Metal modified Mesoporous ZSM-5 as catalysts for the oligomerization of 1-hexene

By

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DECLARATION

I declare that **Metal modified Mesoporous ZSM-5 as catalysts for the oligomerization of 1-hexene** is my own work, that it has not been submitted previously for any degree or examined in any other university, all the sources I have quoted have been indicated and acknowledged as complete references.

Name: Kenneth Mpemane Mlimi Date: 03 February 2021

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ABSTRACT

The use of diesel engines in vehicles and heavy machinery throughout the world has been slowly increasing in the past few decades. This has led to high demand for diesel and gasoline with high octane number. Diesel and gasoline are in high demand due to its qualities as fuels containing low or no sulfur and nitrogen compounds, making them environmentally friendly and the anti- knocking properties respectively. With these reasons and more, researchers have been studying processes like the catalytic oligomerization of olefins to produce synthetic fuels with augmented qualities and properties. The effectiveness of the process will depend on the quality of the catalyst.

Solid acid catalysts such as zeolites are commonly used in the petrochemical industry. ZSM-5, a microporous zeolite with unique pore channel characteristics, strong acidity, hydrothermal stability and coke resistant properties make it one of the most significant catalysts in the petrochemical industry. It is used in the oligomerization of olefins such as the conversion of olefins to distillates (COD) process. ZSM-5 remains the preferred choice of catalyst for the oligomerization of olefins due to its acidity and shape selective properties, which offers good activity and selectivity However, ZSM-5 is a medium pore zeolite which limits the degree of branching during oligomerization and suffers from diffusion limitations when long chain hydrocarbons are concerned. In order to increase the efficiency of ZSM-5 in the oligomerization of olefins by increasing activity, selectivity to long chain hydrocarbons(diesel) and increasing branching in gasoline to boost octane numbers, researchers have investigated the modification of the ZSM-5 catalyst. ZSM-5 is modified by introduction of a secondary mesoporous system via treatments such as desilication to enhance accessibility to active sites and facilitate diffusion of branched and long chain hydrocarbons. Metal doping is also seen as a route of developing a bi-functional catalyst that promotes oligomerization to longer chains while also producing high octane gasoline by increasing the degree of branching through isomerization.

This study investigates modifying the physicochemical properties of ZSM-5 via desilication and metal doping for the oligomerization of 1-hexene, a model compound for alkenes oligomerization. The physicochemical properties were studied using characterization techniques such as XRD, HRSEM, HRTEM, EDS, BET and NH_3-TPD. XRD analysis showed that the synthesis of pristine ZSM-5 was successful as the MFI structure with the typical peaks at 8° and 23° 2Theta were clearly observed. XRD also showed that even after desilication of the pristine ZSM-5, as well as the metal doping on the desilicated ZSM-5, the framework of the zeolite is not altered and the crystallinity was maintained. However, the acidity and porosity is altered after both desilication and metal doping treatments. The BET results show that the desilication process was successful with an increase in surface area and pore volume in the desilicated ZSM-5 and the introduction of mesopores with a maximum of 5-9 nm in size. After desilication the acidity of the strong acid sites decreased and an increase in weak acid sites was observed. Metal doping led to a decrease in surface area as well as micropore volume suggesting that the metals were in the pores of the zeolite. It also caused further decrease in strong acid sites and an increase in weaker ones. However, a significant increase in both weak and strong acid was observed with cobalt doping The HRSEM, HRTEM, and EDS results show that the metals were added successfully with the actual loading equal to the theoretical loading of 1 wt% metal (i.e. Ni, Zn, Cr andCo).

The catalytic performance improved after desilication. An increase in conversion of more than 20% was observed. The desilicated ZSM-5 produced more dimers compared to the pristine ZSM-5 i.e. the selectivity to diesel increased from about 30% to 45%. This was attributed to the improved diffusion properties and accessibitlity to active acid sites in the desilicated ZSM-5.. The monometallic 1%Zn/ZSM-5 outperformed the other metal doped catalysts that were tested when it came to oligomerization by further increasing selectivity to diesel range products to above 55%. The 1%Co/ZSM-5 however exhibited excellent performance as an isomerization catalyst. RONs of more than 140 were obtained. Thus a bi-functional catalyst that simultaneously promoted oligomerization and isomerization by enhancing selectivity to diesel range hydrocarbons and increasing branching in gasoline range products respectively, was envisaged by synthesizing a bimetallic catalyst with Zn and Co. It was found that the Zn:Co ratio in the bimetallic catalysts had a remarkable influence on the catalytic activity and selectivity. An increase in the cobalt loading from 0.3Co-0.7 Zn/ZSM-5 to 0.7Co-0.3Zn/ZSM-5 showed an increase in isomers which correlated with an increase in the RON. The 0.3Co-0.7 Zn/ZSM-5 catalyst which had the lowest cobalt content also showed an enhancement in the oligomerization reaction when compared to the other bimetallic catalysts which favoured the formation of isomerized C6 products. It also showed the highest selectivity to C_{12}+ products compared to all other catalysts. However the overall selectivity to diesel of the 0.3Co-0.7 Zn/ZSM-5 was comparable with the desilicated ZSM-5 and was only slightly better than the pristine ZSM-5 in terms of gasoline RONs. Therefore, the modifications of ZSM-5 via desilication and metal doping were successful in improving the catalytic performance of ZSM-5 in the oligomerization of 1-hexene. Increased selectivity to diesel and high octane gasoline were achieved. However, it may be worthwhile investigating Zn:Co ratios with less Co in future to further enhance diesel selectivity while still producing high octane gasoline.

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Nomenclature

Abbreviation	Description
AlO4	Alumina
Al	Aluminium
SiO4	Silica
Si	Silicon
BET	Brunauer Emmett and Teller
COD	Conversion of Olefins to Distillate
EDS	Energy Dispersive Spectroscopy
FID	Flame Ionisation Detector
FCC	Fluid Catalytic Cracking
GC	Gas Chromatography
C6-C9	Gasoline range
HRSEM	High Resolution Scanning Electron Microscopy
HRTEM	High Resolution Transmission Electron Microscopy
LPG	Liquid Petroleum Gas
MTO	Methanol to Olefins
MOGD	Mobil Olefins to Gasoline and Distillate
MOR	Mordenite
PetroSA	Petroleum Oil and Gas Corporation of
PXRD	Powder X-ray Diffraction
PBU	Primary Building Unit
SBU	Secondary Building Unit
SDA	Structure Directing Agent
TPD	Temperature Programmed Desorption
TPA	Tetrapropylammonium
WHSV	Weight Hourly Space Velocity
ZSM-5	Zeolite Socony Mobil

THESIS STRUCTURE

The thesis is outlined as follows:

Chapter 1: This chapter contains a general introduction to the dissertation and briefly presents the petroleum industry and catalysis. The importance of catalysts in the petrochemical industry is highlighted.

Chapter 2: The literature review is divided into three sections: An introduction to zeolites and in particular ZSM-5, modification which includes desilication via post alkaline treatment and metal doping of the ZSM-5 zeolite, and the oligomerization of olefins.

Chapter 3: In this chapter the experimental methods and procedures used to achieve the objectives are outlined. The research is broken into two main parts. Part one is the synthesis of the pristine ZSM-5, desilication of ZSM-5, and metal-doping of ZSM-5. Part two is the evaluation of the synthesized zeolites as catalysts for the oligomerization reaction using 1-hexene as feed.

Chapter 4: This chapter is divided into four parts which consists of a comparison between the pristine and desilicated ZSM-5, monometallic doping with various transition metals, bimetallic doping and finally a comparison of the synthesized ZSM-5 and its various modifications. The results obtained in the experiments, including the characterization of the synthesized catalysts and the evaluation of the catalysts in the oligomerization of 1-hexene is discussed.

Chapter 5: This chapter summarizes the finding of the experiments and presents the conclusions of the study.

CHAPTER 1: GENERAL INTRODUCTION

1.1 Catalysis.

Catalysis is a process of increasing the rate of a reaction by introducing a catalyst to a reaction. A catalyst is a substance that increases the rate of a reaction by providing an alternative reaction path that has lower activation energy. The catalyst is not consumed in the reaction but instead regenerated. A good catalyst must be highly selective, highly active, and must have a long lifetime. Catalysts can be classed into two main groups, namely homogeneous and heterogeneous catalysts. Homogeneous catalysts are in the same phase as the reactants, whereas the heterogeneous catalysts are in a different phase as the reactants.

Homogeneous catalysts possess certain advantages over the heterogeneous catalysts such as enhanced mixing between the reactants and moderate reaction conditions. However, they also possess disadvantages which include difficulty in separation from the reactants and products, stability problems, and regeneration [1], [2]. Catalysts are used in many chemical processes, such as the production of sulfuric acid, methanol, ammonia, and the production of fuel in the petrochemical industry [3].

1.2 Function of Catalysts in the Petroleum Industry.

The petroleum industry is a vital one in the functionality of modern society, as it provides energy and transportation fuel. Petroleum is a composition of hydrocarbons. Ideally, a chemical reaction of petroleum (i.e. combustion) should yield water and carbon dioxide; however, this is not the case. Combustion of petroleum yield mixture of products that include oxygenated hydrocarbons, carbon monoxide, and nitrogen compounds, since this reaction takes place in the presence of air, these products is harmful to the environment.

Petroleum is also known as crude oil, and it is often used as a raw material in the production of various chemicals such as solvents, plastic, pharmaceuticals, and pesticides. Crude oil is a non-renewable source of energy. The world’s crude oil reserves are plummeting, to compensate for this, the combustion of fossil fuel and the use of natural gas has been employed. These processes led to the increase of greenhouse gasses hence global warming. In recent years, the need for environment-friendly fuels has increased. The research field, as well as the chemical industry, are in the continuous development of effective catalysts to fulfil environmental, economic, political demands[4], [5].

The petroleum industry uses a lot of catalytic processes to refine crude oil and produce environmentally friendly gasoline and diesel fuels. These processes include but are not limited to reactions such as catalytic cracking, isomerization, hydrogenation, and catalytic oligomerization. Catalytic cracking is a process in which a long hydrocarbon chain is broken down into smaller hydrocarbons. These are heavy crude oils or tars which are cracked to olefins over zeolite catalysts.

Thermal cracking, steam cracking, hydrocracking and fluid catalytic cracking (also known as FCC) are cracking processes that are heavily employed to convert high molecular weight hydrocarbons to valuable gasoline and olefins. Isomerization is a process that introduces branching in linear hydrocarbons. This process is very important in the production of high-octane gasoline. Hydro-isomerization is used to introduce some branching to the linear hydrocarbons for applications such as jet fuel production. Oligomerization is a chemical reaction that converts monomers to larger molecules through a finite degree of polymerization. Oligomerization is the process that is utilized for the conversion of olefins to gasoline and distillates products. These processes mainly use heterogeneous catalysts in the chemical industry such as solid acids, in particular zeolites because of the advantages they have compared to homogeneous catalysts [6].

1.3 Commercial uses of various catalysts

Some examples of zeolite catalysts utilized commercially are Zeolite Y based catalysts in FCC of an olefinic naphtha (Superflex process), platinum supported on mordenite zeolite(Pt/MOR) for isomerization and hydroisomerization of C_5-C_6 alkanes (e.g. Su¨d-Chemie Hysopar, Procatalyse IS 632 and UOP HS-10) and ZSM-5 in the oligomerization of olefins. . ZSM-5 is used for the oligomerization of C_3-C_6 olefins to gasoline and diesel range hydrocarbons such as in the Mobile Olefins to Gasoline and Distillates process (MOGD).

The MOGD is an oligomerization process that uses the ZSM-5 zeolite as a catalyst as it offers good activity and selectivity to gasoline and diesel fuels as well has good catalyst stability. Since the MOGD uses olefins as a feed stock and one of the by-products in the Fischer Tropsch Synthesis process (FTS) are lower olefins which is produce in large quantities, a modified MOGD process to run specifically olefins(C_3-C_6) from FTS was developed namely the Conversion of Olefins to Distillates (COD) process [7], [8].

1.4 The Conversion of Olefins to Distillates (COD) process

The COD process typically operates under conditions 200–280 °C, 1–5 MPa and WHSV between 0.1 and 5 h^{-1} over a microporous HZSM-5 zeolite as catalyst and produces high quality distillates(REF Winnie paper). The diesel produced possesses excellent properties for use in compression ignition engines. The use of diesel engines in industrial or in passenger vehicles has increased drastically in recent years. This increase has led to a high demand of diesel and middle distillates/gasoline products. Efforts to improve on oligomerization processes such as COD technology to meet the current demands for diesel and high octane gasoline are of vital importance. Hence improvements in terms of catalytic performance of these technologies that help meet these demands are being heavily researched.

1.5 Zeolites

Zeolites such as ZSM-5 remain the preferred choice of catalyst due to its hydrothermal stability, strong acidity and unique pore structure. However, due to the microporous nature of ZSM-5 it suffers from internal diffusion limitations as well as reduced accessibility of active sites. This can result in lower conversions and longer contact times as larger molecules slowly diffuse from the catalyst. They may undergo unwanted side reactions leading to lower long chain hydrocarbon selectivity. The formation of carbonaceous deposits consequently results in a quicker deactivation of the catalyst as pore blockage occurs. Two ways that are typically used to improve the overall activity of the zeolite catalyst are modifications of the porosity and acidity. Porosity can be modified via an introduction of a secondary mesopore system that enhances diffusion. To overcome diffusion limitation challenges desilication and dealumination treatments are used to introduce mesopores thereby forming a bimodal pore system known as hierarchical zeolites[13], [14].

Hierarchically structured zeolites may have a multi-distribution of pore systems. The micropores still serve in a shape selective process for molecules, while meso- and macropores provides a facile diffusion pathway for molecules to and from the active sites within the pores (Ref Winnie). Furthermore, it is known that the constrained pores can have a considerable effect on the nature of products. ZSM-5 zeolite has been shown to limit the degree of branching. Thereby introducing larger mesopores may results in an increase in the degree of branching which will enhance the octane rating of gasoline products.

Secondly, metals are added to alter the acidity of the zeolite catalyst. The metals may have promotional effects leading to increased catalytic performance. Introduction of certain metals such as Cobalt, Zinc Nickel and Chromium are known to enhance reactions such as isomerization, aromatization and oligomerization. For example, it is known that the ethylene reactivity in the acid catalysed oligomerization is very low and solid acids containing transition metals such as nickel are required for this reaction [9]. Nickel was also added to ZSM-5 which showed an increase in weak acid site, a decrease in strong acid site and consequently an increase in activity was observed as well for the ethylene oligomerization reaction [10]. Therefore modification of ZSM-5 through alterations in porosity and acidity or a combination of both may lead to enhanced catalytic performance in terms of increased selectivity to diesel range products as well as highly branched gasoline products with a higher octane rating

This project focuses on developing ZSM-5 zeolite catalysts with improved performance in the oligomerization of olefins. The pore structure of ZSM-5 is modified via the desilication process while the physicochemical properties of the zeolite is altered by the addition of various. Cobalt, Zinc, Nickel, and Chromium are loaded onto the ZSM-5 zeolite in the monometallic form and the effects of the different metals are compared. With the aim of developing a catalyst that produces high quality diesel and gasoline with high octane number a catalyst with a bimetallic configuration is synthesized. The catalysts are applied in the conversion of 1-hexene, a model compound for the oligomerization of olefins, hence applicable in the production of environmentally friendly fuels. The research conducted and the experience gained will ensure development of human capital and will be of significance to academia and industry.

