the nature of elements present in a catalyst [59]. The characteristics of X-ray produced when the electron form inner shell gets knocked out of from the atom and the outer shell electron fills the vacant site. The particular atom characteristics is the amount of energy released and the excess energy released, that corresponds to the X-ray range [58, 60].

A clear evaluation in the morphology and as well as distribution of elements in the catalyst and the support materials was conducted by EDS and SEM. Prior to microscope, the powder samples were mounted into stubs and coated with gold. SEM micrographs and the images were attained utilizing a LEO 1450 SEM and also the EDS was carried out using Jeol JSM 6100 SEM equipped with a Bruker EDS detector. The detector was placed 20 nm from the specimen in order to collect as many X-rays as possible at an accelerating voltage of 3 eV.

2.3.4 Fourier transform infrared spectroscopy

Fourier transform infrared spectroscopy (FTIR) is a diagnostic tool utilized for the determination of functional groups present in the catalyst. In heterogeneous catalysis FTIR is basically used to study molecular structure of catalysts. Identification of the species adsorbed or reaction intermediates and their molecular structures on catalyst and the nature of acid-basic sites present on the surface of the catalyst during the reactions and preparations is done using this technique. Molecules vibrate or rotate at specific frequencies, and these frequencies correspond to vibrational energy levels of molecules and it is on this that IR spectroscopy is based. Inorganic and organic materials can be analyzed. A typical wave-number range covered by the vibrational spectroscopy is from 4000-200 cm^{-1}. The analyses were conducted with a Perkin Elmer Spectrum 100 FTIR equipped with a Universal Attenuated Total Reflectance (ATR) sampling accessory. IR spectra were recorded by placing a small quantity of the powdered catalyst onto ATR crystal and applying a pressure of ~60 gauge to accomplish good contact between the catalyst material and the crystal at room temperature. The spectra were attained for all the MgO as well as VMgO catalysts.

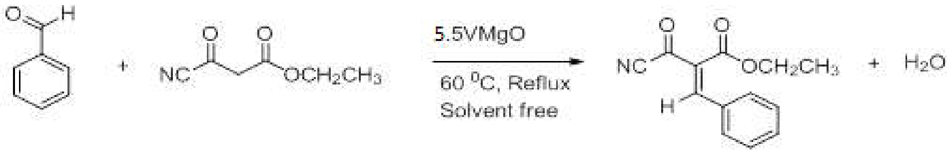
2.4 Catalytic testing

2.4.1 Knoevenagel condensation

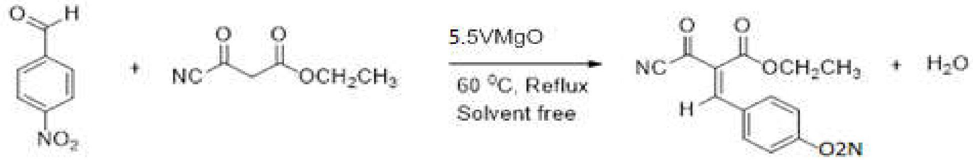
The reactions were carried out in a 100 mL round bottom flask fitted with a reflux condenser, magnetic stirrer and a $CaCl_2$ guard tube. The substrate (10 mmol), active methylene reagents (10 mmol) and catalyst were added to the flask heated in an oil bath at the 60 °C. The mixture was stirred with a magnetic stirrer and refluxed for the required reaction time.

2.4.2 Effect of substrates

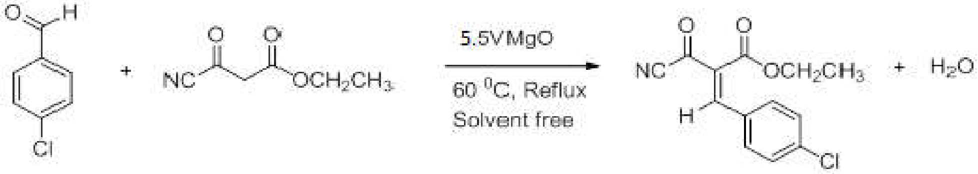
Various aldehyde substrates were used with its reaction with ethyl cyanoacetate to assess the effect on product yield and is demonstrated by the following reaction schemes:



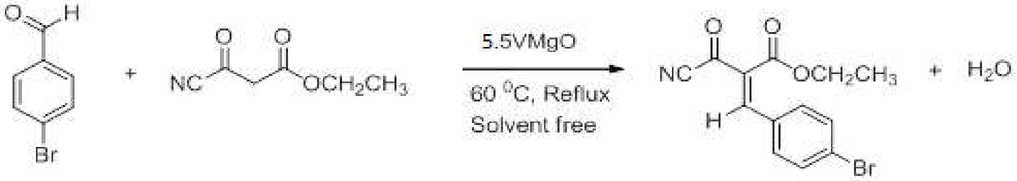
Scheme 2.1: Knoevenagel condensation reaction between benzaldehyde with ethyl cyanoacetate catalyzed by 5.5VMgO.



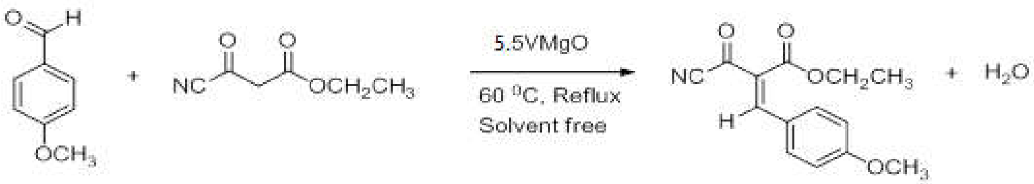
Scheme 2.2: Knoevenagel condensation reaction between *p*-nitrobenzaldehyde with ethyl cyanoacetate catalyzed by 5.5VMgO.



Scheme 2.3: Knoevenagel condensation reaction between *p*-chlorobenzaldehyde with ethyl cyanoacetate catalyzed by 5.5VMgO.



Scheme 2.4: Knoevenagel condensation reaction between *p*-bromobenzaldehyde with ethyl cyanoacetate catalyzed by 5.5VMgO.



Scheme 2.5: Knoevenagel condensation reaction between *p*-methoxybenzaldehyde with ethyl cyanoacetate catalyzed by 5.5VMgO.

2.4.3 Product analysis

The conversion of the aldehyde was determined using gas chromatograph (GC-2014, SHIMADZU) equipped with a capillary column and a flame ionization detector. The GC was calibrated regularly with calibration standards and the column was frequently baked out frequently to ensure a smooth baseline and consistent results. Nitrogen was utilized as a carrier gas and the total run time was 15 min. The sampling was done using a 1.0 μL syringe and directly injected into the GC, without further purification. The sample size injected was 0.1 μL. Appendix B: Table B1 shows the temperature programme and Table B2 shows the GC parameters used in this study.

CHAPTER 3

RESULTS AND DISCUSSION

3.1 Catalyst characterization

Vanadium supported on metal oxides have developed interest in catalysis, owing to their high activity and selectivity, low-cost, environmental benign impacts presented towards significant industrial routes [61]. The physical, textural and chemical properties were carried out to establish a clear evaluation using various techniques. The techniques provision and complement each other and together render the data essential to establish the properties of the catalytic material as well as those properties that impact the catalytic activity. Moreover, every effort has been made to establish the link between material structure and its related influence to activity or reactivity.

3.1.1 Inductively coupled plasma-atomic emission spectroscopy

The chemical compositions of the catalysts were determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) and the results are shown in the Table 3.1. All values obtained in triplicate and the samples were prepared in duplicate, with good agreement in the results obtained from the SEM-EDS analysis. The energy dispersive x-ray spectroscopy (EDS) was also used to analyze the catalysts, which is a localized technique. The vanadium content determined by ICP compared well to those determined obtained by EDS.

Table 3.1 Vanadium loadings in VMgO catalysts.

Catalyst	Nominal loadings	Actual loadings
1.5VMgO	1.50	1.30
3.5VMgO	3.50	3.30
5.5VMgO	5.50	5.20

3.1.2 X-ray diffraction

The powder XRD patterns of the magnesium oxides, prepared by deposition-precipitation and precipitation, are shown in Figure 3.1, whereas Figure 3.2 shows the diffractograms of the vanadium loaded on the MgO prepared by deposition-precipitation.

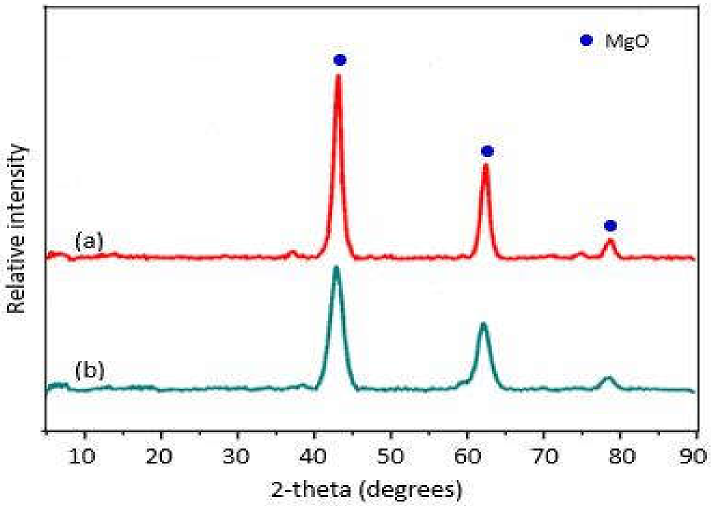


Figure 3.1 XRD diffractograms of (a) MgO(DP) and (b) MgO(P).

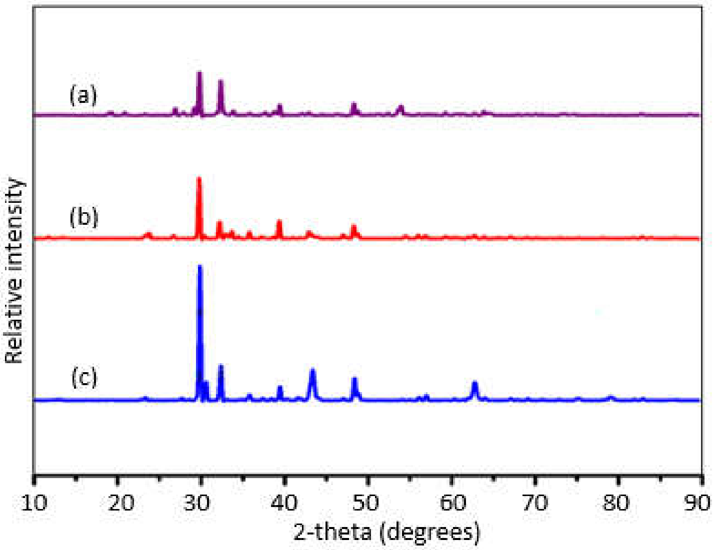


Figure 3.2 XRD diffractograms of (a) 1.5VMgO, (b) 3.5VMgO and (c) 5.5VMgO.

