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Alcohols conversion over transition metal based catalysts

By

Mthobisi Sbonelo Ndebele
Durban university of Technology

Supervisor:
Dr Yusuf Makarfi Isa

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DECLARATION

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DEDICATION

Dedicated to My lovely belated mom…

…C.J Msweli…

ACKNOWLEDGEMENTS

I would like to pass my gratitude to my supervisor Dr Yusuf Isa for his supervision, guidance, support, encouragement and for making this thesis possible. Never forgetting my family and friends for their continuous support on my studies. Further, I would like to acknowledge chemical engineering staff both lecturers and lab technicians for their contribution.

Last but definitely not least, I would like to thank my colleagues; post graduate students for encouragement and support.

ABSTRACT

Ethanol and butanol obtainable through fermentation of lignocellulose biomass have become promising alternative feedstock for production of fuels as they are biodegradable and sustainably regenerated via the photosynthesis cycle. The properties of hydrocarbons produced through alcohol conversion closely resemble those of gasoline. Catalytic systems are reported to play a vital role during alcohol conversion to hydrocarbons. In this study ethanol and butanol were used as a feedstock for production of hydrocarbons over Fe, Zn and Ni catalyst systems supported on zeolite ZSM-5 (Zeolite Socony Mobil-5) and activated carbon (AC).

X- Ray Diffraction (XRD), Scanning Electron Microscope (SEM) coupled with Energy-dispersive X-ray spectroscopy (EDS) and Brunauer, Emmet, and Teller (BET) analyses were employed for catalyst characterization. XRD patterns confirmed the success of metal doping on ZSM-5 and activated carbon supports. Major peaks at 7.96° and 23.97° corresponding to ZSM-5 crystals were observed in ZSM-5, and AC was found to be amorphous. Impregnation with metals reduced the crystallinity of ZSM-5 supported catalysts. Whereas SEM analysis showed that catalysts supported on ZSM-5 exhibited irregular shapes and catalyst supported on activated carbon exhibited disordered structures. The BET analyses confirmed that the surface areas of promoted catalysts decreased after metal doping.

Evaluation of the catalysts were carried out in a ½ inch stainless steel reactor at 400 °C and atmospheric pressure with a weight hourly space velocity (WHSV) of 2.5 h^{-1} (g feed)/ (g catalyst). The ZSM-5 support performed better than activated carbon support. More than 90% conversion was achieved over catalysts supported on ZSM-5. Production of hydrocarbons over catalysts supported on activated carbon were as a result of the active component. Conversion of feedstock was observed to produce more benzene, toluene and xylene (BTX) compounds with an increase in butanol content. 100% conversion was achieved with pure butanol and not more than 99.86% conversion was achieved with pure ethanol.

Catalyst systems supported on HZSM-5 and activated carbon were successfully synthesised. Ethanol, butanol and ethanol-butanol mixtures were successfully converted to liquid hydrocarbons and the conversion was greater than 90%. On the promoted catalysts, production of BTX were suppressed and various metals were observed to perform differently.

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NOMENCLATURE

Abbreviations

AC	Activated Carbon
AKI	Antiknock Index
BET	Brunauer, Emmet, and Teller
BTEX	Benzene, Toluene, Ethylbenzene and Xylene
BTX	Benzene, Toluene and Xylene
BuOH	Butanol
EDS	Energy-dispersive X-ray spectroscopy
EIA	Energy Information Administration
ETG	Ethanol to Gasoline
EtOH	Ethanol
FWHM	Full Width at Half Maximum
GC-MS	Gas Chromatography–Mass Spectrometry
HPLC	High Performance Liquid Chromatography
ID	Inside Diameter
iEA	International Energy Agency
M	Motor octane number
MTH	Methanol-to-hydrocarbons
MTG	Methanol-to-gasoline
MTO	Methanol-to-olefins
OD	Outside Diameter
PID	Proportional–Integral–Derivative
R	Research octane number
SEM	Scanning Electron Microscope
WHSV	Weight hourly space velocity
XRD	X- Ray Diffraction
ZSM-5	Zeolite Socony Mobil-5

Chemical Symbols

Ag	silver
Al	Aluminum
Au	Gold
C_2H_5OH	Ethanol
Ca	Calcium
Ce	Cerium
$CH_3CH_2CH_2OH$	Propanol
CH_3OCH_3	Dimethyl ether
CH_3OH	Methanol
Cl^-	Chlorine ion
CO_2	Carbon dioxide
Cr	Chromium
Cu	Copper
Fe	Iron
Ga	Gallium
Hf	Hafnium
Ir	Iridium
Lr	Lawrencium
Lu	Lutetium
Mg	Magnesium
Mn	Manganese
NH_3	Ammonia
Ni	Nickel
$Ni(CO)_4$	Nickel tetracarbonyl
NiO	Nickel(II) oxide
Pd	Palladium
Pt	Platinum
Re	Rhenium
Rh	Rhodium
Sc	Selenium
Si	Silicon
Sn	Tin
Sr	Strontium

Y	Yttrium
Zn	Zinc

Parameters

B	Full width at half max
d	Particle size of crystalline
Hr	Peak Height of a Reference
Hs	Peak height of a Sample
K	Crystalline constant
λ	X-Ray Wavelength
θ	Brass angle

CHAPTER 1

INTRODUCTION

1.1. Background and motivation

Energy is important in the quality of people's life and modern humans have become more dependent on energy as large volumes of energy are being consumed and consumption growth is high (Pasten and Santamarina 2012; EIA 2016a). Energy consumption has increased gradually in the transportation sector across the globe, with road transportation impacting the most in overall energy transportation consumption. Combined sectors of electricity and transport produced approximately 66% CO_2 emissions in 2007 (EIA 2016b) and other pollution threats have stimulated various countries to be committed in the reduction of greenhouse emission. As part of global community of nations, South Africa has aligned its policies with global implications. From 2005 to 2015 total energy consumption increased significantly as shown in Figure 1-1, the total energy includes consumption from industrial activities, households, services and transportation sectors (EIA 2016b).

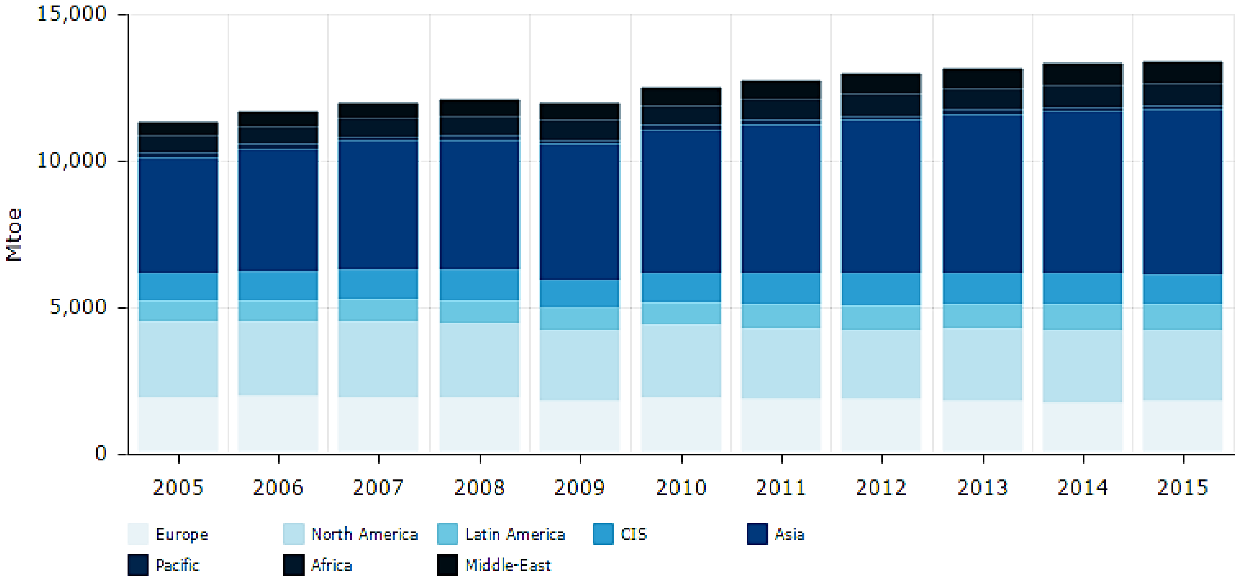


Figure 1-1. Total Energy Consumption (EIA 2016b)

The increase in energy consumption is associated with an increase in CO_2 emissions mainly produced from fossil fuels. This energy increase is connected to the high amount of energy being produced to meet global demand. Fossil fuels are known to be the most widely used source of energy which when burnt give off carbon dioxide, a greenhouse gas which is the main contributor to global warming. The increase in temperature of earth has resulted to flooding of low lying areas, melting of polar ice caps and rise in sea level. With continuous use of fossil fuels, it is estimated that emissions of carbon dioxide rapidly rising will change the climate and the temperature of the earth will increase by 2 to 6 degrees Celsius by year 2100, which is a remarkable increase from the current temperature of 1.7 degrees Celsius (Kitous *et al.* 2016).

While, coal and natural gas have the tendencies of increasing the feedstock base of crude, these fuels also have environmental threatening potentials and thus do not seem to be sustainable. For these reasons, energy sources still stand as a major issue globally and the need to combat the challenges facing the energy industry could not have been timelier. The recent instability in fuel prices as well as numerous debates on the potential threats of fossil fuels to the environment have continued to force researchers and scientists to seek for alternatives to conventional fuel sources. Alcohols, because of their properties which have close resemblance to those of modern gasoline as shown in Table 1-1 have been considered in transportation fuels (Riittonen *et al.* 2012).

Table 1-1. Properties of gasoline, 1-butanol and ethanol (Riittonen et al. 2012)

Fuel	**Energy density/ MJ L^{-1}**	**Air-to-fuel ratio**	**Energy content/ Btu/US gallon**	**Research octane number.**	**Water solubility/%**
Gasoline	32	14.6	114,000	81–89	negligible
1-Butanol	29.2	11.12	105,000	78	7
Ethanol	19.6	8.94	84,000	96	100

Being corrosive and volatile, some alcohols like methanol result in damaging of plastics and rubber components in fuel systems and not being appropriate for use as racing fuels has caused its rejection in transportation fuels (Karpov 2007). In recent years, application of ethanol from renewable biomass as motor fuel has become an area of interest around the globe. Countries like Brazil and USA produce vast amounts of bioethanol through fermentation process using different feedstock. However, the first generation bioethanol production often employs edible food crops like maize and sugarcane as feed stock which has contributed in the increase of food prices by competing with human food and animal feed production (Riittonen *et al.* 2012). To shift away from this problem, second generation biofuels from non-edible raw materials like wood, agricultural waste and other lignocellulose materials have been considered greatly (Riittonen *et al.* 2012).

Application of ethanol as a stand-alone fuel in modern car engines has been associated with different problems due to its physicochemical properties. Its corrosivity, water solubility and limited use in low temperature regions makes it very unfit to be utilised in modern car systems resulting to a need for engine design modifications and fuel filling stations (Tret'yakov *et al.* 2010). Modification of modern car engine includes replacement of some components such as fuel tank, electrical wiring, fuel pump, fuel filter, fuel lines and filler tubes which is very impractical for existing car engines and economically infeasible (Tret'yakov *et al.* 2010). Instead of using ethanol alone, blended biofuels were implemented to improve biofuels properties. Petrol blended ethanol for example E-10 and E-85 have been used in different countries to enhance the octane level and decrease net harmful emissions from car engines (Kim and Dale 2006).

Not very long ago, South African government proposed mandatory blending of petrol and diesel with biofuel from 1 October 2015 as the country encouraged investments in its biofuels sectors to reduce its reliance on imported fuels. Blending of fuels also improves the combustion in engine and reduces the emission of environmentally harmful components in gasoline. E-10 unleaded is a type of gasoline blended with 10 percent ethanol and 90 percent unleaded gasoline. Because ethanol is considered a good cleaning agent thus E-10 blend can help in keeping the engine clean from some impurities. In old engines ethanol can loosen contaminants and other present residues that have already been deposited in the engine or fuel delivery system. In this case the loosened materials collect in the fuel filter which can be removed and replaced once damaged (Karpov 2007). E-85 on the other hand is a type of biofuel blended with 15 percent unleaded gasoline and 85 percent ethanol, which is an environmentally friendly type of fuel and has high oxygen content causing it to burn cleaner than gasoline. This reduces threats like depletion of ozone layer and emissions of CO and benzene.

The production of ethanol from lignocellulosic biomass is a mature technology that has been in existence for many years and the abundance of biomass resources in all geographical locations makes its potential production limitless (Launder 2001; Lin 2001; Lin and Tanaka 2006; Karpov 2007). Biomass has the ability to produce a significant amount of energy if properly utilised, its advantage stems from the fact that it reduces the net emission of a number of greenhouse gases since it is actively engaged in the photosynthesis cycle. Biomass also serves as feedstock for the possible conversion of hydrocarbon rich materials into products of choice.

While it is interesting to note that ethanol can be obtained from various sources, it is likewise of importance to note that moving towards biofuel is very possible. It would be of benefit when these alcohols obtainable from different sources through fermentation are properly converted to fuel range hydrocarbons which are similar to those obtainable from modern gasoline; hence avoiding the need for modern engine modifications. While operating conditions such as temperature and pressure play critical roles in the alcohols conversion, catalysts type and composition will be ultimate in determining the composition of the final products (Meyer *et al.* 2005).

1.2. Historical background of alcohol conversion

Conversion of alcohols to gasoline range hydrocarbons is not a new phenomenon, this was discovered years ago accidentally by two teams of Mobil Scientists; Mobile Oil Central Research Laboratory in Princeton and Mobil Chemical in Edison; the teams were working on different projects towards isobutene methylate with methanol and methanol conversion to ethylene oxide over ZSM-5 catalyst. However, the reactions did not proceed as targeted instead the reactions proceeded to aromatic hydrocarbons formation. Further investigations based on understanding reaction pathways followed and this discovery became popular and triggered lots of researches in this field. During methanol conversion, the complete conversion was achieved. Firstly, methanol was found to undergo dehydration step to dimethyl ether and water, followed by conversion of the equilibrium mixture of methanol to light olefin and water, and the final reaction step results to the product distribution of high olefins, paraffin, aromatics and naphthenes as shown in the reaction equations 1-1 and 1-2 (Keil 1999).

$$2CH_3OH \xleftrightarrow{Dehydration/Hydration} CH_3OCH_3 \xrightarrow{Dehydration} Light\ olefins \tag{1-1}$$

$$Light\ olefins \rightarrow Higher\ olefins + n/iso - paraffins + Aromatics + naphthenes \tag{1-2}$$

Investigations involved a commercial plant that was situated in New Zealand for methanol conversion to gasoline (MTG) from non-petroleum sources. The process underwent two stages, firstly methanol was passed through a first reactor for dehydration and then passed through a second conversion reactor in a form of fixed bed in which reaction took place at temperatures between 350 and 370 °C. About 700 000 tons per day of gasoline was produced through Mobil fixed-bed MTG process (Keil 1999).

Conversion of methanol over ZSM-5 catalysts is not ideal due to high percentage production of durene and benzene which are associated with increment in cost as required for the reduction of durene through distillation. Durene is undesired in transportation due to its high freezing point of 79.2 °C, on the other hand formation of benzene is a problem on its own as this poses a potential for carcinogenicity to humans at high dose and can even lead to development of cancer and other non-cancerous diseases (He *et al.* 2003; Ramasamy and Wang 2013).

To overcome the challenges of product selectivity among others, the production of biofuels is worth investigating. The conversion of alcohols to hydrocarbons similar to those obtainable from petroleum refining industries has been considered as an alternative for fossil fuels. In these processes, catalysts play a crucial role in conversion of the feedstock to fuel range hydrocarbons, thus producing catalyst systems which are highly active in alcohol conversion and product selectivity will be of benefit.

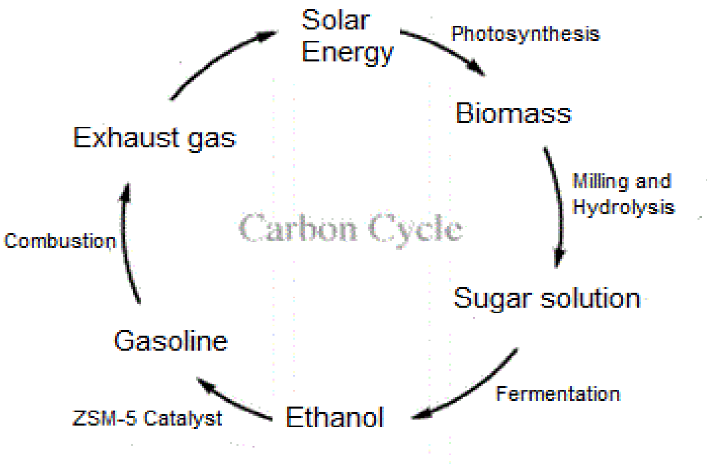


Figure 1-2. CO_2 cycle, adapted from Wigley and Schimel (2005)

In recent years, ethanol and butanol have become the promising alternative feedstock because they are biodegradable and typically regenerative through photosynthesis. Substitution of methanol by ethanol and/or butanol in the very same process of MTG has benefits in reducing water content and the process does not produce by-products like durene. Most interesting part is that the CO_2 released during combustion can be used to grow plants which results to zero net greenhouse gas contribution to global warming as shown in Figure 1-2.

Studies on different alcohols have been reported, however studies on alcohol mixtures have not been reported extensively in the open literature. Comparison of ZSM-5 supports with other zeolites supports have been reported as well in the open literature, however comparisons between ZSM-5 supports and activated carbons supports have not been reported widely in the open literature. Thus this study aims to evaluate the conversion of ethanol, butanol and ethanol-butanol mixtures over zeolite and activated carbon supported catalyst with a focus on product distribution.

1.3. Main aim and the objectives of study

Ethanol and butanol have become promising alternative feedstock for production of fuels as they are biodegradable and typically regenerative through photosynthesis. These bio-alcohols can be produced through fermentation of lignocellulose biomass such as wood and grasses without threatening food security. Furthermore the properties of their conversion products have been found to closely resemble those of modern gasoline. On the other hand, catalytic systems have been reported to play vital role during conversion of these alcohols. Therefore the main aim of this work is to convert ethanol and butanol as samples from the alcohol family over developed catalytic systems.

Objectives of the research include:

- Preparation and characterisation of Iron, nickel and zinc catalysts
- Investigating the effect of iron, nickel and zinc metal catalysts on conversion activity and product selectivity
- Investigating the effect of ZSM-5 and activated carbon support on conversion activity and product selectivity

- Investigating the effect of ethanol-butanol mixtures at different mixing ratios on product distribution and selectivity

1.4. Thesis outline

This thesis has been written over five main chapters:

Chapter 1 provides a brief background of the study and motivation together with the main aim and objectives of this work.

Chapter 2 discusses the theory and the importance of zeolites, transition metals, alcohols, catalysis as and as well as relevant research reported in the literature.

Chapter 3 gives a detailed explanation of the experiments used in the catalyst synthesis as well as characterisation and catalyst testing.

Chapter 4 presents results obtained from the experimental section and discussion.

Chapter 5 provides a conclusion drawn from discussion and recommendations for future work.

CHAPTER 2

LITERATURE REVIEW

2.1. Energy sources

The role of energy in modern days is greatly increasing; however, the resources available for energy generation have to be carefully chosen due to certain environmental and economic reasons. To date energy market has become strongly influenced by a substantial increase in the energy demand which is mostly due to the strong economic growth in developing countries. On the other hand it is observed that the capacity to deliver fossil fuel energy may be limited in the near future (iEA 2004).

2.1.1. Fossil fuels

Fossil fuels still remain the major source of energy globally (Khan 2012) and currently they are the most reliable sources of energy. Fossil fuels are sources of energy which were formed within the earth over millions of years by decay of land vegetation and animals; when layers are compressed and heated over time, deposit of hydrocarbons are formed. These are considered non-renewable since they take long to form (Williams 2002). There are mainly three types of fossil fuels; these are oil, coal and natural gases (Dincer 2000).

Environmental pollution is one of the main shortcoming of fossil fuels, when fossil fuels are burnt to the atmosphere they release a number of harmful gases such as carbon dioxide, carbon monoxide, sulfur oxides and hydrocarbons (Reddy and Venkataraman 2002) resulting in greenhouse gases which are major contributors to global warming. The increase in the temperature of the earth has resulted to flooding of low lying areas, melting of polar ice caps and rise in sea level. With continuous use of fossil fuels, it is estimated that emissions of carbon dioxide that is predominantly due to fossil fuel combustion will change the climate and the temperature of the earth will increase by 2 to 6 degrees Celsius by year 2100, which is a remarkable increase from the current temperature of 1.7 degrees Celsius (Khan 2012).

Accidents can be disastrous with the continuous use of fossil fuels. Accidents involving fossil fuels can cause serious damage and are highly dangerous to the environment and its surroundings. Oil spillages have occurred in the past, oil spills can result to death of aquatic animals including those living offshore and can lead to pollution of water bodies. The environment around the seashore can also be destroyed (Barbir et al. 1990). Emissions due to greenhouse gasses and other toxic compounds as a result of fossil fuel combustion can cause severe health complications such as chronic asthma, low lung functioning, chronic bronchitis and cardiovascular diseases (Wuebbles and Jain 2001).

Fossil fuels are highly liable to price fluctuations and market manipulation (Cherp et al. 2016; Hari et al. 2015). This aspect is greatly felt by developing countries that heavily rely on importation of fossil fuels. Shifting to renewable energy technologies may minimize these price fluctuations and manipulations to a greater degree (Hari et al. 2015). As the world's energy demand is mainly met by fossil fuels, there is a great need to lookout in much consideration for alternatives energy sources.

2.1.2. Biomass

Biomass is an organic matter that is renewable. During photosynthesis, plants use light energy to convert carbon dioxide and water into sugar and oxygen. Biomass can be converted into liquid biofuels such as methanol and ethanol through fermentation process (Demirbaş 2001). Biofuel is a type of energy derived from renewable plants (Hossain et al. 2008) and animal materials which are extracted from biomass (Smith 2013). These may find application vehicle fuels, biodiesel, green diesel and biogases (McKendry 2002a). In biofuel the CO_2 net emission is significantly reduced compared to fossil fuels. The amount of CO_2 released into the atmosphere during burning of biofuel overtime is estimated to be equal to the amount of CO_2

required when biomass grows through photosynthesis and therefore biomass is carbon neutral (McKendry 2002). Biofuel is one of the main focuses in development of sustainable and recoverable source of energy in the world (Khan 2012).

A wide range of feedstock such as Lignocellulosic biomass, sugar, oil plants and waste vegetable oil/ animal fat can be converted into variety fuels and chemicals obtainable from fossil fuels as shown in Figure 2-1.