1.6 Rationale

The petrochemical industry is one of the major contributors to the energy sector. With the world crude oil reserve depleting and growing environmental concerns there is an urgent requirement for renewable energy resources and a need to reduce greenhouse gasses in the atmosphere. There is also a need to increase the quality and meet the ever-growing demands of high octane gasoline and distillates fuels. To help mitigate these demands a lot of research has been undertaken to find alternative ways and processes that produces cleaner fuels. The Conversion of Olefins to Gasoline and Distillates (COD) is one such process. COD an integral part of the Gas to Liquid (GTL) technology used by PetroSA at the Mossel bay refinery. The olefins that are obtained from the Fischer Tropsch process, are oligomerized over an acidic catalyst namely ZSM-5. However, the ZSM-5 catalyst has diffusion limitations due to its smaller pores and it deactivates fast with bulky molecules poisoning the catalyst as well as blocking the active acid sites of the catalysts leading to lower activity, selectivity to desired and products and catalyst stability. Therefore the improvement of the oligomerization process goes hand in hand with the development of effective catalysts. An effective catalyst is one that has good selectivity towards desired products, good activity and longer life span. In this study we investigate the modification of the porosity and acidity of the ZSM-5 zeolite in order to synthesize an effective catalyst with good selectivity towards diesel products while improving the octane number of gasoline, and eliminating steps like skeletal isomerization in the refining process. It is envisaged that introducing secondary porosity as well as doping with metal promoters will enhance the overall performance of the ZSM-5 catalyst in this reaction.

1.7 Aim

The aims of the project were to study the effects of monometallic and bimetallic metal loaded desilicated ZSM-5 on the physicochemical properties and catalytic performance of the zeolite catalysts. The catalysts were evaluated in the oligomerization of 1-hexene.

1.8 Objectives:

The objectives of this research were to:

(i) Synthesise a pristine ZSM-5 Using the hydrothermal method, Desilicate the pristine ZSM-5 using NaOH and compare the effects of desilication on the physicochemical properties and catalytic performance

(ii) Synthesise monometallic and Bimetallic doped ZSM-5(M= Ni, Zn, Cr Co) ZSM-5 via the incipient wetness impregnation method

(iii) Characterize and study the effects of desilication and metal loading on the physicochemical properties such as acidity and porosity

(iv) Evaluate the catalytic activity and investigate the effect of metals and desilication on activity, selectivity and stability of the catalyst in the oligomerization of 1-hexene .

Chapter 2: Literature Review

2.1 Zeolites

Zeolites are crystalline, microporous aluminosilicate materials that are built from an infinitely extending three-dimensional network of [SiO_4] and [AlO_4] tetrahedra linked to each other by oxygen atoms [11]. The AlO_4 is negatively charged, this is charged balanced by a suitable cation while the SiO_4 is charged balanced. The zeolite becomes a solid acid when the charge is balanced by a proton. Zeolites were discovered in 1756 by a Swedish mineralogist Axel Fedrick Cronstedt when he was heating the mineral stilbite and it gave off steam due to the adsorbed water. The word zeolites translate to boil stone, it originates from the Greek word zeo means to boil and lithos meaning stone.

The microporous nature of zeolites allows them to be used as molecular sieves. This means the pores and channels of a zeolite allow smaller molecules to pass through while larger ones are excluded. This makes them very useful in the petrochemical industry as shape selective catalysts. They can be used to remove liquid and gasses impurities at a molecular level. Zeolites are used in in the automotive industry to help improve the air-brakes in trucks, vehicles air-conditioning as well as help reduce vehicles exhaust emissions[12]. They are also applied in laundry detergent, insulated windows, while in the petrochemical industry they are used in the production of lead free gasoline. With these qualities, zeolites have made it possible to produce clean, high quality and high performance petrochemicals in a cost effective way as they offer cheaper ways of producing greener fuel [13], [14].

Zeolites occur in nature and some are synthesized in the laboratory. Synthetic zeolites have an advantage over naturally occurring zeolites, as they are pure with regular voids and channels. The physicochemical properties of synthetic zeolites can be tailored to specific needs. Zeolites are used in different industries for various applications. Differences between zeolites, zeolite like material, and tectosilicates are not easy, as a result of the crystalline solids. The framework density of zeolites is used to differentiate different classes of zeolites and zeolites alike.

The frameworks categories which have been approved by the International Zeolite Association(IZA) detailing the description of these frameworks can be found in the atlas of zeolite framework types. The Linda Type A (LTA), Linde Type L (LTL), Zeolite Beta. (BEA), Faujasite (FAU), and ZMS-5 (MFI) are just some of the different zeolite frameworks you can find

2.2 Structural Overview

Zeolites (Figure 2.1) have an open framework that consists of channels and interconnected voids occupied by water molecules and alkali earth metals. The Group I and Group II cation can be reversibly exchanged for similar size cation when an aqueous solution is passed through the voids. These channels allow particles of a certain size to pass through while restricting particles that are larger hence they act as molecular sieves. These properties make them good catalysts and indispensable in the petrochemical industry[13], [15], [16].

Zeolites are made up of two building units called the primary building units and the secondary building units. The primary Building Units (PBU) are the tetrahedral AlO_4 and SiO_4 which are linked together to form the Secondary Building Units (SBU). These SBU normally form the shapes of the zeolites from a complicated shape like hexagonal-prisms, cube-octahedra to a simple cubic. The SBU is repeated and extended to form the zeolite framework, they also give rise to different types of zeolites structures. There are nine SBU which can be used to explain all known zeolites.

The SBU consist of 4,6,8, and 10 membered rings, in which a 4 membered ring consist of 4 tetrahedral molecules bonded to each other and the SBU can be linked to form different polyhedrons[12], [13], [17]. An empirical formula for a zeolite can be written as $M_ynO.Al_2O_3._xSiO_2._wH_2O$ where "M" represents the exchangeable cations "n" represents the valency of the cation “M”, “x” and “y” represent the total number of tetrahedral per unit cell and “w” the number of water molecules per unit cell. “M” is generally from the elements of group I and II, although other metal, non-metal. Zeolites are very thermal stable even at 700 to 800 °C.

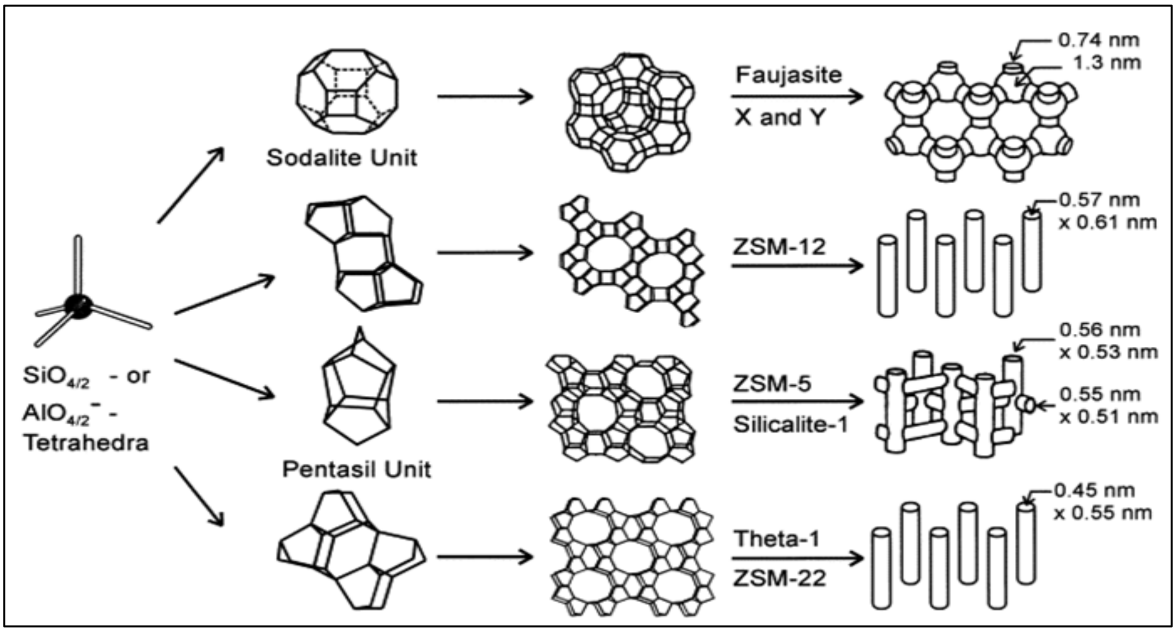


Figure 2.1: Diagram of zeolites. Illustrating their building primary, secondary building blocks, along with the different frameworks of zeolites that can occur

2.3. Type of Zeolites

2.3.1 Natural Occurring Zeolites

Natural occurring zeolites are formed where there are some volcanic activities. They are formed when volcanic ash or rock reacts with alkaline water underground. Some zeolites take a long period to crystallize, ranging from thousands to millions of years, particularly those in the shallow marine basin. It is rare to find pure natural zeolites due to the way they are formed, so most contain other minerals such as quartz and other zeolites. They are approximately 63 known naturally occurring zeolites and 7 of those have been found to occur in abundance. These are chabazite, analcime, mordenite, phillipsite, erionite, ferrierite, and clinoptilolite. They have been efforts to try to synthesize some of the naturally occurring zeolites in the lab, however, only ferrierite and mordenite have been produced in large quantities. The naturally occurring zeolites are used in animal feeding, horticulture, wastewater treatment, odour control, and in construction [11][13], [18].

2.3.2 Synthetic zeolites and their application

Zeolites are formed by the crystallization of alumina, silica, alkali-salts, water, and organic templates under hydrothermal conditions. The first hydrothermal synthesis of zeolite was reported in 1862 by St. Claire Deville and it was called levynite. During the 1930s to the 1950s the synthesis of zeolites was refined by Barrer. From the 1950s onwards zeolites gain interest for commercial use. The main reason for this was the discovery of zeolites A, Y, and X which were found by Milton and Breck. Zeolite A, Y, and X are characterized by larger pour volume, regular crystal structure, internal volume. They also characterised by high catalytic activity and thermal stability in processes such as catalytic cracking and isomerization [7].

Zeolites can be categorized according to their pore diameter and chemical composition. The chemical composition in zeolites refers to the Silica alumina Ratio (SAR). These are classed as low silica (SAR = 1-1.5), medium silica (SAR = 1.5-5), high silica (SAR = 5-several thousands) and Al-free, (Silicates). The nature of the zeolite is affected by the precursors, synthesis conditions such as temperature, pressure, and the pH of the mixture during crystallization. The concentration of OH^- modifies the nucleation time by influencing the transport of silicates from the solid phase to solution[15], [18]–[20]. The hydrothermal synthesis method is a widely used method to produce zeolites. Since then several ways of synthesizing zeolites have been described in the literature such as microwave-assisted hydrothermal synthesis, solvothermal, ion-thermal synthesis [21], [22]. The hydrothermal synthesis which was used in this study is explained in further detail in the following section.

2.3.2.1 Hydrothermal Synthesis

Hydrothermal Synthesis is the conventional way of producing synthetic zeolites. Hydrothermal synthesis can be classified into two categories depending on the temperatures. If the temperature falls in the range of 150°C-240°C this is known as subcritical and if it’s above this range to well over 1000°C it’s called a supercritical. Most hydrothermal syntheses take place in the subcritical range. Hydrothermal synthesis is preferred because of the low energy consumption, reaction interface is easily controlled, there is high reactivity of reactants and reduced pollution. The reaction mixture contains silica acid, base to mobilize the silica, water, structural directing agent(SDA). This mixture is transferred to a Teflon cup which is enclosed in an autoclave, then is placed into an oven ([15], [20]). The following factors affect the synthesis of zeolites such as silica and alumina source, silica and alumina ratio, batch composition, alkalinity, crystallization temperature and reaction time, ageing, structural directing agent and water content [20]. Figure 2.2 below shows a flow-diagram of the hydrothermal synthesis method

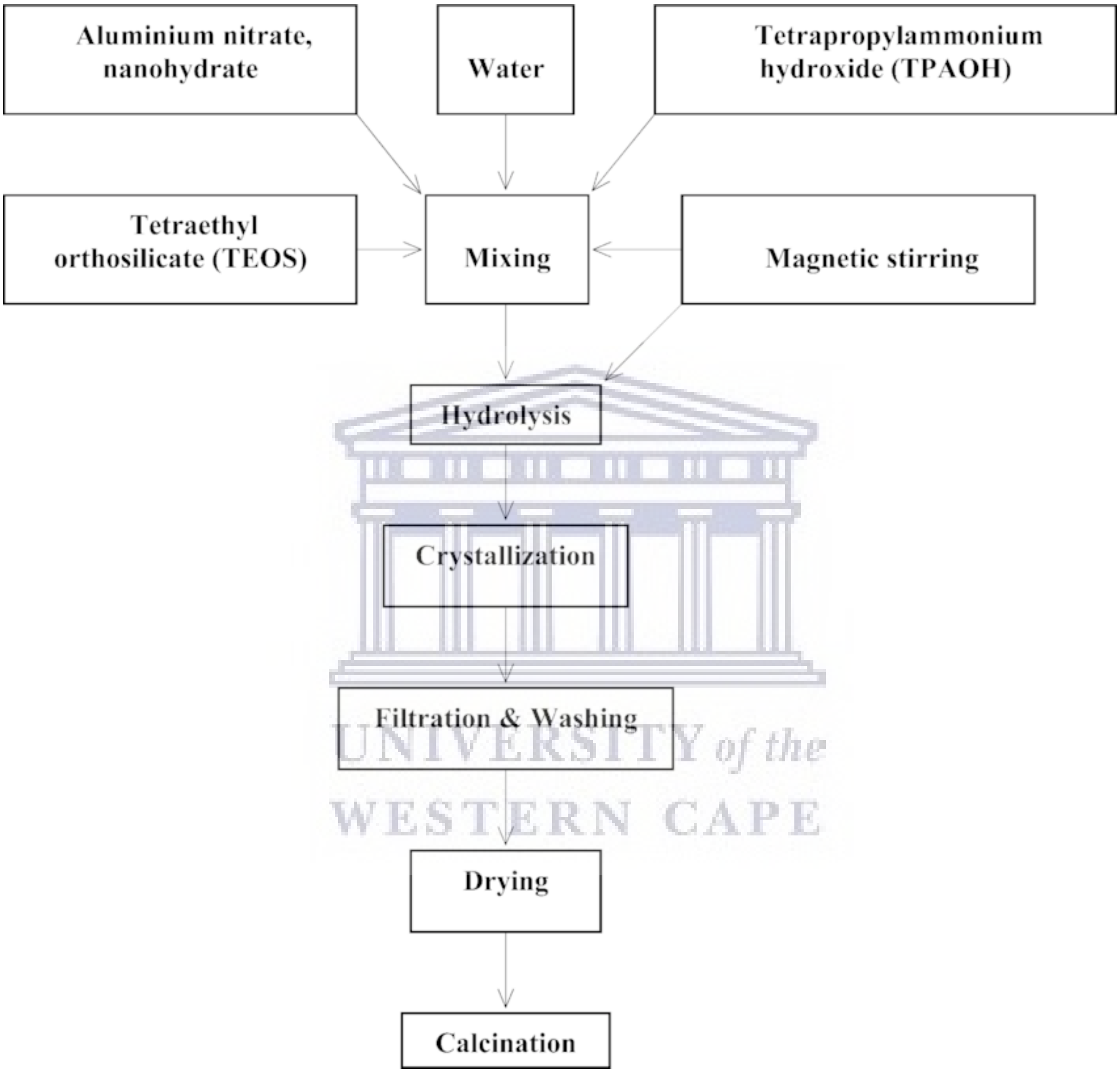


Figure 2.2: Flow-chart that shows the synthesis of zeolite pristine ZSM-5, using the Hydrothermal method

2.3.2.2 Zeolite application

Synthetic zeolites have larger pores than the naturally occurring ones hence these synthetic zeolites are used in processes that involve large molecules. They are used as adsorbents to remove oxygen from argon, purification, and separation of air, catalytic cracking and oligomerization of light olefins, just to mention a few[18], [21]. They are chosen for these processes due to their properties, such as ion exchange capacity, high acidity, resistance to coke deposition, high thermal stability, large adsorption capacity, and uniform structure. Their big internal pore volumes, the diverse framework of chemical, molecular size pore, and uniformity of the crystal structures and composition allows control of structure and properties of the zeolites during synthesis so that it can be tailored for a specific application. Due to the large diversity of structures in which the SBU can be arranged, can result in multiple variations of synthetic zeolites with different pore sizes and pore volume[18][15], [20]. Table 2.1 (below) shows different types of zeolites and their applications in different industries as well as their characteristics.