The X-ray diffraction patterns of all the catalysts are reflective of low crystallinity. The broad diffraction peaks of all the catalysts show the existence of magnesium oxide with its characteristic peaks at 2θ angles of 43°, 63°, and 78°. The diffraction patterns in Figure 3.2 reveal the formation of vanadium phases shown by peaks at 2θ equal 29° , 30°, and 33° due to vanadium and magnesium orthovanadate. A similar observation was reported for the VMgO catalyst in the ODH of short-chain alkanes [62]. The catalyst with low vanadium content (1.5VMgO) shows peaks of low intensity, implying low concentrations or poorly crystalline and highly dispersed. In general, the XRD patterns of the MgO and VMgO catalysts were similar to those previously reported [63-65].

3.1.3 Fourier transmission infrared spectroscopy

IR analysis was performed on all the supports and the vanadium loaded catalysts. Figure 3.3 shows the spectra of MgO(1), MgO(2) and MgO(3), each having seven absorption bands at 586, 1234, 1327, 2484, 2989, 3495 and 3765 cm^{-1}. The bands at 1234, 1327, 2484, 2989, 3495 and 3765 cm^{-1} are assignable to the O-H bending for the combined water molecule and the O-H stretching of the hydroxyl group, whereas the band at 586 cm^{-1} is linked to the bending vibration of Mg-O. MgO was the only phase that existed in these catalysts supports, no other bands were observed in the spectra, as the MgO was prepared from different precursors by calcination.

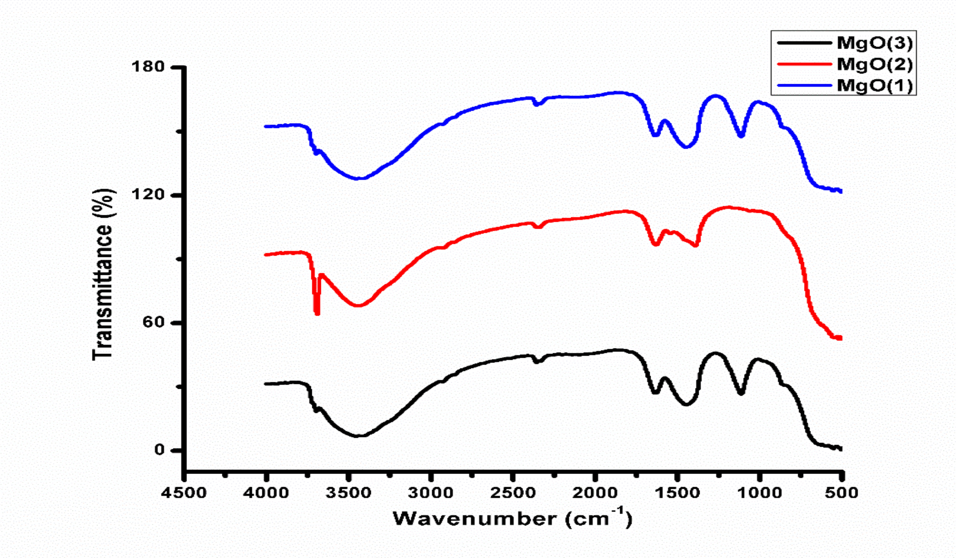


Figure 3.3 FTIR spectra of MgO(1), MgO(2) and MgO(3).

The morphological analysis of the prepared MgO supports by SEM and EDS image mapping showed that MgO was the only phase existed in these catalyst supports, in agreement with the results produced by IR. A similar trend is observed with the IR spectra of MgO(DP) and MgO(P) in Figure 3.4. The spectrum shows the absorption bands at 586, 1234, 1489, 1535, 2407, 3500 and 3600 cm^{-1}. Once again, the band at 586 cm^{-1} is due to MgO bending vibration of Mg-O, while the rest of the bands are assignable to the O-H bending for the combined water molecule (bending mode of water molecule) and the O-H stretching of the hydroxyl group. MgO was the only phase present in the catalyst.

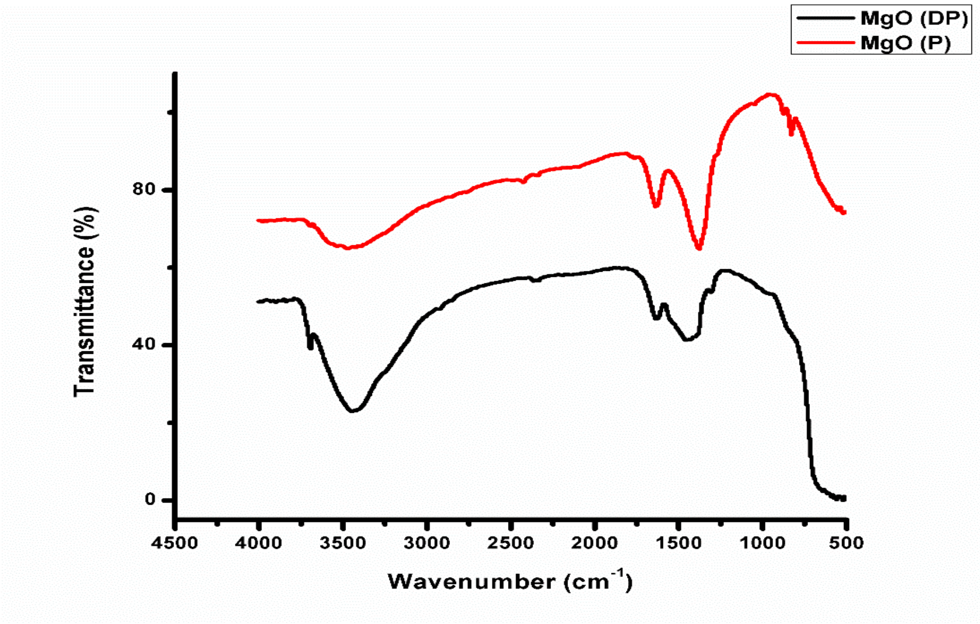


Figure 3.4 FTIR spectra of MgO(DP) and MgO(P).

Infrared spectra of the vanadium loaded catalysts in the region between 500 and 4500 cm^{-1} are depicted in the Figures 3.5. The presence of an intense band at 1697 cm^{-1} associated with pyrovanadate phase. The presence of bands at 1437, 1535, 1636 and 1936 cm^{-1} in the VMgO samples is the indication of the formation of magnesium vanadates phases [63]. However, in the case of the higher vanadium loadings, the pyrovanadate (1697 cm^{-1}), together with an additional orthovanadate phase (asymmetric stretching of the VO_4 group), with a band at 1936 cm^{-1}, are present.

The appearance of these bands has been related to the presence of other magnesium vanadates, i.e. MgV_2O_6 and $Mg_2V_2O_8$, or to be originated from low crystalline $Mg_3V_2O_8$ highly dispersed on the

MgO surface [66]. A noticeable feature is that the presence of pyrovanadate phase is more manifested with different vibration modes compared to that of 1 ,5VMgO and 3,5VMgO catalysts. The existence of different vibration modes between different phases is due to different interactions as the vanadium concentration increases. With it C_{2v} point group of symmetry, the pyrovanadate could vibrate either through the terminal VO_3, or the skeletal VOV bridge [63].

The bands at 1697 and 1936 cm^{-1} are due to the asymmetric stretching of the VOV group in the pyrovanadate and the asymmetric stretching of the VO_4 group in the orthovanadate, respectively. The band at 3600 cm^{-1} shows the absorption of free hydroxyl groups which is typical free for Mg-OH surface groups. For the higher vanadium loadings, the intensity of this band decreases after incorporation of vanadium, probably due to vanadium ions interacting initially with Mg-OH groups forming magnesium vanadate like species [66].

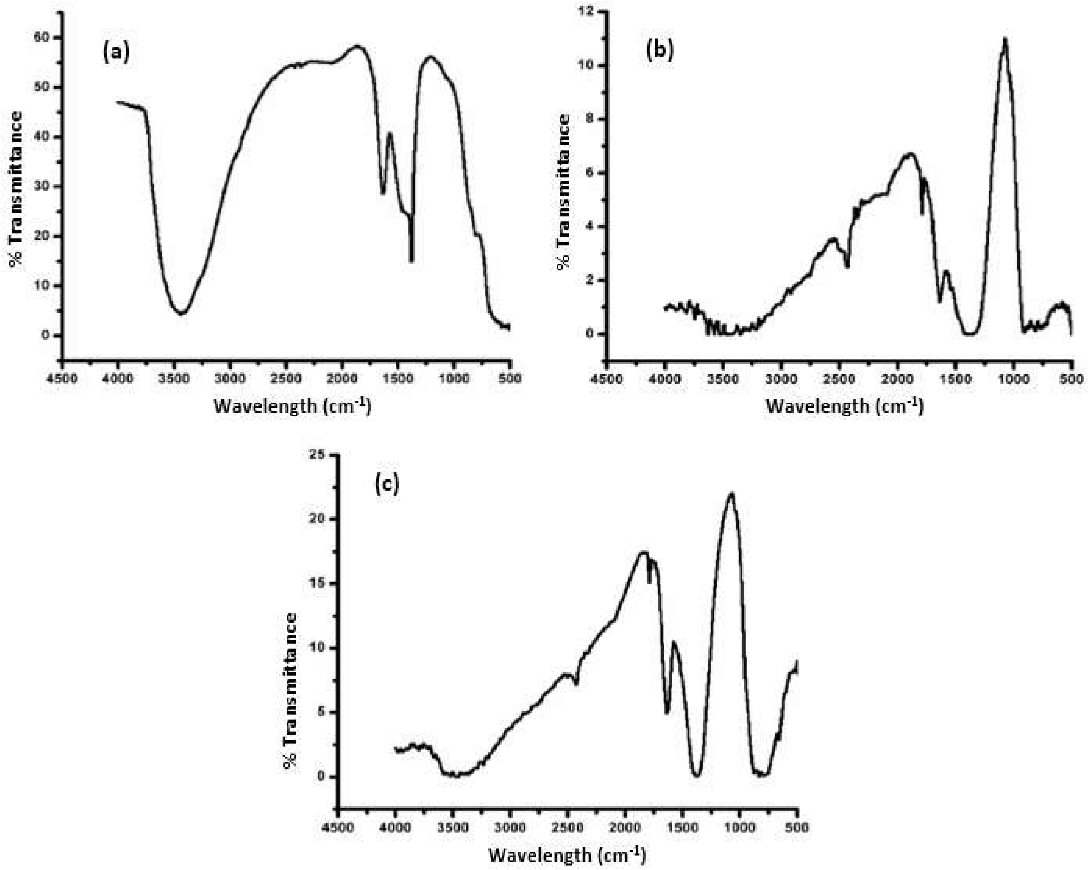


Figure 3.5 FTIR spectra of (a) 1.5VMgO, (b) 3.5VMgO and (c) 5.5VMgO.