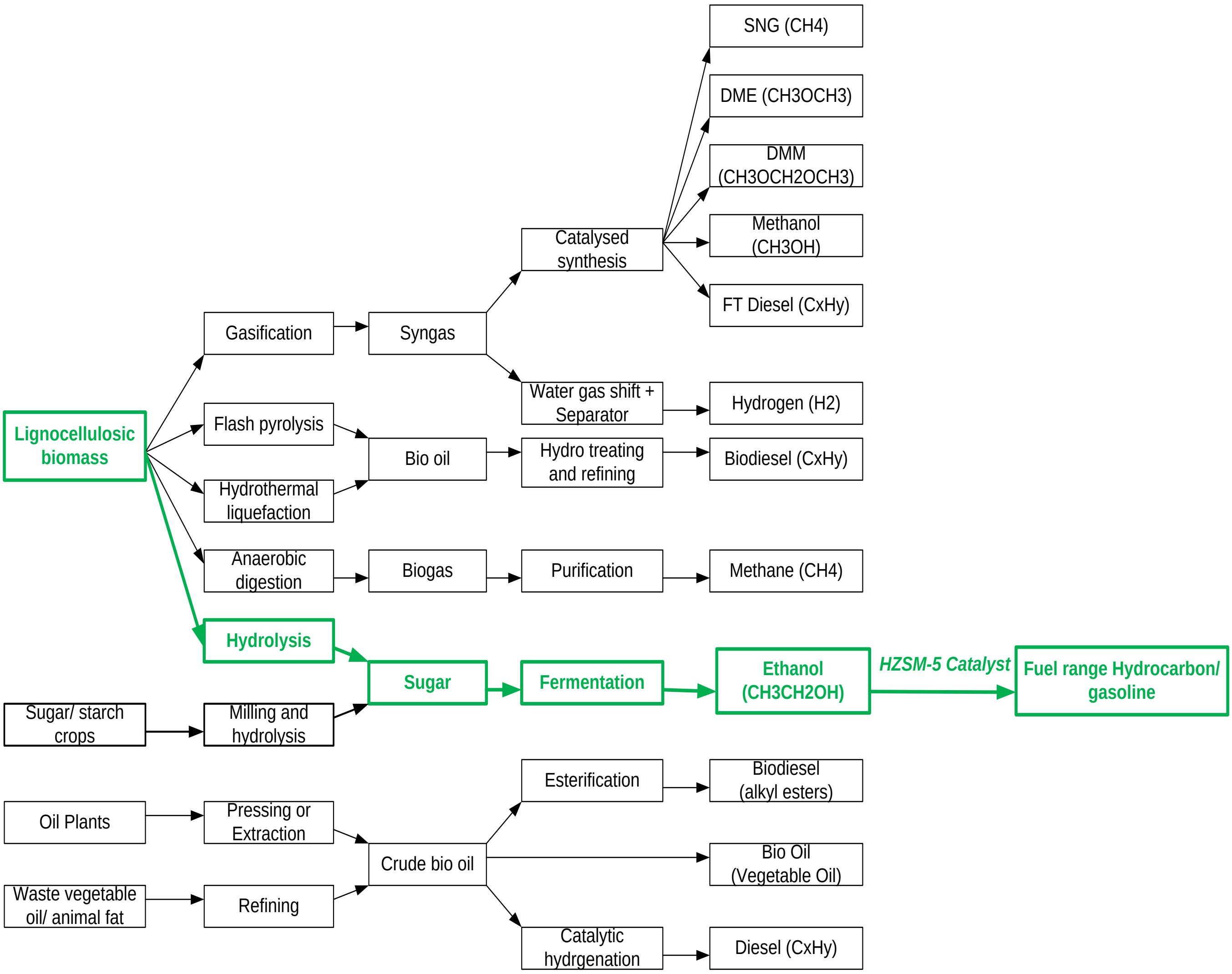


Figure 2-1. Platform of converting bioenergy to fuel chemicals, adapted from Hamelinck and Faaij (2006).

Two biomass sources of sugar, namely; lignocellulosic biomass (second generation biomass) and sugar (first generation biomass) undergo hydrolysis and or milling to form sugar. Sugar is then subjected to fermentation process for production of ethanol. After this stage, the bioethanol produced from fermentation processes can go through catalytic processes, ETG, for production of gasoline/ gasoline range hydrocarbons (Hamelinck and Faaij 2006).

2.2. Gasoline

Gasoline is usually produced from crude oil. Each crude oil is unique and is a complex mixture of thousands of compounds. Most compounds in crude oil are hydrocarbons. Other than carbon and hydrogen compounds, there are also small, but important amounts of other elements such as sulfur, nitrogen and certain metals. The compounds that make up crude oil range from the smallest and simplest hydrocarbon molecule (methane) to large, complex molecules containing up to 50 or more carbon atoms (Barbeira *et al.* 2007).

Paraffins, aromatics, and naphthenes are natural constituents of crude oil, and are produced in various refining operations as well. Olefins usually are not present in crude oil; they are produced in certain refining operations that are dedicated mainly to gasoline production (Barbeira *et al.* 2007).

Gasoline is a complex mixture of approximately 300 various components, mainly volatile hydrocarbon compounds. Gasoline is blended from several refinery process streams, including any of the various naphtha streams from direct distillation of crude oil at atmospheric pressure by catalytic and thermal cracking processes (EUCAR 2003). In some gasoline grades, oxygenated compounds are also part of automotive gasoline components. Table 2-1 represents typical composition for an automotive gasoline.

Table 2-1. Composition by hydrocarbon type of typical automotive gasolines (EUCAR 2003).

Composition	Range
Alkanes	4-8 wt. %
Alkenes	2-5 wt. %
Isoalkanes	25-40 wt. %
Cycloalkanes	3-7 wt. %
Cycloalkenes	1-4 wt. %
Total aromatics	20-50 wt. %
Benzene	0.5-2.5 wt. %
Paraffins	30-90 vol. %
Olefins	0-30 vol. %
Aromatics	10-50 vol. %

2.2.1. Octane rating

The octane rating is a measure of a fuel's ability to avoid knock. Knock occurs when fuel is prematurely ignited in the engine's cylinder, which degrades efficiency and can be damaging to the engine. The fuels contain an oxygenate that prevents knock by adding oxygen to the fuel and this oxygenate is commonly referred to as octane.

Gasoline is rated based on its antiknock index (AKI) which is a measure of octane rating. The AKI determines the fuel ability to resist engine knock. The AKI is calculated as the average of the research octane number (R) and motor octane number (M). A low research octane number could cause a speed knock and run-on after the engine has been shut down while a low motor octane number may course engine knock during acceleration where power is needed in certain cases like climbing hills (Karpov 2007). Some properties of typical gasoline are tabulated in Table 2-2.

Table 2-2. Gasoline fuel properties (Eccleston and Cox 1977)

Property	**Value**
Energy density	32 MJ L^{-1}
Water solubility	negligible
Air-to-fuel ratio	14.6
Energy content	114,000 Energy content/B tu/US gallon
Research Octane Number	81–89

2.2.2. Benzene, Toluene, Ethylbenzene and Xylene (BTEX) Complex

The BTEX complex is a hydrocarbon mixture of benzene, toluene, ethyl-benzene and xylene. Commonly knowns as gasoline aromatics, these compounds are refined from low-octane petroleum products into a high-octane gasoline additive. While some volume of BTEX is native to gasoline, it is also added to finished gasoline to boost its octane rating. The total volume of BTEX (aromatics) in finished gasoline depends on the desired octane value and other desired fuel properties (EIA 2013).

2.3. Alcohols production and alcohol fuels

Alcohols are a group of compounds that contain hydroxyl group –OH which is attached to an alkyl group (Weissermel and Arpe 2008). These are alkanes at which single hydrogen has been replaced with an –OH group. Alcohols are less volatile with higher, melting point but have greater water solubility compared to corresponding hydrocarbons (Vollhardt and Schore 2011). Alcohols are abundant in nature as methanol, ethanol, propanol butanol and so on; they can be found in all carbohydrates (sugar) compounds (Pretsch *et al.* 2009). Alcohols like methanol have been considered in transportation fuels for some particular engine design (Hahn-Hägerdal *et al.* 2006), however they are highly corrosive and more volatile which results in damaging of plastics and rubber components in fuel systems (Karpov 2007). In recent years, application of ethanol from renewable biomass as motor fuels has become an area of interest around the globe. This is because of its potential to reduce the utilisation of fossil fuels (Hahn-Hägerdal *et al.* 2006).

2.3.1. Fermentation

Fermentation is a series of reactions which release energy from organic molecules. Yeast is added to sugar and fermentation takes place. The energy that was in sugar is being returned to ethanol. The production of ethanol is achieved by conversion of simple sugar using enzymes which are produced by living microorganisms. These bacteria are classified according to the tolerance of oxygen. Aerobic bacteria are those that use oxygen and anaerobic are those that do not use oxygen. Facultative are those that continue to grow even after available oxygen has been consumed, the facultative anaerobic is the yeast being used for ethanol production (Stewart 1982).

During fermentation process, about 5 percent of the sugar is being utilised by the yeast for the production of new cells and other minor products including acetic acid, lactic acid and glycerol. Yeasts are single cell fungi that are wildly distributed in nature which are responsible for enzymes in conversion of sugar to ethanol. Genus Saccharomyces are type of yeast used for ethanol production, these are very sensitive to operating conditions of ethanol production. They are effective at pH and temperature range of 3.0 to 5.0 and 27 °C to 35 °C respectively. The period for conversion of mash to ethanol depends on number of yeast cells per quantity of sugar (Stewart 1982).

2.3.2. Ethanol and ethanol production

Ethanol is a clear, colourless liquid phase material with agreeable odour. Ethanol CH_3CH_2OH is an alcohol group of organic chemical compounds which constitutes a hydroxyl group –OH, bonded to carbon atom. Generally, ethanol melts at -114.1 °C, boils at 78.5 °C with a density of 0.789 g/ml at standard temperature of 20 °C (Lin 2001), other properties are listed in Table 2-3.

Table 2-3. Ethanol fuel Properties at 1 atm. (Gautam and Martin 2000).

Property	**Value**
Molecular weight	74.122 g/mol.
Melting point	- 130 ^{0}C to – 112 ^{0}C
Boiling point	78.2^{0}C - 78.5^{0}C
Vapour pressure	59 mm Hg at 20 ^{0}C
Energy density	19.6 MJ L^{-1}
Water solubility	100
Air-to-fuel ratio	8.94
Energy content	84,000 Energy content/ Btu/US gallon
Research Octane Number	96

Ethanol can be obtained through fermentation of sugar (Launder 2001; Lin 2001; Lin and Tanaka 2006; Karpov 2007). Simple sugar is converted through zymase as an enzyme catalyst into ethanol and carbon dioxide as illustrated by equation 2-1 (Stewart 1982; Lin 2001):

$$C_6H_{12}O_{6\,(aq)} \xrightarrow{Zymase\ (\ 27\ to\ 35\ degres\ celcuis\ )} 2C_2H_5OH_{(aq)} + 2CO_{2\,(aq)} + heat \tag{2-1}$$

Ethanol produced from fermentation has concentration of about 14 % and thus can be further concentrated through distillation of aqueous solution to obtain composition of about 96 % ethanol and 4 % water. In order to obtain absolute ethanol, dehydrating agent can be used to remove remaining water (Lin 2001). The ethanol original application was as a gas extender when foreign oil prices increased rapidly in 1970s in U.S. Due to phasing out of leaded gasoline it became very popular as a booster of octane quality. It was then used as an emission reducing oxygenate as it has a high oxygen content and thus burns completely and reduces pollution (Karpov 2007).

2.3.3. Butanol and butanol production

Butanol is a clear neutral liquid with a strong vinous odour. Butanol ($CH_3CH_2CH_2OH$) is immiscible with most of solvents like other alcohols, ketones, aldehyde, etc. Generally, butanol melts at -114.1 °C, boils at 78.5 °C and has a density of 0.789 g/ml at standard temperature of 20 °C (Lin and Tanaka 2006), other properties are listed in Table 2-4.

Butanol can also be produced through fermentation of sugar from lignocellulosic materials. Butanol has shown excellent fuel characteristics with oxygen content of around 22 percent which when used as a fuel extender results in a complete fuel combustion (Ezeji *et al.* 2006). Application of butanol fuel in car engines results to clean air by reducing emissions such as carbon monoxide and unburned hydrocarbons.

Table 2-4. Butanol fuel Properties at 1 atm. (Gautam and Martin 2000).

Property	Value
Molecular weight	74.122 g/mol.
Melting point	-89 °C
Boiling point	117.7 °C
Vapour pressure	0.6 kPa
Energy density	29.2 MJ L^{-1}
Water solubility	7
Air-to-fuel ratio	11.12
Energy content	105,000 Energy content/Btu/US gallon
Research Octane Number	78

2.4. Catalysis

Catalysts plays crucial role in many chemical reactions of industrial application (Yilmaz and Müller 2009), this include petroleum cracking (Degnan Jr 2000), synthesis of methanol from carbon monoxide and hydrogen gas (Kiatphuengporn *et al.* 2016), production of fertilizers (Leggo 2015) and alcohol conversion to gasoline hydrocarbons (Weckhuysen and Yu 2015). Catalysts are capable of producing materials or enhancing suitable chemical reactions for production of designated products (Roberts and Poignant 2003). Catalysts are very special substances, looking back to their definition- substances that increases the rate of reaction without being used up in the reaction (Moulijn *et al.* 1993).

A catalyst affects the reaction kinetics by lowering the activation energy (Scott and Lukehart 2013), it provides low energy pathways for chemical reactions. In solid catalysts like zeolites, it provides enough surface area for reactions to take place especially in sites of the catalyst which are active (Weckhuysen and Yu 2015). Activity of the catalyst is one of the main features which makes reaction possible, a catalyst does not only speed up the reaction, but it also improves the selectivity in reaction or product distribution. The activity of the catalyst is however not everlasting, there is a point where the catalyst does not perform to its full capacity and that point is termed catalyst deactivation (Richardson 2013). Catalyst deactivation may be due to various stresses such as mechanical stress, thermal stress and chemical stress (Bartholomew 2001).

2.4.1. Mechanical stress

These are caused by friction and are predominately due to mixing, continuous stirring and conversion inside the reactor. Fouling is also one of the causes for deactivation which basically blocks the active sites in a catalyst.

2.4.2. Thermal stress

At high temperature conditions, the catalyst components may be lost or transformed, which destroys the catalyst in a way that it undergoes different changes such as phase and surface change, and particle sintering.

2.4.3. Chemical stress

Chemical stress involves coking and poisoning in the catalyst. Poison may be any substance present that can result in poor adsorption to the catalyst sites by blocking active sites. Poisoning partially depends on the temperature, may be a reversible or irreversible poisoning. Coking on the other hand is the deposition of carbonaceous materials which accumulates in the catalyst surface and tends to block active sites.

2.4.4. Types of catalysts

2.4.4.1. Homogeneous catalysts

In homogeneous catalyst, both catalyst and reactants are in the same fluid phase (Cornils and Herrmann 1996; Chorkendorff and Niemantsverdriet 2006; Van Leeuwen 2006) and usually they are present in liquid phase (Chorkendorff and Niemantsverdriet 2006; Van Leeuwen 2006). They are highly active and or selective in many reactions (Cornils and Herrmann 1996; Sheldon 2012) and they are molecularly dispersed with the fluid reactants (Cornils and Herrmann 1996), which in turn makes the separation very difficult and expensive as they are even molecularly dispersed in product. Their applications are limited because of their stability only in mild conditions. The application of homogeneous catalysts in chemical industries is significantly very small compared to heterogeneous catalysts. They are abundantly used in pharmaceutical and polymer industries, especially for polymerization and oxidation of alkenes (Cornils and Herrmann 1996).

2.4.4.2. Biological catalysts

Biological catalysts are enzymes catalyst that speed up the rate of biochemical reactions. When they are used in reactions, they are 1015 times faster compared to the uncatalysed reactions. These are proteins with specific functions and very active under mild conditions. They play crucial role in lowering free energy of the reaction transition state (Najafpour 2015). Enzymes catalyst are dominantly involved in reactions that takes place in photosynthesis and fermentation process (Cornils and Herrmann 1996).

2.4.4.3. Heterogeneous catalysts

Heterogeneous catalysts are present in different phases from that of the reactants, usually the reactants are in gas or liquid phase and the catalyst is in solid form. They are significant because after reaction they are easily separated from reactants and products (Jens *et al.* 2014) which makes them more interesting in industrial applications. In most heterogeneous catalysts, the reaction usually takes place at the surface of the catalyst because of its large surface area and its porosity. These catalysts can be supported on porous, nanoparticle material, which may be inert or active while inert support materials such as activated carbon do not interfere with the actual catalyst an active support like zeolite actively interferes with the actual catalyst (Thomas and Thomas 2014). Therefore, any porous materials can be used as catalyst support such as zeolites, activated carbons, binary oxides and silicon carbides, because it assist in dispersing the catalyst.

The performance of a catalyst is determined by its activity in conversion, selectivity in product distribution and catalyst life which is well defined by catalyst deactivation (Centi *et al.* 2012). Nevertheless, the solid catalyst properties such as distribution of active species, nature and composition of the various phases and the surface morphology are well pronounced as coordination of surface atoms takes the largest part transformation during catalyst life (Figueiredo 2012). Aspects such as catalyst preparation, activation, transformation, deactivation, catalyst support and regeneration are important in catalyst systems. Each of these aspects plays an important role in catalyst synthesis and they have to be well considered when producing catalyst systems for particular production (Centi *et al.* 2012). Heterogeneous catalysts are widely used in petroleum refineries during production of fuel hydrocarbons. Zeolite based catalysts and some precious metals have been successfully employed in variety of commercial processes in petroleum and petrochemical industries.

2.5. Zeolites theory

Zeolites are microporous crystalline aluminosilicates (Somorjai and Li 2010) with high surface area and complex structure which is a tetrahedral network enclosed with cavities and channels (Baerlocher *et al.* 2007) interconnected by small windows (Modi and Trivedi 2012). Their structure is three dimensional coming from a framework of $[SiO_4]^{4-}$ and $[AlO_4]^{5-}$ coordination polyhedral that are connected to one another by sharing all oxygen to form interconnection cages and channels (Somorjai and Li 2010).

2.5.1. Zeolite structure

Zeolite is made of SiO_4 and AlO_4 tetrahedral which is the elementary building unit in zeolite structure whereas each of four oxygen anions in tetrahedral are shared with silica or alumina tetrahedron. The schematic diagram in Figure 2-2 represents the development of zeolite structure from aluminosilicates. (Meier and Olson 1992).

The ZSM-5 and its silica and analogue silica-1 are formed from pentasil unit and they show intersecting system of ten-membered-ring pore which are sinusoidal and straight in structure. The framework of zeolite ZSM-5 has configuration of linked tetrahedral, the connection of the sheets of HZSM-5 leads to a formation of dimensional framework of channel structure (Baerlocher *et al.* 2007). The cross section of both straight and sinusoidal channel comprises of 10 oxygen atoms. The straight channel and opening is of 0.54 x 0.65 nm in dimension and 0.51 x 0.55 nm sinusoidal. The silicon to aluminium (Si/Al) ratio is the one responsible for the strength of acid site of the zeolite and its hydrophobicity observed in ZSM-5 catalyst while channel structure and its dimensions are responsible for high stability and strong shape selective action (Weitkamp and Puppe 2013).

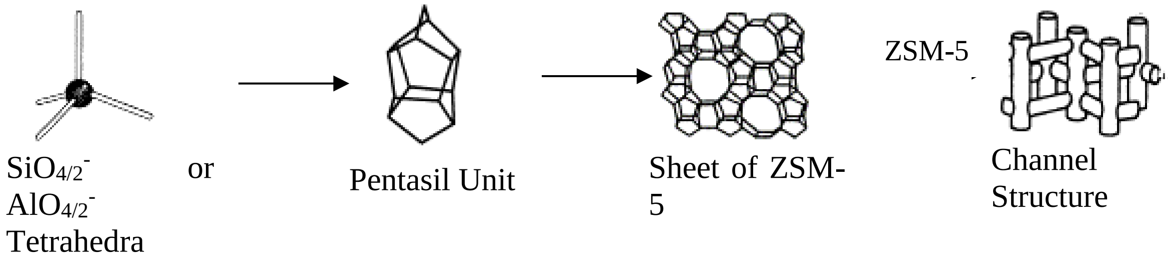


Figure 2-2. Development of zeolite structures from aluminosilicates (Meier and Olson 1992)

This type of structure allows the catalytic reaction to take place according to shape selectivity. The product selectivity usually takes place when part of the product formed at the active sites diffuses out of the lattice, and other part of product are larger to leave the zeolite lattice which may further react to produce smaller molecular size that can diffuse out from zeolite or may lead to catalyst deactivation. Catalyst deactivation may be due to coke formation. ZHSM-5 catalyst are much less sensitive to coke deactivation compared to other zeolite types due to its pore size (Armengol *et al.* 1997).

2.5.2. Zeolite acidity

The acidity in zeolite is mainly due to the presence of Bronsted Acid sites, after high temperature treatment, which makes it very special in catalytic reactions. Lewis acid sites may also be present. The diagrams in Figure 2-3 depict an example of acid sites in zeolite (Barthomeuf 1991).

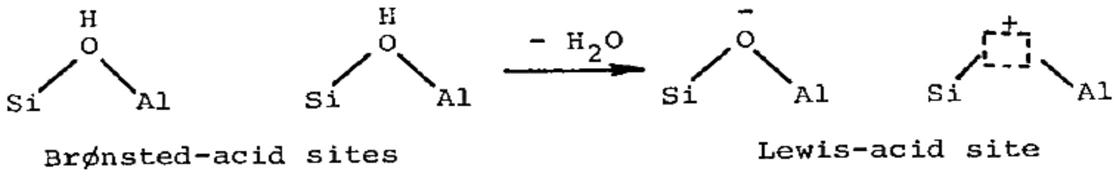
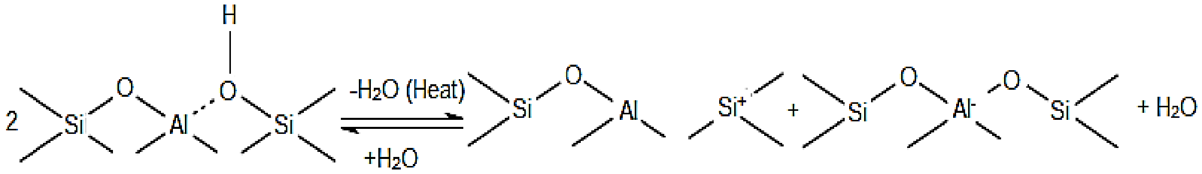


Figure 2-3. Zeolite acidity (Barthomeuf 1991)

The availability of these two acid sites depends on the reaction conditions and activation procedure. Bronsted acid sites can be obtained in treatment of acid stable zeolites like ZSM-5 with ammonium chloride or nitrates especially in converting zeolite Na-HZSM-5 to its proton form H-ZSM-5. And Lewis acid sites can be obtained by dihydroxylation of two neighbouring hydroxyl groups by heat treatment with temperature above 477 °C where by water will be removed and coordinated unsaturated Al^{3+} ion is formed (Barthomeuf 1991; Armengol *et al.* 1997). This is demonstrated schematically in Figure 2-4.



Bronsted Acid Sites

Lewis Acid Sites

Figure 2-4. Zeolite acidity dehydration (Armengol *et al.* 1997)

An acidity and the stability of the zeolite is influenced by the framework charge of the zeolite. ZSM-5 has been considered as high silica zeolite due to infinite silica to alumina ratio. Varying Si/Al ratio has several effects in zeolite properties or performance in catalysis. The zeolite stability in high temperature reactions and its activity depends on Si/ Al ratio. ZSM-5 is very stable in high temperatures up to 1027 °C, low Si/Al ratio zeolites like zeolite X and Y are destroyed at pH less than 4 while ZSM-5 zeolites are stable in boiling concentrated acid solutions (Baerlocher *et al.* 2007).