Table 2.1: Tabulation of the different types of synthetic zeolites and their applications.

Zeolite Type	**Oxygen numbers at the ring-opening**	**Dimensions of the zeolite and framework.**	**Pore-size, width in Angstrom**	**Application**
Chabazite, SAPO-34, SSZ-13	8	3D	3.8	Gas Separation
Zeolite A,	8	3D	4.4	Pervaporation, Membrane Reactors
Ferrierite, ZSM-35/ ZSM-5	10	2D/3D	5.4	Pervaporation, Gas Separation and acid catalysed reactions
MEL-ZSM-11	10	3D	5.4	Pervaporation
Mordenite, Zeolite Y	12	1D	7.0	Pervaporation and Gas Separation, catalysed reactions

Zeolite A was the first zeolite to be used in a commercial process, *i.e.* it was used as an adsorbent to remove oxygen from argon at the Union Carbide plant, it is also used as an anhydrous laundry detergent. Zeolites are used in many different areas for various applications from biochemical and biomedical to produce medical grade oxygen to agriculture it where they are used to treat the soil. In addition, the Zeolite Socony Mobil-5 (ZSM-5) has become a very important zeolite in the petrochemical industry as it is used in many chemical reactions to produce high-quality gasoline and distillates fuels and chemicals [14], [23], [24]. ZSM-5 zeolite is discussed in further detail in the section below.

2.4. Zeolite Socony Mobile-5 (ZSM-5)

The Zeolite ZSM-5 was first synthesized by Arguer and Landolt in 1972. ZSM-5 is a medium pore zeolite with the MFI framework structure. It is a 10 membered ring with the following formula $Na_nAl_nSi_{96-n}O$, where n is a number between 0 and 27 [22]. ZSM-5 has high thermal stability and Bronsted acidity, the pore size is believed to be in this range 5.3-5.6 Angstrom [25]. This is classified as microporous since it is less than 20 Angstrom. Mesoporous is when the pore sizes are between 20-500 Angstrom, and any pores greater than 500 Angstroms are referred to as macroporous..

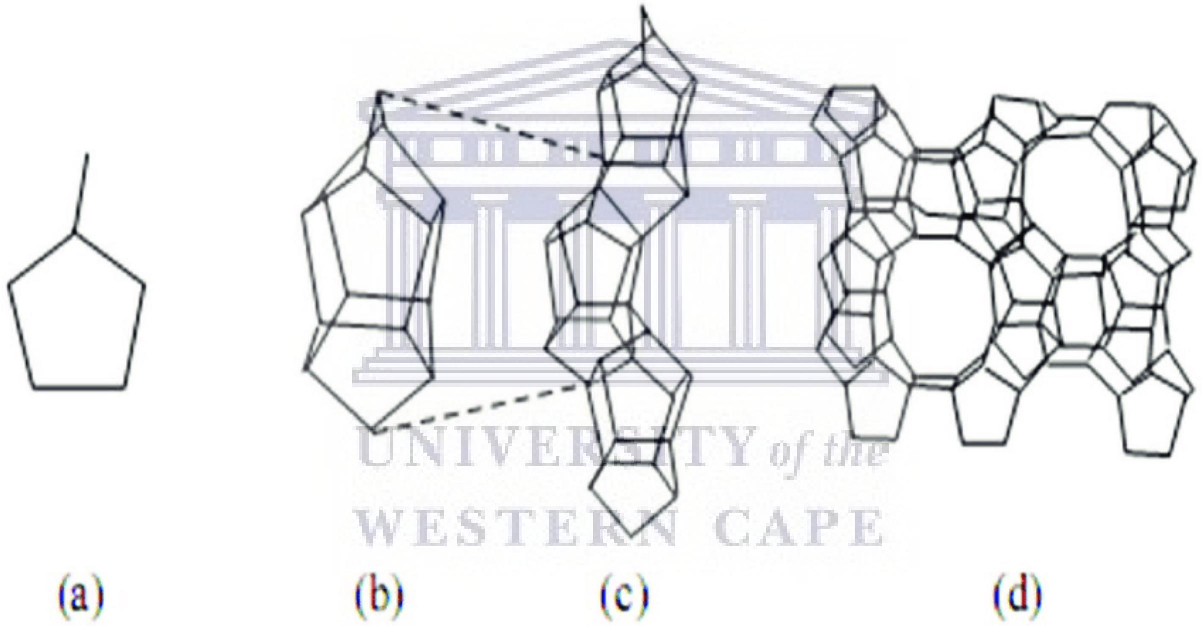


Figure 2.3: Building block of a ZSM-5 zeolite. (a) Type 5-1 SBU secondary construction unit. Assembly of secondary building units (b) in pentasil group, (c) in chain, and (d) in layers of tetrahedra.

Figure 2.3 shows the structural components of ZSM-5. A ZSM-5 consist of several pentasil which are linked together by oxygen atoms and each pentasil is composed of eight, five membered ring. The linked pentasil form a 10 membered ring forming a tetrahedral, depicted in figure 1.4 [22], [26].

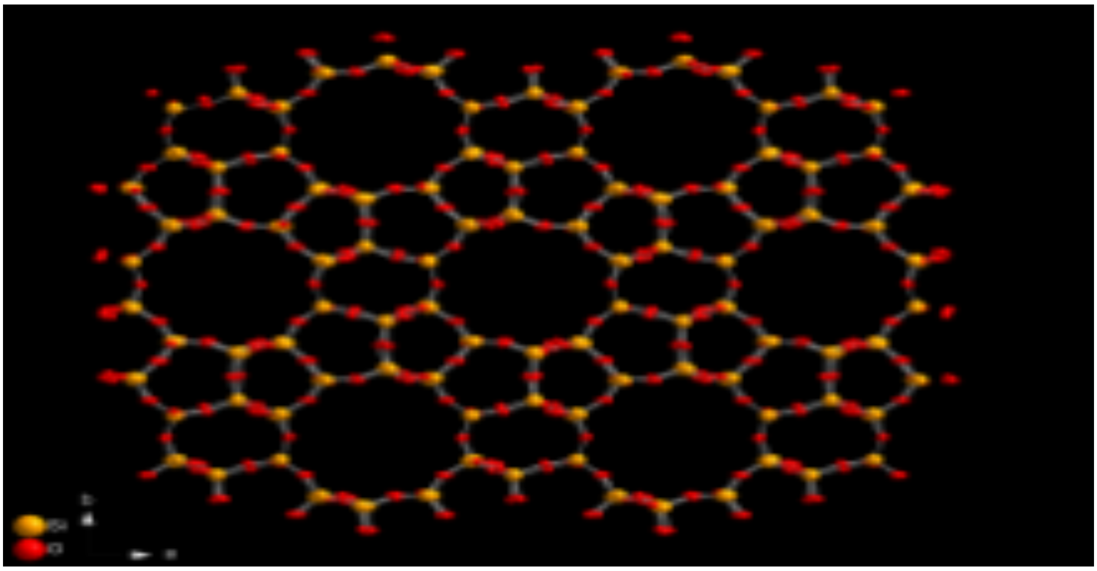


Figure 2.4: Pristine ZSM-5 molecular structure

The ZSM-5 catalyst is typically synthesized using the hydrothermal method [25]. The synthesis usually involves three solutions, (i) Source of the silica, (ii) source of sodium ion, alumina, and hydroxide ions, and (iii) tetra-propylammonium cation which is a template. These three solutions are mixed to form a tetrapropylammonium-ZSM-5. ZSM-5 has a high acidity and a very unique channel structure which makes them very useful in shape-selective reactions. The ZSM-5 is mostly used in the petrochemical industry in many acids catalysed reactions[22], [27], [28]

2.4.1. ZSM-5 in the Petrochemical Industry

The morphology of a catalyst has a big influence on the physicochemical properties of catalysts. Features like pore size, acidity, and pore volume affect the selectivity and activity of the catalyst. ZSM-5 has a high SAR and when the Al^{+3} replaces a Si^{+4} the positive charge (proton) is needed to balance the charge in the zeolite, hence making it more acidic. ZSM-5 possesses regular micropores of molecular dimensions which allow them to be used as shape selective catalysts. One application in which ZSM-5 is used is the isomerization of meta-xylene to para-xylene. An example of the reaction is shown below in Figure 2.5.

Figure 2.5: Depicts an Isomerization reaction over a ZSM-5 catalyst from Meta-Xylene on the left to Para-Xylene on the right .

Figure 2.5 above illustrates an isomerization reaction over a ZSM-5 catalyst. This reaction illustrates the shape selectivity of the ZSM-5, as there are three possible outcomes which are ortho-xylene, meta-xylene and para-xylene. However the para-xylene is almost always favoured to be produced due to shape selectivity [29]. The ratio in which they are produced is 1000:10:1 para-xylene: meta-xylene: ortho-xylene respectively. The main reason for this is attributed to sieving functionality of the ZSM-5 as the channel size of the ZSM-5 are comparable to the size of the para-xylene which has a higher diffusion coefficient (0.53 nm), while the other two isomers have a lower diffusion coefficient(meta-xylene = 0.61 and ortho-xylene = 0.66nm) and larger steric hindrance [29], [30].

ZSM-5 is used in many petrochemical reactions which includes the production of propylene, in improving gasoline octane number in catalytic cracking, alkylation, oligomerization, cracking, hydrogenation and isomerization of hydrocarbons [5], [29]–[31]. The Zeolite ZSM-5 is used in catalytic cracking of naphtha into olefins, which in turn are used in the conversion of olefins to distillate and gasoline products over a ZSM-5 type catalyst. ZSM-5 is sometimes used as a support in which a metal or transition metal is deposited on the surface and internal pores of the ZSM-5 catalyst. In the oxidation of ethanol to acetaldehyde, copper is deposited on the ZSM-5. Ni-ZSM-5 is used in the hydrogenation of polymethyl-benzenes. These observations clearly show the significance of the ZSM-5 in the petrochemical industry[32], [33].

However, ZSM-5 has several challenges due to its micro-porosity which causes diffusion limitations. Bulky molecules and the formation of coke during reactions tend to block the pores and hence poison the catalyst reducing catalyst activity and catalyst life. To overcome these diffusion challenges researchers have been modifying the microporous ZSM-5 to a mesoporous ZSM-5 using different techniques such as desilication and dealumination. These aim at increasing the accessibility to the catalytic active sites for bulky molecules, the life of the catalyst, and acidity while preserving the crystallinity and structural framework of the zeolite[27]. The desilication method which has been used in this study to introduce secondary porosity to the ZSM-5 zeolite is explained in further detail.

2.5 Desilication (Forming hierarchical pores)

The diffusion limitations in the zeolite are overcome by introducing mesoporosity in the zeolite structure. The introduction of the mesoporosity leads to the formation of a bimodal pore system. These zeolites are known as hierarchical zeolites, which contains both micropores and mesopores. There are two main ways in which the mesoporosity can be introduced. There is a top-down approach and the bottom-up approach. With regards to the top-down approach, the secondary pore system is introduced via desilication or dealumination which are post-synthesis methods. The bottom-up approach route creates a zeolite synthesis method that will induce micropores and mesopores directly or indirectly by using or not using a mesopore template agent[27], [34].

2.5.1 The Bottom-up approach

The bottom-up route which involves templating is generally of two kinds. It uses both hard and soft templates and mesoporosity is created upon the removal of these templates. Soft templating (Endo-templating) is when the templating agent is included in the synthesis of the zeolite. Soft templating uses Van der Waals forces, hydrogen bonding, and covalent bonds to interact with the zeolite framework. Hard templating (Exo-templating), a solid template is included in the synthesis of the zeolite and it is removed at a high temperature creating mesopores where the hard template was situated. The template-free approach requires a vital control of the crystallization of the zeolites [27], [35]. The templating method presents a lot of challenges and more room for errors, (i.e. they are hard to remove post synthesis and are not cost effective), however it does offer better control of the pore size and formation. Hence the top-down approach methods are widely used and it is cost-effective[27].

2.5.2 Top-down approach

The top-down approach involves desilication or dealumination. Desilication is a process of extracting the silica from a microporous zeolite framework without disrupting the framework of the zeolite whereas dealumination is the extraction of alumina from the framework. Both these are post-synthesis methods. Dealumination was first reported by Barrer in the 1960s in the extraction of alumina in clinoptilolite. The dealumination process is achieved via leaching or by steaming processes assisted by the hydrolysis of the -Si-O-Al- bonds. The combination of the two dealumination methods yields better results compared to either of them. Dealumination has been used mostly to dealuminate zeolite Y to form its ultra-stable form, which has a high SAR and used in catalytic cracking [27], [36]. Figure 2.6 below shows the effect desilication and delamination on the pristine zeolite, the much-improved transportation properties to and from an active acid site.