3.1.4 Electron microscopy

3.1.4.1 Scanning electron microscopy

Analysis by means of SEM was carried out to obtain a clear evaluation of the morphology of the support and the catalysts as well as the elemental distribution of the catalyst samples. The pure morphology of MgO(1), MgO(2), and MgO(3), portrayed by SEM micrographs in Figure 3.6 (a), (b) and (c) reveal the irregular plates-like porous, fluffy particles and rough surfaces, respectively. The support (MgO) for these three catalysts was obtained by treating the precursors ($MgCO_3$, $Mg(CH_3COO)_2•4H_2O$ and $Mg(NO_3)_2•6H_2O$) under calcination at 500 °C for 12 hours. An obvious feature in the SEM image of MgO(3) portrayed by Figure 4.8 (c), is the large aggregates, moreover the cubic geometry of these aggregates can also be seen as bright particles that are randomly scattered over the catalyst surface.

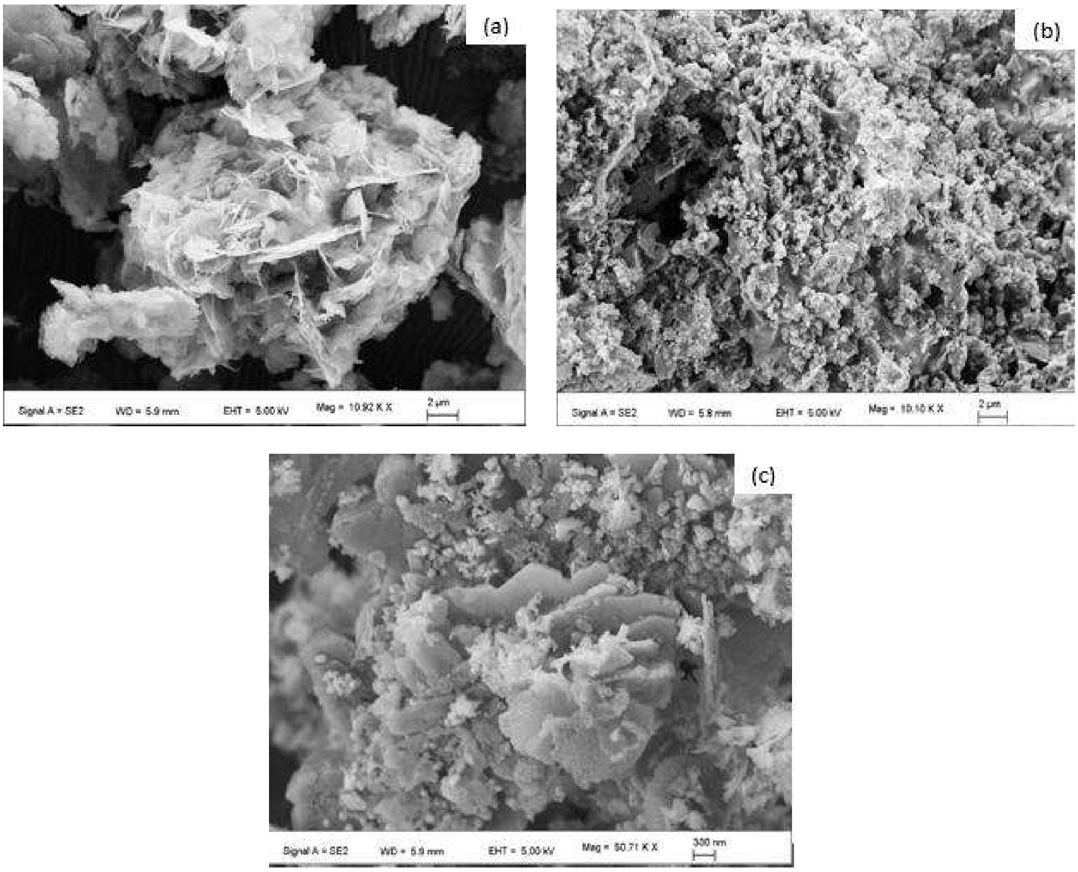


Figure 3.6 SEM micrographs of (a) MgO(1), (b) MgO(2), and (c) MgO(3).

The differences in the particle size and morphology in the micrographs maybe due to the different type of methods used on the precursors to prepare the supports MgO(1), MgO(2), and MgO(3). In summary, the SEM images indicate that the surface morphology was different over the catalysts and the surface morphology was more affected because of different precursors that MgO was prepared from rather than the chemical differences of these precursors [67].

Figure 3.7 displays the SEM images of magnesium oxide prepared by deposition precipitation and precipitation methods. The morphology of MgO(DP) reveals the large, round particles on the surface of the catalyst, while the morphology of small fluffy particles on the catalyst surface is displayed by the SEM image of MgO(P). Hence, it can be observed that the surface morphology is influenced by catalyst preparation method [67].

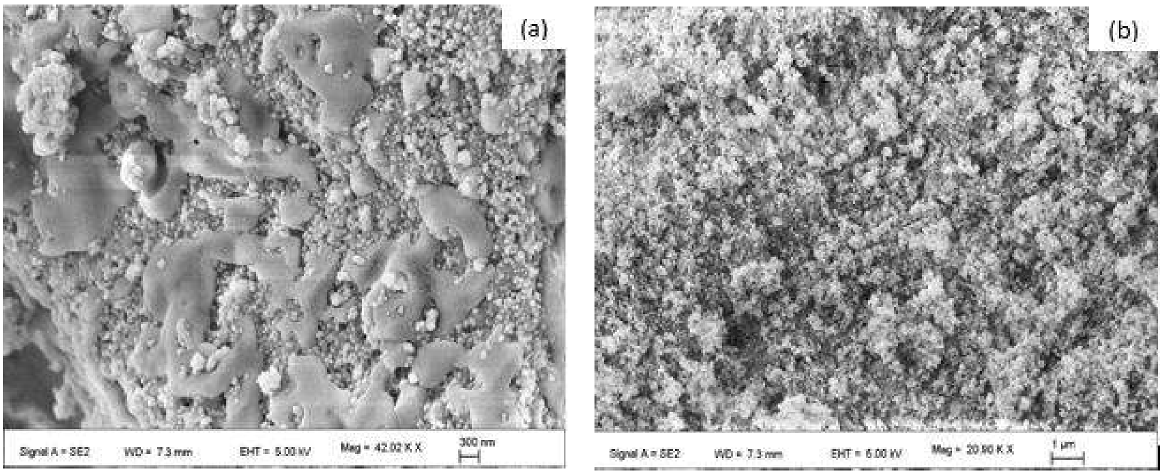


Figure 3.7 SEM micrographs of (a) MgO(DP), (b) MgO(P).

Much of the small platelets-like structures observed on the catalyst (1.5VMgO) surface displayed by the SEM micrograph (Figure 3.8(a)). With the low concentration of vanadium, the platelets-like structure becomes smaller, possibly undergoing fragmentation due to incorporation of vanadium. For the 3.5VMgO catalyst, aggregates of vanadium seem distributed over the surface of the catalyst. However, when reaching higher vanadium concentration (5.5VMgO), the surface of the catalyst becomes rough and increasingly stacked with cubic plates of nanovanadia being reflected on the image. In this regard, these SEM images indicate that the 1.5VMgO possessed the most uniform distribution of the vanadium on the surface of the catalyst [53].

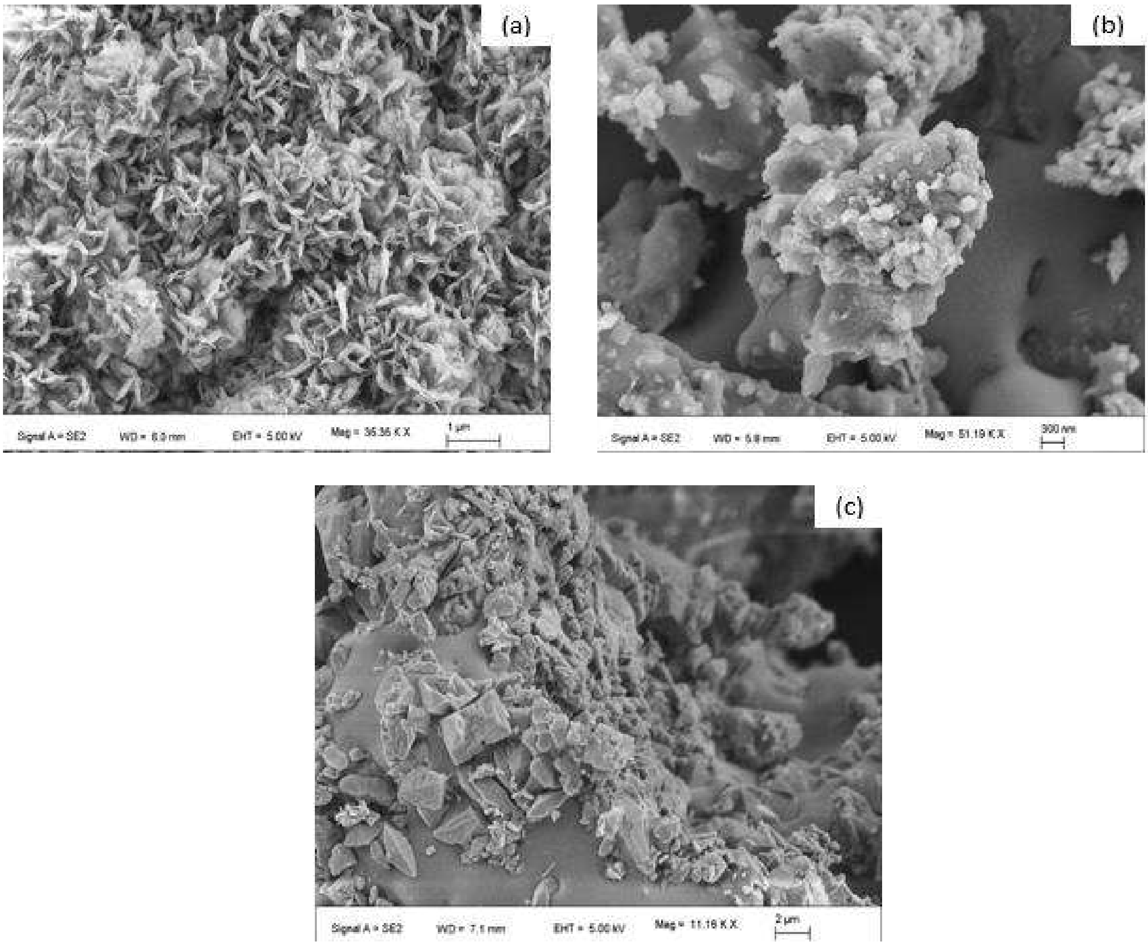


Figure 3.8 SEM micrograph of (a) 1.5VMgO, (b) 3.5VMgO, and (c) 5.5VMgO.