Increasing the silica to alumina ratio however results in the decrease in concentration of cations in a sense that they are function of the Al content in the zeolite. This further affects the specific interactions in the catalyst and cations exchange selectivity is predominantly affected. The change in structure of the whole zeolite building unit is also one of the features.

2.5.3. Zeolites applications

Zeolite catalyst has one of the most interesting applications in industries; it is widely used as catalyst in industries such as Petroleum refining, Synfuels Production and Petrochemical production. Catalytic cracking followed by hydrocracking is by far the largest application in petroleum refining sectors. Other uses of zeolites are in the hydro- Isomerisation and waxing mostly by application of ZSM-5 and mordenite (Bekkum *et al.* 1991). Zeolites are also used as adsorbents especially in the removal of heavy metals in industrial waste water (Csicsery and Rabo 1976). Zeolite has one of the applications in the separation processes such as production of branched paraffins from n-paraffins (Bekkum *et al.* 1991). Other zeolite applications include manufacturing of detergents, animal feed supplements and soil improvement (Weitkamp and Puppe 2013).

2.5.4. Zeolite in catalysts

The medium pore zeolite ZSM-5 has shown potential in conversion of alcohols to hydrocarbons containing aromatics. The conversion is being achieved through acidic nature of ZSM-5 as well as its silica to alumina ratio. During catalyst conversion of alcohols, the reaction path involves dehydration, oligomerization of light olefins to heavier olefins and isomerisation, cyclization and aromatization (Cornils and Herrmann 1996). In synfuel production, ZSM-5 has been applied in alcohol to gasoline processes (Baerlocher *et al.* 2007) and in conversion of alcohols to other organic compounds such as aromatic hydrocarbons (Inaba *et al.* 2006).

2.5.5. Zeolite as support for metals

Zeolite supported metals are used in chemical industries especially for enhancement of reactions for conversions of different organic compounds to selective products. For maximum activity with minimal metal content, metal dispersion is of importance. Zeolite is able to enhance high atomic metal dispersion due to its structure and pores. Metal particles become stabilized by zeolite lattice inside pores that provide large surface area. Zeolites as supports become bifunctional catalyst with a metal function and acid Bronsted sites function, apart from everything, they are very stable in reaction conditions and acquire high surface area up to 800 m^2/g (Weitkamp and Puppe 2013).

2.6. Transition metals

2.6.1. Transition metals in general

Transition metals are generally located between the group 3B and group 2B on the periodic table. These elements have at most two electrons in the outer s-orbital and d-orbital which are incompletely filled with electrons. Transition metals are categorised in to d-block and f-block metals. The d-block consists of 3d elements staring from scandium (Sc) to cupper (Cu), 4d elements from yttrium (Y) to silver (Ag) and 5d elements from hafnium (Hf) to gold (Au). The f-block metals consist of lanthanide series from lanthanum (La) to lutetium (Lu), and actinide series from actinium (Ac) to Lawrencium (Lr) (Khandelwal 2007). Most of these transition metals are highly coloured compounds containing complex formulas (Gutmann 2012).

2.6.2. Chemistry of transition metals

Transition metals are generally coordinated with ligands also known as metal complexes. These metals complexes are neutral or are in a form of ionic substances, usually cations. Neutral ligands includes ammonium (NH_3), carbon monoxide, etc. Examples of ionic ligands are Cl^-, $C_5H_5^-$, etc. The main difference between the two is that neutral ligands are stable molecules in their free state on their own independent of metals, while ionic ligands become stable only when they are coordinated to central metals (Khandelwal 2007).

2.6.3. Transition metals catalyst

In various chemical reactions, transition metals and other compounds have shown catalytic activity. The catalytic activity is due to metals' ability to demonstrate multiple oxidation states and formation of complexes. The common example of these metals as heterogeneous catalyst is based in car exhaust where by Pt/Ph alloy supported ceramic converts the mixture of CO_2, CO, NOx and hydrocarbons in exhaust gases to H_2O, CO_2 and N_2 (Khandelwal 2007). For conversion to occur, the reaction require only metals as they possess Lewis acid sites or metals in compound form with ligands which possess Lewis base (Crabtree 2009).

2.7. Activated carbons

Activated carbon is a member of a family of carbons ranging from carbon blacks to nuclear graphites, from carbon fibres and composites to electrode graphites. All come from organic parent sources but with different carbonization and manufacturing processes. In a very general manner, activated carbons can be described as the porosity (space) enclosed by carbon atoms. This is considered as a unique material because of the way it is filled with holes (voids, spaces, sites, pores) the size of molecules. The most important part of these holes is that although they are spaces of zero electron density, these pores possess intense van der Waals forces; from the near proximity of carbon atoms (Marsh and Reinoso 2006).

Activated carbon structure (Figure 2-5) consists of hexagonal carbon rings, many of which have undergone cleavage, are randomly orientated, and lack the directional relationship with one another that is present in single graphite crystals. The overall structure is thus very disordered. Further, the distance between the layers is greater than that found in graphite, 3.6 Ȧ (McDougall 1991).

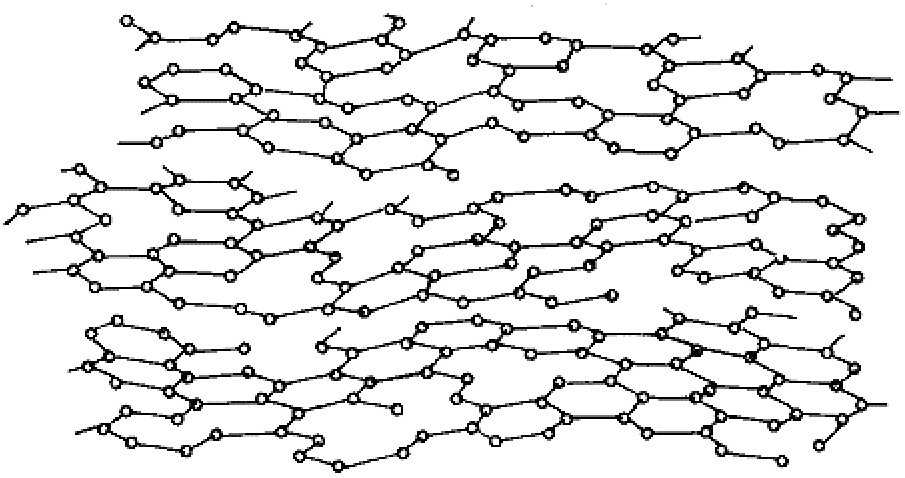


Figure 2-5. Activated carbon structure (McDougall 1991)

The surface area of the activated carbons are generally defined as larger than 400 m^2/g through BET analysis. The pore volume on the other hand is known to be greater than 0.2 ml/g and the width of the pores varies from 3 Å to thousands angstroms. Pores are classified in terms of diameters. Materials exhibiting pores between 500 Å to 20 00 Å are Macropores, 100 Å to 500 Å are Mesopores and 8 Å to 100 Å are Micropores (Marsh and Reinoso 2006).

2.8. Alcohol valorisation

Methanol-to-hydrocarbons (MTH), methanol-to-Olefins (MTO) and methanol-to-gasoline (MTG) reactions have been considered very attractive in research especially for ethanol conversion (Song *et al.* 2010). Following the developments of ZSM-5 applications, the Exxon Mobil's discovery MTG processes in 1970s has inspired researchers in understanding reaction mechanism of alcohols over zeolites catalyst particularly HZSM-5 (Ramasamy and Wang 2013). Ethanol and butanol can be converted to number of hydrocarbons which are similar to those obtained in gasoline range hydrocarbons, these includes benzene, toluene, xylene, light olefins among others.

2.9. HZSM-5 catalysis in alcohol conversion

Ramasamy and Wang (2013) studied alcohols transformations to transportation fuels over HZSM-5 (30) and Inaba *et al.* (2006) applied HZSM-5 (29) and HZSM-5 (190) in ethanol conversion to benzene, toluene and xylene (BTX). Even though the silica to alumina ratios of these catalysts of 30 and 29 were closer to each other, however the targeted products was not the same. Ramasamy and Wang (2013) and Inaba *et al.* (2006) were concerned with producing fuel range hydrocarbons and BTX respectively.

Alcohols feed stock for production of fuel hydrocarbons were methanol, ethanol, 1- propanol and 1– butanol. Catalyst life and product distribution were compared amongst all alcohol conversion process. The catalyst life for 1-propanol and 1-butanol conversion were found to be much longer than that of methanol and ethanol conversion, which is due to the low activation energy required by high alcohols for oligomerization compared to dehydration of smaller alcohols (Ramasamy and Wang 2013).

The acid sites strengths play crucial role in alcohol conversion, product distribution and product selectivity (Inaba *et al.* 2006; Song *et al.* 2009; Ramasamy and Wang 2013), the product distribution classified to paraffin, olefins, aromatics, naphthalene and naphthene compounds were present for all alcohols studied. The variation of product selectivity depends on alcohol class (Ramasamy and Wang 2013) and Si/Al ratio (Song *et al.* 2009). High alcohols produce more liquid hydrocarbons compared to methanol as suggested by Rahman *et al.* (2006), on the other hand smaller alcohols produce high gas fraction which is incondensable at room temperature (Ramasamy and Wang 2013) at which these may be classified as natural gases-ranging from C1 to C4 hydrocarbons. HZSM-5 (30) has high Si/Al ratio (Rahman *et al.* 2006) as results suggested that an increase in aluminium content increases the surface acidity (Rahman *et al.* 2006).

In the conversion of ethanol to BTX over HZSM-5 (29), the formation of BTX hydrocarbons favoured mostly xylene. Other products include diethyl ether, ethylene, C3+ olefins and paraffin. About half of product was BTX and the other half was shared amongst other products. HZSM-5 (190) formed ethylene at high selectivity which suggests that solid acidity of the catalyst is crucial in this reaction. No BTX was formed in ZSM-5 (190) which suggests that presence of large number of acid sites does not always favour the formation of BTX. By evaluation of both HZSM-5 (29) and HZSM-5 (190) it was suggested that low Si/Al ratio is ideally essential for high hydrocarbons production from ethanol (Inaba *et al.* 2006; Song *et al.* 2009), and high Si/Al ratio favours ethylene production (Song *et al.* 2009).

2.10. Metal: M/ HZSM-5 catalysts in alcohol conversion

Various metals such as Mo, Sr, Al, Pt, Sn, Na, Mg, Cr, Cu, Ga, Ru, Rh, Ag, Re, Ir, Au, Ca, Ba, Mn, Ce and Pd have been supported on zeolite catalyst for alcohol conversion (Inaba *et al.* 2006). HZSM-5 catalyst has shown 100% conversion of ethanol (Song *et al.* 2009) and the product composition such as ethylene, paraffin, aliphatic and aromatics have been found to depend strongly on Si/Al ratio (Song *et al.* 2009). Reaction temperatures (Inaba *et al.* 2006), acid strength (Park and Ihm 2000), slilica to alumina ratio (Goto *et al.* 2010) and weight hourly space velocity (WHSV) (Ramasamy and Wang 2013) have been reported to affect the product distribution and selectivity. High temperature reactions favour the formation of ethylene through intramolecular dehydration of ethanol (Park and Ihm 2000) and an increase in SiO_2/ Al_2O_3 ratio tends to reduce the surface acidity on HZSM-5 and lower SiO_2/ Al_2O_3 ratio favours the ethylene production (Song *et al.* 2009).

Platinum (Pt) supported on ZSM-5, ZSM-22 and H-β have been reported to be very active in hydrocracking due to strong acid sites compared to other catalyst supports like SAPO-11/ Al-MCM-41 and H-Y catalyst (Park and Ihm 2000). The activity of Pt/H-β was found to be high through TPD analysis even though similarities of pore sizes and metal dispersion between Pt/H-β and Pt/H-Y existed. Through Pt/ZSM-5, Pt/ZSM-22 and Pt/H-β catalyst, hydrocracking activity increased with conversion, thus Pt enhance the conversion of alkenes to alkanes and it was suggested that highly dispersed Pt favours hydrogenation compared to hydrocracking (Park and Ihm 2000). Studies have shown that some metals supported on ZSM-5 can enhance the production of benzene, toluene and xylene (BTX) while others suppresses their formation (Inaba *et al.* 2006).

Catalyst promoted with Mg, Ca and Ba have been found to increase the formation of ethylene and reduce propylene yield in ethanol conversion due to the reduction of HZSM-5 acidity caused by metal cation loaded on the catalyst. On the other hand metals such as Ni and Ca have been found to increase the formation of C5+ aliphatic and aromatics hydrocarbons while the yield of ethylene significantly decreases using these metals (Song *et al.* 2009). Other metals like Cr, Ce, Pd, Ti, Zr, Mo and W have been reported to enhance both formations of ethylene and propylene yield, while Zr was discovered to improve hydrothermal stability of zeolite (Song *et al.* 2009) which prevents the zeolite structure to undergo dealumination (Song *et al.* 2009; Goto *et al.* 2010). Thus the catalyst promoted metals improve the catalyst performance (Goto *et al.* 2010).

2.11. Fe/HZSM-5 catalyst in alcohol conversion

Inaba *et al.* (2007) applied the incipient wetness impregnation technique to load Fe (10%) on HZSM-5 (29) catalyst for production of olefins from ethanol. Several sources of Fe tabulated in Table 2-5 were used.

All catalysts prepared were tested in a fixed bed reactor packed with 0.2 g catalyst at a temperature of 400 °C. Fe promoted HZSM-5 catalysts were found to be active in the formation of gaseous products such as ethylene, C3+ olefin, paraffin and aromatic compounds. The formation of aromatics was suppressed by Fe loading while the formation of ethylene and C3+ olefin was heightened (Inaba *et al.* 2007). An increase in calcination temperature of Fe catalyst from 500 °C to 900 °C was observed to influence the ethylene and aromatics selectivity irrespective of the Fe sources exclusive $FePO_4$, which showed a very high selectivity to ethylene and a very low selectivity to other products such as C3+ olefins. Expansively the higher the selectivity of aromatics, the lower selectivity of C3+ olefins (Inaba *et al.* 2007).

Table 2-5. Metal precursors (Inaba *et al.* 2007)

Fe source Chemical Name	Fe source Chemical formula
Iron (III) nitrate Nona hydrate	$Fe(NO_3)_39H_2O$
Iron (III) sulphate n- hydrate	$Fe_2(SO_4)_3.nH_2O$
Iron (III) chloride hexahydrate	$FeCl_3.6H_2O$
Iron (III) oxalate dihydrate	$FeC_2O_4.2H_2O$
Iron (III) Phosphate n-hydrate	$FePO_4.nH_2O$

The selectivity of all products changed with time on stream (Inaba *et al.* 2007; Ramasamy and Wang 2013), the selectivity of aromatics compound was decreased with time on stream while that of ethylene was increased on the other hand (Inaba *et al.* 2007). This was further verified by Ramasamy and Wang (2013), as they reported that complete conversion of ethanol to ethylene is achieved even if the catalyst deactivation for liquid hydrocarbons has been reached. This further suggest that ethanol dehydration occurs on weak acid sites and coke deposition on strong acid strength does not predominantly affect ethanol dehydration as long as traces of acidity are still present (Ramasamy and Wang 2013). Thus, the primary dehydration and secondary reactions occur at different acid sites.

The behaviour in phases and crystallite diameter of a loaded catalyst were observed by Inaba *et al.* (2007) through XRD pattern of Fe sources before and after the reactions. The loaded Fe catalyst from $Fe(NO_3)_3$ source before the reaction was found existing as Fe_2O_3 while during the reaction it was reduced to Fe_3O_4 for calcined catalyst at 500 °C and 700 °C while at 900 °C no change was observed. Inaba *et al.* (2007) further stressed that the catalyst prepared from Fe source of $Fe_2(SO_4)_3$ calcined at 500 °C did not show XRD pattern of FeOx before the reaction, suggesting that Fe may exist as FeSOx species which is the result of aromatics compound formation and carbon deposition. Catalyst prepared from Fe source of $FePO_4$ calcined at 700 °C also revealed no XRD pattern before and after the reaction, for this reason it was suggested that this was effective for ethylene formation while on the other hand it was not effective for C3+ olefins and aromatic hydrocarbon formation (Inaba *et al.* 2007).

2.12. Ni/HZSM-5 catalyst in alcohol conversion

The effect of metal content in ethanol conversion to higher hydrocarbons over metal nickel modified HZSM-5 catalyst was studied by Van der Borght *et al.* (2015). Nickel metal from $Ni(O_3)_3.6H_2O$ was impregnated into HZSM-5 (15) at different percentage loadings. The catalyst test was performed in a tubular reactor packed with 0.0005 kg catalyst and HZSM-5 (15) was used as reference catalyst. It was reported that addition of small amount in nickel loading resulted in the slight increase of ethylene formation, while ethylene formation was decreased when metal loading was decreased (Van der Borght *et al.* 2015).

The crystallinity of HZSM-5 was not affected by metal promotion and the smaller nickel content showed no XRD peaks for metal oxides. The persecutor of metal oxide phases of NiO was displayed for higher metal content, however no pure metals was observed on the XRD patterns. Product classes such as C3-C5 olefins, C2-C5 paraffin, aromatics and C5 hydrocarbons were achieved. By doping nickel into HZSM-5, Van der Borght *et al.* (2015) reported that there were no additional functionalities included in the catalyst and even no additional reaction pathways were observed in the reaction mechanism. Further it was reported that no oligomerization to 1-olefin was observed. It was suggested that this may be due to temperature and high pressure since oligomerization usually occurs at low temperatures and high pressures (Van der Borght *et al.* 2015).

Low metal content does not affect structural properties of the catalyst such as surface area and pore volume (Van der Borght *et al.* 2015) . Loading of nickel in HZSM-5 through impregnation resulted in the formation of nickel as cation added for small metal cluster which were not observable in the XRD or TEM. High metal loading showed metal oxides and metal cluster was observed. The catalyst properties such as acid sites, porosity and surface area were reduced due to pores blockage. Van der Borght *et al.* (2015) concluded that, the lower metal loading has a positive effect in the production of C3+ hydrocarbons. This is due to the accessibility of the acid sites while on the other hand high metal loading was found to decrease the production of high hydrocarbons due to bulky metal resulting to pore blockage and decrease in acid strength.

2.13. Zn/ HZSM-5 catalyst in alcohol conversion

Zn/HZSM-5 catalyst prepared by impregnation method in methanol to gasoline (MTG) process was studied by Fattahi *et al.* (2016). Prepared catalysts were tested in a fixed bed reactor at 370 °C, ambient pressure. It was highlighted that slow deactivation rate in the methanol conversion to hydrocarbons was observed over Zn/HZSM-5. The catalyst was found to be active in production of gasoline hydrocarbons such as xylene, toluene, methyl-ethylbenzene and tri-methylbenzene. It was reported that with time on stream, the formation of toluene and xylene products decreased while the formation of tri-methylbenzene and C10 aromatics increased, and the amount of light olefins was negligibly very small. Zinc promoted zeolite was found to be stable and longer in catalyst life, furthermore it was observed to improve the formation of aromatics hydrocarbons (Fattahi *et al.* 2016).

2.14. Reaction pathways for alcohols conversion

Reactions involved in Exxon Mobil process for Methanol-to-Gasoline have been proposed after detailed investigation of MTG processes as shown in reaction scheme in Figure 2-6. Over HZSM-5 catalyst, methanol follows the intermolecular dehydration to form diethyl ether. It then undergoes further dehydration to form olefin, ethylene in this case (Keil 1999; Ramasamy and Wang 2013). The ethylene formation in methanol reaction requires the formation of carbon-carbon bond between C1 reactant (Inaba *et al.* 2007). Olefin is then further subjected to oligomerization, dehydrocylization and hydrogenation reaction towards the formation of gasoline range hydrocarbons.

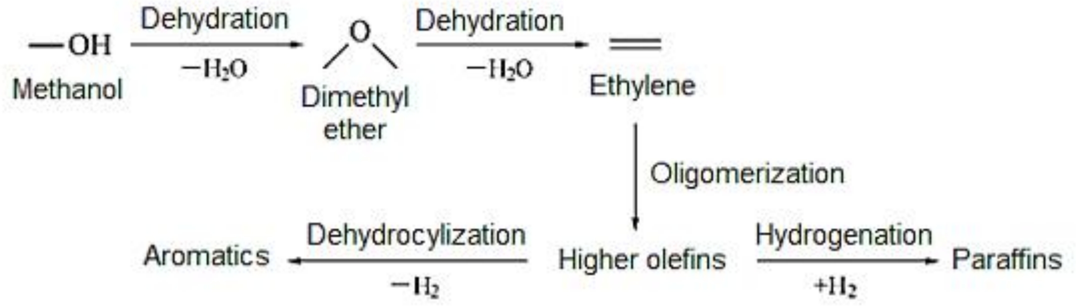


Figure 2-6. Reaction mechanism for methanol conversion over ZSM-5, adapted from Ramasamy and Wang (2013)

Ethanol conversion reaction mechanism is presented in Figure 2-7. The conversion of ethanol-to-gasoline also follows the same mechanism for methanol except that ethanol undergoes intramolecular dehydration to form ethylene (Ouyang *et al.* 2009; Van der Borght *et al.* 2015) in one step. Unlike methanol, the ethanol reaction eliminates the need for the indirect routes for hydrocarbon pool mechanism (Van der Borght *et al.* 2015) and this reaction can proceed in acid sites (Inaba *et al.* 2007). Other alcohols such as propanol and butanol were also observed to follow the same reaction network as ethanol reaction mechanism. 1- propanol and 1-butanol undergo intramolecular dehydration to form propylene and 1-butylene respectively.

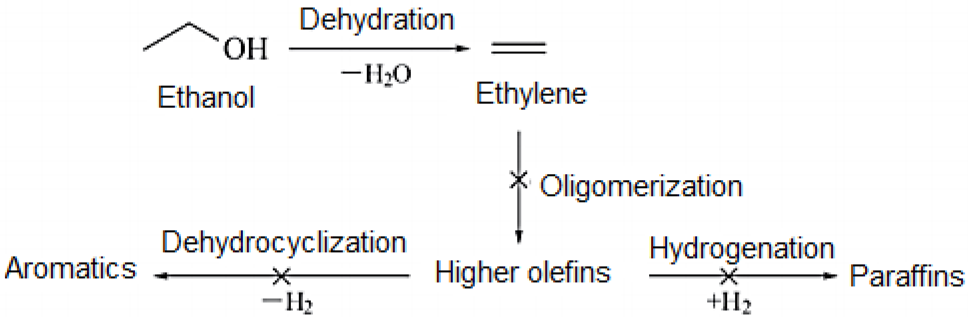


Figure 2-7. Ethanol conversion reaction mechanism over ZSM-5, adapted from Ramasamy and Wang (2013)

The oligomerization process follows to form higher olefins which can undergo dehydrocylization to form aromatics and or be hydrogenated to form paraffins (Ramasamy and Wang 2013), these reactions occur at acid sites of the zeolite support (Inaba *et al.* 2007). However, Inaba *et al.* (2006) proposed that ethanol can undergo similar MTG reaction pathways through ethanol intermolecular dehydration at low temperatures to form diethyl ether, followed by intramolecular dehydration of ethanol to ethylene at high temperature as shown in Figure 2-8.