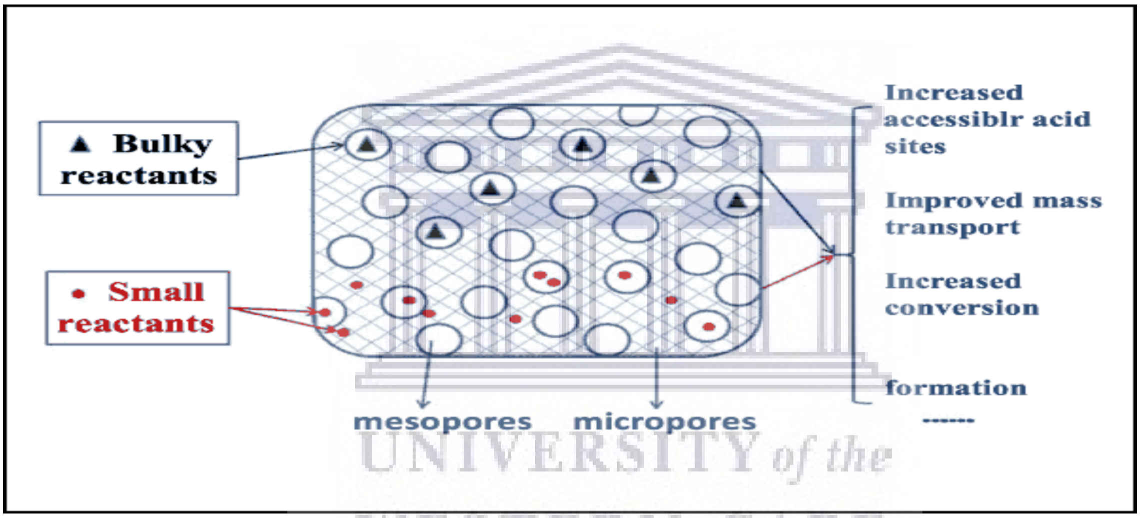


Figure 2.6: Depicts the effects of hierarchical zeolites on the zeolites itself.

A zeolites framework comprises silica, along with small amounts of alumina, therefore a significant dealumination will disrupt the zeolite framework. Dealumination of a zeolite can also alter the Si/Al ratio (SAR), strength and distribution of the acidy. A partial collapse of the zeolites framework can occur due to silanol nets formations. The silanol nets are formed due to extraction of Al from the zeolites framework. Dealumination offers no controlling over the size and shape of the mesopores [27].

Desilication was first reported in 2000 by Ogura, where the ZSM-5 was desilicated successfully without destroying the framework of the zeolite [37]. This was achieved via alkaline post-synthesis treatment. They also showed that desilication is influenced by SAR. The 25-50 SAR has been identified as the best range at which optimal hierarchical pores are introduced. Any SAR lower than 25 leads to Al blocking the extraction of Si, due to the Al zoning in the framework and the large crystal size. SAR higher than 50 extractions lead to an excess of Si extraction the formation of bigger pores, hence the damage of the zeolite framework. Figure 2.7 shows the effects of SAR in desilication of the ZSM-5 zeolite[27],[13], [36].

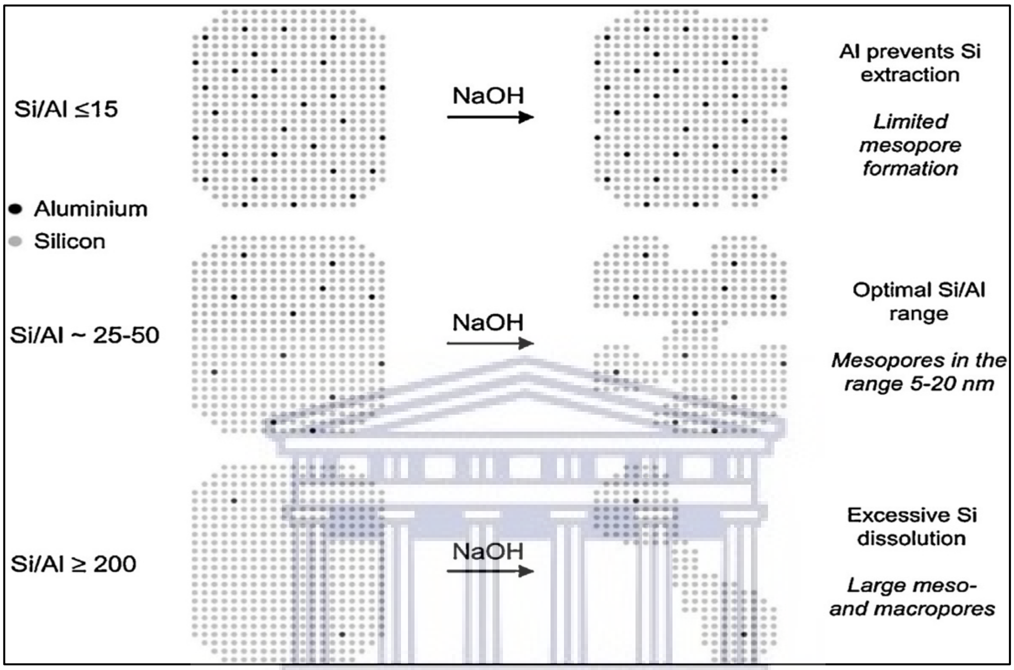


Figure 2.7: Illustration of the effects of SAR in the desilication of zeolites [27].

The desilication of the ZSM-5 zeolite is a post-synthesis method, which is a top-down approach for creating a hierarchical zeolite. The microporous zeolite is treated in an alkaline solution containing NaOH. The NaOH is sometimes coupled with pore directing agents such as surfactants TPA^+ and CTA^+. Pore directing agents may also be cation, anions, and non-ionic. The ZSM-5 is added to 0.2M of NaOH which is gently stirred for 30 minutes at 65 °C, then this mixture is cooled down and filtered. The filtered product is dried in an oven for 2 hours at 100°C. There are attempts to use an organic base instead of inorganic because the NaOH is too harsh on zeolites with a particular SAR, as it is sensitive towards the SAR. Organic bases such as TPAOH, TMAOH, and TBAOH have been used to desilicate various zeolites. Organic bases are not as selective to Si as NaOH and offer better control of the mesoporosity formation. The TPAOH can be used to desilicate zeolite with higher SAR and lesser stable framework zeolite, like zeolite beta. Figure 1.6 below shows desilication effects via an organic base and NaOH.

The organic base treatment requires about 5-8 hours at a higher temperature in comparison to the NaOH route. Recently, fluoride has also been used to desilicate zeolites. Fluoride was successfully used in desilicating the zeolite, as it has a strong mineralization (solidifying) effect so it can be used for zeolites with large crystals and few silanol defects [27].

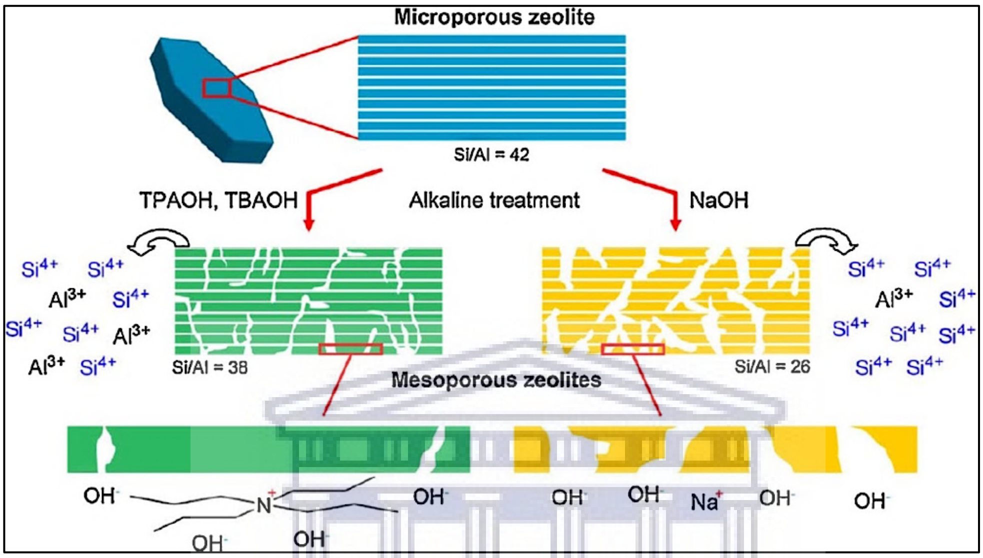


Figure 2.8: Illustration of the desilication of zeolite by TPAOH, TBAOH, and NaOH [1], [27]

The acidity of ZSM-5 is altered by desilication, in which the amount of protonic site is reduced and the acid sites are more accessible. According to literature in which the effect of desilication on the acidity of ZSM-5 was studied by pyridine adsorption and IR which were used to quantify the amount and type of acid sites on the ZSM-5 and desilicated ZSM-5[9], [13]. It was found that the concentration of Bronsted and Lewis acids are altered as well. Generally, the concentration of Bronsted acid sites decrease and the concentration of Lewis acid sites increase. Selectivity and catalytic activity is also affected by desilication. A study in which the effect of desilication on catalytic performance was investigated they found that desilicating a zeolite with a lower SAR< 25 tends to be selective towards cracking heavy hydrocarbons and formation of heavy aromatics. On the other hand, zeolites with a higher SAR > 25 favours the formation of gasoline range products and olefins [38]. Another reaction in which they showed that desilication improves the catalytic performances *i.e.* activity and selectivity is the Friedel-Crafts acylation of anisole and propionic anhydride to produce p-methoxy-propiophenone. [39]. When the mesopore ZSM-5 was compared to the micropore

ZSM-5, the mesopore ZSM-5 improved the selectivity towards the product by a factor of 1.7 higher than the unmodified ZSM-5and catalytic activity by 1.5 times compare to the unmodified ZSM-5 and the conversion was improved from 90% to 96% towards the desired products[8], [39].

2.6 Metal doping

After NH_4^+ ion exchange and calcination ZSM-5 is converted to the H-form. . The H atom in the ZSM-5 is used as a compensation ion and therefore easy to exchange with other cation such as metal ions [40]. Zeolites are sometimes used as support in which metal/transition metals are introduced using various methods. These metals are introduced in the ZSM-5 framework due to their promotional effects in various catalytic applications. The metals may alter the acidity of the ZSM-5 thereby affecting the activity, selectivity and stability of the ZSM-5 an hence overall performance of the catalyst [41]. Different metals have different effects, hence different metals are used for different reactions. In some cases, the same metal is used for different reactions but with different reaction conditions. It is well known that zeolite ZSM-5 has high thermal stability, selectivity, and catalytic activity with good acid properties [41], [42]. Following these observations, a lot of metals have been studied/ used to increase catalytic activity, selectivity, and stability.

Theses metals are introduced using various methods such as the incipient wetness impregnation method, ionic exchange, deposition precipitation and co-precipitation just to mention a few. The ion exchange method and impregnation methods are generally used to prepare industrial and commercial catalysts. This is due to the ease of synthesis as well as high metal dispersion which can be obtained without destruction of the zeolite crystal structure [43]–[45].

Acid catalysed reactions play an important part in the chemical/ petrochemical industry. Hence the acid catalysed reaction of hydrocarbons is a vital one. Reactions such as catalytic cracking, isomerization, dehydration, and oligomerization are all acid catalysed reactions. In this review the effect of metal promotion in the oligomerization of olefins is discussed in further detail. Several studies have shown that adding metal ions in the ZSM-5 improves the catalytic activity, enhances acidity, improves selectivity to diesel range hydrocarbons while other metals may boost the octane number of gasoline, and increased stability of the H-ZSM-5[37]. Nickel, Zinc, Chromium, and Cobalt were the metals used in this study to synthesise M/ZSM-5 (M = Ni, Zn, Cr, and Co)

2.6.1 Nickel (Ni) as a promoter

The biomass Catalytic Pyrolysis on Ni/ZSM-5, Effects of Nickel Pre-treatment and Loading, shows that the use of nickel supported by ZSM-5 improves catalytic activity and selectivity. This study was done by loading a different amount of nickel and compared it to the pristine ZSM-5 by comparing the selectivity, activity and deactivation times [40], [46]. Different loading percentages of the metals correlate with the silica-alumina ratio (SAR) of the ZSM-5 zeolite. ZSM-5 with higher SAR (SAR > 60) forms a Ni/ZSM-5 with strong acidity which increases the hydrophobicity of the catalyst leading to its fast deactivation. While a SAR < 20 hinder the formation of nickel particle and decreases the catalytic activity. The SAR between 25-30 was shown to be the optimum one [32], [40], [45]. The Ni/ZSM-5 is also used in hydrogen production by reforming phenol, catalytic cracking and together with Zn/ZSM-5 can be used to convert alkanes to aromatic hydrocarbon as well as olefins [41].

The oligomerization of ethene and 1-hexene over nickel modified ZSM-5 zeolite has been studied. The Ni/ZSM-5 has shown an improvement in the catalytic activity as well as selectivity in ethene oligomerization. Over 80% selectivity towards the C_{10+} products was obtained which is similar to the products obtained when 1-hexene is used as feed. The was possible because the textural properties of the pristine ZSM-5 were also modified to improve the diffusion properties [47]. In a separate study a bifunctional catalyst which included nickel impregnated on Al-MCM-41 for the oligomerization of ethylene was investigated. They showed that the Nickel incorporated into the catalyst improve catalytic activity, stability and selectivity towards C_{5+} products. It was suggested that these effects were the results of the presence of Ni^{2+} ions however further investigation need to be done to elucidate this hypothesis. It was noted that the formed species was more dependent on the amount and strength of the Bronsted acid on the nickel modified catalyst, which increases selectivity towards C_{5+} [46], [48].

2.6.2 Zinc (Zn) as a promoter

Zinc has been shown to have similar properties to the nickel when deposited on the zeolite framework. A small amount (0.5wt% <) of metal loading shows that the metal ions act as compensation as ions, while a loading (> 0.5wt%) has a better distribution on the zeolite framework. The Zn/ZSM-5 in which the loading was achieved by the wet impregnation method possesses both the ZnO/ZSM-5 and H-ZSM-5 species. And the transportation of the ZnO species from the surface of the zeolites to the channels helps increase the active Lewis-acids site [41], [49].

Zinc modified ZSM-5 is typically used as aromatization catalysts. A comparison study was conducted in which one ZSM-5 was alkaline treated and the other was not treated. Both were then doped with Zn. These catalysts were tested on the aromatization of n-hexene. The addition of Zn to the both alkaline treated and untreated ZSM-5 showed that the density of Bronsted acid sites decrease while the density of the Lewis acid sites increases. The treated alkaline ZSM-5 was shown to be more stable, with high activity and high selectivity when compared to the untreated one especially on 1-hexene aromatization[50]–[52]. A lot of studies have been conducted on the effects of Zn doped ZSM-5 on the aromatization of propane and shown that the catalytic performance is improved by this modification [53], [54].

The use of Zn as promoter in this study was based on the stated effects above and we wanted to investigate if zinc modified ZSM-5 can increase the selectivity towards aromatics in the 1-hexene oligomerization reactions. This may result in increases in the octane number. As metal doping of Zn is also similar to Ni in its effects on acidity, the effects on doping a desilicated ZSM-5 for oligomerization to diesel range products will be investigated.