Additional images of all the support materials and catalysts are shown in the Appendix A. SEM images in Figure A1 of MgO(1), MgO(2), and MgO(3) shows the large cubic MgO particle on 50 000x magnification, giving a clear cubic particle shapes. SEM image in Figure A2 of MgO(DP) and MgO(P) shows the small round MgO shapes for both samples. MgO(DP), however, present a clear round shape of particles compared to the MgO(P). Mg(DP) was the best method and the catalysts support used to synthesize the VMgO catalysts. SEM images in Figure A3 of 1.5, 3.5 and 5.5VMgO shows the small platelets structures, round MgO shapes and large stacked cubic shapes, respectively. This also agrees with the effect on vanadium loading in the catalysts. The higher the vanadium loading the bigger the particle shape and the rougher the surface becomes.

3.1.4.2 Energy dispersive spectroscopy

Energy dispersive spectroscopy (EDS) analysis performed on the MgO(DP) support showed an even distribution of magnesium in the spectrum (Figure 3.10) and back scattered electron (BSE) mapping, Figure 3.9, showed the elemental composition which agreed with that obtained by ICP-AES.

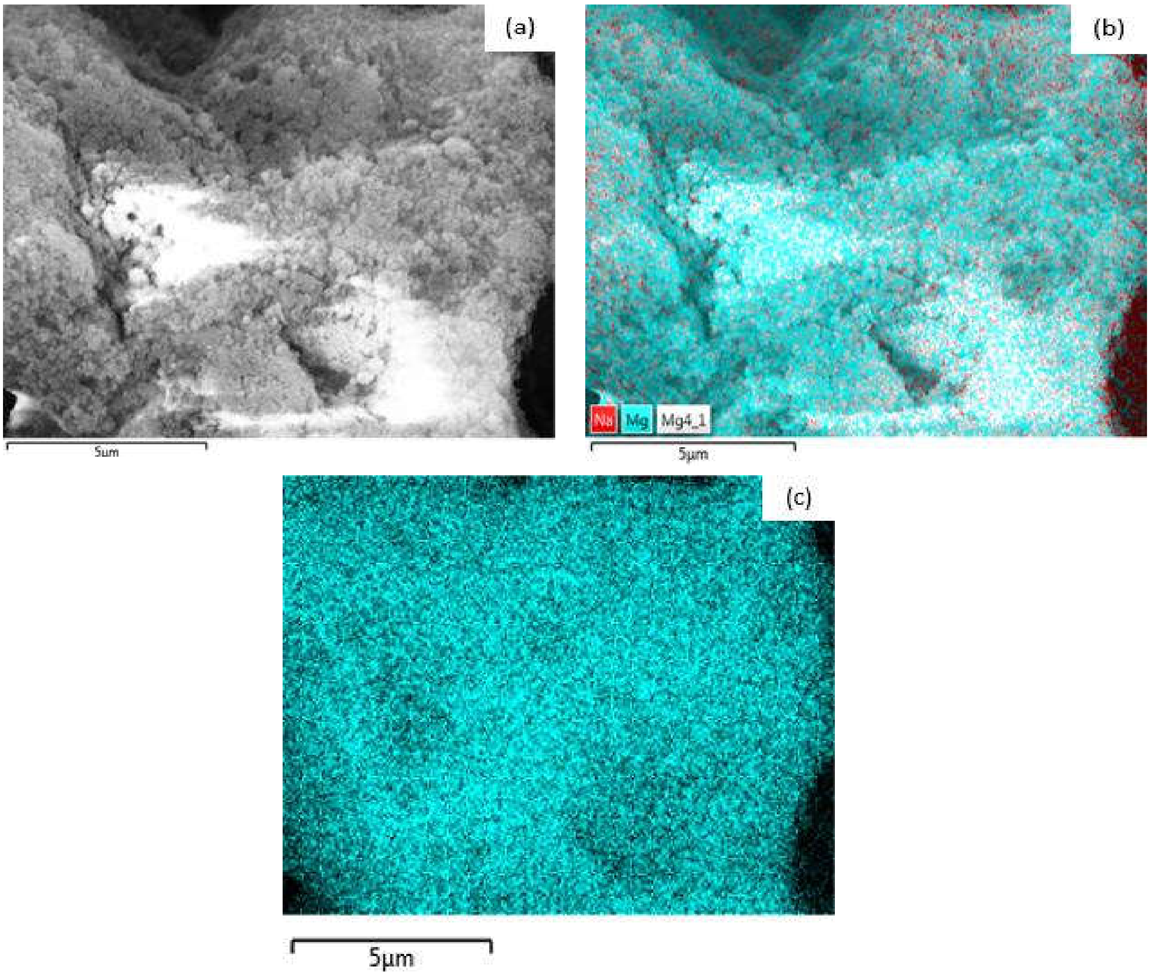


Figure 3.9 BSE SEM images of (a) MgO(DP), (b) overlay of elemental maps in MgO(DP) and (c) elemental map of magnesium.

The examination of the SEM images of the 1.5VMgO catalyst showed that a few porous platelets-like particles were present. EDS analysis performed on these platelets-like particles showed that they were composed of vanadium and magnesium. These elements are distributed over the catalyst as shown in Figure 3.11. This is in full agreement with the elemental analysis obtained from the ICP-AES. The EDS spectrum in Figure 3.12 also showed the elemental composition which agreed with that obtained by ICP-AES. The SEM images and BSE SEM mappings of the 3.5 and 5.5VMgO vanadium-loaded catalysts are shown in the Appendix A. BSE SEM mapping in Figure A4, EDS spectrum in Figure A5 of 3.5VMgO shows the elemental distribution of vanadium and magnesium over the catalyst and this is in agreement with the ICP-AES results obtained. BSE SEM mapping in Figure A6, EDS spectrum in Figure A7 of 5.5VMgO shows that vanadium and magnesium elements are distributed over the catalyst and this also is in agreement with the ICP-AES results obtained.

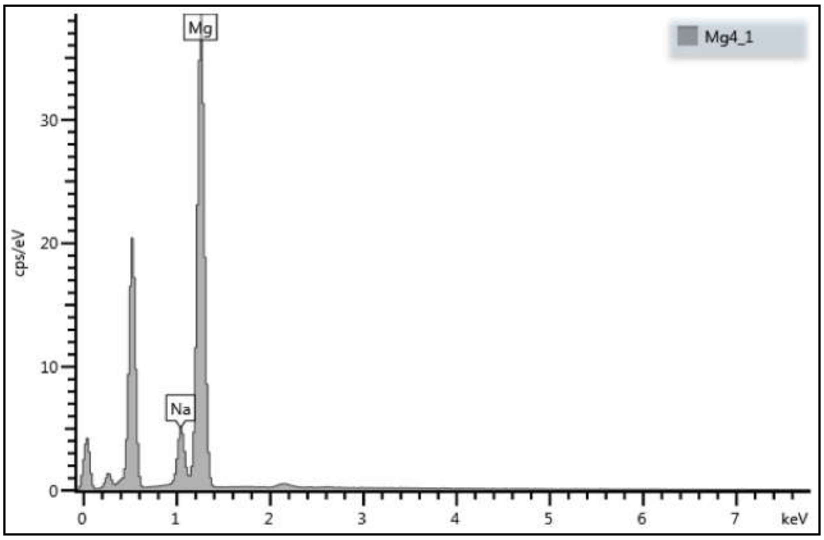


Figure 3.10 EDS spectrum of MgO(DP).

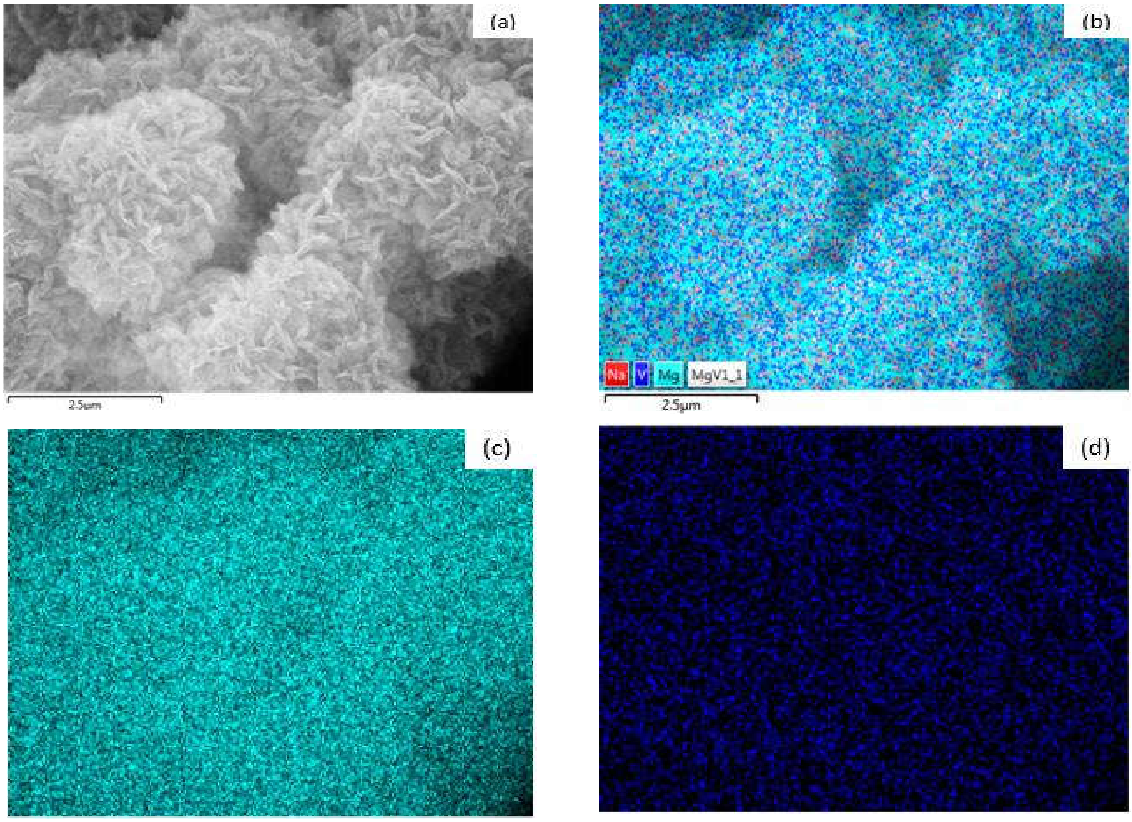


Figure 3.11 BSE SEM images of (a) 1.5VMgO, (b) overlay of elemental maps of magnesium and vanadium in 1.5VMgO, (c) elemental map of magnesium and (d) elemental map of vanadium.