Diethyl ether can be converted to ethylene and to C4 olefins through dehydration at high temperatures. Both diethyl ether products can undergo oligomerization, aromatization, H-transfer and cracking reactions to form olefin, paraffins and BTX hydrocarbons. In last stage, the compound undergoes carbonization to form carbon deposits (Inaba *et al.* 2006, 2007). The effect of metal modified catalyst on reaction pathways was investigated by Van der Borght *et al.* (2015). No additional reaction functionalities were found to be included in the catalyst and no extra reaction pathways were observed to be added in reaction mechanism.

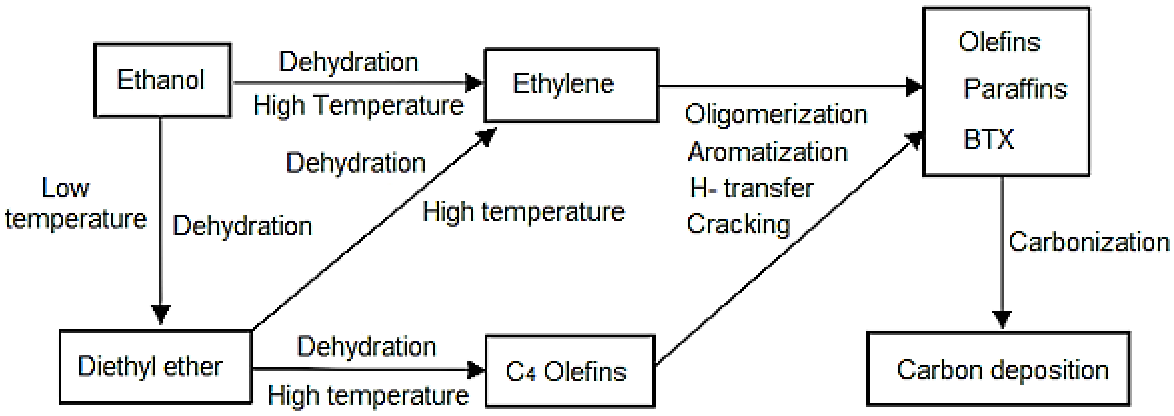


Figure 2-8. Supposed reaction mechanism for ethanol conversion, adapted from Inaba *et al.* (2006)

2.15. Characterisation techniques

2.15.1. X- Ray Diffraction (XRD)

XRD is a characterization technique used to determine the properties of a material such as crystal structure and phase composition. Solid matters can be described as amorphous or crystalline. In amorphous materials, atoms are arranged in a random manner as found in liquids while in crystalline materials, atoms are arranged in a regular pattern. Most solid materials can be pronounced as crystalline through XRD. The diffraction pattern is produced when x-rays interacts with crystalline substances. The x-ray diffraction pattern of a substance is thus like a fingerprint of a substance which is unique for every substance, and the same substance always gives the same patterns, where in mixtures, each substance will give off its pattern independently of the others (Jenkins and Snyder 1996).

When a solid material is bombarded with an x-ray beam, then electrons around the atom of the solid material gets excited and begin to oscillate with the same frequency as the incoming beam. Destructive interference will then occur in almost all directions with no energy leaving the solid sample. Because atoms in crystal are arranged in a regular pattern, thus constructive interference will occur in few directions. The signals of these diffracted rays are detected on a detector and get recorded (Jenkins and Snyder 1996).

2.15.2. Scanning Electron Microscope (SEM) - Energy-dispersive X-ray spectroscopy (EDS)

The scanning electron microscope (SEM) is a technique used for imaging particles with a high-energy beam of electron in a raster scan pattern. When the SEM is coupled with EDS, the mechanism allows the analysis of elemental composition in solid material. In SEM-EDS, electron optical system to produce an electron probe is required. Other components employed in SEM-EDS are specimen stage to place the specimen, a secondary electron detector for secondary electron collection which is responsible for topographic picture generation, and the image display unit (Goldstein *et al.* 2012).

Samples are bombarded with electrons from electron gun and signals are generated through secondary electron, detection of backscattered electron which generates the picture based on the mass of the element, and X-ray which is used in element composition identification and spectrum generation. The interaction takes place between the electron and atoms making up the sample that provides signals which carries the information of the topology and composition (Goldstein *et al.* 2012).

2.15.3. BET (Brunauer, Emmet, and Teller)

BET is a characterization method that employs the physical adsorption of gas molecules on a solid surface and serves as a basis for analysis technique for the measurement of the surface area of the solid material. This technique is based on the adsorption and condensation of N2 at liquid Nitrogen temperature. Nitrogen is usually used because of its availability in high purity and its strong interaction with most solids. Because the interaction between gaseous and solid phases is generally weak, the surface is cooled using liquid N2 to obtain detectable amounts of adsorption. Known amounts of nitrogen gas are then released stepwise into the sample cell.

Relative pressures less than atmospheric pressure is achieved by creating conditions of partial vacuum. After the saturation pressure, no more adsorption occurs regardless of any further increase in pressure. Accurate pressure transducers monitor the pressure changes due to the adsorption process. After formation of adsorption layer, the sample is removed from the nitrogen atmosphere and heated to cause the adsorbed nitrogen to be released from the material and quantified. The data collected is displayed in the form of a BET isotherm, which plots the amount of gas adsorbed as a function of the relative pressure. (Brame and Griggs 2016).

2.15.4. Gas chromatography, GC-MS

Gas chromatography (GC) is an analytical technique used for organic compounds analysis based on their boiling points. This uses the application of chemical mixtures separation into individual components based on their volatilities and or polarity. When good separation is achieved, individual compounds can be quantified. When Gas chromatogram is coupled with mass spectroscopy (GCMS) it allows better identification of individual compounds. GC is a very sensitive instrument to which samples of one microliter or less are injected through the column. The components required in a GC for analysis are the injector ports through which samples are being loaded, the column at which components are being separated, carrier gas (usually Helium) which carries the sample throughout the instrument, a detector and a data processor (Hites 1997).

Samples to be analysed are typically loaded at the injector port, then the injector port is heated in order to volatilize the sample. Once the sample is in a gas phase, it is carried out into a column by the carrier gas (mobile phase). On the other hand, the application of mass spectroscopy involves the fragmentation of the compound into small ions. These ions are then reorganised based on their mass-to-charge ratios in a mass analyser and collected by a detector to produce mass spectrum. Each molecule has its unique mass spectrum and thus this is used to identify the unknown compounds (Hites 1997).

CHAPTER 3

EXPERIMENTAL AND ANALYTICAL METHODS

3.1. Material description

Zeolite (ZSM-5): Chemical obtained from Zeolyst International (CBV 5524G-1000G), SiO_2/Al_2O_3 = 50, in an ammonium form. White powder of fine particles. This was used as a starting material for HZSM-5 which was used as a catalyst support for metals.

Activated carbon (AC): Chemical obtained from Donau Carbon. Black powder of fine particles. This was used as a catalyst support for metals.

Ethanol: Chemical obtained from Lichro Chemical and Laboratory, 95 % Ethanol, Analytical Reagent (AR) grade, Colourless Liquid. Ethanol was used as a feed stock for production of hydrocarbons.

Butanol: Chemical obtained from Lichro Chemical and Laboratory, n-Butanol, Analytical Reagent (AR) grade, Colourless Liquid. Butanol was used as a feed stock for production of hydrocarbons.

Iron (III) nitrate nonahydrate: Chemical obtained from Sigma-Aldrich at 98+ %, ACS reagent grade. Grey powder with fine particles. Iron (III) nitrate nonahydrate was used as a precursor for iron in preparation of catalyst systems supported on both HZSM-5 as well as activated carbon for conversion of feedstock (ethanol / butanol).

Nickel (II) nitrate hexahydrate: Chemical obtained from Sigma-Aldrich, ACS reagent grade. Green powder with fine particles. Nickel (II) nitrate hexahydrate was used as a precursor for nickel in preparation of catalyst systems supported on both HZSM-5 as well as activated carbon for conversion of feedstock (ethanol / butanol).

Zinc nitrate hexahydrate*:* Chemical obtained Sigma-Aldrich at 98 %, ACS reagent grade. White powder with fine particles. Zinc Nitrate Hexahydrate was used as a precursor for zinc in preparation of catalyst systems supported on both HZSM-5 as well as activated carbon for conversion of feedstock (ethanol / butanol).

3.2. Catalyst preparation

3.2.1. Zeolite transformation from ammonium form to hydrogen form

ZSM-5 zeolite in ammonium form (CBV 5524G with SiO2/Al2O3 = 50) obtained from Zeolyst International was calcined in a muffle furnace at 600 °C in atmospheric environment for 5 hours (Van der Borght *et al.* 2015). Calcination directs the ammonia to be released from the zeolite framework which turns into zeolite in a protonic form.

3.2.2. M/HZSM-5 (M: Zn, Fe, Ni)

5 wt. % Metals (Zn, Fe and Ni) were deposited using incipient wetness impregnation technique on HZSM-5 as an active support. Metal salt was mixed with deionised water for preparation of metal solution. The samples were oven dried at 110 °C overnight for removal of water and calcined at 550 °C for 6 hours to get rid of organic impurities (Van der Borght *et al.* 2015). Samples obtained were designated as Zn/HZSM-5, Fe/HZSM-5 and Ni/HZSM-5.

3.2.3. M/AC (M: Zn, Fe, Ni)

5 wt. % Metals (Zn, Fe and Ni) were deposited using incipient wetness impregnation technique on activated carbon as an inert support. Metal salt was mixed with deionised water for preparation of metal solution. The samples were oven dried at 110 °C overnight for removal of water and calcined at 550 °C for 6 hours on a muffle furnace under atmospheric environment

to get rid of organic impurities (Van der Borght *et al.* 2015). Samples obtained were designated as Zn/AC, Fe/AC and Ni/AC.

3.3. Catalyst characterization

3.3.1. X- Ray Diffraction (XRD)

XRD measurements for catalysts were performed on a BRUKER AXS D8 Advance XRD machine powder diffraction system. Copper radiation source was used and the x- ray generator settings for scans were conducted with 40 KV and 40 mA with a scanning range of 0.5° to 90°.

3.3.2. Scanning Electron Microscope (SEM) - Energy-dispersive X-ray spectroscopy (EDS)

FEI Nova NanoSEM 230 fully equipped with an EDS system was used in the present study. This system was employed for obtaining the elemental composition of the catalyst samples. The catalyst samples were coated with graphite to reduce charge problems. The EDS system was also used to get an idea of the elemental composition including Si, Al, O, Fe, Ni and Zn present in samples.

3.3.3. BET (Brunauer, Emmet, and Teller)

Surface area studies was performed in a BET analyser TriStar II 3020 2.00 model. Catalyst samples for BET specific surface area analysis were outgassed using helium. BET surface area analysis was carried out at -195.8 °C in surface area analyser, using nitrogen.

3.4. Alcohol conversion

3.4.1. Catalyst test

Reactions were carried out in a down flow fixed bed stainless steel reactor tube (Length = 0.42 m, ID= 0.009 m and OD= 0.012 m) as depicted in Figure 3-1.The reactor was packed with 0.5 grams of catalyst supported with quartz wool for each experiment. Heating was achieved through an external tube furnace coupled with a relay receiver input from PID Temperature controller. A thermocouple was inserted at the centre of the furnace closest to the catalyst bed to ensure the temperature of the bed was controlled accordingly. Feed was fed using HPLC pump into the reactor.

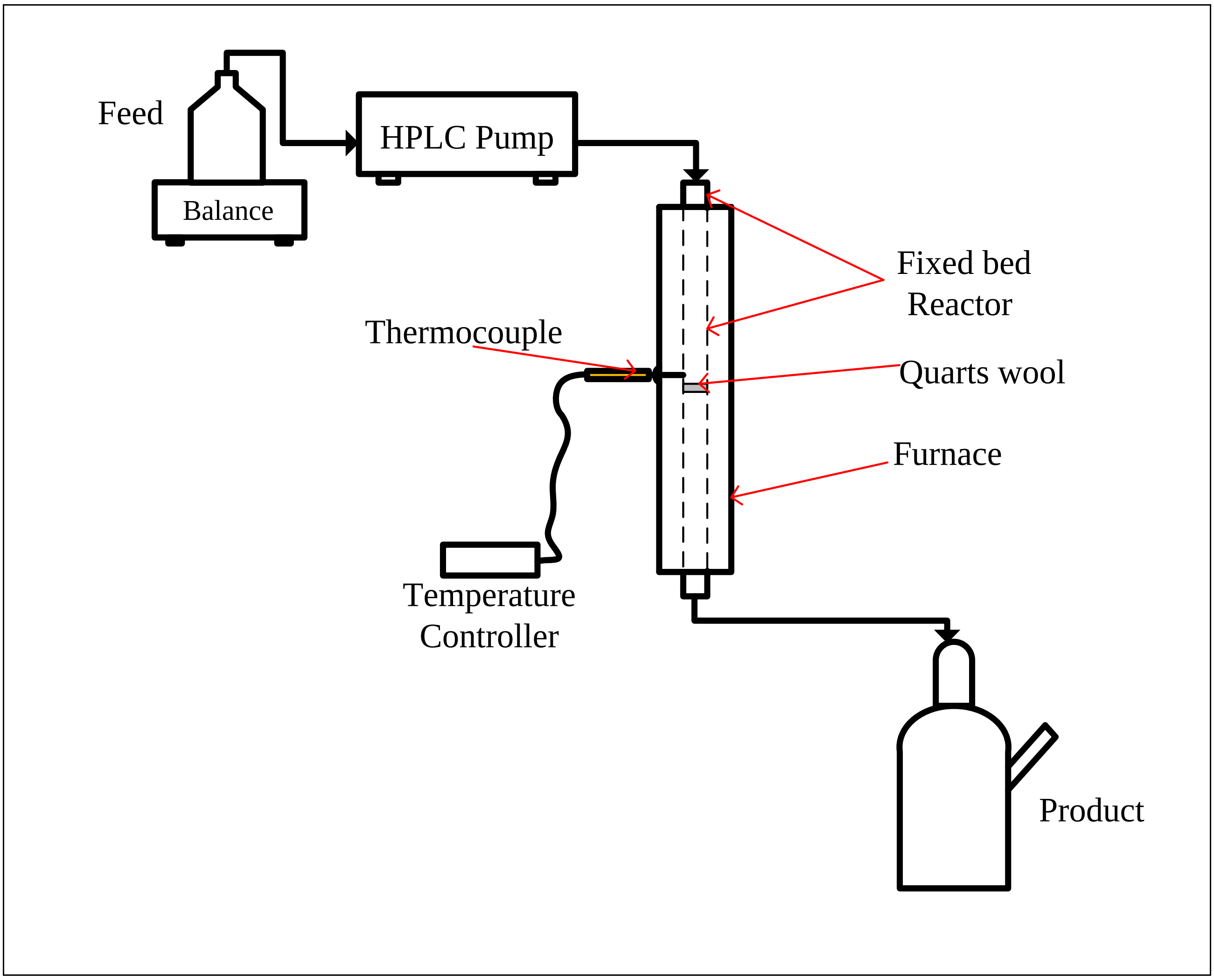


Figure 3-1. Process Flow Diagram

All experiments were carried out at weight hourly space velocity (WHSV) of 2.5 g/h^{-1} g cat. The reactor was operated at 400 °C and atmospheric pressure. Before any experimental run, catalyst was preheated for activation. Feed stock was passed through the catalyst in a reactor and the product was sent to a collecting vessel with gas outlet. Liquid samples were then sent for analysis (Van der Borght *et al.* 2015).

3.4.2. Gas chromatography mass spectroscopy (GC-MS)

The Liquid products were analysed using offline Shimadzu gas chromatograph mass spectroscopy (GCM-SQP-2010 Ultra), equipped with the capillary column of 30m x 0.25 x 0.25um DB5MS and FID detector. One microliter of sample was introduced into an injector port (split mode) with a detector temperature of 250 °C. The temperature of the column was initially at 50 °C with a temperature increase gradient of 4 °C/ min up to 280 °C and helium at a flowrate of 0.9 ml/ min was used as a carrier gas.

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1. Catalyst characterization

4.1.1. X- Ray Diffraction (XRD)

4.1.1.1. Zeolite transformation from ammonium to hydrogen form

XRD analysis was carried out to assess the crystallinity of the ZSM-5 zeolites used in this study. The XRD Patterns of ZSM-5 received from the supplier in ammonium form and zeolite calcined at 600 °C to hydrogen form are shown in Figure 4-1. It was confirmed that the calcination process did not affect the crystallinity of zeolite. ZSM-5 or ZSM-5 calcined (H-ZSM5) characteristic peaks in the XRD patterns are normally found at 2θ diffraction angles of 7.96, 8.91, 14, 14.87, 20.92, 23.28, 23.97, 24.52 and 26.66 degrees corresponding to zeolite crystals.

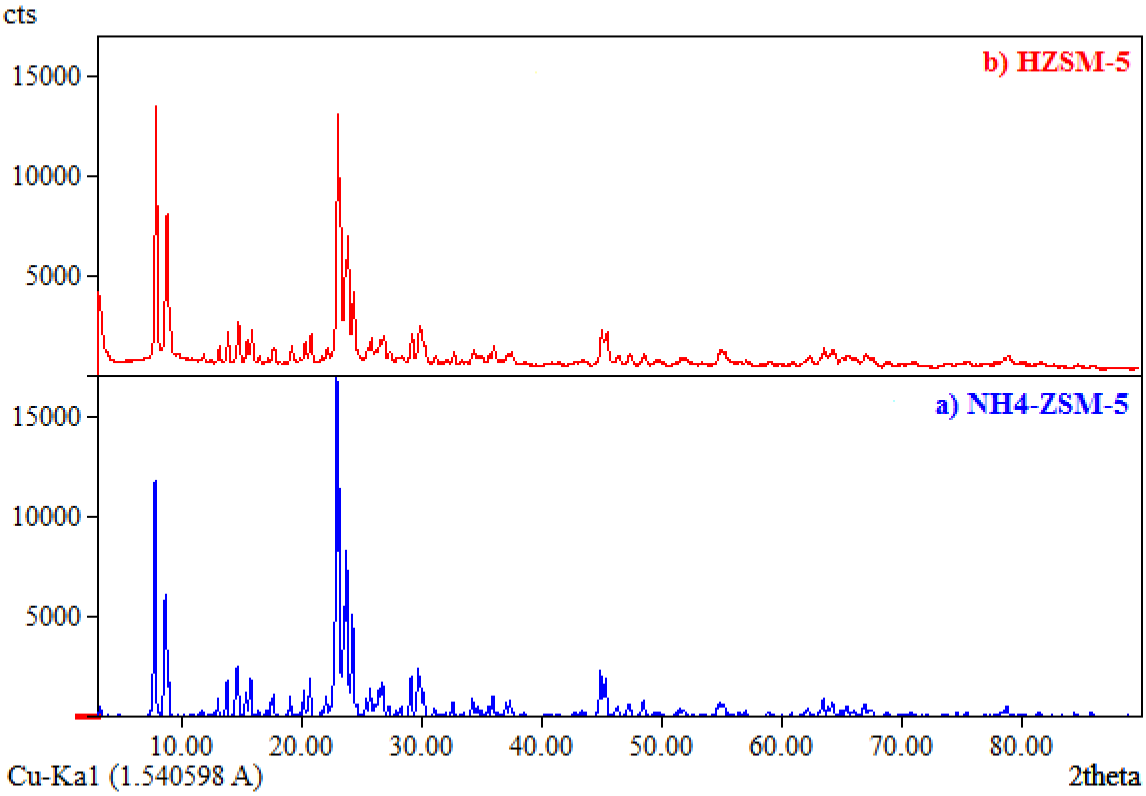


Figure 4-1. XRD Pattern of ZSM-5 a) NH_4-ZSM-5 and b) HZSM-5

4.1.1.2. Zeolite promoted metals: Fe, Ni and Zn

XRD patterns showed no significant changes in the crystallinity of modified zeolite. All sample structures of HZSM-5, Fe/HZSM-5, Ni/HZSM-5 and Zn/HZSM-5 show similar characteristic peaks of 2 theta at 7.94, 7.95, 8.01, 8.84, 8.88 degrees with different intensities. The relative crystallinity of prepared catalyst samples were calculated (refer to Appendix A).

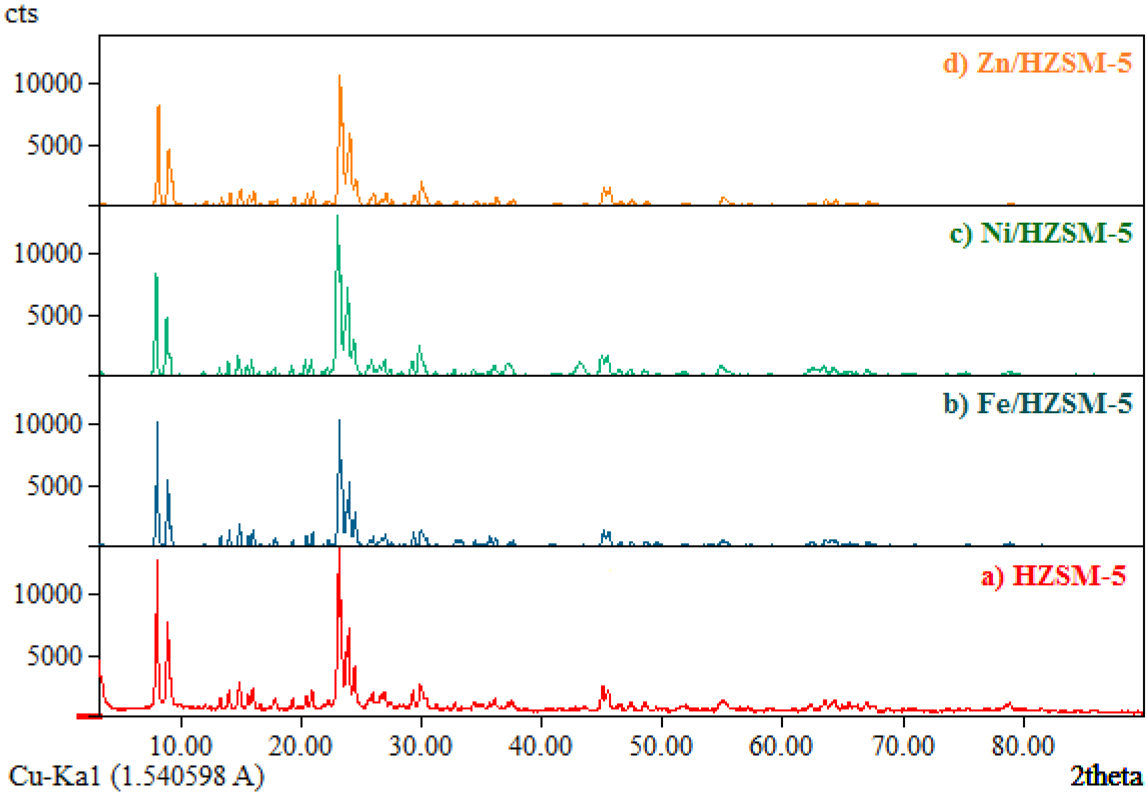


Figure 4-2. XRD Patterns for HZSM-5 and M/HZSM-5

ZSM-5 Calcined: This is a parent catalyst for this study and was used as a reference for all catalyst prepared. The particle size of the crystalline was calculated using Debye Scherrer equation to be 29.46 nm (refer to Appendix B) and the catalyst sample was found to possess monoclinic crystal system.