2.6.3 Chromium (Cr) as a promoter

Chromium is normally supported in ZSM-5 for use in the oxidative dehydrogenation of ethane and propane as well as catalytic cracking[55], [56]. However, the study of 1-hexene and 1-octene oligomerization over a solid catalyst by conducted by Arno de klerk looks at the chromium doped Cr/ZSM-5 catalyst [7]. The study investigated the properties needed in a catalyst for high olefin oligomerization. Oligomerization is normally focused on C2-C5 olefins. One of the main reasons for this is the diffusion limitations in the catalysts. `De klerk looked at different catalysts with different physical and acid properties namely MCM-41, ZSM-5, zeolite-Y, zeolite-Omega, amorphous silica-alumina, solid phosphoric acid, sulphated zirconia, nickel and chromium doped ZSM-5 [7], [55], [56]. It was shown that the catalysts with pores size that are 10nm or larger performed better in terms of selectivity towards heavier oligomers, and has better activity as well longer catalyst life compare to the ones with smaller pore sizes[7]. This was because heavy oligomers were less readily trapped in the catalyst.

The Cr/ZSM-5 has CrO_2^+ which is co-ordinating in the cationic position of the zeolite catalysts and prevent cyclisation while promoting dehydrogenation [53]. Chromium may improve the selectivity of ZSM-5 if added in a ZSM-5 with larger pores. This was shown in literature, where they study the oligomerization of 1-hexene and Octene over a solid acid catalyst. The selectivity towards lubricating oil increased drastically over a chromium doped large pore H-MCM-41 catalyst. It is known that chromium has the ability to selectively catalyse olefin trimerization, as well as olefin oligomerization and polymerization. The high selectivity to lubricating oil may be due to a change in the oligomerization mechanism. The mechanism was likely to be coordination and alkene insertion by the metal which was different from the acid catalysed oligomerization of the other catalysts [7][55]. These observations motivated the study of Chromium promoting effects on a desilicated ZSM-5 which has larger pores compared to the pristine ZSM-5, in the oligomerization of 1-hexene.

2.6.4 Cobalt (Co) as promoter

The effects of cobalt as a promoter are well known for isomerization and hydrocracking. However, little is known about its effects on oligomerization. Cobalt supported on a bimodal ZSM-5 system has shown to have a good performance in the Fischer Tropsch Synthesis, when compared to cobalt supported on commercial ZSM-5 and Microporous ZSM-5. In this study where they looked at the performance of a Co/ZSM-5 in the Fischer-Tropsch Synthesis, it was shown that Co/ZSM-5 improves activity and selective towards C5-C20 while decreasing selectivity towards (CH4) [59],[61]. The mesopores on the bimodal ZSM-5 provided better mass transfer to and from acid sites as compare to the other catalysts, which in turn promoted hydrocracking of longer hydrocarbon chains, resulting in high activity and selectivity towards C_5-C_{20} hydrocarbons [57]. While the oligomerization of 1-butene over cobalt supported on carbon showed good selectivity towards linear 1-octene production about 80%. The product profile from this study also contain branched C12 products [58].

These observations were vital in choosing cobalt as a promoter for the study as one of the objective of the study is to produce a highly branched products, thus increasing the octane number of the gasoline fuel. .

The oligomerization of olefins in the C_2-C_5 is well studied and used in production of high octane gasoline and distillates products. However, the use and study of olefins in C_{5+} is limited due to several reasons. One of the reasons is due to the lack of a good catalyst that can be used. Oligomerization normally uses zeolites as a catalyst in the petrochemical industry, especially ZSM-5. The ZSM-5 is an effective catalyst, however due its diffusion limitation, is easily poisoned by bulky molecules. Thus it is less effective in the oligomerization longer chain olefins. The modification of the ZSM-5 via desilication which will induce mesopores in the microporous ZSM-5 may enhance the overall catalytic performance in the oligomerization of longer chain olefins. The additional metal may also lead to further promotion of oligomerization leading to an enhanced selectivity to diesel range products or other reactions such as isomerization and aromatization which may result in gasoline range products with improved octane numbers.

2.7. Oligomerization

The petrochemical industry uses multiple reactions to produce transportation fuel as well as various chemicals that are used in our daily life. One of the widely used reactions is catalytic cracking. Catalytic cracking is used to convert crude oil into various products. One of the by-products that are formed is lower (C_2-C_6) olefins. Fischer Tropsch Synthesis is also one of the processes that produce a lot of lower olefinic by-products. These products are upgraded to more valuable fuels in a process such as oligomerization. Thus the catalytic oligomerization process is an important one in the petrochemical industry as it converts lower olefins to middle distillates, as this assists in meeting the global demands for middle distillates [16],[47].

Oligomerization is a process in which few oligomers/monomers are used as reactants which join to form longer hydrocarbon chains normally with ($2 > n > 100$) where n is the number of monomers. While polymerization is defined as having $n > 100$ [59]. In the 1930s, the Universal Oil Products commercialised the oligomerization process in which propene/butene was converted to middle distillates over a phosphoric acid catalyst. They were the first to do so, however the disadvantage with the phosphoric acid catalyst is the short catalyst life and lack of flexibility. To overcome these challenges, zeolites were introduced into the oligomerization process and hence the development of the Mobil olefins to gasoline and distillates also known as the MOGD process [59]. The oligomerization process has since been studied in detail in terms of reaction conditions, catalyst type, product distribution and mechanism. A brief summary is given herein.

2.7.1 Oligomerization Commercial processes

Oligomerization has been in use commercially since the 1930s. However, it was used mainly for C_2-C_5 oligomerization, for the production of lubricant oil and high octane gasoline. The reason for this narrow focus was due to the fact that C_{5+} olefins can be upgraded by refining pathways such skeletal isomerization or be incorporated to the fuel directly [7], [8]. The catalytic polymerization UOP process was one of the first oligomerization processes to be commercialized. Mobil olefins to gasoline and distillates process(MOGD) was developed to help mitigate the demands of middle distillates and high octane gasoline. MOGD uses oligomerization, and can be used to oligomerize C_{5+} olefins. The Conversion of olefins to distillates (COD) was developed for upgrading the Fischer Tropsch Synthesis products (Olefins). These processes are used commercially for oligomerization of olefins in the range C_2-C_6, even heavier olefins can be oligomerized [7], [8]. A list of commercial technologies applying the oligomerization process for fuel production is listed in Table 2.2.

Table 2.2: list commercial processes that uses oligomerization of olefins, the catalyst and type of product.

Catalyst	**Technology**	**Type of Products**
Solid phosphorus acid (SPA)	CatPoly and InAlk	Gasoline, Jet fuel
Amorphous silica alumina	Polynaptha and Selectopol	Gasoline and Diesel
HZSM-22, HZSM-57	EMOGAS	Gasoline and Jet fuel
HZSM-5	MOGD and COD	Diesel
Homogenous nickel	Dimersol G	Gasoline
EMOGAS	ExxonMobil	Gasoline, jet fuel
Acid resin	NExOCTANE	Gasoline
Montmorillonite	Octol-A	Gasoline

The above mentioned processes are typically catalysed by solid acid catalysts. The catalytic polymerization UOP process uses a solid phosphoric acid (SPA) with an operating temperature range of 150 °C-245 °C, WSHV range of 0.1 hr^{-1} – 50 hr^{-1} and pressure range of 10 to 40 bars. Since oligomerization is an exothermic process, three variations of the UOP process were developed which differ in reaction conditions and in the way the heat is removed from the exothermic reaction [8]. The disadvantage of the solid phosphoric acid catalyst is that it has a shorter life span and that it cannot be regenerated. The life span was found to be around six months in the refineries. SPA catalyst cannot be used for oligomerization of C_{5+} olefins as its activity decreases considerably with an increase in olefin chain length. The possible reason for this deactivation lies in the intermediate product as the SPA does not form carbocation, rather phosphoric esters which limits the formation of bulky molecules and hence distillates products [8].

The processes such as COD and MOGD use zeolite base catalysts, namely the MFI type zeolites such as HZSM-5. A lot of zeolites have been studied for oligomerization, however the ZSM-5 has been found to be the most effective. The reaction conditions, silica alumina ratio (SAR), method used in preparing the catalyst and preheating the catalyst, are some of the factors affecting the product distribution in an oligomerization reaction that use ZSM-5 as a catalysts [8], [22]. Typical reaction conditions of these process are as follows: temperature 150 °C-300 °C, pressure 10 be-50 bar and a WHSV of 0.5 hr^{-1} – 50hr^{-1} .

2.7.2 Oligomerization mechanism

The oligomerization reaction mechanism occurs in several steps. First is the protonation of the olefin which leads to the formation of an alkylcarbenium ion, followed by addition of the second olefin to alkylcarbenium known as the propagation step. The last step is the deprotonation of the formed product. The rate constants of propagation and the rate constants of deprotonation determine if oligomers or polyolefins are formed. If the rate constants are similar an oligomer is formed while if the rate constants of propagation are higher than that of deprotonation a polyolefin is formed. This route of reaction is known as the carbocation chemistry/reaction. Figure 2.7 (below) shows a schematic representation of the reaction mechanism[47], [59], [60].

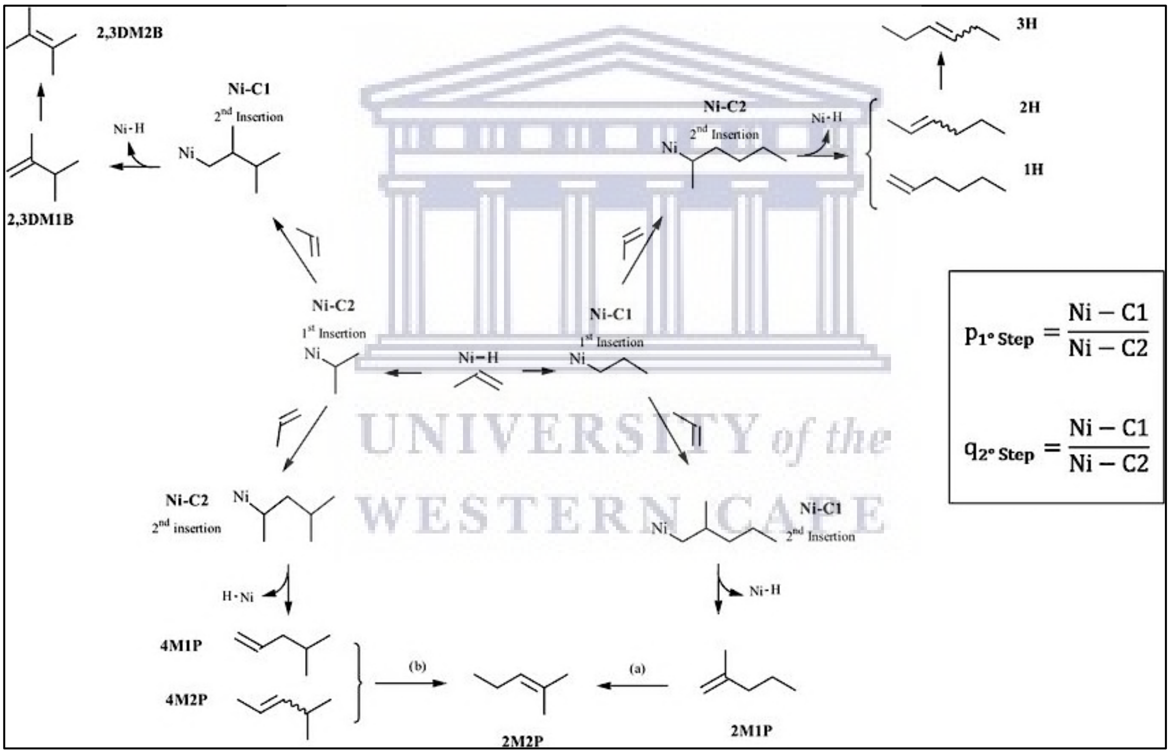


Figure 2.9: Depicts the oligomerization mechanism of propylene [61]

The catalyst ZSM-5, nickel supported zeolites, MCM-41, etc are typical catalysts that are used in oligomerization and offers better activity, selectivity and has a better life span compared to phosphoric acid catalysts. Oligomerization is used to produce a wide variety of chemicals. Oligomerization helps in producing environmentally friendly gasoline and distillates which contain high octane numbers. These fuels can be used to blend to fuels that contain sulphur as fuels produced via oligomerization contains little to no sulphur at all. A good example of this is the bio-jet fuel produced using biomass resources and the conversion of olefins to distillates (COD) process [7], [47], [60]. These characteristics make it an interesting topic for research.

2.7.3 Factors affecting Oligomerization

The oligomerization reaction is affected by both the type of catalyst as well as reaction conditions. The nature of the catalyst, i.e. nature of its porosity and acidity in terms of acid strength and acid site density has an effect on the product type as well as the product distribution. This observation is elucidated by the UOP process, which focus on the oligomerization of C_3-C_4 olefins due to the nature of the SPA catalysts. The SPA catalyst was tested in oligomerization of naphtha with an aim of producing distillates products. However, the interaction between the SPA and C_{5+} olefins was weak as well as hindered by C_3-C_4 olefins, this limited the formation of distillates products [8], [62].

Reaction conditions such as weight hourly space velocity (WHSV), temperature and pressure are the other factors that affect oligomerization. In case of the WHSV the resident time of the feed in the catalyst plays a crucial role. It has been shown that it's impossible to eliminate competing reactions in an oligomerization processes. Reactions like catalytic cracking and isomerization also occur during oligomerization and the greater the resident time the higher the influence from other reactions especial catalytic cracking[8], [16].

Temperature and pressure have a direct promotional relationship with the reaction rate of oligomerization. That is, an increase in temperature induces an increase in the reaction rate of oligomerization. However, this increase in temperature also increases the influence of side reactions, especial catalytic cracking. An increase in pressure sees an increase in molecular weight of products. These observations suggest that activity and selectivity in an oligomerization process are influenced by reaction conditions. This was shown in a study that investigated the effects of reaction condition on 1-butene oligomerization over a ZSM-5 catalyst [8], [16], [62]. It has been shown that to overcome these challenges such as secondary cracking reactions which affect diesel range product selectivity, typically moderate reaction conditions must be used, i.e. a temperature between 100 °C-250°C, pressure of 30 bar-50 bar and WHSV of $0.5\ hr^{-1} – 50hr^{-1}$ [8].

CHAPTER 3: EXPERIMENTAL METHODS

The characteristics and catalytic performances of the modified ZSM-5 materials depend on the synthesis method implemented. The synthesis method and characterization techniques that were used in the preparation and study of the physicochemical properties will be discussed in this chapter. Characterization techniques such as XRD, TEM, SEM, BET, and NH_3-TPD were used to determine the phase composition, morphology, porosity, and acidity respectively. The reactor system utilized for evaluation of the catalytic performances, the use of gas chromatography for the analysis of products obtained during catalytic testing, and determination of the activity and selectivity of the catalysts will be explained in depth.