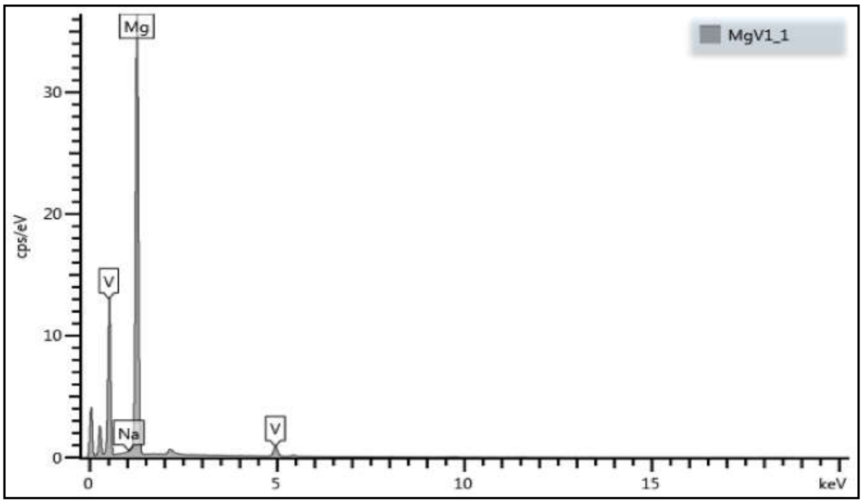


Figure 3.12 EDS spectrum of 1.5VMgO.

3.2 Catalytic testing

The section is focused on the catalytic activity of vanadium supported on magnesium oxide catalysts denoted as VMgO, where numbers preceding represents the nominal weight percentage of vanadium loading. Several investigations were carried out in an attempt to understand the stability and overall performance of these catalysts. Investigations in using different precursors denoted as MgO(1), MgO(2) and MgO(3); where numbers represents the type of the precursor used, effects by varying the amount of the catalyst, effect of different methods; where DP and P in MgO(DP) and MgO(P) catalysts represents the type of methods employed in the synthesis of the supports, and the effect of using different substrates were also carried out. The Knoevenagel condensation was carried out under solvent free condition in the presence of MgO and VMgO catalysts. Reactions were carried out in triplicate at constant temperature (60 °C) and reaction time (30 minutes). Reactions without the presence of the catalyst were carried out under similar conditions.

Magnesium oxide is amongst the most employed metal oxides in the discipline of catalysis, commonly used as a support, although its use as a catalyst is also reported in literature [63] Magnesium oxide has been used as a catalyst in oxidation of coupling methane [68], dehydrogenation-dehydration of alcohols [69], dehydrohalogenation of halogenated hydrocarbons [70], benzylation of aromatics [71], synthesis of pyranopyrazole derivatives [72] and Claisen-Schmidt condensation [73].

In this study, three magnesium supports were synthesized from different precursors, characterized and tested in Knoevenagel condensation reaction and the results are shown in Table 3.1 and Figure 3.13. Here, the effect of varying the amount of catalyst was assessed in the reaction of benzaldehyde with ethyl cyanoacetate. MgO(1) gave yields between 59 and 68 %, whereas MgO(2) and MgO(3) produced yields of between 44 and 65% and 53 and 73%, respectively. These results confirm that the varying the amounts of catalysts on the different types of supports had an effect on the conversion of the product. Increasing the amount of the catalyst leads to better yields. However, 0.05g of MgO(3) showed to be the better catalyst with a yield of 73 %. To estimate the aldehyde condensation that was due to factors other than the catalyst, the blank reaction was carried out under same experimental conditions, however no conversion was observed.

Table 3.2 The Knoevenagel condensation of benzaldehyde (10 mmol) with ethyl cyanoacetate (10 mmol) catalyzed by MgO(1), MgO(2) and MgO(3) catalysts at 30 minutes reaction time.

			Amount (g) of catalyst and yields (mol %)		
			0.01	**0.03**	**0.05**
Entry	**Catalyst**		**Yield**	**Yield**	**Yield**
1.	MgO(1)		57	61	68
			59	64	68
			60	62	68
		Average	59	62	68
2.	MgO(2)		43	52	67
			44	53	63
			44	54	66
		Average	44	53	65
3.	MgO(3)		51	59	73
			53	61	72
			55	64	73
		Average	53	61	73

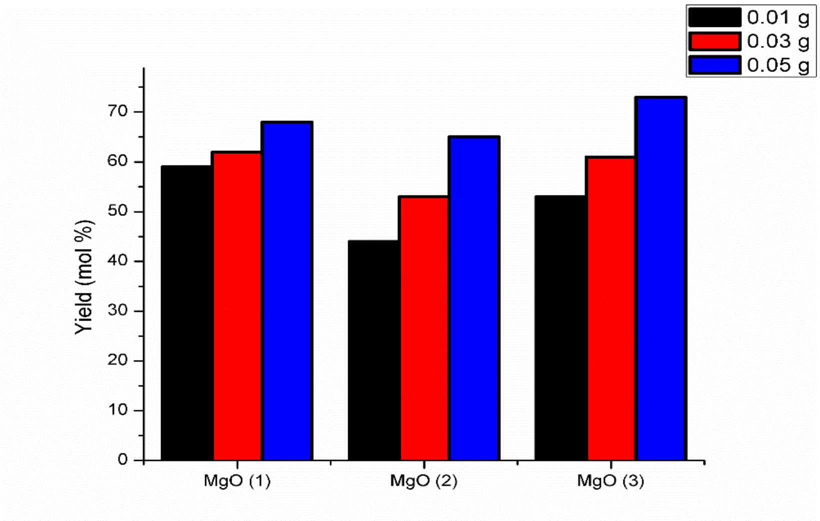


Figure 3.13 The Knoevenagel condensation of benzaldehyde (10 mmol) with ethyl cyanoacetate (10 mmol) catalyzed by MgO(1), MgO(2) and MgO(3) catalysts at 30 minutes reaction time.

Table 3.3 and Figure 3.14 show the effect of the precipitation method of magnesium oxide on the catalytic activity. Based on the results, the MgO prepared by deposition precipitation was catalytically more superior than the MgO prepared by precipitation for the Knoevenagel reaction. The 0.05 g of catalyst was chosen for the evaluation on the effect of different methods because it was the amount that gave the optimum yield (73 %) on the MgO(3), Table 3.2.

Table 3.3 The Knoevenagel condensation of benzaldehyde (10 mmol) with ethyl cyanoacetate (10 mmol) catalyzed by 0.05 g of MgO(DP) and MgO(P) catalysts at 30 minutes reaction time.

Entry	Catalyst		Yield (%)
1	MgO(DP)		80.88
			81.15
			83.05
		Average	81.69
2	MgO(P)		72.47
			70.25
			72.27
		Average	71.65

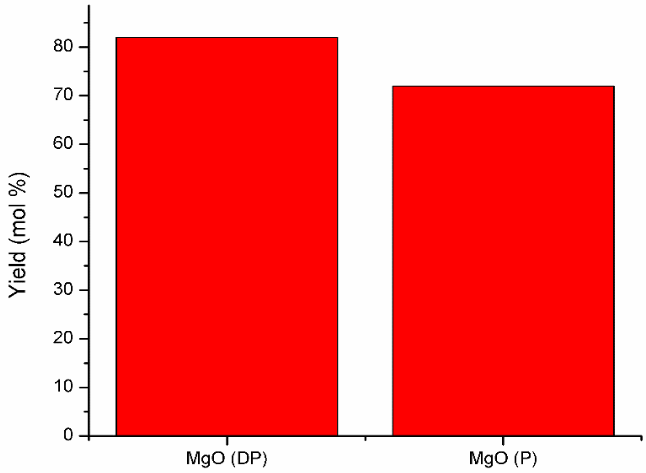


Figure 3.14 The Knoevenagel condensation of benzaldehyde (10 mmol) with ethyl cyanoacetate (10 mmol) catalyzed by 0.05g of MgO(DP) and MgO(P) catalysts at 30 minutes reaction time.

Due to its behavior in aqueous solutions, MgO is usually classified as a basic support. Chemically, an interesting feature related to MgO is that it is an irreducible oxide, with a very electropositive cation (Mg^{2+}), and the oxygen vacancies when formed are indeed anion vacancies with trapped electrons. Structurally, MgO is an oxide with a rock-salt structure, which means that on the surface each Mg^{2+} is surrounded by five O^{2-} ions. Magnesium oxide was reported to exhibit surface defects such as edges, corners and kinks; these surface defects were believed to play a role in the splitting of the chemical bonds of the adsorbed molecules and, thereby, may influence the catalytic performance of the MgO. Generally, the anhydrous surfaces of metal oxides possess two active sites, *viz*. the cations M^{n+} and the anions O^{2-} [63]. For the adsorption of organic molecules, an important step in the catalytic testing, the cations are likely to be the active sites and the metal oxide surface is predominantly acidic. MgO was used as support for vanadium to synthesize catalysts (VMgO catalysts) that were used for the Knoevenagel condensation with aromatic aldehydes and ethyl cyanoacetate. In these VMgO catalysts, the tetrahedral vanadium species are believed to constitute the active centres, with the general acceptance that the reaction mechanism takes place through the reduction–oxidation cycle between V^{5+} and V^{4+} [74]. Mg^{2+} is known for its low reduction potential, which makes it unlikely for MgO to get easily reduced to Mg^{1+} or Mg^0 during the catalytic testing. Thus, an important difference between V^{5+} in the VMgO system and Mg^{2+} is that the former, unlike Mg^{2+}, may easily be reduced to V^{4+} in the reduction-oxidation cycle that is believed to take place during the catalytic testing. Thus, in contrast to the VMgO system, the redox mechanism is unlikely to take place when MgO is employed as a catalyst, and as a consequence differences in the catalytic performance are expected [63]. Based on the information from the literature, and yield (82 %) obtained on MgO(DP), further investigations were carried to ascertain the effects of varying vanadium loading in the catalyst in an attempt to better understand the influence of vanadium on the condensation of benzaldehyde with ethyl cyanoacetate. The incorporation of vanadium onto MgO support was prepared using wet impregnation method. Table 3.4 shows the catalytic activity on the effect of vanadium loading using MgO(DP) support on 1,5, 3.5 and 5.5VMgO catalysts for the reaction of benzaldehyde with ethyl cyanoacetate gave the product yields of 85, 91 and 97 %, respectively. The yields are illustrated graphically in Figure 3.15.

Table 3.4 The Knoevenagel condensation of benzaldehyde (10 mmol) with ethyl cyanoacetate (10 mmol) catalyzed by 0.05 g of 1.5VMgO, 3.5VMgO and 5.5VMgO catalysts at 30 minutes reaction time.