Fe/HZSM-5: HZSM-5 was modified through impregnation with 5% Iron (Fe). The XRD pattern is presented in Figure 4-2. Iron modification did not change the crystalline structure of zeolite catalyst. However, the relative crystallinity of the catalyst was reduced to 75%

compared to that of the parent catalyst. The particle size of the crystalline at 2theta of 23° increased from 29.46 nm to 49.75 nm after iron impregnation. On the other hand, the crystal system of the catalyst did not change; it remained as monoclinic. Phases of iron crystallinity were not detected in this sample, this suggests that ions of iron were finely dispersed at the sites of the zeolite which caused them not to be detected.

Ni/HZSM-5: Catalyst modified with nickel was evaluated and 5% nickel was impregnated into zeolite catalyst. The pattern for this catalyst system is presented in Figure 4-2 showing no change in crystallite structure and the relative crystallinity was 80%. Particle size of the crystalline at 2theta of 23° was reduced to 16.36 nm and the crystal system did not change from monoclinic after nickel impregnation. Nickel was detected in a form of NiO crystalline phases at 2theta of 37°, 43° 63°, 75° and 79°.

Zn/HZSM-5: Figure 4-2 shows XRD pattern of HZSM-5 doped with Zinc metal. However, zinc impregnation did not affect the crystallinity of the catalyst but the relative crystallinity was 70%. The particle size of the crystalline for a peak at 2theta = 24.34° was reduced to 19.92 nm and the crystal system was found to exhibit both monoclinic and orthorhombic after zinc impregnation. Diffraction peaks appearing at 2theta of 32°, 34.5°, 36°, 47°, 56.5°, 66°, 67° and 68° indicated that the Zn existed in the catalysts in the form of ZnO.

4.1.1.3 Activated carbon promoted metals: Fe, Ni and Zn

XRD pattern of activated carbon and activated carbon promoted metals is shown in Figure 4-3. Promoted activated carbon revealed significant peaks that confirms the successful impregnation of metals.

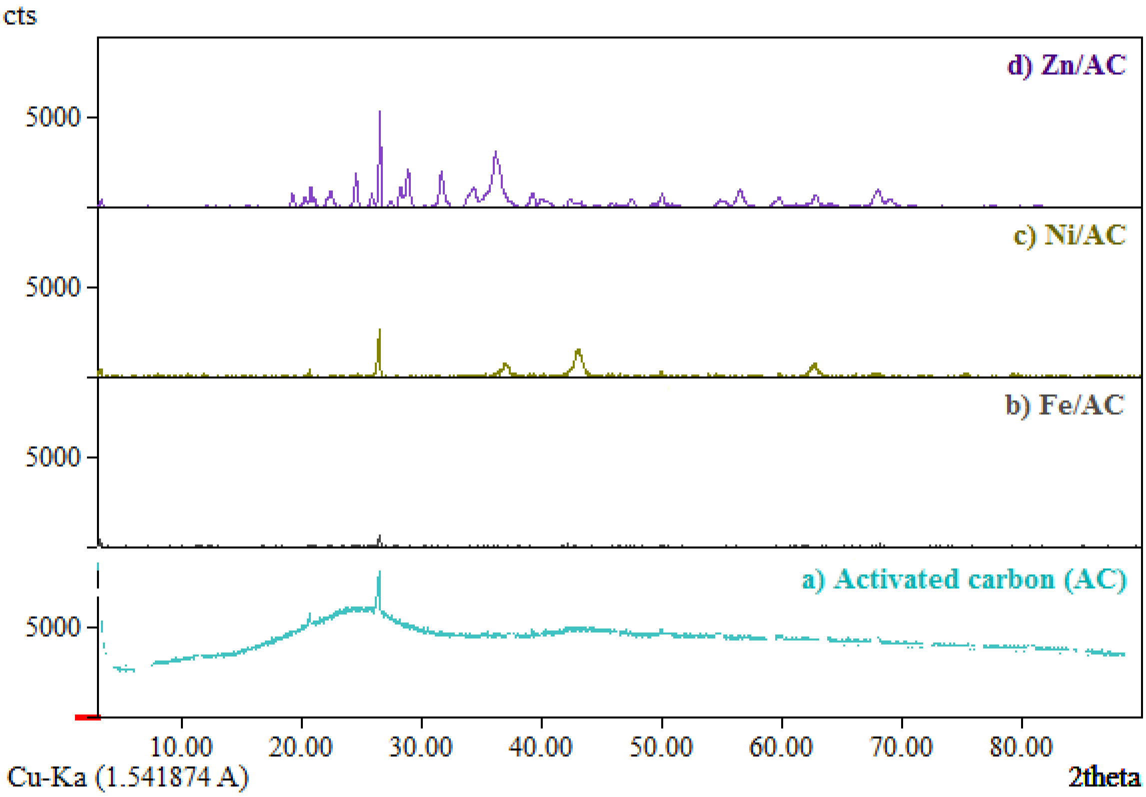


Figure 4-3. XRD Pattern for Activated carbon promoted metals

Activated Carbon (AC): Activated carbon was used as an inert support for metals. XRD pattern for activated carbon is shown in Figure 4-3. XRD pattern showed that activated carbon exhibits amorphous structure and the major peak at 2theta angle of 26.5° corresponds to carbon.

Fe/AC: The XRD pattern of Iron supported on activated carbon is shown in Figure 4-3. Phases of iron crystalline were not detected in Fe/AC, suggesting that this metal is present at high dispersion on activated carbon. Major peak at 2theta of 26.5°corresponds to carbon.

Ni/AC: Nickel supported activated carbon showed a number of major peaks compared to Fe/AC catalyst as represented in Figure 4-3. The sharp peak represents the presence of carbon at 2theta of 26.5°. Nickel in the form of NiO crystalline phases was detected at 2theta of 37°, 43°, 63°, 75° and 79°.

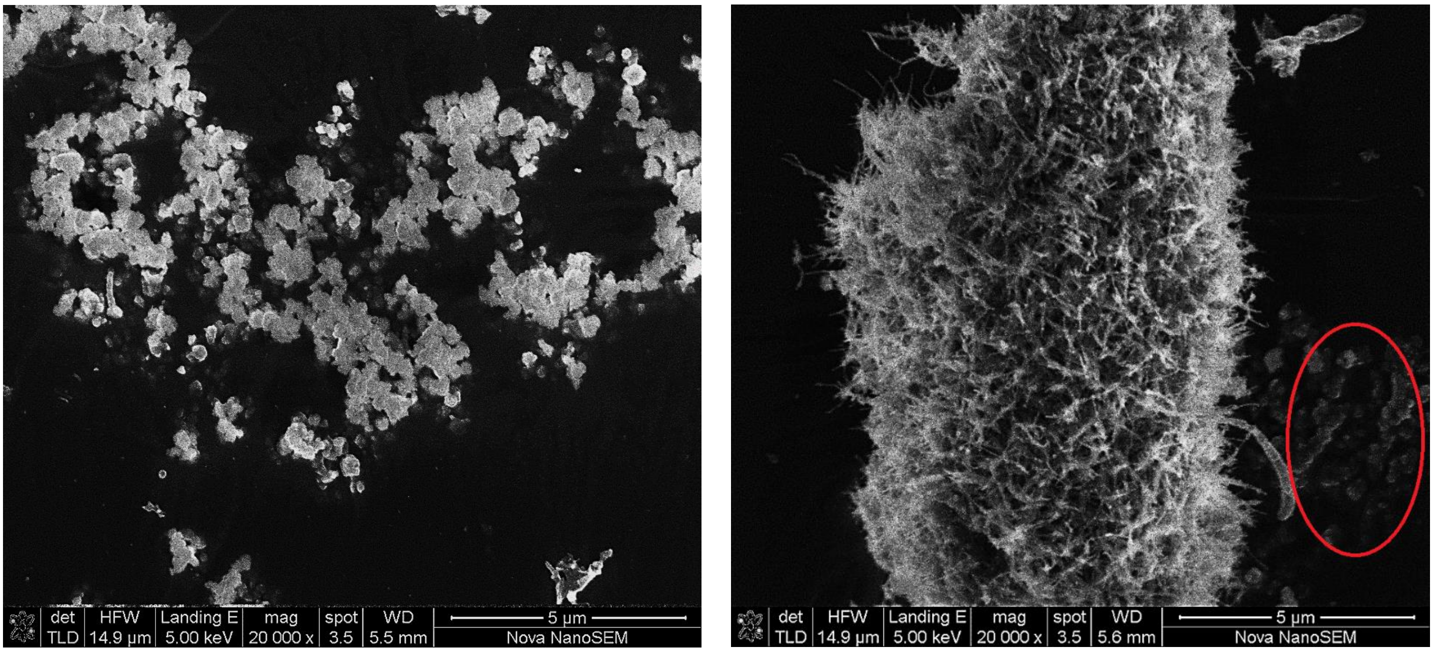
Zn/AC: Zinc supported activated carbon showed several number of major peaks as presented in Figure 4-3. Carbon element was detected at 2theta of 26.5° and zinc in the form of ZnO crystalline phase was detected at 2theta values of 32°, 34°, 36°, 47.5°, 56.5° and 67°.

4.1.2. Scanning Electron Microscope (SEM) and Energy Dispersive X-Ray Spectroscopy (EDS)

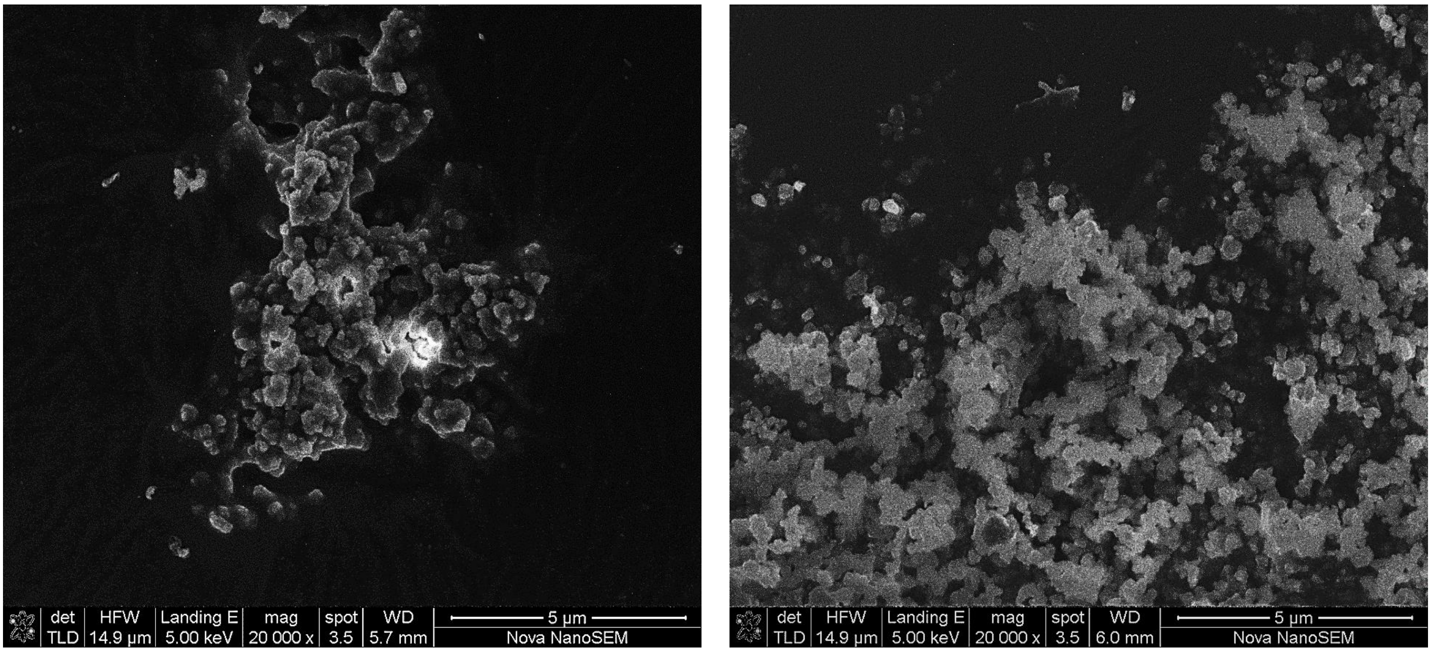
4.1.2.1. Zeolite and zeolite promoted metals: Fe, Ni and Zn

The crystal morphology of zeolite and zeolite promoted metals were analysed by SEM analyser as shown in Figure 4-4. The SEM images were taken at magnification of 20 000 times. HZSM-5 was observed to exhibits irregular shapes, even though it was difficult to conclude based on the shapes of this particles it can be seen that they are of relative size.

Formations of small crystals were observed following the shape of fibres clustered together during promotion with zinc. The portion circled with red colour (Figure 4-4 b) exhibited different particle shape which can be related to spherical and are clustered. Impregnation with nickel showed development of particles with irregular shapes stuck together. Zinc promoted HZSM-5 revealed particles of irregular shapes, it can be seen that the Zn/HZSM catalyst exhibits shapes which relates to that of HZSM-5 alone. Further, EDS analysis was conducted in order to check the composition of the catalyst.



a) HZSM-5 b) Fe/HZSM-5



c) Ni/HZSM-5 d) Zn/HZSM-5

Figure 4-4. SEM Images for *a)* HZSM-5 *b)* Fe/HZSM-5 *c)* Ni/HZSM-5 and *d)* Zn/HZSM-5

Fe/HZSM-5: Figure 4-5 shows compositions of Fe/HZSM-5; presence of iron was observed as well as oxygen, aluminium and silicon as elements of zeolite catalyst. The Fe loading calculated from EDS results was 5.18 % which is closer to targeted loading of 5%.

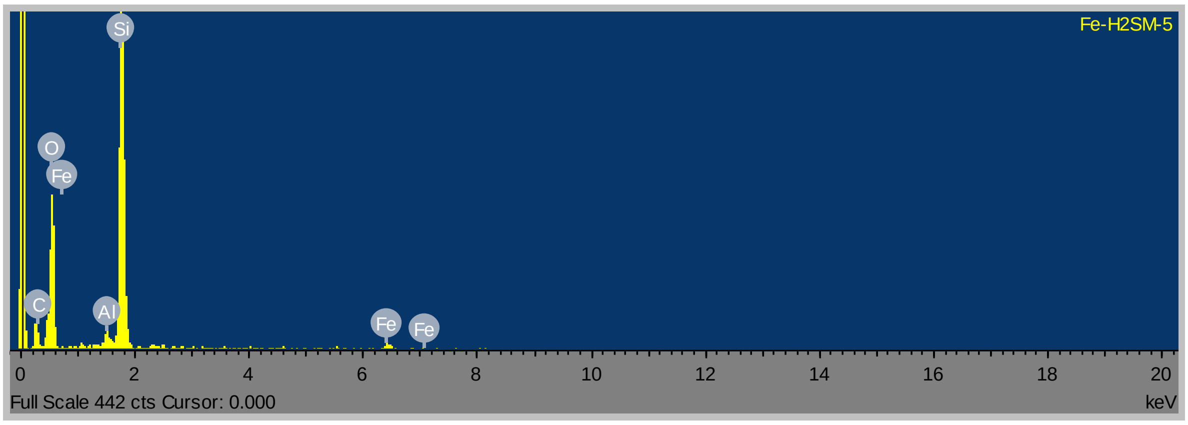


Figure 4-5. EDS Graph for Fe/HZSM-5 Catalyst

Ni/HZSM-5: Shown in Figure 4-6 is nickel supported HZSM-5 catalyst composition. Nickel was detected in the sample verifying the success of metal impregnation. Other elements from zeolite structure such as oxygen, silicon and aluminium were detected as well. Moreover, carbon detected was from the film. The Ni loading was calculated from these results was 4.67 % which is closer to targeted 5% loading.

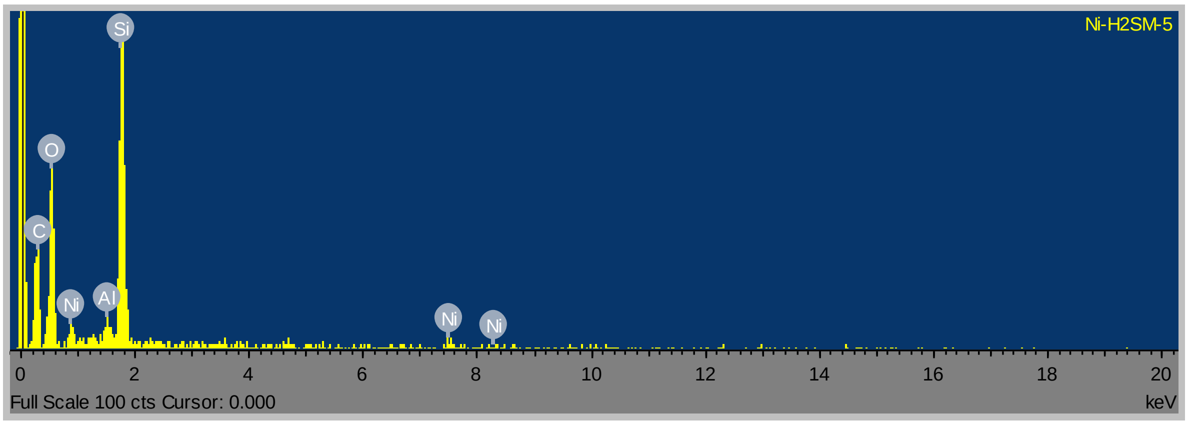


Figure 4-6. EDS Graph of Ni/HZSM-5 Catalyst

Zn/HZSM-5: As shown in Figure 4-7 no traces of zinc were detected by EDS analyser. This does not mean that the catalyst was not impregnated with zinc, it is because zinc metal in the portion selected to bombard the sample with a focus beam of electron was not well dispersed. This was verified by the XRD results which revealed traces of zinc in this sample.

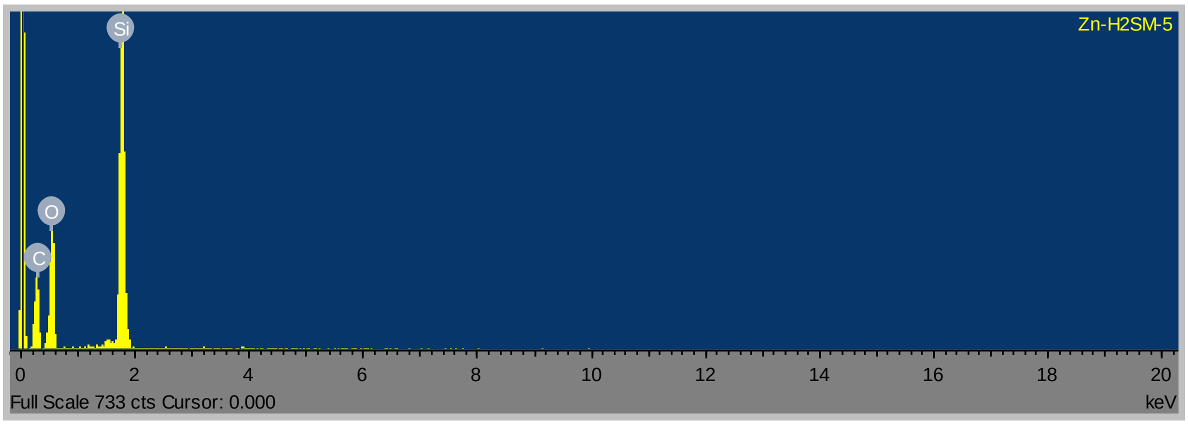


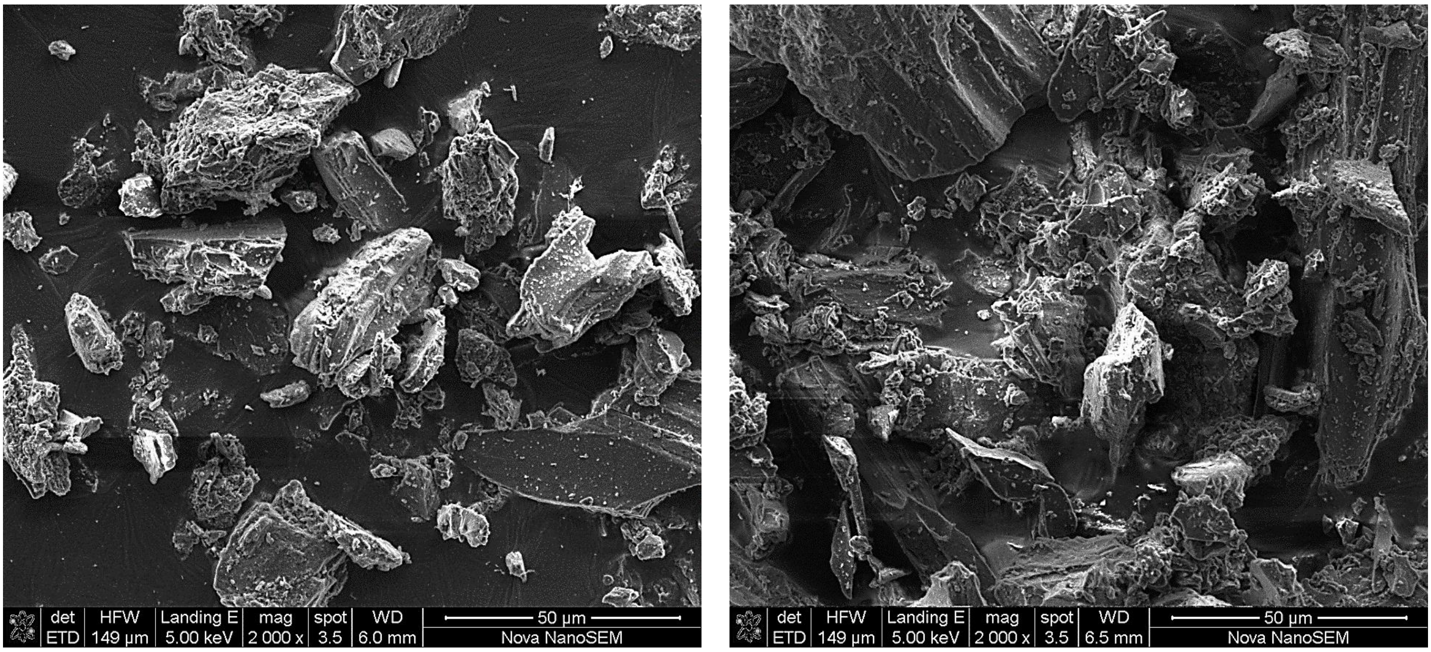
Figure 4-7. EDS Graph of Zn/HZSM-5 Catalyst

4.1.2.2. Activated carbon and activated carbon promoted metals: Fe, Ni and Zn

The morphology and composition of activated carbon and activated carbon promoted metals were analysed by SEM-EDS analyses as depicted in Figure 4-8. The SEM images were taken at a magnification of 20 000 times.