3.1 Materials

The pristine ZSM-5 catalyst was synthesized using Sodium Aluminate ($NaAlO_2$), Sodium Hydroxide (NaOH,) and tetra propylammonium bromide (TPABr) which was used as a structural directing agent. Nickel nitrate ($Ni (NO_3)_2.6H_2O$), zinc nitrate ($Zn (NO_3)_2.6H_2O$), cobalt nitrate ($Co (NO_3)_2.6H_2O$), and chromium nitrate ($Cr (NO_3)_2.6H_2O$), were used to modify the desilicated ZSM-5. Ammonium nitrate ($NH_4(NO_3)$) was used to make up a solution for ion exchange of Na-ZSM-5. The NaOH was used to desilicate the pristine ZSM-5 to introduce mesopores into the zeolite structure. 97% 1-hexene was used as a feed in the evaluation of the catalyst. All reagents were obtained from Sigma Aldrich (St. Louis, Missouri, USA).

3.2 Synthesis of the ZSM-5 Zeolite

3.2.1 Synthesis of pristine ZSM-5

About 1.7 g NaOH and 0.87 g of Sodium aluminate were dissolved in 50ml of distilled water, The mixture was stirred to obtain a homogenous solution A. Then a solution B was prepared by dissolving 4.95 g TPABr in 50 ml of distilled water. Lastly, solution C was a mixture of 30 ml of ludox gel and 39 ml of distilled water. Solution A was added to solution C and the mixture was stirred for 1 hour using an overhead stirrer until it reaches homogeneity. Then Solution B was added to the mixture and stirred for a further 1 hour until homogeneity was reached. The resulting gel was transferred into a 1000 ml stainless-steel Parr™ autoclave and heated to 150 °C for 72 hours. The precipitated product was filtered from the mother liquor and washed with distilled water until all Br^- ions are removed (verified by the $AgNO_3$ test). Moreover, the solid was dried overnight in an oven at 100 °C. The structure-directing agent was removed by calcinating the dried solid product in a furnace for 5 hours at 550 °C, resulting in our product of interest, the pristine ZSM-5.

3.2.2 Desilication of pristine ZSM-5

The desilication was achieved by alkaline treatment of pristine ZSM-5. The samples of ZSM-5 were treated with an aqueous basic solution at 65 °C, to selectively extract silica from the zeolite framework. This process was performed for over 30 minutes. Exactly 5 g of the pristine ZSM-5 was weighed and placed in a 500 ml round bottom flask containing the solution (500 ml distilled water) of NaOH (4 g). After every 30 minutes had elapsed the mixture was left to settle then filtered. The solid samples were then washed thoroughly with distilled water, dried in an oven at 100 °C and calcined in a furnace at 550 °C for 5 hours to obtain the desilicated ZSM-5.

3.2.3 Metal modification of the desilicated ZSM-5

The metal modification was carried out using the incipient wetness impregnation method. Catalysts with metal loading of 1 *wt%* were prepared *i.e.,* 1%M/ZSM-5 where M = Cr, Co, Ni, and Zn. A total of 5 g of metal modified ZSM-5 was prepared, in which 4.95 g was the desilicated ZSM-5 and the 0.05 g was from the metal added. To prepare the metal modified ZSM-5, the following calculations were carried out. The metal Nickel was used as an example

The total mass of the catalyst = 5 g
1% of 5g is 0.05 g of the Nickel.
Zeolite = 4.95 g
Molar mass of nickel nitrate = 290.79 g/mol
Molar mass of nickel = 58.6934 g/mol
Mass of nickel nitrate to be weighed = (290.79 g/mol * 0.05g/ 58.6934 g/mol)
= 0.25 g

In one beaker a minimal amount of water was used to suspend the zeolite powder. In a separate beaker, the nickel nitrate salt was dissolved and added dropwise to the zeolite powder in solution. The mixture was stirred while heated to get rid of the excess water then dried in an oven for an hour at 100°C. The resulting product was calcinated for 5 hours at 550°C.

3.2.4 Metal (Bimetallic) modification of the desilicated ZSM-5

The bimetallic modification was carried out using the incipient wetness impregnation method. Three catalysts with the following metal loading 0.7Zn/ 0.3Co, 0.5Zn/0.5Co and, 0.3Zn/0.7Co wt% were prepared, with the both metals combining to 1%M/ZSM-5, M = Zn and Co. A total of 5 g of metal modified ZSM-5 was prepared, in which 4.95 g was the desilicated ZSM-5 and the 0.05 g was from the metals added. To prepare the metal modified ZSM-5, the following calculations were carried out. The catalyst 0.7%Zn-0.3%Co/ZSM-5 was used as an example

The total mass of the catalyst = 5 g
1% of 5g is 0.05g of the combine metals
(0.7) = 70% of 0.05g is 0.035 and (0.3) = 30 % of 0.05 is 0.015
Desilicate Zeolite = 4.95 g
Molar mass of zinc nitrate = 189.36 g/mol and Molar mass of cobalt(ii)nitrate = 291.03 g/mol
Molar mass of zinc = 65.38 g/mol and molar mass of cobalt = 58,93 g/mol
Mass of zinc nitrate to be weighed = (189,36 g/mol * 0.035g/ 65,38 g/mol)
= 0.10 g
Mass of cobalt nitrate to be weighed = (291,03g/mol * 0.015 g / 58,93 g/mol)
= 0.07 g

In one beaker a minimal amount of water was used to suspend the zeolite powder. In two separate beakers, one containing the zinc nitrate salt the other cobalt nitrate, the metal nitrate salts were dissolved and added drop-wise to the zeolite powder in solution. The zinc was added first until it was well mixed. There after the cobalt solution was added. In all the bimetallic catalyst preparations the zinc solution was added first, and then followed by the cobalt solution. The mixture was stirred while heated to get rid of the excess water, then dried in an oven for an hour at 100°C. The resulting product was calcined for 5 hours at 550 °C.

3.3 Characterization Techniques

3.3.1 NH3-Temperature programmed desorption (NH3-TPD)

The quantity and strength of the acid sites in the ZSM-5 and 1%M/ZSM-5 were determined using the NH_3-Temperature Program Desorption (TPD). The NH_3-TPD profile was obtained from an Autochem II Micromeritics Chemisorption Analyzer (Figure 2.1). Normally 0.1 g of the sample was added to quartz U tube reactor and quartz wool was used to support the sample. The sample is then heated up to 500 °C, this temperature is maintained for 20 minutes while flushing the sample with helium at a flow rate of 30 ml/minute, this activates the sample. Then the sample is cooled to 120 °C still under the flow of helium. NH_3 was adsorbed by the sample at 120°C for 0.5 hrs, this was achieved by switching the helium gas with 5% NH_3 balanced by helium and flown at 15 ml/minute. After the 0.5 hrs has passed helium was flown again to remove the physisorbed NH_3. The temperature was increased to 700 °C at a rate of 10 °C/minute while the helium was flown at a rate of 25ml/minute throughout. The signal was identified using a thermal conductivity detector (TCD) and recorded on a computer.

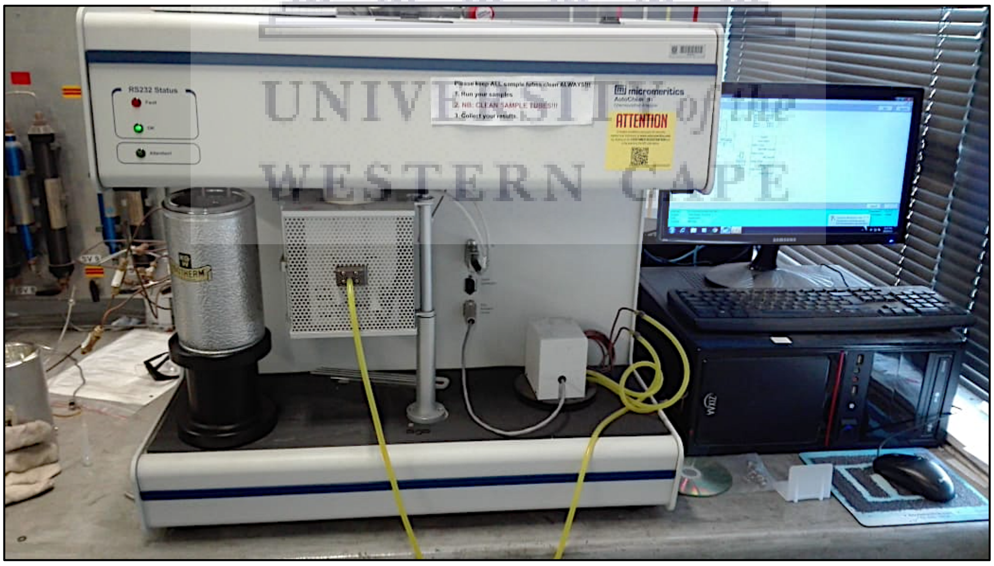


Figure 3.1: Imaging of the Autochem II Micrometrics chemisorption analyser

3.3.2 Brunauer-Emmett-Teller (BET)

The measurements of surface area, pore-volume, and porosity were attained using the BET multipoint method. The Micrometrics 3-Flex analyser was used to obtain the N_2 adsorption/desorption Isotherm at -196 °C. Before the N_2 physisorption, the catalysts were degassed at 90 °C for an hour, followed by another round at 400°C for 4 hours while flowing an inert gas to remove moisture

3.3.3 High-resolution scanning electron microscopy (HRSEM) and High-resolution transmission electron microscopy (HRTEM)

All the micrographs that were obtained from the HRSEM, were attain using High Resolution-SEM EHT 40 kV. The samples were carbon-coated before imaging. The HRSEM was equipped with energy-dispersive ray spectroscopy (EDS) spectrometer. The technicalG2-F20 S-Twin MAT high-resolution microscopy was used to obtain the TEM micrographs. The instrument is 200 kV FEG-TEM equipped with energy-dispersive ray spectroscopy. The samples were dissolved in ethanol, and the solution was added drop-wise to a copper grid before being analyzed in the TEM instrument.

3.3.4 Powder x-ray diffraction (PXRD)

The existent components in the catalyst were determined through phase analysis utilizing Powder x-ray diffraction. The PXRD patterns were obtained using the BRUKER AXS D8 advance in a range 0f 2θ, 5° -90° (Cu-Kα radiation $\lambda K\alpha 1 = 1.5406$ Angstrom) 40 kV. The crystallinity of the catalysts was calculated from the PXRD pattern.

3.4 Catalyst Evaluation

The catalysts were evaluated in the oligomerization of 1-hexene to higher hydrocarbons. Oligomerization is a well-established method of converting light olefins to middle distillates and high-octane gasoline. Oligomerization is used in the Mobil olefins to gasoline and distillates process also known as MOGD. PetroSA operates a technology i.e. the Conversion of olefins to distillates (COD) which is an oligomerization process that converts light olefins to gasoline and distillates at Mossel Bay in the Gas to Liquid refinery[47]. This forms part of upgrading olefinic products obtained from the Fischer-Tropsch process.

3.4.1 Reactor set up

The experiments were carried out using a microscale fixed bed reactor. The microreactor tube is 70 cm in length with a diameter of 1.57 cm and two inlets. One inlet is for the liquid feedstock and the other is for the nitrogen gas used to pressurize the system. Figure 3.2 and Figure 3.3 (below) illustrates the sketch of the fixed reactor tube used in the COD experiment and the microreactor used for oligomerization experiments, respectively. Table 3.1(below) presents the properties of the reactor tub

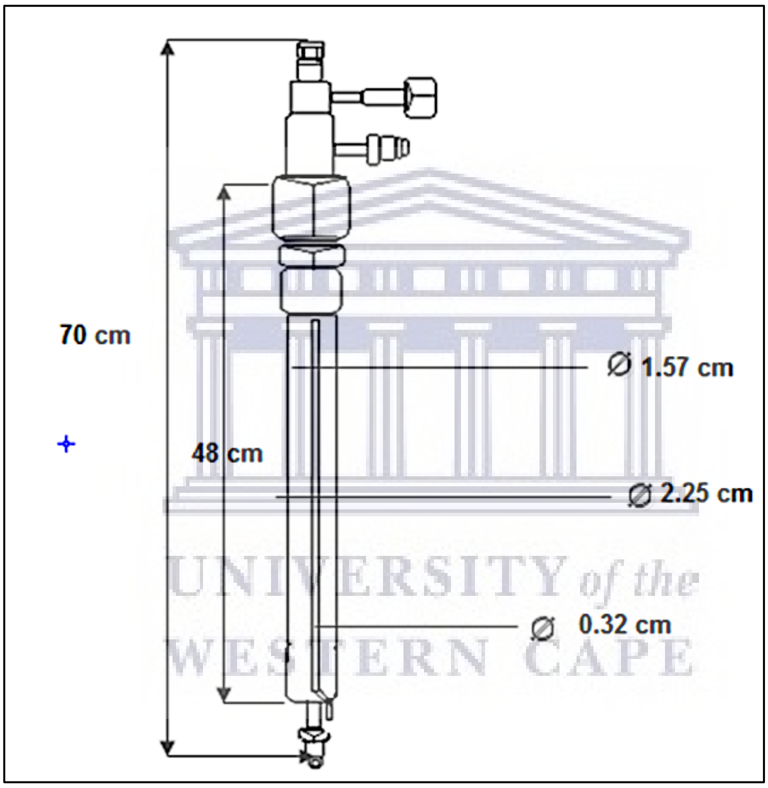


Figure 3.2: Depicts the sketch of the fixed reactor tube used in the COD experiments.

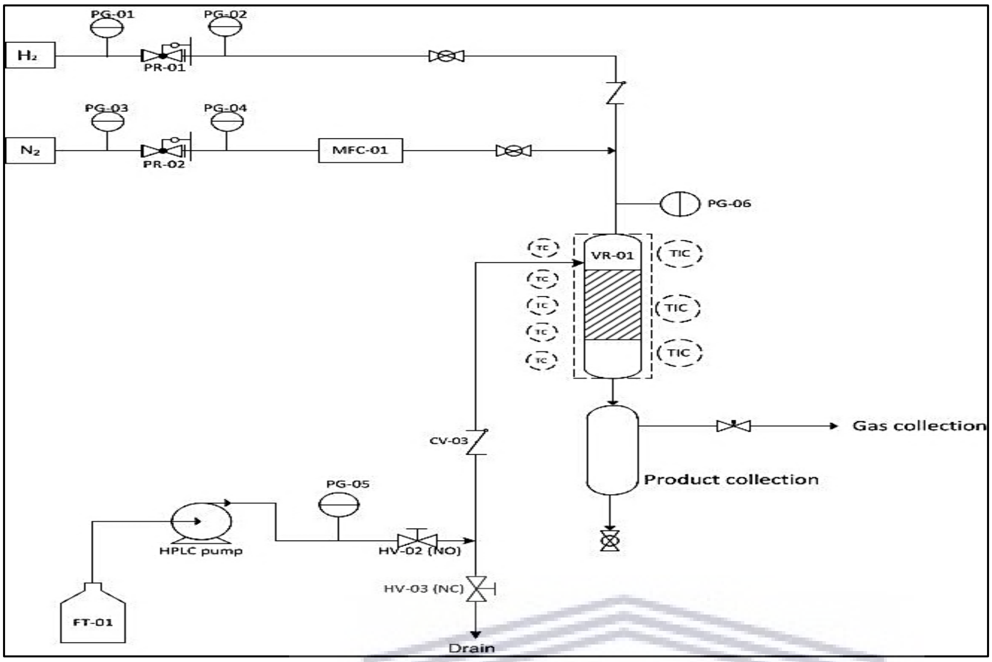


Figure 3.3: Imaging of the microreactor used for oligomerization experiments.