Entry	**Catalyst**		**Yield (mol %)**
1	1.5VMgO		84.64
			85.89
			83.03
		Average	84.52
2	3.5VMgO		90.35
			90.64
			90.95
		Average	90.65
3	5.5VMgO		96.21
			96.50
			97.20
		Average	96.64

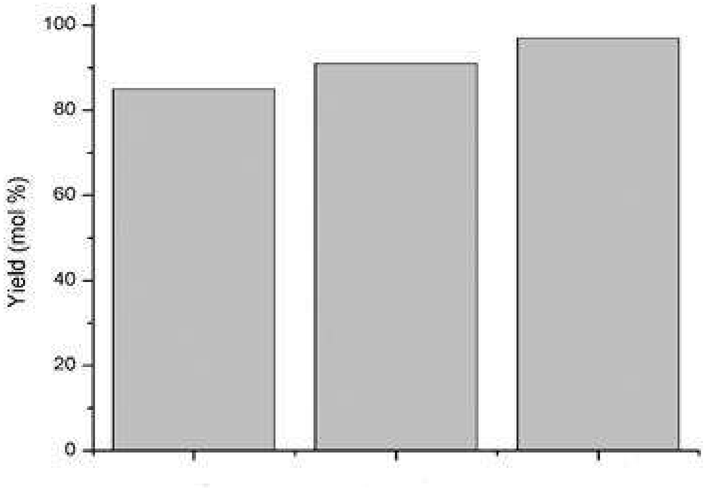


Figure 3.15 The Knoevenagel condensation of benzaldehyde (10 mmol) with ethyl cyanoacetate (10 mmol) catalyzed by 0.05 g of 1.5VMgO, 3.5VMgO and 5.5VMgO catalysts at 30 minutes reaction time.

The increase of vanadium on the supports resulted in the increased yields rather than with MgO(DP) alone; 82 % versus 97 % after 30 minutes. This catalyst was further used to study the catalytic activity on the effect of various aromatic aldehydes with ethyl cyanoacetate.

Because of its good catalytic activity (5.5VMgO with 97 % yield) in the reaction of benzaldehyde with ethyl cyanoacetate, the Knoevenagel condensation reactions of different aldehydes with ethyl cyanoacetate were carried out over the 5.5VMgO catalyst. The 5.5VMgO catalyst was utilized because it presented the excellent yield compared to 1.5 and 3.5VMgO catalysts. The reaction conditions: Aldehyde (10 mmol), ethyl cyanoacetate (10 mmol), 5.5 wt. % VMgO (0.05 g), temperature (60 °C), time (30 min), reaction ratio (1:1), solvent free. All conversions of aldehydes were above 91 %. The reactions of benzaldehyde, *p*-nitrobenzaldehyde, *p*-chlorobenzaldehyde, *p*-bromobenzaldehyde and *p*-methoxybenzaldehyde with ethylcyanoacetate gave products yield of 97, 94, 93, 96 and 95 % respectively and these results are summarized in Table 3.5 and Figure 3.16.

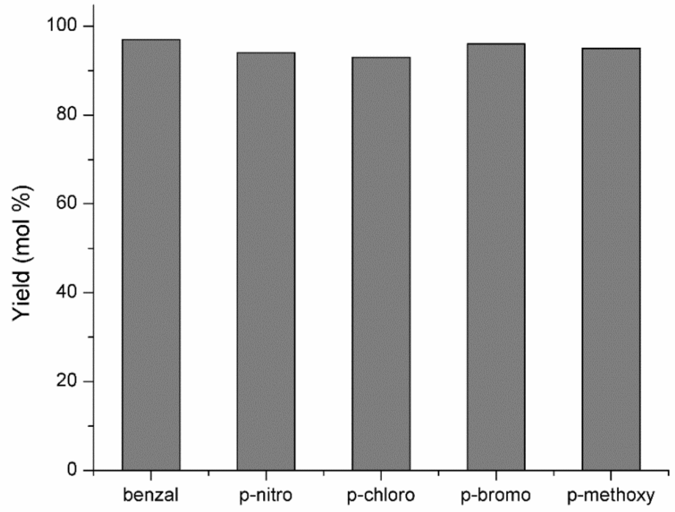
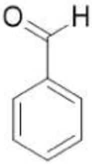
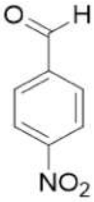
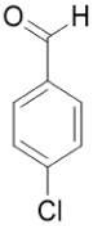
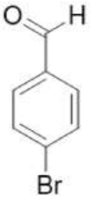
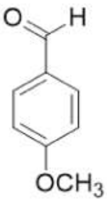


Figure 3.16 The Knoevenagel condensation of aromatic aldehydes with ethyl cyanoacetate catalyzed by 0.05 g of 5.5VMgO catalyst.

Table 3.5 The Knoevenagel condensation of aromatic aldehydes with ethyl cyanoacetate catalyzed by 0.05 g of 5.5VMgO catalyst.

Entry	Aldehyde	Ester	Yield (mol %)
1		-CN; COOEt	97
2.		-CN; COOEt	94
3.		-CN; COOEt	93
4.		-CN; COOEt	96
5.		-CN; COOEt	95

CHAPTER 4

SUMMARY AND CONCLUSIONS

The MgO supports were synthesized from three different precursors ($MgCO_3$, $Mg(CH_3COO)_2•4H_2O$ and $Mg(NO_3)_2•6H_2O$). The catalysts were characterized by ICP-AES, PXRD, FTIR and SEM and EDS. The MgO(3) showed the good catalytic activity using a mass of 0.05 g. The increment of the catalyst amount leads to a better catalytic activity. The magnesium nitrate precursor was also used to prepare the MgO using deposition precipitation and precipitation method. MgO(DP) showed good catalytic conversion (82 %). The effect of using different methods for supports synthesis was well manifested. The morphological analysis of the prepared MgO supports by SEM and EDS image mapping, showed that the MgO was the only phase existed in these catalyst supports and in agreement with the IR results. The elemental composition of the MgO prepared by precipitation and deposition precipitation methods were in agreement with SEM and EDS mapping, as magnesium and vanadium were the elements present in the catalysts.

Vanadium magnesium mixed oxide catalysts with variable vanadium loadings were successfully synthesized using a wet impregnation method and tested for the Knoevenagel condensation of benzaldehyde with ethyl cyanoacetate. The incorporation of vanadium into magnesium oxide showed the significant influence on physicochemical properties. Magnesium oxide and magnesium orthovanadate were found to be the only phases present in all catalysts. FITR spectra of 1.5VMgO, 3.5VMgO and 5.5VMgO, showed the band at 3600 cm^{-1} in the hydroxyl region shows the absorption of free hydroxyl groups which is typical free for Mg-OH surface groups. MgO(DP) and MgO(P) possess this band in the hydroxyl region and this band disappears after incorporation of vanadium, it can be concluded that vanadium ions interact initially with Mg-OH groups forming magnesium vanadate like species. VMgO showed weak bands attributed to pyrovanadate and ortho vanadate phases present in small quantities. SEM and EDS image mapping revealed that magnesium and vanadium were the present in all the catalysts and ICP results were in agreement. Electron microscopy showed that the surface morphology was more affected by different methods of catalysts preparation rather than the chemical differences.

5.5VMgO exhibits excellent catalytic activity (97 %) on the reaction of benzaldehyde with ethyl cyanoacetate. The increase of vanadium on the supports resulted in the increased yields rather than with MgO(DP) alone; 82 % versus 97 % after 30 minutes. It is believed that phase cooperation between the two phases present on the catalyst surface results in enhanced catalytic performance. The effect on various aldehydes was also tested successfully using 5.5VMgO and benzaldehyde showed the highest catalytic activity (97 %). In contrast to this, this catalyst facilitates the reaction under solvent free conditions with good catalytic performance. The objectives were achieved and the Knoevenagel condensation procedure is convenient and highly efficient since the compounds are produced in good to excellent yields after short reaction times. This project provides another alternative application of 5.5VMgO in organic synthesis and can replace existing homogenous catalysts and as well as other heterogeneous catalysts, therefore ideal for industrial applications with green methodologies.

The use of supports like alumina and silica supported on vanadium and possibly, by selecting various transitional metals such as zinc, iron, nickel etc. on the solvent-free Knoevenagel condensation reaction will be done in future. Additionally, the recyclability studies of the catalyst with high yield will be conducted to enable the product up-scale.

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APPENDIX A

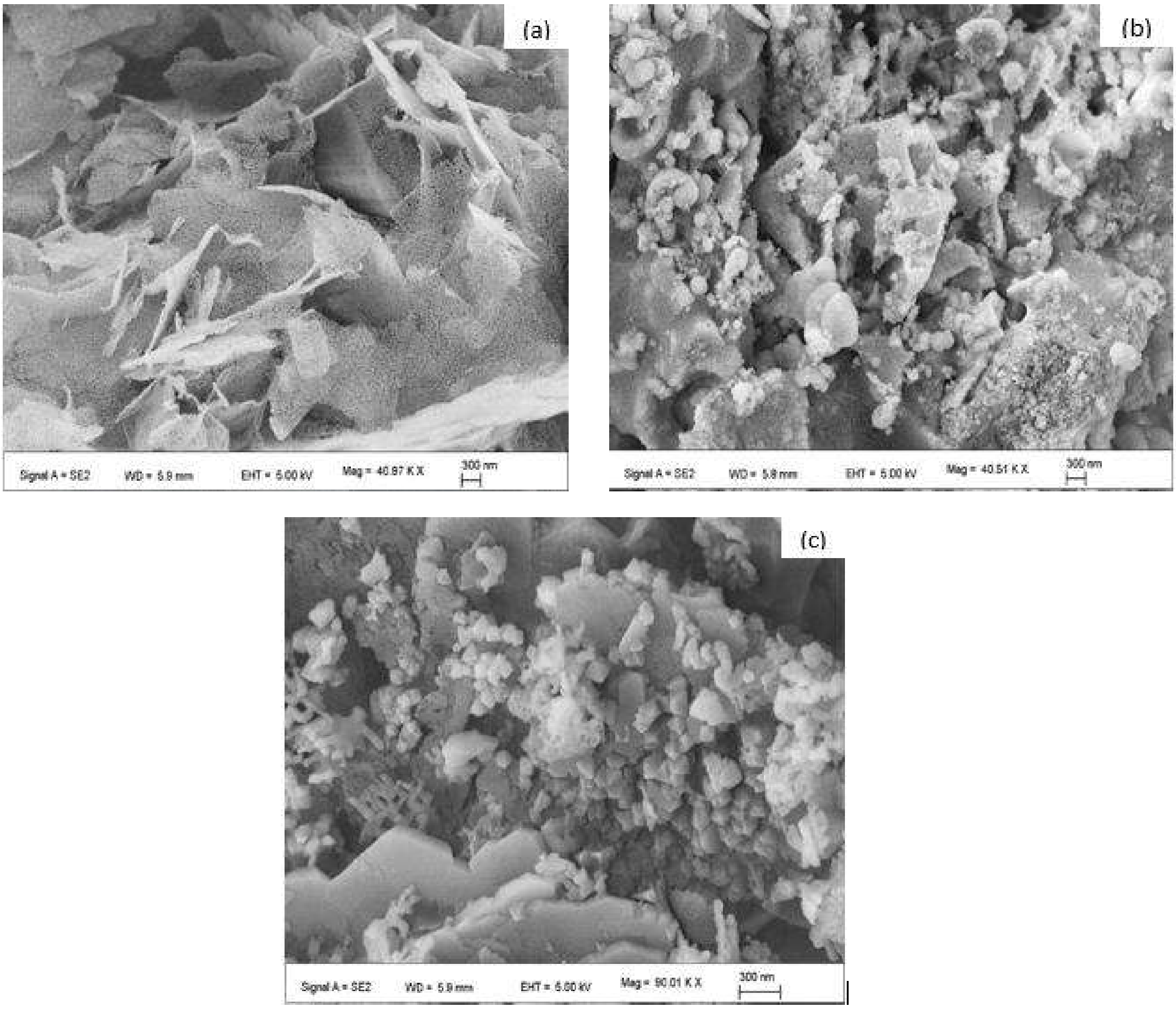

Figure A1 SEM micrographs of (a) MgO(1), (b) MgO(2), and (c) MgO(3).