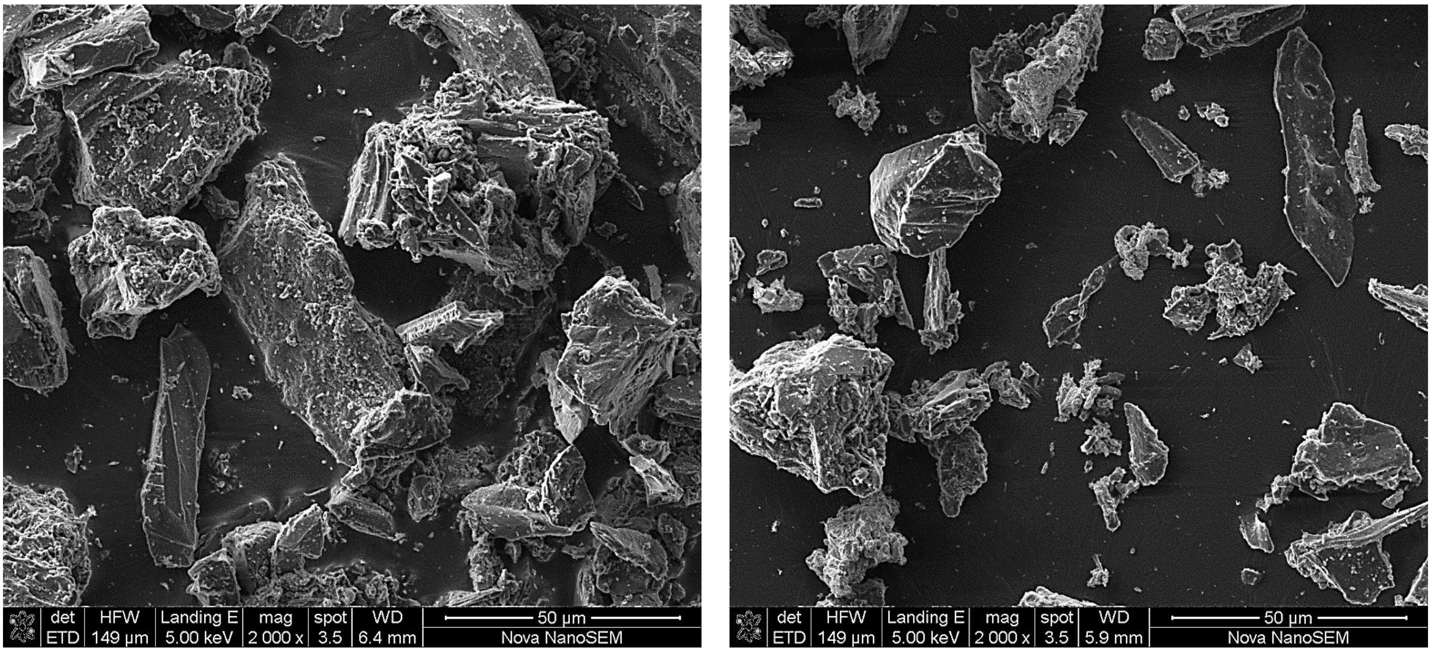
All samples of activated carbon and activated carbon supported metals, M: Fe, Ni and Zn, exhibited disordered structure. The particles possess rough surface with plane sheets that had irregular shapes. At some positions these shapes are clustered together. Further, EDS analysis for catalyst supported with activated carbon was conducted to verifying the success of metal impregnation by checking catalyst composition.

Fe/AC: Composition of iron supported activated carbon catalyst is shown in Figure 4-9. Iron metal was detected confirming the success of Fe impregnation. Other elements such as carbon, oxygen and phosphate were detected.



a) Activated Carbon (AC)

b) Fe/AC



c) Ni/AC

d) Zn/AC

Figure 4-8. SEM Image for *a)* AC *b)* Fe/AC *c)* Ni/AC and *d)* Zn/AC

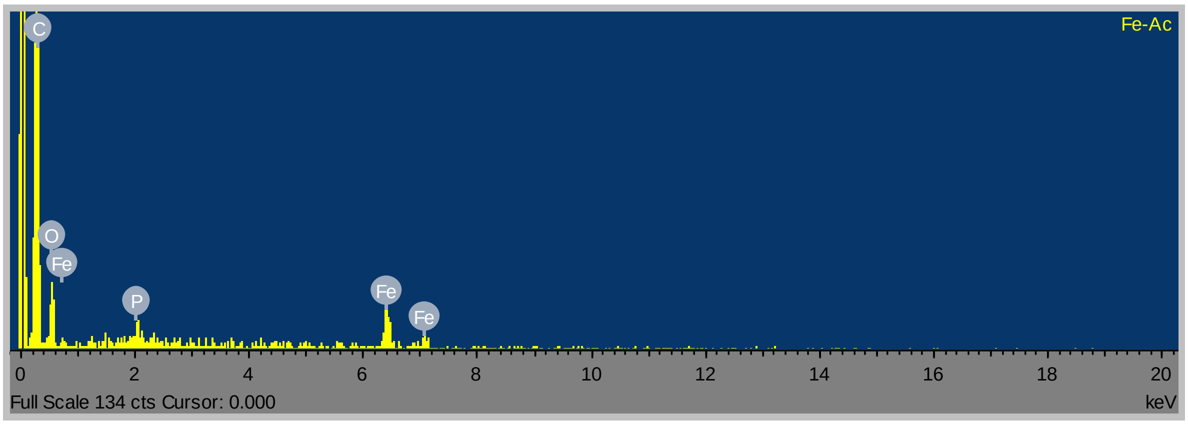


Figure 4-9. EDS Graph for Fe/AC Catalyst

Ni/HZSM-5: Nickel supported activated carbon composition is presented in Figure 4-10. Nickel was detected verifying the success of impregnation. Also other elements such as oxygen, and phosphorus were detected while carbon was from the film.

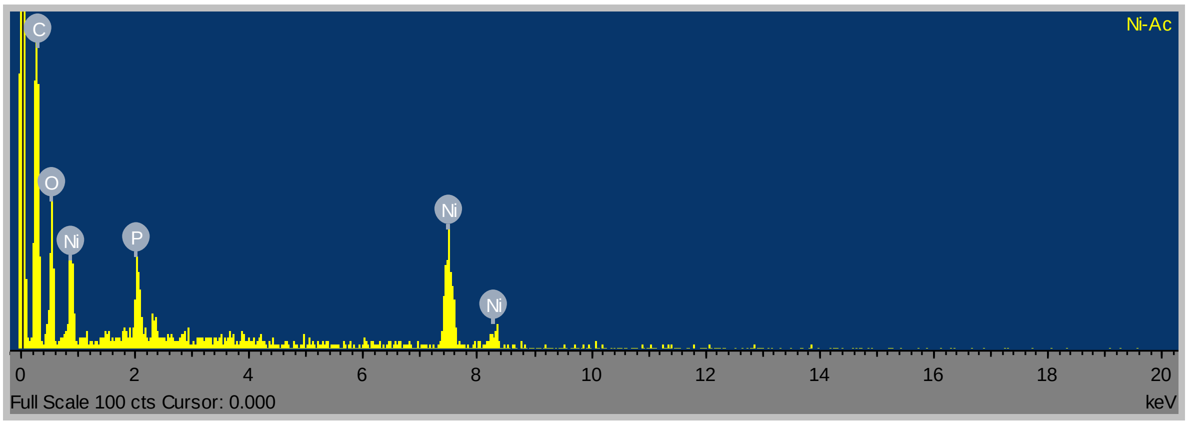


Figure 4-10. EDS Graph for Ni/AC Catalyst

Zn/AC: Zinc supported activated carbon is shown in Figure 4-11. Zinc metal was detected and other elements such as oxygen, phosphate and silicon.

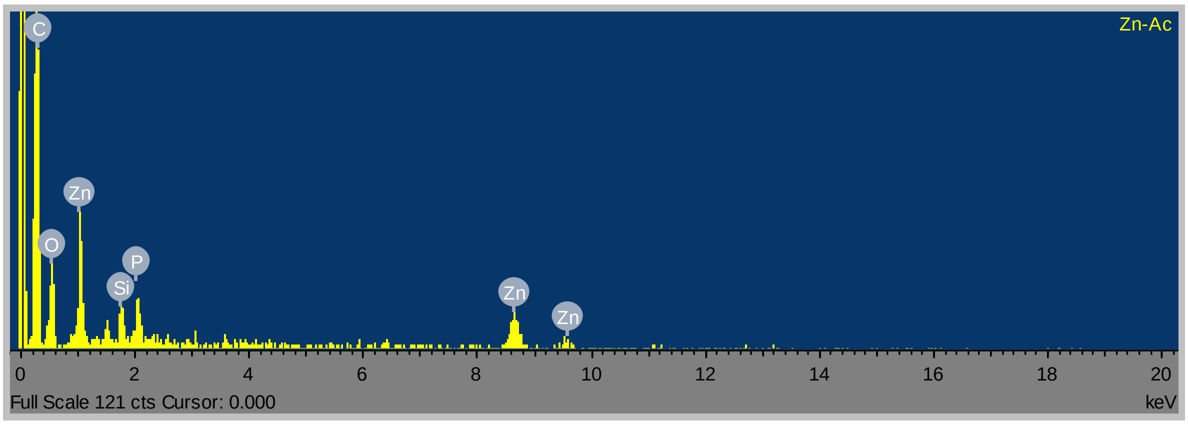


Figure 4-11. EDX Graph of Zn/AC Catalyst

4.1.3. Surface area measurements- Brunauer, Emmet, and Teller (BET)

BET analysis was performed on activated carbon supports in order to study the surface area of catalytic systems. Zeolite was obtained from the supplier with a total surface area of 425 m^2/g and activated carbon was obtained from the supplier with a total surface area of 500 m^2/g. BET surface area of prepared activated carbon supported metal catalysts are tabulated in Table 4-1.

Table 4-1. BET surface area for activated carbon supported catalyst

Catalyst samples	**S_{BET} (m^2/g)**
Fe/AC	300.28
Ni/AC	284.91
Zn/AC	226.58

When activated carbon was promoted with Fe, Ni and Zn, the surface area dropped to 300.28 m^2/g, 284.91 m^2/g, and 226.58 m^2/g respectively. This high decrease may be due to calcination after impregnation of metals. These catalysts were impregnated at same conditions and time, noting that the surface areas differ from each other, this suggests that metal type also contributed on the reduction of the surface area of activated carbon.

4.2. Catalyst test: Alcohol conversion

The activity of different catalytic systems such as HZSM-5, Fe/HZSM-5, Ni/HZSM-5, Zn/HZSM-5, Fe/AC, Ni/AC and Zn/AC were evaluated using a fixed-bed down flow stainless steel reactor at 400°C, atmospheric pressure and a WHSV of 2.5 h^{-1} (g alcohol)/ (g catalyst). Ethanol, butanol and ethanol-butanol mixtures were used as a feedstock for the activity tests.

4.2.1. The effect of catalyst support on product distribution

4.2.1.1. Ethanol conversion

Comparison between HZSM-5 and activated carbon supports during ethanol conversion was considered for different metals and products distribution as shown in Table 4-2. More than 93% ethanol conversion was achieved with catalysts supported on HZSM-5 and not more than 21.8% of conversion was achieved with catalysts supported on activated carbon. The yield of liquid hydrocarbons produced from catalysts supported on ZSM-5 ranged from 15.1% to 42.95%, and that from catalysts supported on activated carbon was obtained to range from 9.4% to 21.8%. Catalysts supported on HZSM-5 produced paraffins, ethylbenzene, BTX, indane and naphthalene. Catalysts with activated carbon support did not produce compounds such as ethylbenzene, xylene, indane and naphthalene while paraffins, benzene and toluene were produced.

4.2.1.2. Butanol conversion

The effect of Catalyst supports on product distribution during conversion of butanol was studied. Product distribution of butanol conversion over various catalysts is shown in Table 4-3. 100 % butanol conversion was achieved in all catalysts supported on HZSM-5 and not more than 46% butanol conversion was achieved in catalysts supported on activated carbon. 17.5% to 52.2% liquid hydrocarbons yield was obtained from catalysts supported on HZSM-5, and 9.6% to 20.4% yield was obtained from catalyst supported on activated carbon. Paraffins, ethylbenzene, BTX, indane and naphthalene were generated from catalyst supported on HZSM-5. Catalyst supported on activated carbon did not produce ethylbenzene, xylene, indene and naphthalene.

4.2.1.3. Overall discussion

Owing that ZSM-5 supports are active in conversion of alcohols, it was deduced that the formation of high liquid hydrocarbons such as benzene, toluene, ethylbenzene, toluene and xylene (BTEX) were due to the activity of ZSM-5. Unlike activated carbon, ZSM-5 poses Lewis and Bronsted acid sites, whereas Lewis acid sites are sufficient for formation of high liquid hydrocarbons (BTEX) and Bronsted acid sites catalyses dehydration of alcohols. Further, these acid sites allows the possible reactions to take place inside the frame work of the zeolite. This was also attributed to channel structure system of the HZSM-5.

On the other hand activated carbon was observed as inert supports, the production of hydrocarbons over catalysts supported on activated carbons were due to metals doped on activated carbon support. The reaction took place on the sites of metals; it is also suggested that the formation of liquid hydrocarbons is due to metal dispersion on activated carbon since there was no interactions between activated carbon and metals in terms of increasing or reducing the metal sites.

Table 4-2. Product distribution of ethanol conversion over various catalyst at 400 °C, 1 atm. and WHSV of 2.5 h^{-1}

Catalyst type	**Ethanol Conversion (%)**	**Product distribution (wt. %)**							
		Paraffins	**Ethylbenzene**	**Benzene**	**Toluene**	**Xylene**	**Indane**	**Naphthalene**	**Other hydrocarbons**
Zn/HZSM5	98.50	0.02	2.98	6.11	21.9	19.99	0.50	0.90	45.88
Zn/AC	16.00	5.92	-	0.11	0.56	-	-	-	9.41
Fe/HZSM5	99.86	0.20	2.28	2.99	13.91	18.98	0.40	3.11	57.89
Fe/AC	21.80	4.11	-	0.13	6.30	-	-	-	11.26
Ni/HZSM5	93.12	0.30	0.98	5.50	13.50	17.74	0.35	6.56	48.05
Ni/AC	10.10	-	-	-	-	-	-	-	10.11

Table 4-3. Product distribution of butanol conversion over various catalysts at 400 °C, 1 atm. and WHSV of 2.5 h^{-1}

Catalyst type	**Butanol Conversion (%)**	**Product distribution (wt. %)**							
		Paraffins	**Ethylbenzene**	**Benzene**	**Toluene**	**Xylene**	**Indene**	**Naphthalene**	**Other hydrocarbons**
Zn/HZSM5	100.00	0.36	2.10	7.04	22.44	29.95	3.89	7.09	27.13
Zn/AC	46.00	20.01	-	0.17	7.55	-	-	-	18.27
Fe/HZSM5	100.00	0.18	3.85	3.48	17.9	28.94	2.83	2.40	40.42
Fe/AC	35.90	1.00	-	0.17	6.45	-	-	-	28.28
Ni/HZSM5	100.00	0.45	1.56	6.54	23.20	30.00	-	8.90	29.34
Ni/AC	34.90	9.55	-	0.15	6.56	-	-	-	18.63

4.2.2. The effect of feed ratio on product distribution over HZSM-5 supported catalysts

The effect of feed ratio on product distribution for zinc promoted catalyst was studied and results are tabulated in Table 4-4. More than 92% conversion was achieved during valorisation of ethanol-butanol mixtures over zinc promoted catalyst. Pure ethanol produced 48 wt. % of benzene, toluene and xylene (BTX) and as the ratio of ethanol decreased, the amount of BTX increased. Pure ethanol favoured the production of toluene and all other alcohol mixtures favoured the production of xylene. Paraffins was the least produced in all mixtures.

Table 4-5 shows product distribution of ethanol-butanol mixtures conversion over iron supported HZSM-5. More than 99 % conversion was achieved. The production of BTX increased (35.9%< 38.5%< 46.1%< 46.9%< 50.3%) with a decrease in ethanol ratio (pure ethanol>75%- 25%> 50%- 50% > 25%- 75%> pure butanol) respectively. All mixtures favoured the production of xylene. Paraffins was the least product produced by all mixtures.

Results for product distribution of ethanol-butanol mixtures over nickel promoted catalyst are tabulated in Table 4-6. More than 93 % conversion was achieved and a decrease in ethanol ratio (pure ethanol>75%- 25%> 50%- 50% > 25%- 75%> pure butanol) has shown an increase in feed conversion (93.1%< 94.5%< 96.8%< 99.6%< 100%). Pure ethanol produced high amount of BTX as compared to other mixtures. Pure ethanol, 50% ethanol-50% butanol mixture, 25% ethanol-75% butanol mixture and pure butanol favoured the production of xylene while 75% ethanol-25% butanol mixture favoured the production of toluene.

In overall results, when ethanol was mixed with butanol it was observed that the formation of BTX hydrocarbons increased. High alcohols like butanol have been reported to generate more liquid hydrocarbons, thus addition of butanol to ethanol is expected to improve the generation of BTX hydrocarbons. Pure ethanol conversion undergoes dehydration to form ethylene as a primary reaction as proposed from the literature. Further, when butanol is added into ethanol, we suggest that dehydration of butanol to butane begins and both ethylene and butane then undergo oligomerization process to form high olefins. By evaluating results obtained, it was observed that both dehydrocyclization and hydrogenation took place since there was production of paraffins and aromatics. Therefore an increase in BTX formation at increasing ethanol ratio was due to addition of butanol.

Table 4-4. Product distribution of ethanol-butanol mixtures conversion over zinc supported on HZSM-5 at 400 °C, 1 atm. and WHSV of 2.5 h^{-1}

%EtOH- %BuOH	**Ethanol-Butanol Conversion (%)**	**Product distribution (wt. %)**							
		Paraffins	**Ethylbenzene**	**Benzene**	**Toluene**	**Xylene**	**Indane**	**Naphthalene**	**Other hydrocarbons**
100%- 0%	98.50	0.02	2.98	6.11	21.9	19.99	0.50	0.90	45.88
75%- 25%	96.27	0.28	6.95	3.5	17.5	30.2	1.01	1.64	34.92
50%- 50%	100.00	0.21	2.58	6.18	21.72	25.13	2.52	4.01	37.51
25%- 75%	92.98	0.16	2.79	4.54	14.97	27.42	5.36	7.79	29.95
0%- 100%	100.00	0.36	2.10	7.04	22.44	29.95	3.89	7.09	27.13

Table 4-5. Product distribution of ethanol-butanol mixtures conversion over iron supported on HZSM-5 at 400 °C, 1 atm. and WHSV of 2.5 h^{-1}

%EtOH- %BuOH	Ethanol-Butanol Conversion (%)	Product distribution (wt. %)							
		Paraffins	Ethylbenzene	Benzene	Toluene	Xylene	Indane	Naphthalene	Other hydrocarbons
100%- 0%	99.86	0.20	2.28	2.99	13.91	18.98	0.40	3.11	57.89
75%- 25%	100.00	0.20	2.31	3.11	15.41	19.98	0.51	4.42	54.05
50%- 50%	100.00	0.21	3.56	3.65	16.11	26.33	1.81	2.78	45.51
25%- 75%	100.00	0.13	3.60	3.12	16.32	27.44	2.00	2.63	44.74
0%- 100%	100.00	0.18	3.85	3.48	17.90	28.94	2.83	2.40	40.42

Table 4-6. Product distribution of ethanol-butanol mixtures conversion over nickel supported on HZSM-5 at 400 °C, 1 atm. and WHSV of 2.5 h^{-1}

%EtOH- %BuOH	Ethanol-Butanol Conversion (%)	Product distribution (wt. %)							
		Paraffins	Ethylbenzene	Benzene	Toluene	Xylene	Indane	Naphthalene	Other hydrocarbons
100%- 0%	93.12	0.30	0.98	5.50	13.50	17.74	0.35	6.56	48.04
75%- 25%	94.45	0.28	1.00	6.11	18.22	17.10	0.29	5.66	44.68
50%- 50%	96.78	0.38	9.11	6.65	20.01	27.28	0.15	8.11	25.00
25%- 75%	99.59	0.40	2.00	6.00	21.65	29.11	0.11	7.44	32.87
0%- 100%	100.00	0.45	1.56	6.55	23.20	30.00	-	8.90	29.34

4.2.3. The effect of feed ratio on product distribution over activated carbon supported catalysts

The effect of feed ratio on product distribution for zinc supported on activated carbon catalyst was studied and results are tabulated in Table 4-7. Less than 47 % conversion was achieved. All mixtures favoured the production of paraffins and no generation of ethylbenzene, xylene, indane and naphthalene were detected. When butanol was added to decrease the ethanol content, it was observed that quantities of paraffins, benzene and toluene were increasing.

Table 4-8 shows product distribution of ethanol-butanol mixtures conversion over iron supported on activated carbon. Less than 26.76% conversion was achieved. Exclusive of 25% ethanol-75% butanol mixture, all mixtures produced paraffins, benzene and toluene.

Results for product distribution of ethanol-butanol mixtures over nickel supported on activated carbon catalyst are shown in Table 4-9. The conversion achieved was not more than 34%. Pure ethanol, 75% ethanol-butanol mixture and 50% ethanol-butanol mixture did not produce paraffins, ethylbenzene, and BTX, indane and naphthalene hydrocarbons. When the amount of butanol was more than 50% in the mixture, there was production of paraffins, benzene and toluene while on the other hand no detection of ethylbenzene, xylenes, indane and naphthalene were noticed.

In overall results, an increase in butanol content resulted in an increase of paraffins, benzene and toluene. On the other hand pure butanol was observed to show high conversion in all cases, this high conversion reported for butanol is due to the high activity for the transformation of this alcohol over the tested catalyst. These observations are also suggested to be the result of butanol as a higher alcohol.

Table 4-7. Product distribution of ethanol-butanol mixtures conversion over zinc supported on AC at 400 °C, 1 atm. and WHSV of 2.5 h^{-1}

%EtOH-%BuOH	Ethanol-Butanol Conversion (%)	Product distribution (wt. %)							
		Paraffins	Ethylbenzene	Benzene	Toluene	Xylene	Indane	Naphthalene	Other hydrocarbons
100%- 0%	16.00	5.92	-	0.11	0.56	-	-	-	9.41
75%- 25%	16.60	6.02	-	0.13	0.57	-	-	-	9.88
50%- 50%	34.00	13.00	-	0.14	4.01	-	-	-	16.85
25%- 75%	33.00	13.89	-	0.15	4.55	-	-	-	14.41
0%- 100%	46.00	20.01	-	0.17	7.55	-	-	-	18.27

Table 4-8. Product distribution of ethanol-butanol mixtures conversion over iron supported on AC at 400 °C, 1 atm. and WHSV of 2.5 h^{-1}

%EtOH- %BuOH	Ethanol-Butanol Conversion (%)	Product distribution (wt. %)							
		Paraffins	Ethylbenzene	Benzene	Toluene	Xylene	Indane	Naphthalene	Other hydrocarbons
100%- 0%	21.80	4.11	-	0.13	6.30	-	-	-	11.26
75%- 25%	26.48	3.92	-	1.11	2.11	-	-	-	8.32
50%- 50%	27.50	3.95	-	1.00	2.11	-	-	-	18.41
25%- 75%	26.76	-	-	-	-	-	-	-	26.76
0%- 100%	35.90	1.00	-	0.16	6.45	-	-	-	28.28

Table 4-9. Product distribution of ethanol-butanol mixtures conversion over nickel supported on AC at 400 °C, 1 atm. and WHSV of 2.5 h^{-1}

%EtOH- %BuOH	**Ethanol-Butanol Conversion (%)**	**Product distribution (wt. %)**							
		Paraffins	**Ethylbenzene**	**Benzene**	**Toluene**	**Xylene**	**Indane**	**Naphthalene**	**Other hydrocarbons**
100%- 0%	10.10	-	-	-	-	-	-	-	10.10
75%- 25%	7.10	-	-	-	-	-	-	-	7.13
50%- 50%	18.00	-	-	-	-	-	-	-	18.00
25%- 75%	17.60	12.98	-	0.18	0.52	-	-	-	3.92
0%- 100%	34.00	9.55	-	0.15	6.56	-	-	-	18.63

4.2.4. Effect of metal type on product distribution

4.2.4.1. Ethanol conversion

The effect of metal impregnation and metal type on product distribution was studied. Comparisons amongst the parent catalyst HZSM-5 and all other metal promoted catalyst for ethanol and butanol conversion were conducted as presented on the chart in Figure 4-12 and Figure 4-13.