Table 3.1: Tabulation of the properties of the reactor tube

Pressure limit	100 bar
Reactor Length	70 cm
Reactor Body Length	48 cm
Reactor body dimension	OD:0.191 cm, ID: 0.157 cm
Reactor top dimension	OD:2.25 cm, ID:1.57 cm
Thermowell Dimension	OD:0.32 cm
The material used for construction	Stainless steel

3.4.2 Experimental procedure

The performance of the ZSM-5 and 1%M/ZSM-5 were evaluated in the conversion of 1-hexene to gasoline and distillates products. The reactor tube is loaded in such a way that the catalysts are placed in the middle of the reactor. The reactor volume is then filled using inert glass beads. The bottom beads offer support to the catalyst. The amount of the beads added was determined based on the dimensions of the reactor tube. To ensure that the beads do not fall out of the reactor tube about 3 cm of glass wool was added at the very bottom and top of the glass beads as well in the middle to separate glass beads and catalysts. The catalysts in the middle of the reactor are mixed with a small amount (about 3ml) of glass beads to ensure even heat distribution. A 1000 ml bottle was used as a feedstock reservoir.

The oxygen in the system was removed by flushing the system with nitrogen by three series of pressuring and depressurizing. The system was then pressurized at 40 bars with nitrogen gas and the temperature was set to 250°C. The weight hourly space velocity (WHSV) was calculated to be 1.33 h^{-1}. The feedstock was flown into the reactor using an HPLC pump. Before the experiment began the pump was primed and the reason for this was to fill up the line with the feedstock which eradicates dead time factor. The feedstock was delivered at a rate of 0.1 ml/minute. The feedstock was transported in a descending flow, the liquid product was collected every 2 hrs after the system had reached a steady-state which took about 6 hrs on average. Each reaction ran for approximately 72 hrs. Each sample was weighed on a mass balance, the reactor pressure and temperature recorded as well at the time. After the 72 hrs of running a single experiment, the reactor was cooled down and the pump switched off. The reactor tube was cleaned with acetone before every experiment performed

3.5 Product analysis by Gas Chromatography (GC)

3.5.1 Operation of the gas chromatography

The liquid hydrocarbon products were collected and analyzed using an offline gas chromatograph (GC), the Bruker 450 series GC. The GC was equipped with the flame ionization detector (FID). An autosampler was used to introduce the sample to the GC injection port. The GC has three injectors the front, middle a, and the rear one. The autosampler is set with a 1.0 µL syringe, while the GC comprises a tray sample that can carry 100 samples at a time. The samples are contained in 2ml vials. Before sampling, the injector is washed three times with the sample. Contamination through carryovers is eliminated in this manner, ensuring that the samples are analyzed effectively

3.5.2 Analysis method of the GC

The liquid products hydrocarbons were analysed using an offline gas chromatography (GC) The standard solution obtained from PetroSA Mossel Bay, pure 1-hexene from Sigma Aldrich were used to calibrate the GC. The calibration showed products in the range C_3-C_{17}.The detailed hydrocarbon analysis (DHA) software was used to analyze the data. The table below show the parameters of the offline GC that was used in the analysis of the liquid samples.

Table 3.2: Characteristics of the offline GC use for liquid hydrocarbon analysis

Instrument	**Bruker-450-GC**		
Column	Rtx ®-100-DHA - 100m X 0.25 mm ID X 0.5μm film: non-polar column with a maximum temperature of 340°C.		
Detector	FID		
Temperature	350 °C		
Gas	Helium		
GC injection program			
Injection temperature	250 °C		
Injection mode	Split 150:1		
Injection volume	1.0 μl		
GC pressure program			
Flow control mode	Constant flow 2ml/min		
Oven temperature program			
	Rate (°C/min)	Final temp (°C)	Hold time(min)
		0	15
	1	50	0
	2	130	0
	4	270	0

3.5.3 Calculation of conversion and selectivity.

The calculations for selectivity and conversion were carried out as shown below.

Conversion of 1-hexene was calculated using the formula below:

$$\%1 - \text{Hexene Conversion} = \frac{\text{Feed}_{\text{in}} - \text{Feed}_{\text{out}}}{\text{Feed}_{\text{in}}} \times 100$$

(1)

$Feed_{in}$ is 1-hexene and $Feed_{out}$, is the 1-hexene that is not converted to other products and this includes some isomers of 1-hexene. The selectivity was calculated by grouping the products into three groups. The first group comprises of C_3-C_5 hydrocarbons, the second group was composed of C_6-isomers, C_7-C_{10}, C_{12}-dimers hydrocarbons and the last group had hydrocarbon with C_{12+} and higher. The following C6 Isomers were considered reactants, t-2-hexene, c-2hexene, t-3-hexene and c-3-hexene i.e. positional isomers. However C6 isomers such as c-4methyl-2-2-pentene, t-4methyl-pentene, 2,3-dimethyl-1butene, 2-methyl-1petene, which underwent skeletal changes were considered products.

Equation 2 below illustrates how selectivity of a particular component C_i was calculated.

$$\%S = \frac{Mass\ \%\ of\ component\ Ci}{\sum Ci} \qquad (2)$$

where S is the mass percentage selectivity for component C_i

CHAPTER 4: RESULTS AND DISCUSSION

Introduction

Over the last thousand years, crude oil has been a major source of energy and continues to play a significant role in the energy sector, where it accounts for a majority of the world's energy consumption. However, crude oil is a non-renewable resource and many researchers have indicated that the world's crude oil reserves are plummeting. Additionally, the combustion of fossil fuel and crude oil extraction has led to the increase of greenhouse gasses hence global warming. In recent years, the need for environment-friendly fuels has increased. Processes like catalytic cracking, isomerization, and catalytic oligomerization have been used to produce environmentally friendly fuels. Catalytic oligomerization is a significant and widely used process in the petrochemical industry for producing environmentally friendly fuels by converting olefins in the C_2-C_6 range to gasoline and distillate range products.

The oligomerization reaction is an acid-catalyzed reaction and traditionally zeolites have been utilized as catalysts in this process. Zeolites are microporous materials with a three-dimensional structure, which offer good activity and selectivity when it comes to the oligomerization of olefins, specifically the ZSM-5 zeolite. As the demand for high octane gasoline and high-quality diesel continues to grow, research has focused on developing gasoline containing more branched isomers, as this increases the octane number while minimizing secondary processes as well as catering for the growing demand of diesel. The inherent microporous nature of ZSM-5 may limit diffusion and hinder the formation of highly branched products and limit selectivity to longer chain products. Introducing mesoporosity via desilication is seen as a possible solution to these problems, as well as the introduction of transition metals which may affect the acidity and alter branching of the products.

This chapter will discuss the characterization of the pristine ZSM-5, Desilicated and %M/ZSM-5 catalysts where M is Nickel, Zinc, Chromium and Cobalt and the effects of mesoporosity and metal modification on the catalytic performance in terms of activity, selectivity to fuels and catalyst stability is evaluated. The following characterizations techniques were used to determine the physicochemical properties of the materials i.e. NH3-

TPD, BET, PXRD, HRSEM-EDS, and HRTEM-EDS. The catalytic behaviors of the materials were evaluated in the oligomerization of 1-hexene using a fixed bed reactor.

4.1. Results and Discussion

4.1.1 Characterization of the Pristine and Desilicated ZSM-5.

4.1.1.1 XRD-analysis

Powder- X-ray diffraction was used to determine the phase purity and relative crystallinity of the materials. The XRD patterns of the pristine and desilicated ZSM-5 samples are displayed in Figure 4.1.

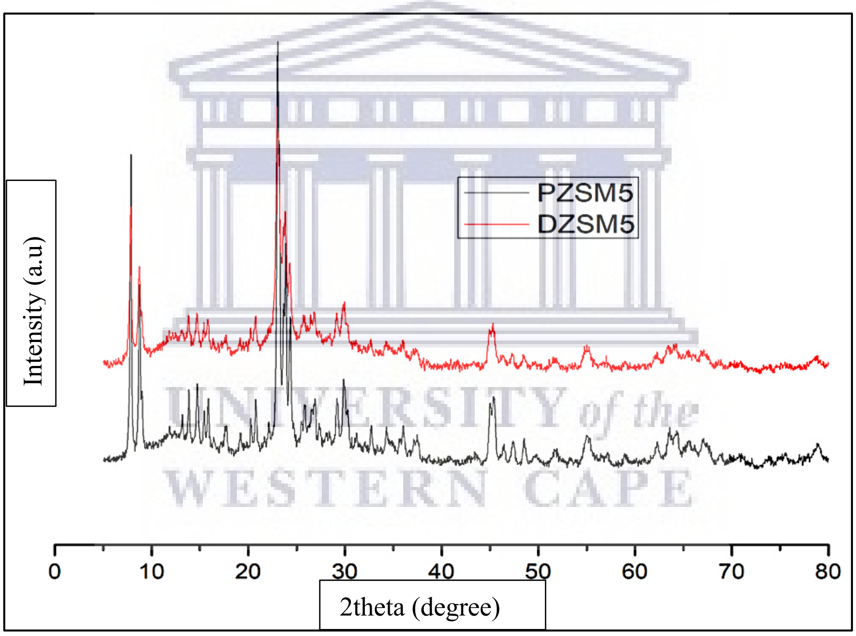


Figure 4.1: XRD pattern showing the successful synthesis of the pristine and desilicated ZSM-5

XRD patterns were recorded using BRUKER AXS D8 advance in a range 0f 2θ, 5° -90° (Cu-Kα radiation λKα1 = 1.5406 Angstrom) 40 kV. The intense peaks observed in the 2θ range 8-10° and 22-25° are indicative of the typical MFI zeolite ZSM-5 structure. [63]. The presence of sharp intense peaks following the desilication, is an indication that the framework of the zeolite remains unaffected, although the intensity of the peak's decrease slightly. The diffraction peaks for Pristine catalyst are sharp and intense, illustrating the high relative crystallinity of the zeolite. While, the diffraction peaks of the desilicated show a decrease in intensity. This is a result of the removal of Si species which is typically accompanied by a change in crystallinity[27], [37]. The crystallinity of the pristine ZSM-5 was taken to be 100% and that of the of the desilicated ZSM-5 was calculated to be 90% of the pristine ZSM-5 *i.e.,*10% of crystallinity was lost in the desilication process. Hence the ZSM-5 structure can be said to be preserved after desilication.

4.1.1.2 B.E. T and NH_3-TPD analysis

The surface, textural and acidity properties were obtained by the using BET and the NH_3-TPD techniques respectively. Table 4.1 shows the surface areas, pore volumes and amount of acidity of the pristine and desilicated ZSM-5 samples.

Table 4.1 Tabulates the B.E.T and NH3-TPD

Catalyst	**S_{BET} (m^2/g)**	**M, Area (m^2/g)**	**E, S_{area} (m^2/g)**	**M, V (cm^3/g)**	**P, V (cm^3/g)**	**T_{min} (°C)**	**T_{max} (°C)**	**Q_{min} (µmol /g)**	**Q_{max} (µmol /g)**
Pristine ZSM-5	328	240	88	0.111	0.069	188	388	276	125
Desilicated ZSM-5	425	274	151	0.115	0.160	196	394	537	48

S_{BET} = BET surface area
M, Area = Micropore Area
E, S_{area} = External Surface Area
M, V = MicroVolume
P, V = PoreVolume
T_{min} = Minimum Temperature (NH_3-TPD)
T_{max} = Maximum Temperature (NH_3-TPD)
Q_{min} = Acid site quantity minimum temperature (NH_3-TPD)
Q_{max} = Acid site quantity maximum temperature (NH_3-TPD)

The table displays a change in the BET surface area (328 m^2/g to 425 m^2/g) and pore volume (0.069 cm^3/g to 0.160 cm^3/g) upon desilication under the given desilication conditions and similar trends have been reported in previous literature[27], [34]. Micropores are the main contributors to the total surface area of the pristine and the desilicated catalysts. Mesopore area increases from 88 m^2/g in the pristine ZSM-5 to 151 m^2/g in the desilicated sample and pore volume from 0.069 cm^3/g to 0.160 cm^3/g respectively. This is an indicator of mesopore development in the ZSM-5 sample.

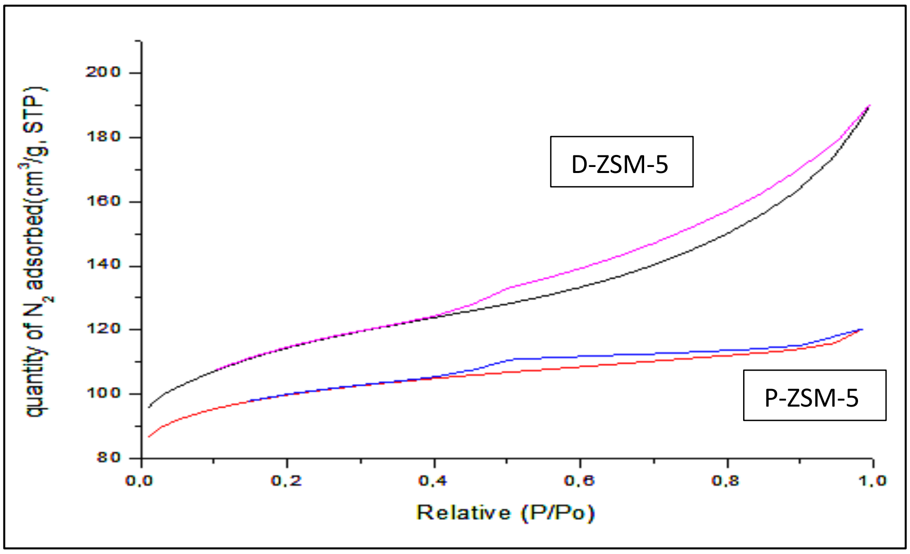


Figure 4.2: N_2 adsorption/desorption isotherms of the pristine and desilicated ZSM-5

The N_2-adsorption-desorption isotherms of the pristine and desilicated ZSM-5 samples are shown in Figure 4.2 above. The N_2 adsorption-desorption isotherm exhibits a type I isotherm implying a uniform distribution of micropores for the pristine ZSM-5. This is typical of a microporous ZSM-5 zeolite[39].On the other hand, the desilicated ZSM-5 shows a type IV isotherm with a hysteresis loop. These are well-known characteristics of a bimodal pore system There is high N2 up take at higher relative pressures ($0.4 < P/P_0 < 1.0$) which is indicative of the presence of mesopores[39], [64].