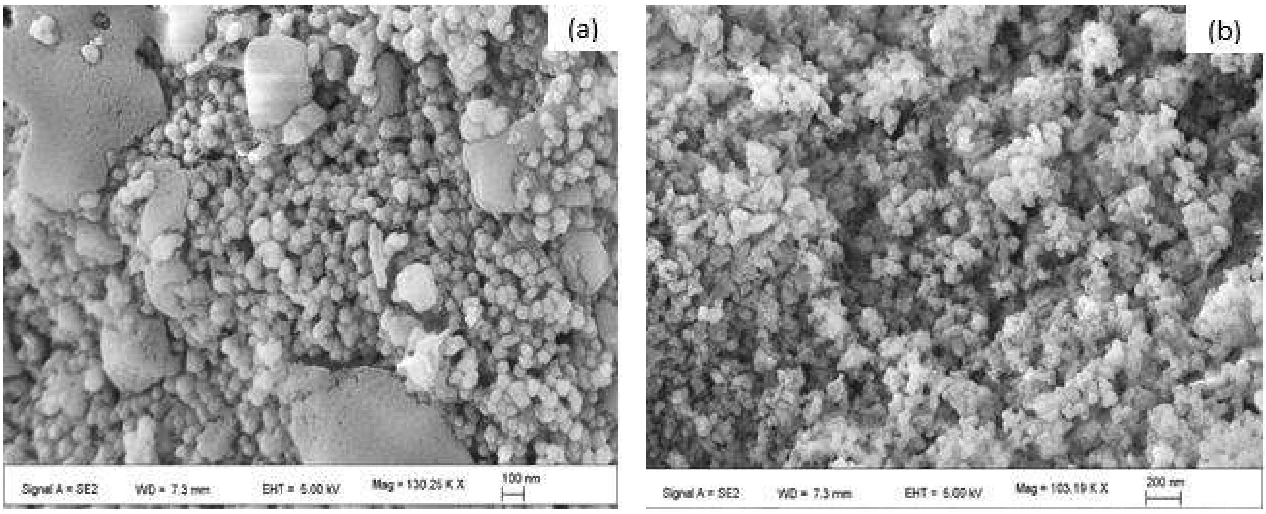

Figure A2 SEM micrographs of (a) MgO(DP) and (b) MgO(P)

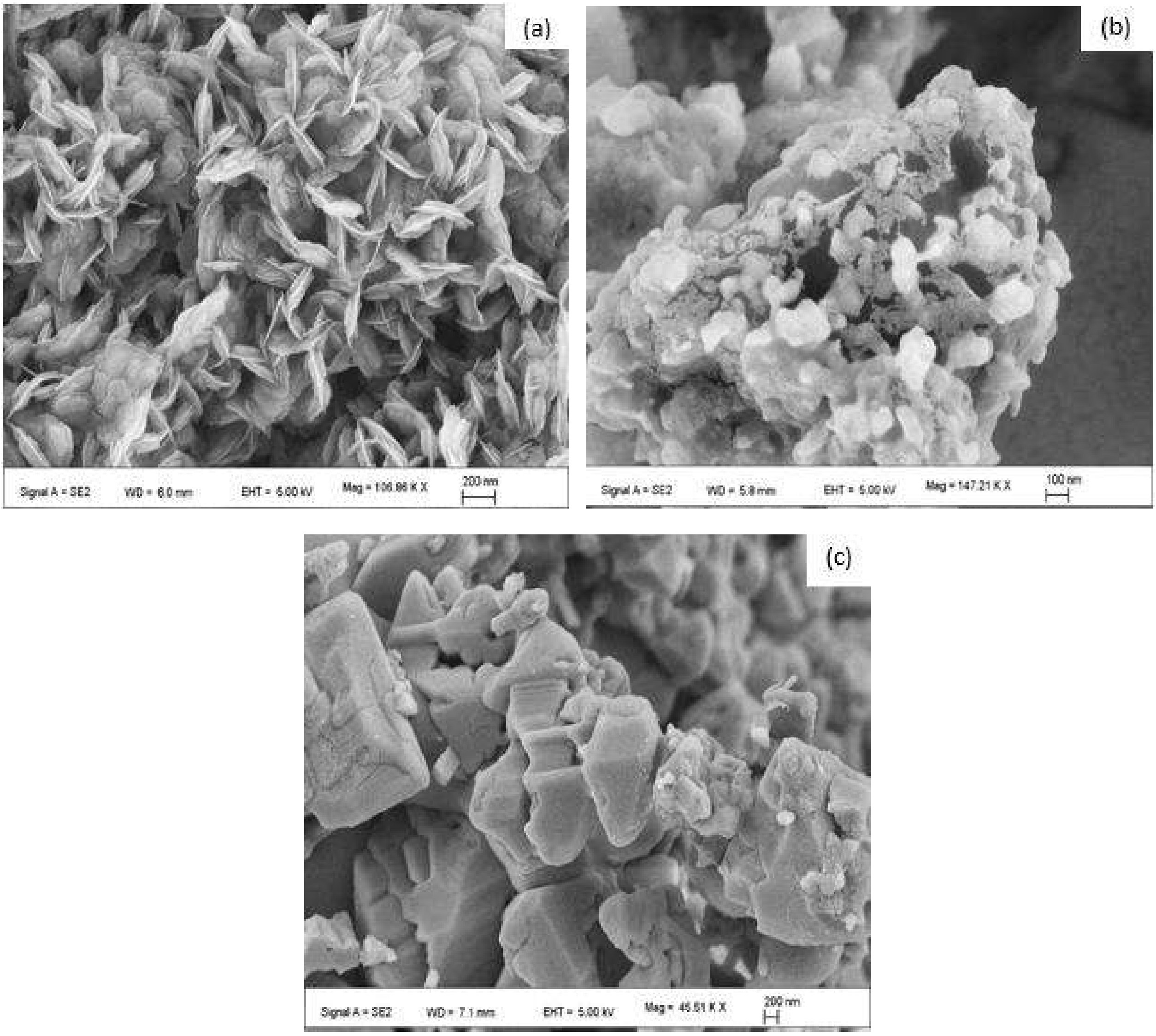

Figure A3 SEM micrographs of (a) 1.5VMgO, (b) 3.5VMgO, and (c) 5.5VMgO.

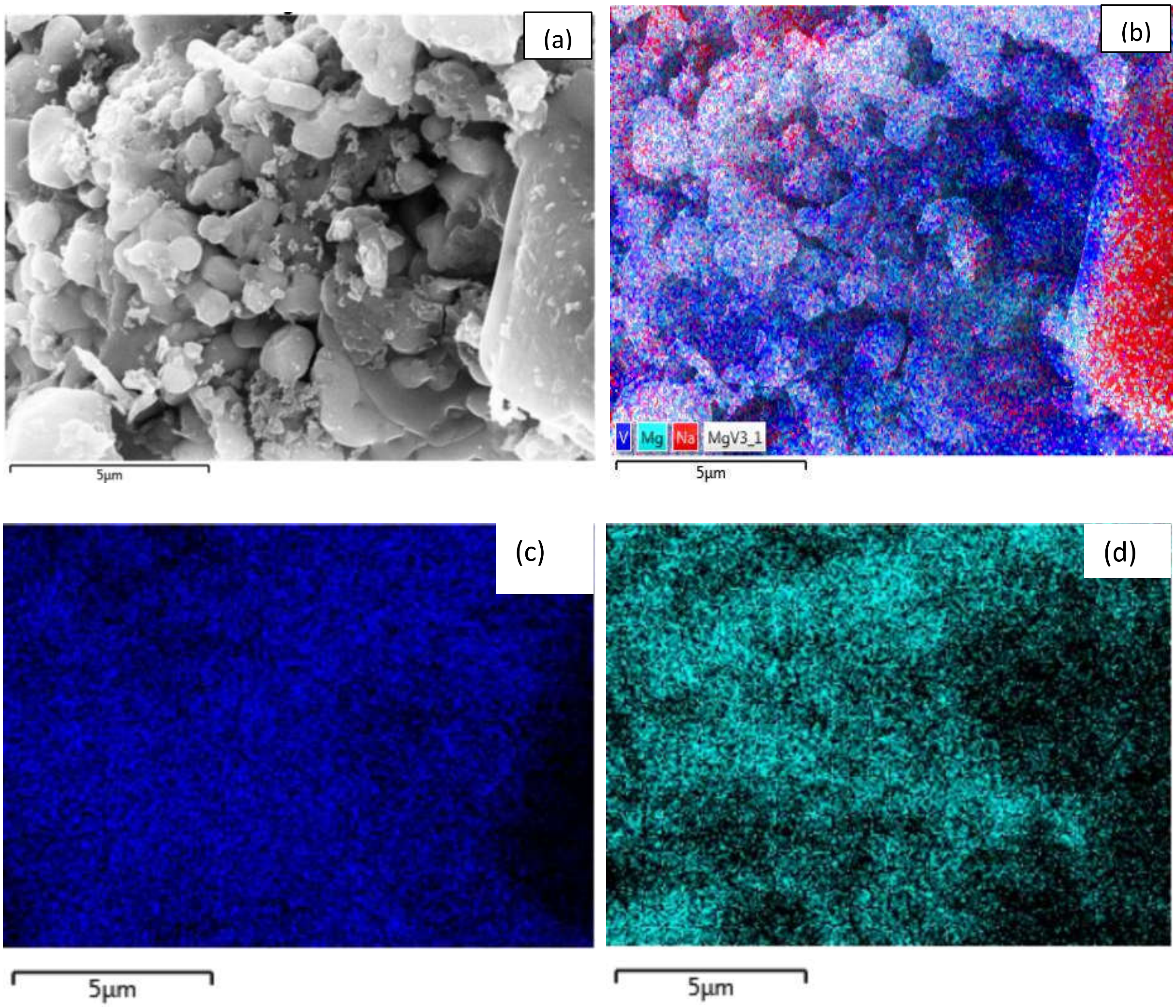

Figure A4 BSE SEM images of (a) 3.5VMgO, (b) overlay of elemental maps of sodium, magnesium and vanadium in 3.5VMgO, (c) elemental map of magnesium and (d) elemental map of vanadium.