Shown in Figure 4-12 is the representation of prepared catalysts and product distribution for conversion of ethanol as a feedstock. 99.45 % ethanol conversion was achieved and HZSM-5 alone favoured the production of BTX (57.4%) and no paraffins were detected. Ethylbenzene, indene and naphthalene were found to be 4%, 7.6 % and 2, 93 % respectively.

Modification of ZSM-5 with zinc showed 98.5% conversion and the production of paraffins (0.02%) were enhanced, while production of ethylbenzene (2.98%), BTX (48%), indene (0.5%) were enhanced and naphthalene (0.9%) was supressed.

Modification of HZSM-5 with nickel showed 93.12% conversion, the production of paraffins, and naphthalene was enhanced to 0.3%, and 0.6% respectively. BTX (36.7%), indane (0.35%) and ethylbenzene (2.98%) were suppressed on the other hand.

Modification of ZSM-5 with iron showed 99.86% conversion and the production of paraffins (0.2%) and naphthalene (3.11%) were enhanced. on the other hand, the production of ethylbenzene (2.28%), BTX (35.9%) and indane (0.4%) were supressed.

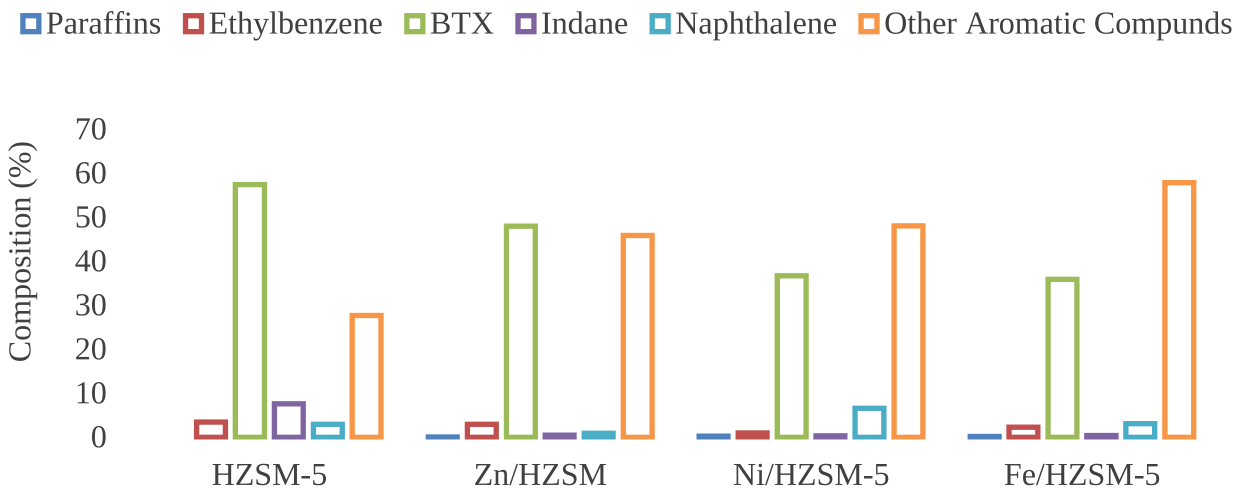


Figure 4-12. Product distribution during ethanol conversion over various metals at 400 °C, 1 atm. and WHSV of 2.5 h^{-1}

4.2.4.2. Butanol conversion

Figure 4-13 shows product distribution for various catalysts supported on HZSM-5 during butanol conversion. All catalyst systems (HZSM-5, Zn/HZSM-5, Ni/HZSM-5 and Fe/HZSM-5) showed 100 % conversion. HZSM-5 produced paraffins, ethylbenzene, BTX, indane and naphthalene during butanol conversion. The catalyst showed high production to BTX (63.2%) amongst products. Quantities of paraffins, ethylbenzene, indane and naphthalene in the liquid product were 0.22%, 4.1%, 6.3% and 0.36% respectively. Promotion with zinc metal enhanced the production of paraffins (0.36%), and naphthalene (7.1%) while production of ethylbenzene (2.1%), BTX (59.4%) and indane (3.9%) were supressed.

Promotion of HZSM-5 with nickel enhanced the production of paraffins and naphthalene from 0.22% and 0.36% to 0.45% and 8.9% respectively while on the other hand, production of ethylbenzene (1.6%) and BTX (59.8%) were supressed. No indane was detected in products. Promotion with iron enhanced the production of naphthalene, while on the other hand production of paraffins (0.18%), ethylbenzene (3.85%), BTX (50.3%) and indane (2.83%) were suppressed.

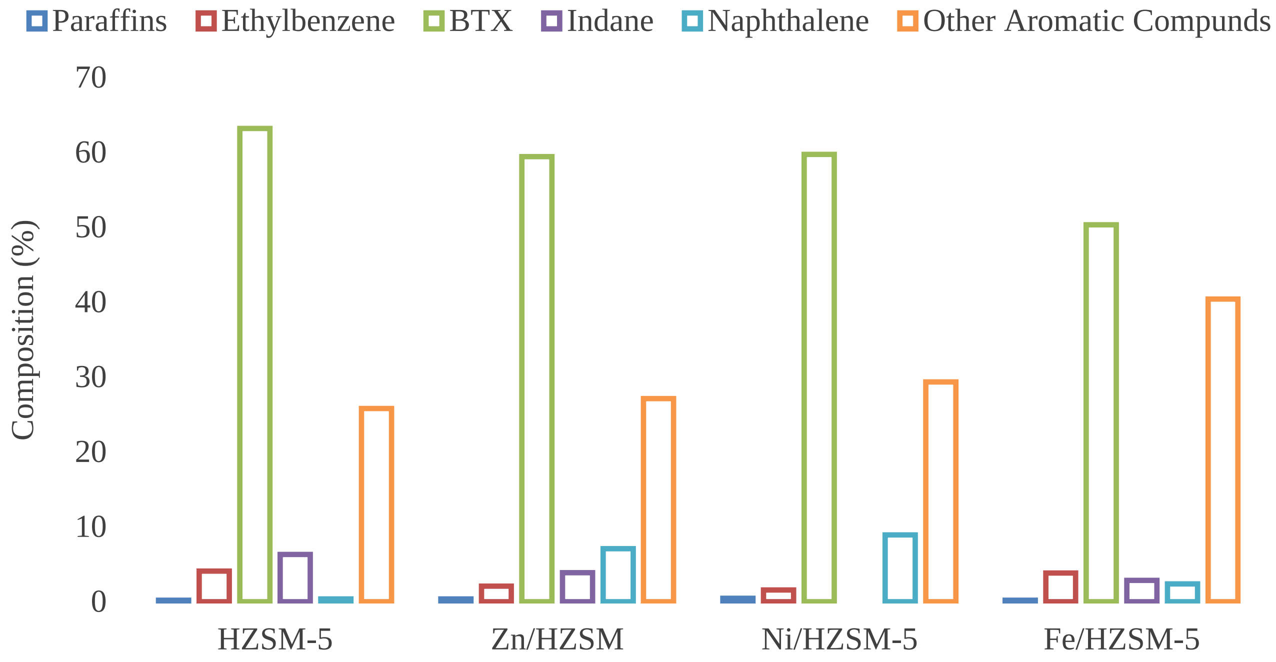


Figure 4-13. Product distribution during butanol conversion over various metals at 400 °C, 1 atm. and WHSV of 2.5 h^{-1}

4.2.4.3. Overall discussion

In all cases, promotion of HZSM-5 with Zn, Ni and Fe enhanced the production of paraffins and or naphthalene. HZSM-5 catalyst showed better results for generation of BTX hydrocarbons. High amount of BTX produced by HZSM-5 catalyst was influenced by the amount of xylenes, in other words HZSM-5 catalyst was selective to xylene production. Promotion with metals enhanced the production of benzene and zinc showed high selectivity to benzene amongst all metals in both ethanol and butanol conversion. In some cases, metals like zinc and iron enhanced the production of toluene. In overall, the formation of aromatics hydrocarbons were supressed when HZSM-5 was impregnated.

This observation may be due to the reduction of HZSM-5 acidity caused by metal doping on HZSM-5. Impregnation with metals is followed by calcination at high temperature, this may also decrease the amount of acid sites of HZSM-5 through ion-exchange of framework aluminium of ZSM-5 with the introduced metal cation (Inaba *et al.* 2007). Reduction of acid sites inhibits the secondary reaction to generate high liquid hydrocarbons. Other factors such as the location of metals in HZSM-5 channel and physical blocking of the channel structure itself may also influence these observations.

4.2.5. Effect of feed type on product distribution over:

4.2.5.1. HZSM-5 catalyst

Results from comparative study between ethanol and butanol as a feedstock for conversion over HZSM-5 catalyst to hydrocarbons are shown in Figure 4-14. The effect of feed type on product distribution was studied for HZSM-5. Ethanol and butanol conversions achieved were 99.45% and 100% respectively. No production of paraffins were detected during ethanol conversion over HZSM-5. Quantities of ethylbenzene, BTX, indane and naphthalene produced from conversion of ethanol were 3.4%, 57.4%, 7.4% and 2.9% respectively. When ethanol was substituted with butanol at the same reaction conditions and catalyst, there was an increase in production of ethylbenzene and BTX by 19.2% and 10% respectively.

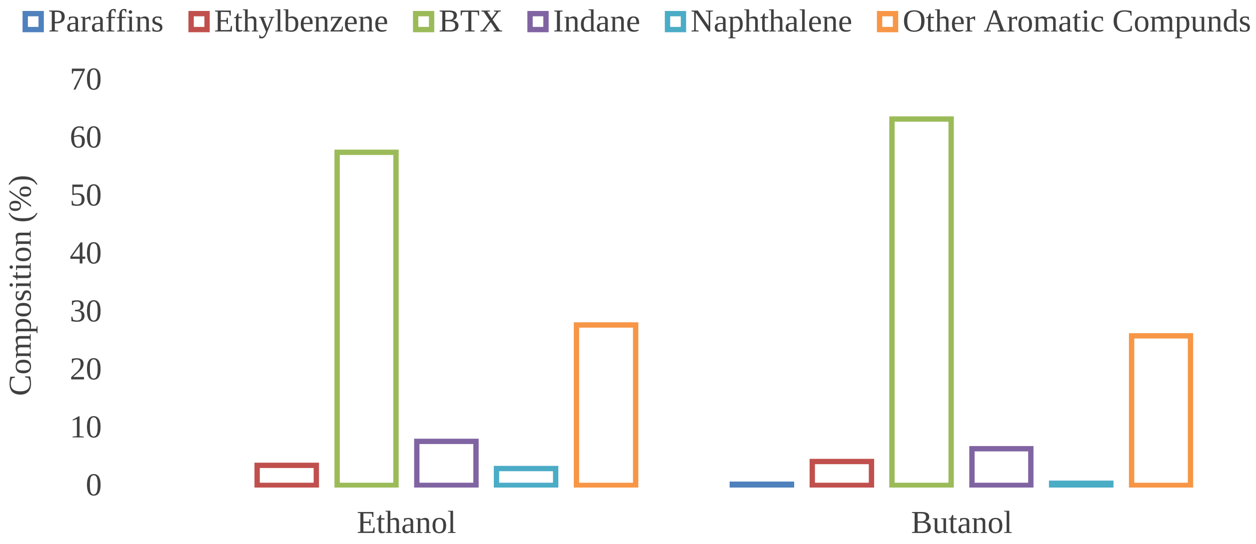


Figure 4-14. Product distribution for conversion of ethanol over HZSM-5 at 400 °C, 1 atm. and WHSV of 2.5 h^{-1}

4.2.5.2. Fe/HZSM-5 catalyst

Figure 4-15 shows results of product distribution and feed type for Fe/HZSM-5 catalyst. Conversion of 99.86 % and 100 % for ethanol and butanol was achieved respectively. Production of paraffins (0.2%), ethylbenzene (2.3%), BTX (57.9%), indane (0.4%) and naphthalene (3.1%) were achieved during ethanol conversion. Exclusive paraffins and naphthalene, the production of paraffins, ethylbenzene BTX and naphthalene were increased when ethanol was substituted with butanol at the same reaction conditions and catalyst system. The increment was 68.9% for ethylbenzene, 40.2% for BTX and indane increased to 2.83%.

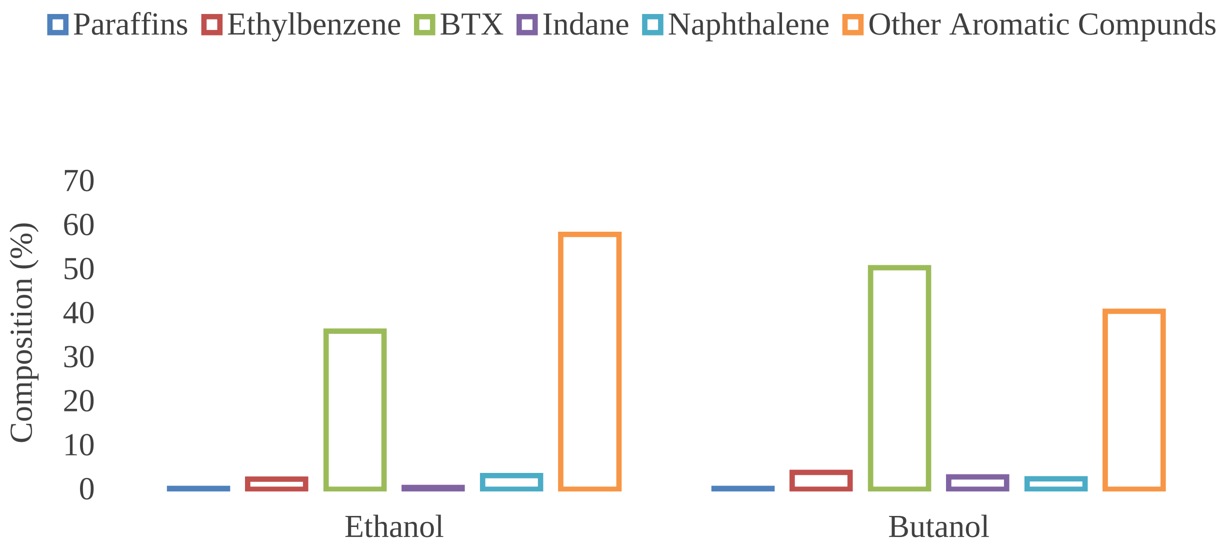


Figure 4-15. Product distribution during alcohol conversion over Fe/HZSM-5 at 400 °C, 1 atm. and WHSV of 2.5 h^{-1}

4.2.5.3. Zn/HZSM-5 catalyst

Figure 4-16 shows results of comparative studies between ethanol and butanol over Zn/HZSM-5. 98.5% ethanol conversion and 100% butanol conversion were achieved. When ethanol was used as feedstock over Zn/HZSM-5 catalyst, products such as paraffins (0.02%), ethylbenzene (3%), BTX (48%), indane (0.5%) and naphthalene (0.9 %) were formed.

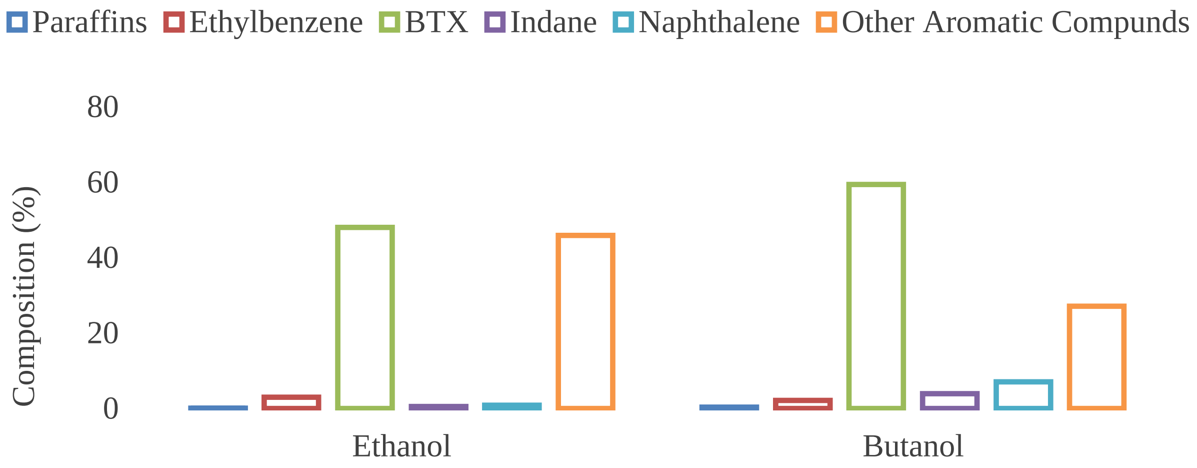


Figure 4-16. Product distribution during alcohol conversion over Zn/HZSM-5 at 400 °C, 1 atm. and WHSV of 2.5 h^{-1}

When butanol was used, instead of ethanol at same reaction condition and same catalysts type, paraffins, BTX, indane and naphthalene increased to 0.36%, 59.4 %, 3.9% and 7.1% respectively. On the other hand ethylbenzene was decreased to 2.1%.

4.2.5.4. Ni/HZSM-5 catalyst

Figure 4-17 shows results of comparative studies between ethanol and butanol over Ni/HZSM-5. 93.12 % ethanol conversion and 100% butanol conversion were achieved. Amount of paraffins, ethylbenzene, BTX, indane and naphthalene produced from conversion of ethanol were 0.3%, 1%, 36.7%, 0.4% and 6.6% respectively. When ethanol was substituted with butanol at the same reaction conditions and catalyst system, there was an increase in products like paraffins, ethylbenzene, BTX and naphthalene to 0.5%, 1.6%, 59.38% and 8.9%. There was no production of indane during conversion of butanol.

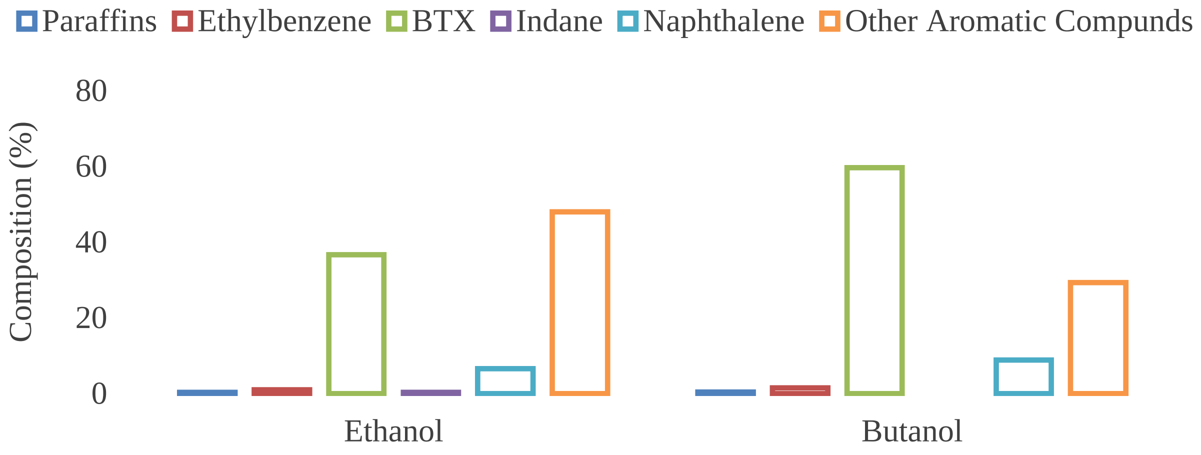


Figure 4-17. Product distribution during alcohol conversion over Ni/HZSM-5 at 400 °C, 1 atm. and WHSV of 2.5 h^{-1}

4.2.5.5. Overall discussion

Both alcohols product distribution were paraffins, ethylbenzene, BTX, indane and naphthalene. The production of BTX from butanol conversion was always higher compared to that of ethanol conversion. This verified that butanol improves the production of BTX. Higher alcohols like butanol have a tendency to form carbocation more readily than lower alcohols counterparts. These carbocation formed are suspected to be the key intermediated that forms BTX aromatics. This is in agreement with Gujar *et al.* (2009) as proposed that high alcohols generate more liquid hydrocarbons. In addition, the formation of BTX may be attributed by the high reaction temperature of 400 °C with a low WHSV of 2.5 h^{-1}. The low WHSV gives the feed enough time to be in contact with the catalyst, this allow enough time the reaction to take place in active sites of the catalyst.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1. Conclusions

Catalysts of metals (M: Fe, Ni and Zn) supported on ZSM-5 and activated carbon were prepared and characterized through XRD, SEM and BET analysis. Through XRD, it was confirmed that catalyst synthesis was successful. Transformation of zeolite from ammonium form to hydrogen form by calcination did not change the crystallinity and crystal system of the zeolite. The metal impregnation on HZSM-5 did not have any effect on crystallinity and crystal system of the zeolite except for zinc catalyst, which exhibited both monoclinic and orthorhombic structure. The crystallinity of all samples promoted with metals decreased compared to the crystallinity of the parent catalyst. Metal loading affected the size of the catalyst systems, while impregnating with Fe led to an increase on the particle size of the crystalline, impregnating with Ni and Zn led to a decrease on the particle size of the crystalline as evaluated at 2theta between 23° to 25°. Iron metals was found to be finely dispersed in zeolite and activated carbon.

Metals were successfully impregnated into activated carbon as verified by the XRD and have proved that activated carbon are not crystalline materials. In both zeolite and activated carbon, zinc and nickel were found to exist in a form of ZnO and NiO respectively. With the SEM images of activated carbon promoted metals taken at a magnification of 2000 times confirmed that activated carbon exhibits particles with plane surface, disordered structure with rough surface which are stick together at some positions. On the other hand, SEM images of ZSM-5 promoted metals taken at magnification of 20 000 times show that HZSM-5 calcined exhibits particles with irregular shapes and relative size. Metal impregnation on activated carbon and calcination reduced the surface area of the catalyst.

The addition of metals into HZSM-5 and activated carbon as catalysts supports had an impact on product distribution and as well as the selectivity of hydrocarbons. Most metals enhanced the production of paraffins and naphthalene while on the other hand, production of ethylbenzene, BTX and indene were supressed. Pure butanol showed up to 100% conversion in all reactions, and it was found to be the best feedstock for production of valuable hydrocarbons such as paraffins, BTX and naphthalene. The mixtures of ethanol and butanol feedstock also performed well on product distribution, compared to pure ethanol and addition of butanol to ethanol increased conversion.

HZSM-5 was the better catalyst support compared to activated carbon. Owing that HZSM-5 is an active material and activated carbon is an inert, it can be concluded that the formation of hydrocarbon is influenced by Lewis acid sites which are sufficient for formation of high liquid hydrocarbons (BTEX) and Bronsted acid sites catalyses dehydration of alcohols. Catalyst supported on activated carbon have proven that metals alone show potential of producing hydrocarbons and the reactions took place in metal active sites, however the conversions were very low.