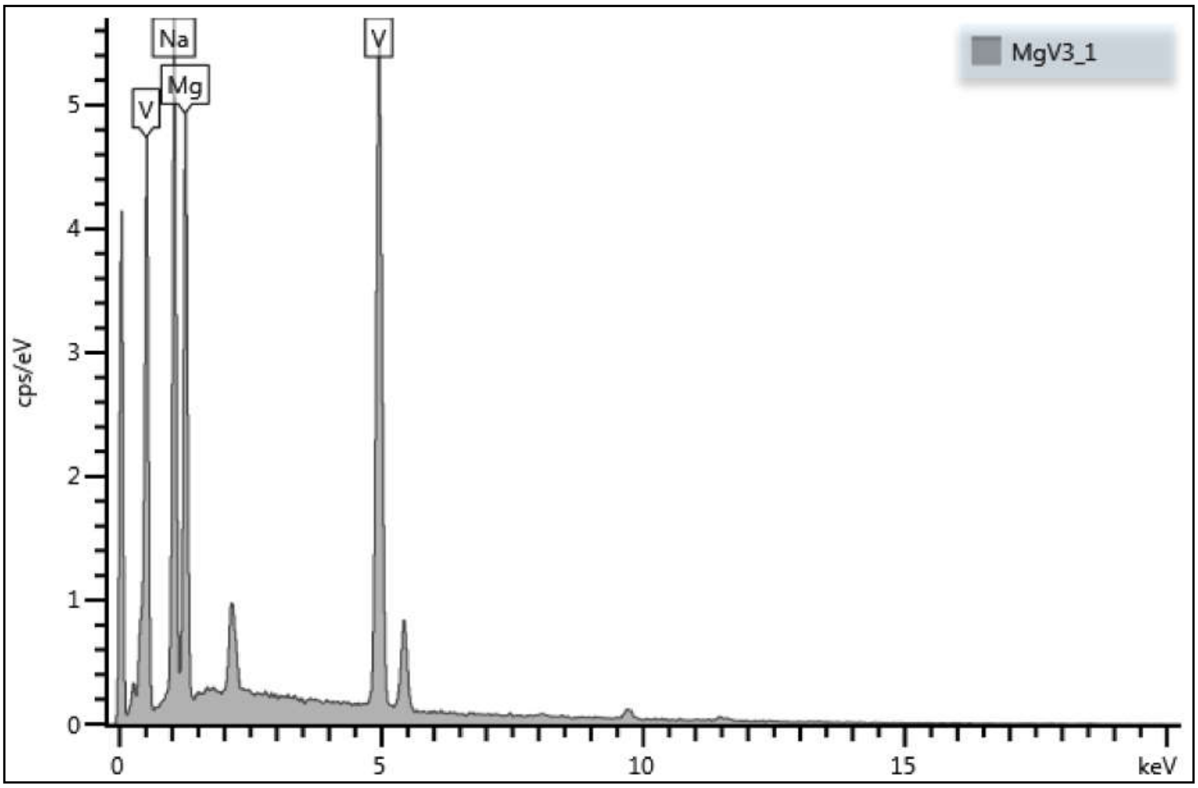

Figure A5 EDS spectrum of 3.5VMgO.

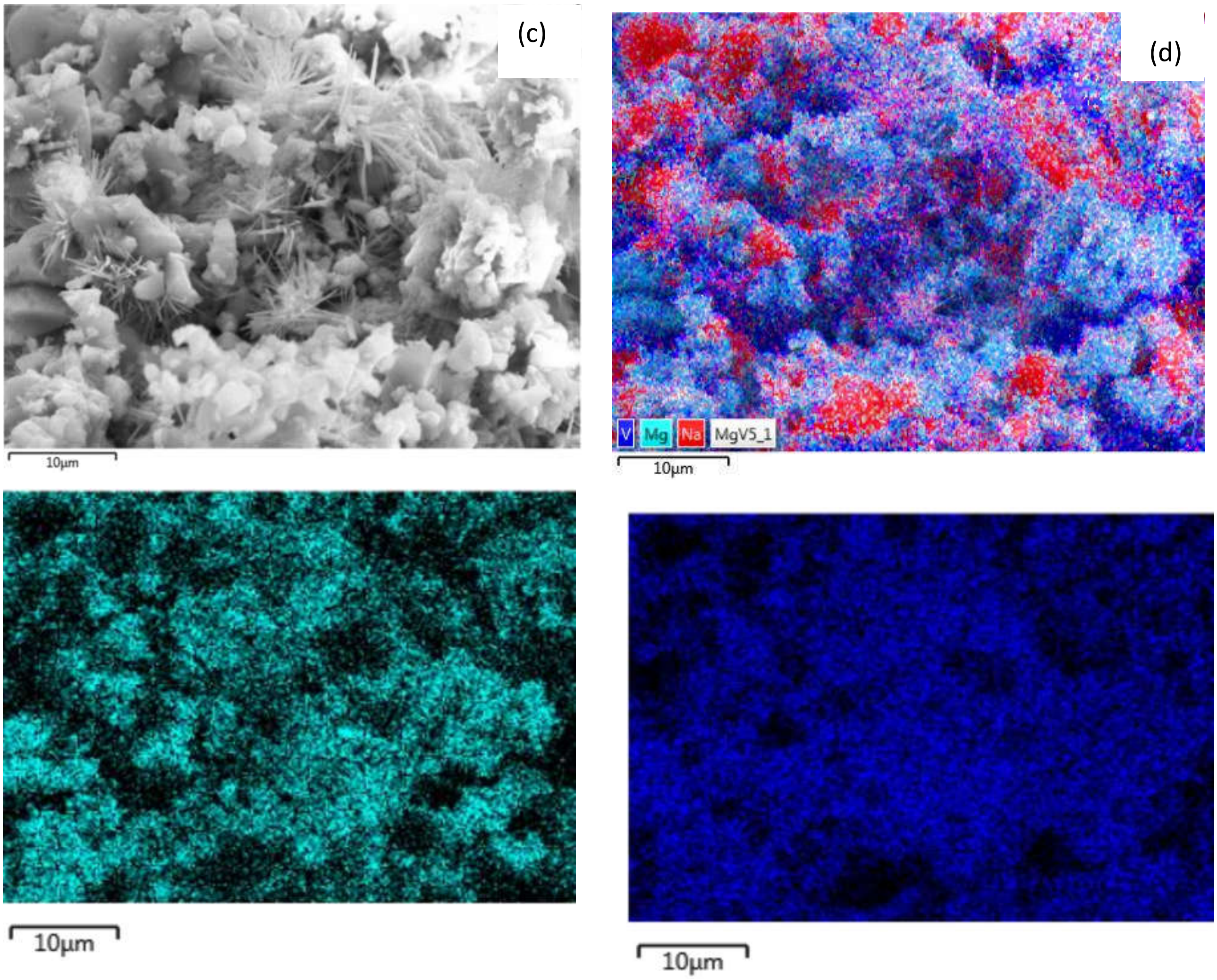

Figure A6 BSE SEM images of (a) 5.5VMgO, (b) overlay of elemental maps of sodium, magnesium and vanadium in 5.5VMgO, (c) elemental map of magnesium and (d) elemental map of vanadium.

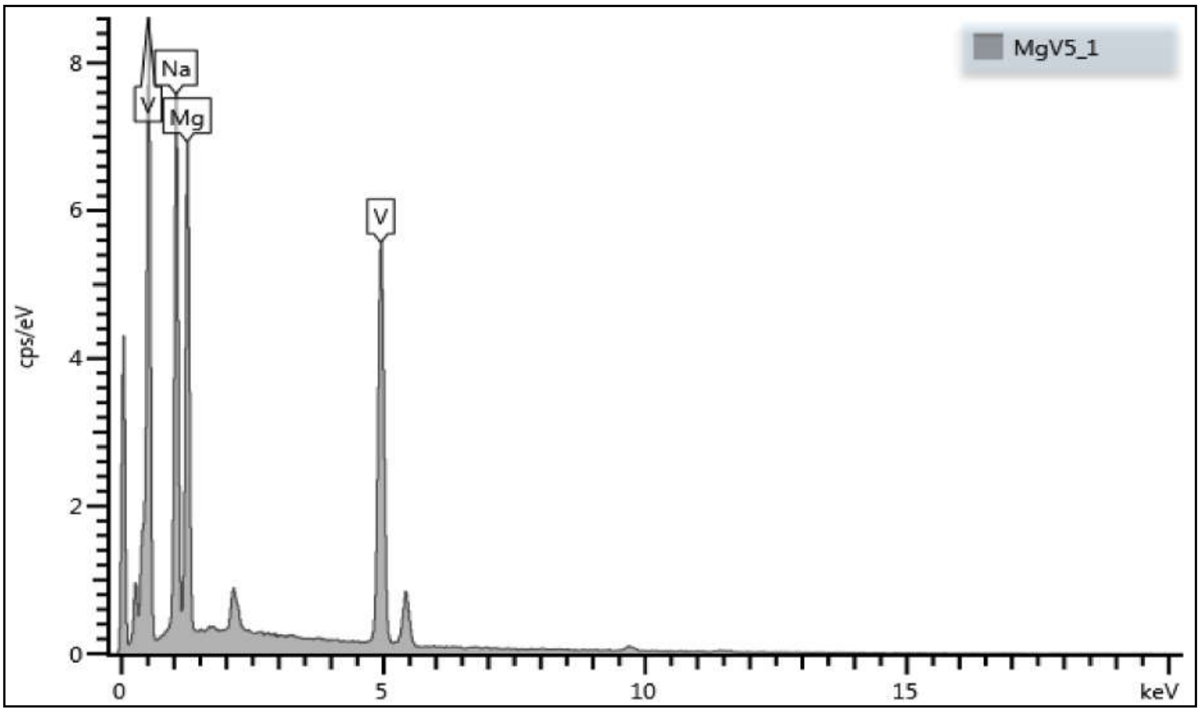

Figure A7 EDS spectrum of 5.5VMgO.

APPENDIX B

Table B1 GC-FID temperature programme.

Rate (°C/min)	Temperature (°C)	Ramp (min)
	50	
10	80	1.00
10	180	1.00
10	240	20.0

Table B2 GC-FID parameters.

Inlet		Column	
Mode	split	Type	capillary
Init. T	50 °C	Model	ZB5-MS
Split ratio	200 °C	Length	30.0 m
Total flow	245 mL/min	Film thickness	0.25 µm
Gas	N_2/Air	Diameter	0.25 mm ID
Linear velocity	30.0 cm/sec	flow	1.21 mL/min
Pressure	89.8 kPa	Max. T	350 °C
Purge flow	3.0 mL/min		