5.2. Recommendation

Mixtures of ethanol and butanol have shown positive results in production of hydrocarbons through metal supported HZSM-5. It is recommend that other alcohol mixtures be investigated as well.

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7. APPENDICES

7.1. Appendix A: Relative crystallinity

The relative crystallinity of zeolite was calculated using the following equation:

$$\%\ XRD\ Relative\ Crystallinity\ ZSM5 = \frac{H_s}{H_r} \times 100$$

$$\%\ XRD\ Relative\ Crystallinity\ Zn/HZSM5 = \frac{29634.84}{42487.41} \times 100 = 70\ \%$$

Where as $\mathrm{H_s}$ is the Peak height for the Sample/catalyst

$\mathrm{H_r} =$ Peak height for the reference catalyst

7.2. Appendix B: Average crystallite size (Debye scherrer equation)

The following equation was used for calculation of particle size of the crystalline structure:

$$d = \frac{K\lambda}{BCos\theta}$$

Where as:

d is the Particle size of the crystalline structure

K is the constant dependent on crystillite shape $= 0.89$

λ is the X − Ray wavelength $= 0.154056$

B is FWHM (Full width at halfmax

θ is a Brass Angle

Table 7-1. Particle size of the crystalline structure

Catalyst Type	2Theta (Degrees)	FWHM (Rad)	Particle size of the crystalline Structure (nm)
NH4ZSM-5	23.75	0.005063	35.15
HZSM-5	23.96	0.005587	29.46
Fe/HZSM-5	23.81	0.003492	49.75
Ni/HZSM-5	23.94	0.010127	16.36
Zn/HZSM-5	24.31	0.007508	19.92

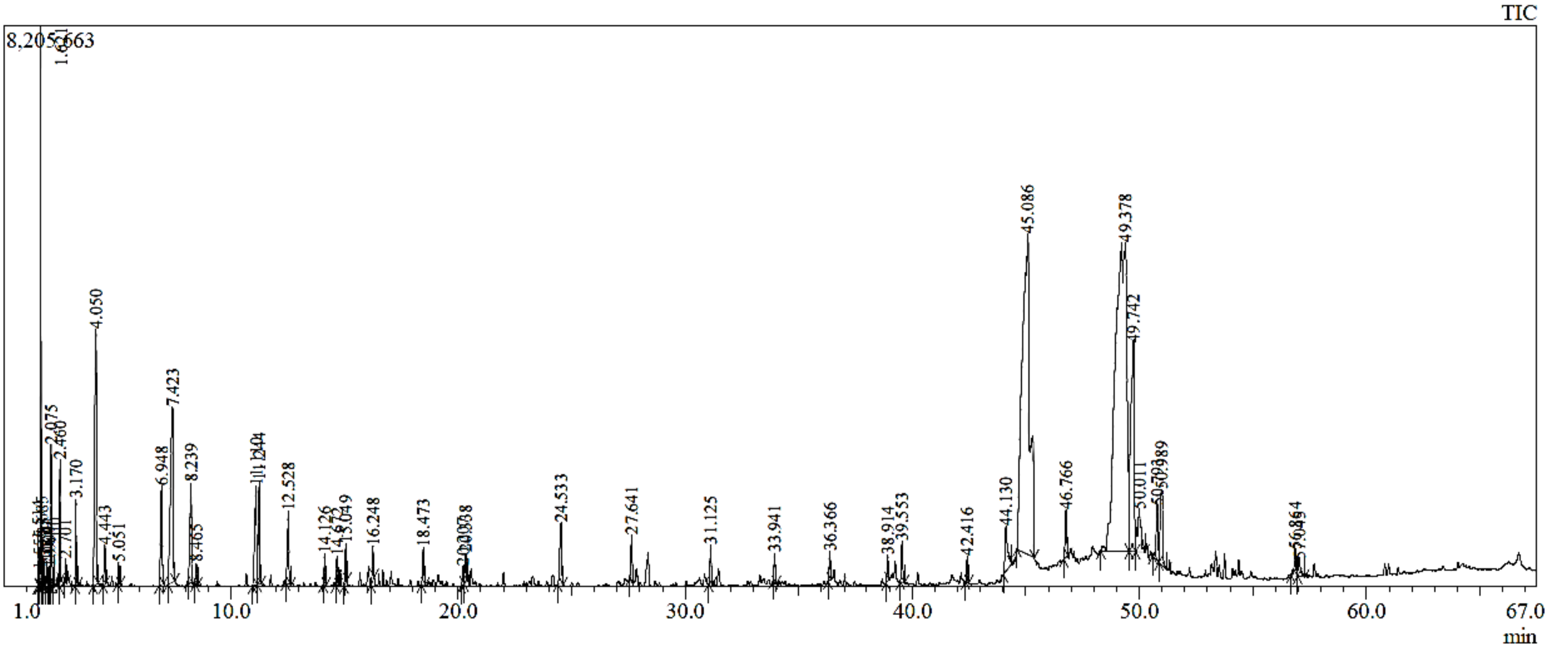
7.3. Appendix C: Miller indices

Table 7-2. Crystal systems

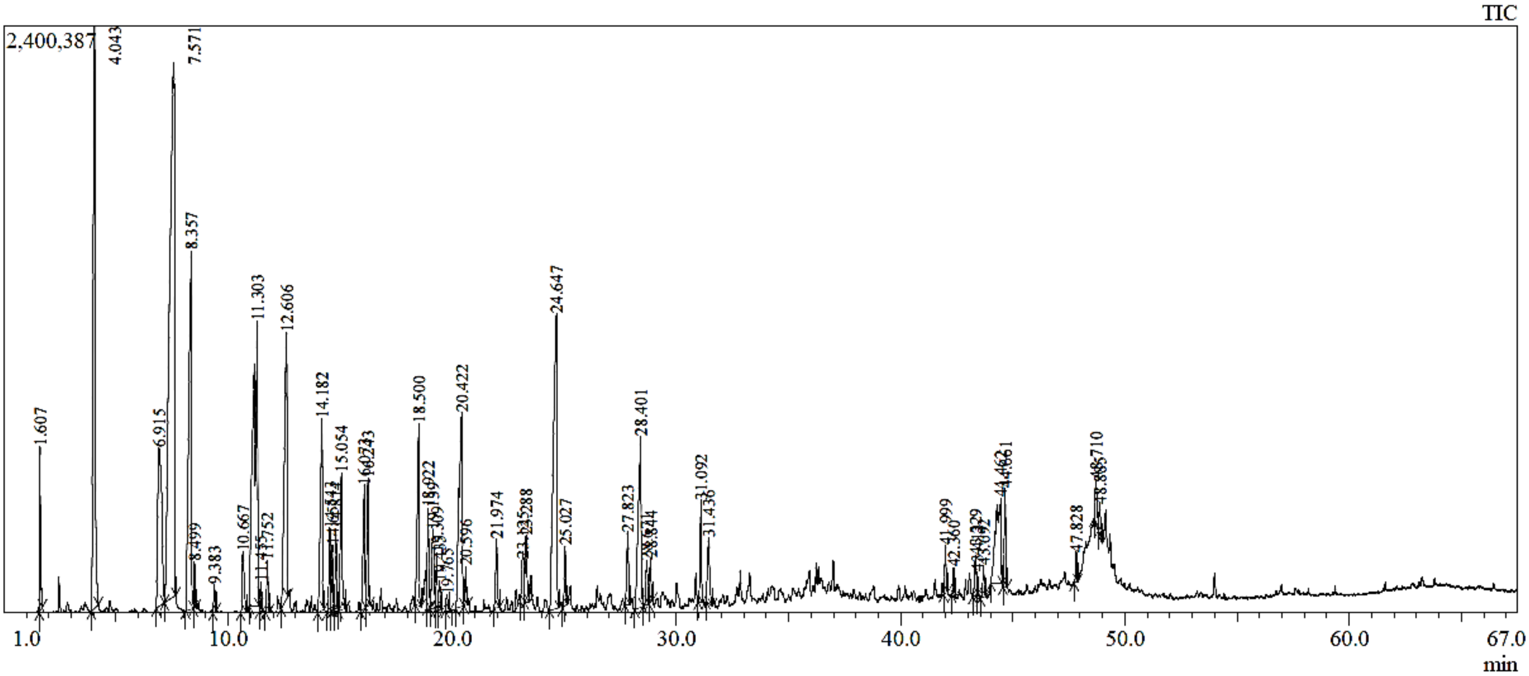
Catalyst Samples	2Theta	h	k	l	M	Crystal System
HZSM-5	7.99	0	k	l	4	Monoclinic
	8.83	0	k	0	2	
	23.04	0	k	l	4	
	23.94	h	0	l	2	
NH4ZSM-5	7.74	h	0	l	2	Monoclinic
	8.64	0	k	0	2	
	22.93	0	k	l	4	
	23.75	h	l	l	4	
Fe/HZSM-5	7.92	h	0	l	2	Monoclinic
	8.76	0	k	0	2	
	23.09	0	k	l	4	
	23.94	h	0	l	2	
Ni/HZSM-5	7.63	h	0	l	2	Monoclinic
	8.57	0	k	0	2	
	22.8	0	k	l	4	
	23.85	h	k	l	4	
Zn/HZSM-5	7.97	0	0	l	2	Monoclinic and Orthorhombic
	8.92	h	k	0	2	
	23.12	0	k	l	4	
	24.07	h	k	l	4	

7.4. Appendix D: Samples of GC-MS Analysis

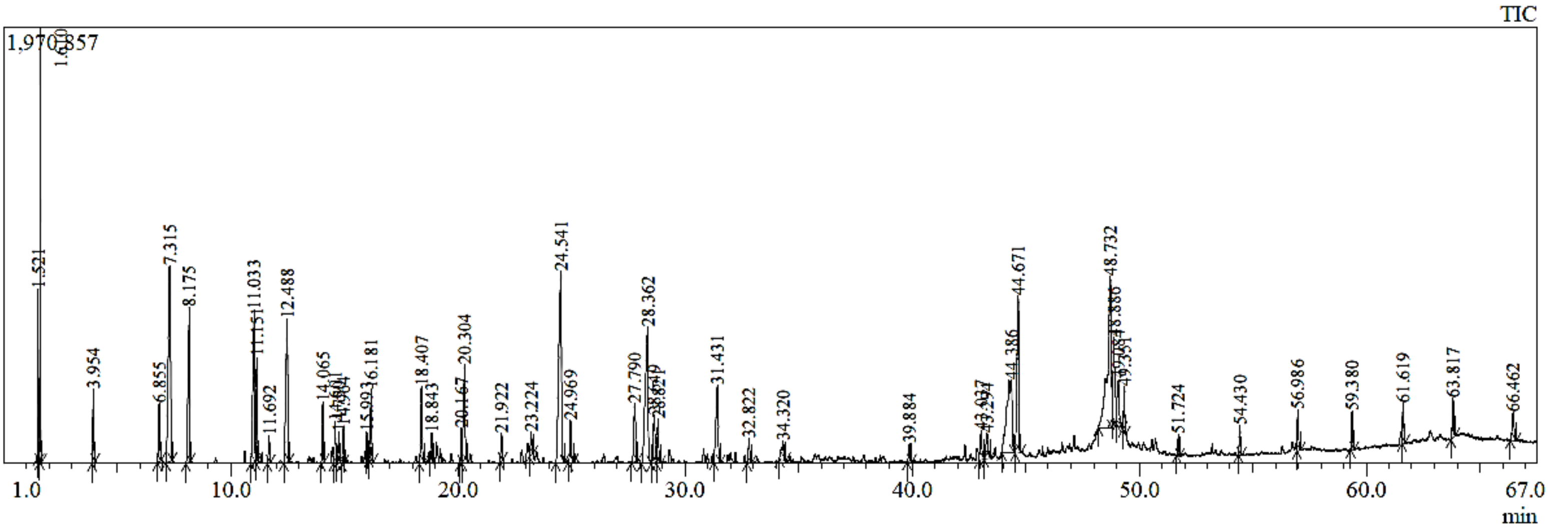
7.4.1. Ethanol conversion over HZSM-5 catalyst



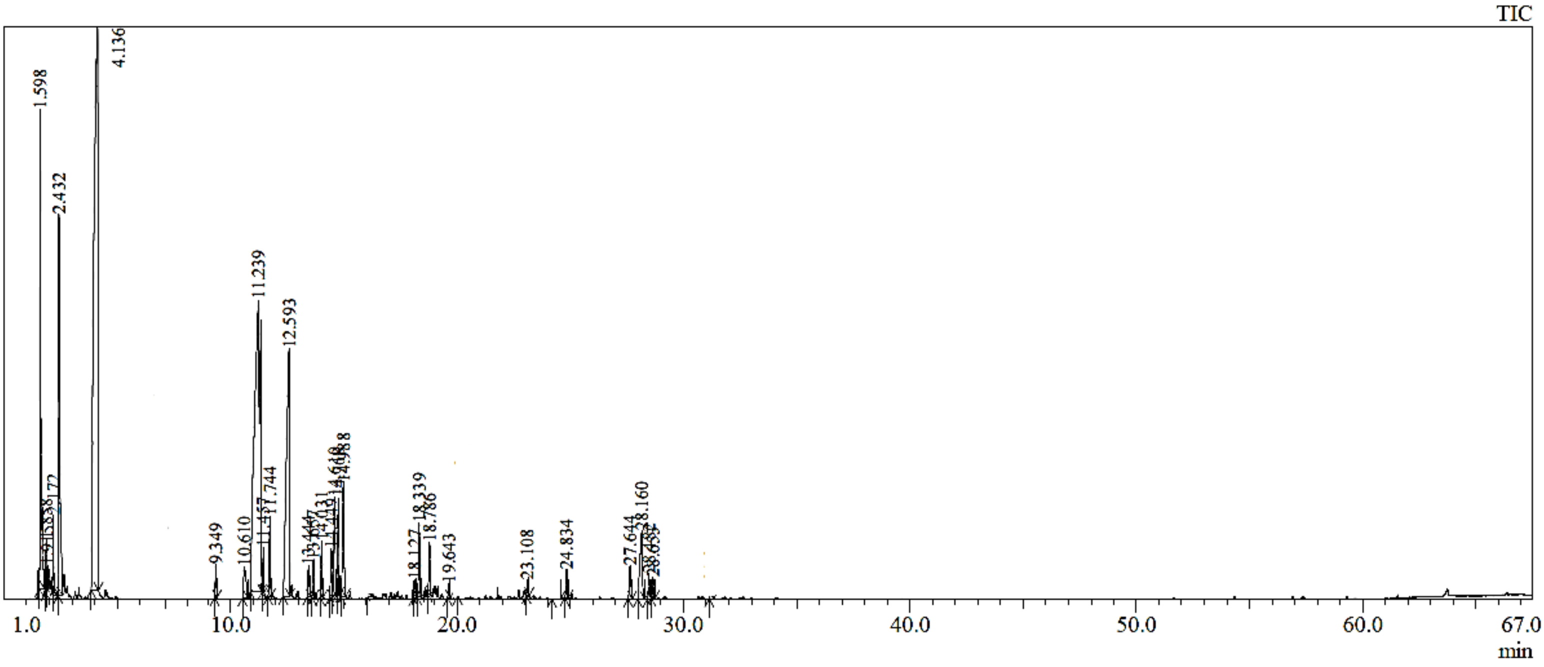
7.4.2. Butanol conversion over HZSM-5 catalyst



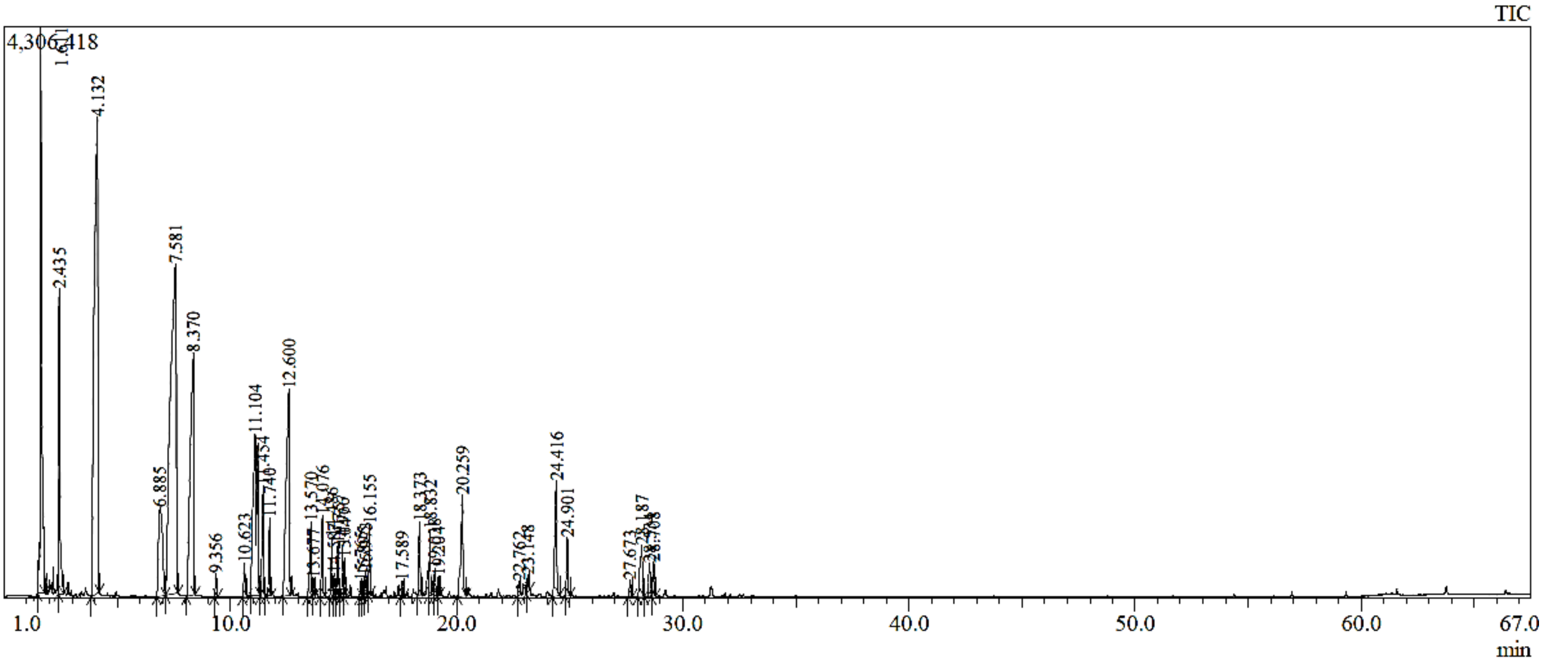
7.4.3. 50% Ethanol-50% Butanol mixture conversion over HZSM-5



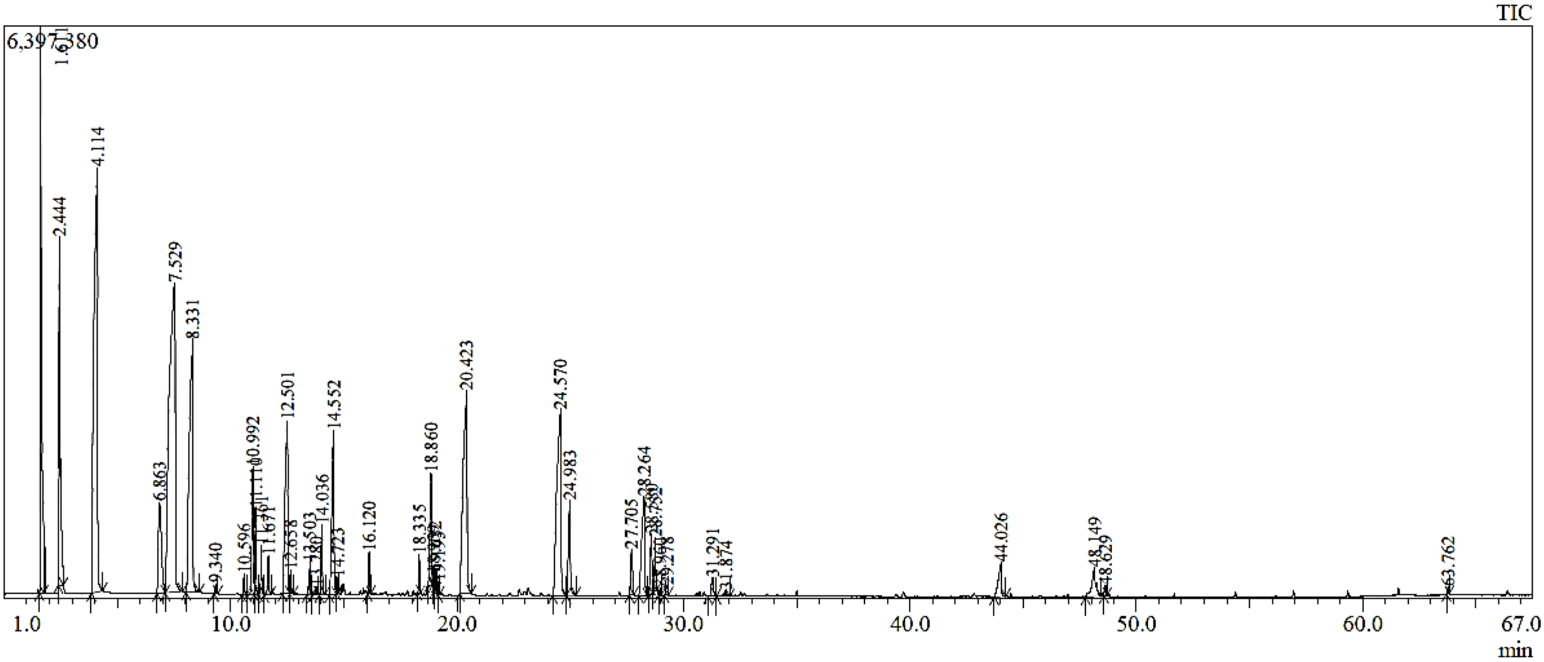
7.4.4. Butanol conversion over Zn/AC catalyst



7.4.5. Ethanol conversion over Zn/HZSM-5 catalyst



7.4.6. Butanol conversion over Zn/ HZSM-5 catalyst



7.4.7. List of retention times and compound names

Retention Time	Compound name
1.514	Water
1.621	Ethanol
1.702	Butanol
1.721	2-Methyl-1-butene
1.858	Butane, 2,3-dimethyl-
1.867	Cyclopentane
1.915	Pentane, 3-methyl-
2.460	Benzene
4.050	Toluene
4.757	Octane
6.948	Ethylbenzene
7.423	Xylene
10.596	Benzene, propyl-
11.110	Benzene, 1-ethyl-2-methyl-
12.548	Trimethylbenzene
12.730	Decane
14.126	Indane
14.587	Benzene, 1,4-diethyl-
14.672	Benzene, 1,3-diethyl-
14.757	Benzene, 1-methyl-3-propyl-
15.047	Benzene, 2-ethyl-1,4-dimethyl-
15.895	Benzene, 1-ethyl-2,4-dimethyl-
16.155	Benzene, 1-ethyl-3,5-dimethyl-
17.589	Benzene, 1,2,3,5-tetramethyl-
19.038	Naphthalene, 1,2-dihydro-
19.204	Naphthalene, 1,2,3,4-tetrahydro-
20.338	Naphthalene
24.570	Naphthalene, 2-methyl-
28.960	Naphthalene, 2-ethenyl-
29.278	Naphthalene, 1,3-dimethyl-
31.291	Naphthalene, 1,6,7-trimethyl-