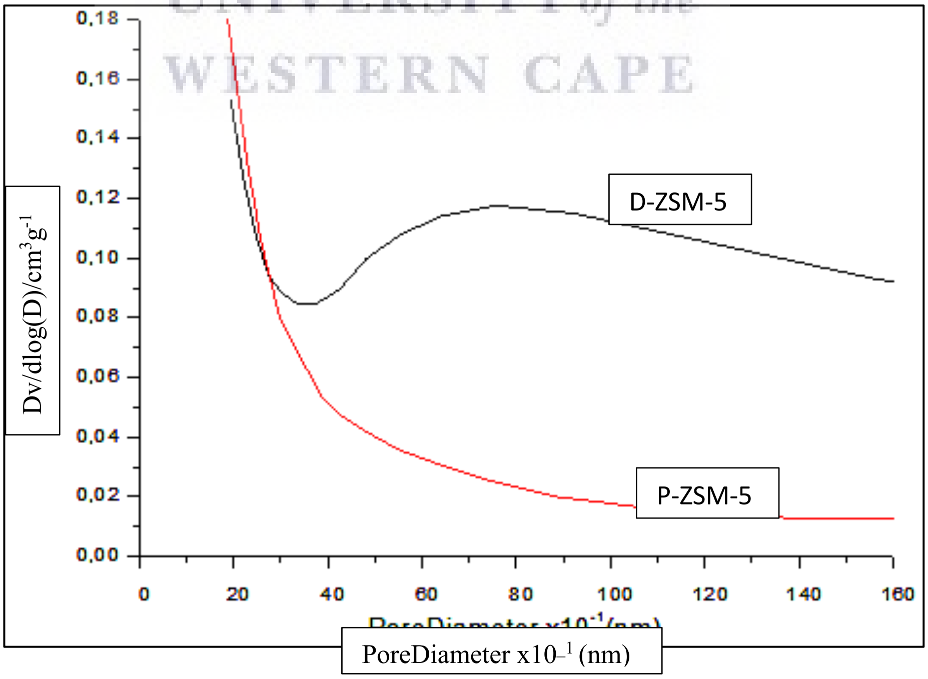


Figure 4.3: Displays the BJH pore distribution derived from the adsorption isotherms of the pristine (P-ZSM-5) and desilicated ZSM-5 (D-ZSM-5)

Figure 4.3 above shows the Barrett-Joyner-Helenda (BJH) graph which depicts the pore size distribution of both the pristine and desilicated ZSM-5. The pore distribution of the pristine ZSM-5 is represented by the decaying curve. It is evident that the pristine ZSM-5 has no mesopores present. The zeolite pore system was affected by desilication as a broad peak is noticed on the desilicated ZSM-5 curve. The desilicated ZSM-5 indicates a wide distribution of pores between 4 and 16 nm, with a maximum at 5-9nm, resulting from the newly created mesopores[65][39].

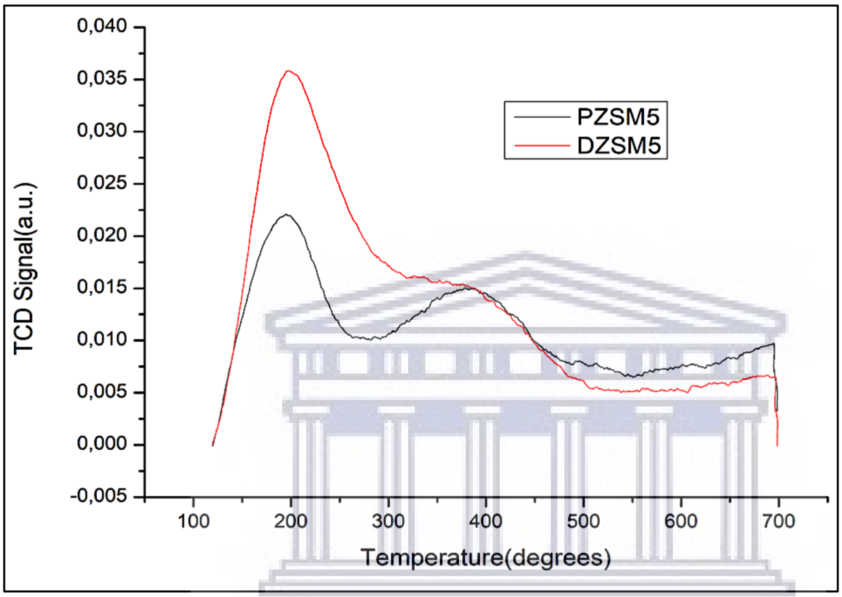


Figure 4.4: NH_3-TPD profile of the pristine and desilicated ZSM-5

Figure 4.4 above displays NH_3-TPD profiles. The pristine ZSM-5 has two distinct NH_3 desorption peaks at approximately 187 °C (low temperature) and 395°C (high temperature). These two peaks are normally associated with weak and strong acid sites respectively. The peak at lower temperature is generally attributed to weak Lewis acid sites, while peak at a higher temperature is associated with strong Bronsted acid site [1], [19], [27]. The area under these peaks is the quantity of the acid sites represented in µmol/g.

The desilicated ZSM-5 also has two peaks. A broad peak at lower temperature approximately at 200 °C is observed and a small flattened peak at higher temperature, approximately 400 °C. The amount of the weak acid sites increases from 276 µmol /g on the pristine ZSM-5 to 537 µmol /g on the desilicated ZSM-5. It is also noticed that the amount of strong acid sites decreases from 125 mmol/g on the pristine to 48 µmol /g on the desilicated. This observation is expected since the acidity of a zeolite is dependent on the aluminum content available[66]. Desilication is a process in which silica is selectively extracted from the zeolite framework structure. The desilication process has altered the SAR from 46 in pristine ZSM-5 to 23 SAR in Desilicated-ZSM-5. As the results have shown the acidity of the desilicated ZSM-5 is altered compared to the pristine ZSM-5. The amount of the strong acid site decreases after desilication which may be due to the removal of the Si species from the zeolite framework which induces lattice defects and may result in a removal of aluminum as well. Hence there is a reduction of the strong acid sites and an increase in weaker sites as possible weaker Bronsted and Lewis acid sites are created. The weaker sites may be attributed to the Si-OH on the external surface and extra framework aluminum[67], [68].

4.1.1.3 SEM and TEM analysis

The morphology of the pristine and the desilicated ZSM-5 were studied using the scanning and transmitting electron microscopy. There is an apparent difference in the SEM micrographs while the TEM micrographs also shows there are differences in the morphology of the two catalysts.

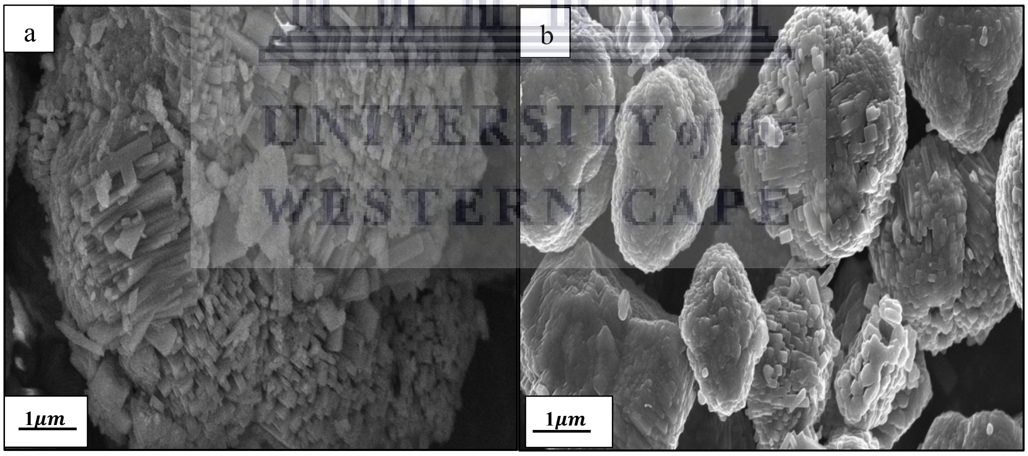


Figure 4.5: SEM micrographs (a) Pristine ZSM-5, (b) Desilicated ZSM-5

The SEM micrographs are shown in Figure 4.5 (a) for the pristine (b) desilicated ZSM-5 zeolite. It is evident that there are small particles of few nanometers in size that have agglomerated to form spheroids which range from 5 μm to 12 μm. It is clear from the micrograph of the desilicated sample that after desilication the surfaces of the spheroids appear rougher. This also correlates with the increase in external surface area observed from BET analysis.

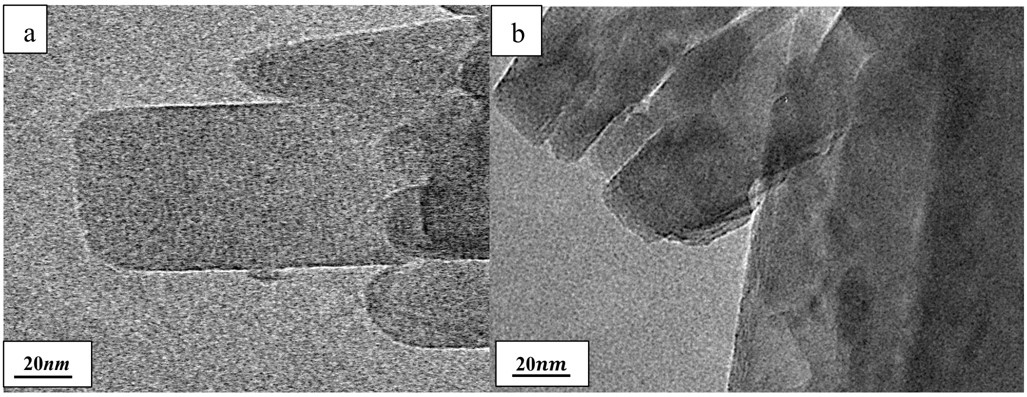


Figure 4.6: TEM micrographs (a) Pristine ZSM-5, (b) Desilicated ZSM-5

The TEM micrographs of the pristine and the desilicated ZSM-5 are shown in Figure 4.6. It can be observed that the pristine ZSM-5 (fig 4.6a) it has smooth surface as well as uniformly distributed micropores with pore dimension of no more than 2 nm. The desilicated ZSM-5 TEM images shows pores that in the range of 2 nm to 12 nm. The pores are not uniformly distributed.

The observations in TEM micrographs correlate with the findings from BET analysis displayed in Table 4.1 as well as the BJH pore distribution plot results in Fig 4.4. Similar results have been reported in the literature [27], [69].

4.1.2 Pristine and desilicated ZSM-5 Catalyst Evaluation

The pristine and Desilicated were both evaluated in the oligomerization of 1-hexene at identical reaction conditions. They were evaluated over a 72 hrs period at 220 °C, with Weight Hourly Space Velocity (WHSV) of 1.5 h^{-1} and a pressure of 40 bars. An optimally functioning catalyst is characterised based on its selectivity, stability, and catalytic activity. Figure 4.7 below shows the conversion of 1-hexene over both the pristine and the desilicated ZMS-5 in an oligomerization process. The results show that the desilicated ZSM-5 with improved textural properties and acidity has better catalytic activity and selectivity towards dimers of 1-hexene and is more catalytically stable compared to the pristine ZSM-5.

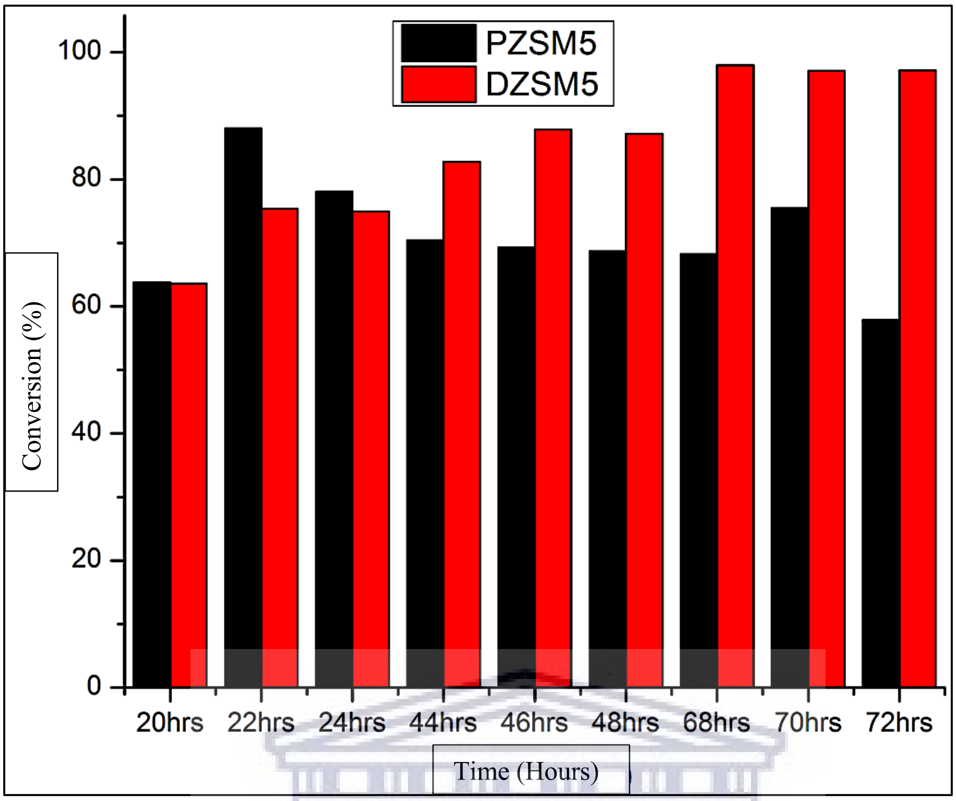


Figure 4.7: Conversion of 1-hexene over pristine and desilicated ZSM-5 in an oligomerization process

The conversion of 1-hexene in the first 20 hrs is I approximately 63 % for both catalysts. Since this is an exothermic reaction, when the 1-hexene makes contact with the fresh catalyst the temperature may increase resulting in higher conversion until steady state is reached. This reaction is temperature dependent. The two catalyst take different times to reach steady state. The pristine ZSM-5 reached its highest conversion in the 22nd hrs of approximately 88% after which it decreased. It took about 44 hrs to reach a steady state after which the conversion remained stable until the 70th hrs. It then decreased from 75% to below 60%. The decrease in 1-hexene conversion may indicate that the catalyst begins to deactivate.

The desilicated ZSM-5 conversion of 1-hexene increases gradually from the initial time on stream and reaches a steady state reached after 68 hrs with the conversion staying around the 97% mark. The desilicated ZSM-5 seems that it may remain active and stable beyond the 72 hrs as the conversion of 1-hexene remain stable at 72 hrs compared to the pristine which started decreasing at the 70th hour mark. The desilicated ZSM-5 is clearly shown to have a significantly higher activity compared to the pristine ZSM-5. The difference in the activity may be due to the improved diffusion and the easy accessibility of active sites on the desilicate ZSM-5.

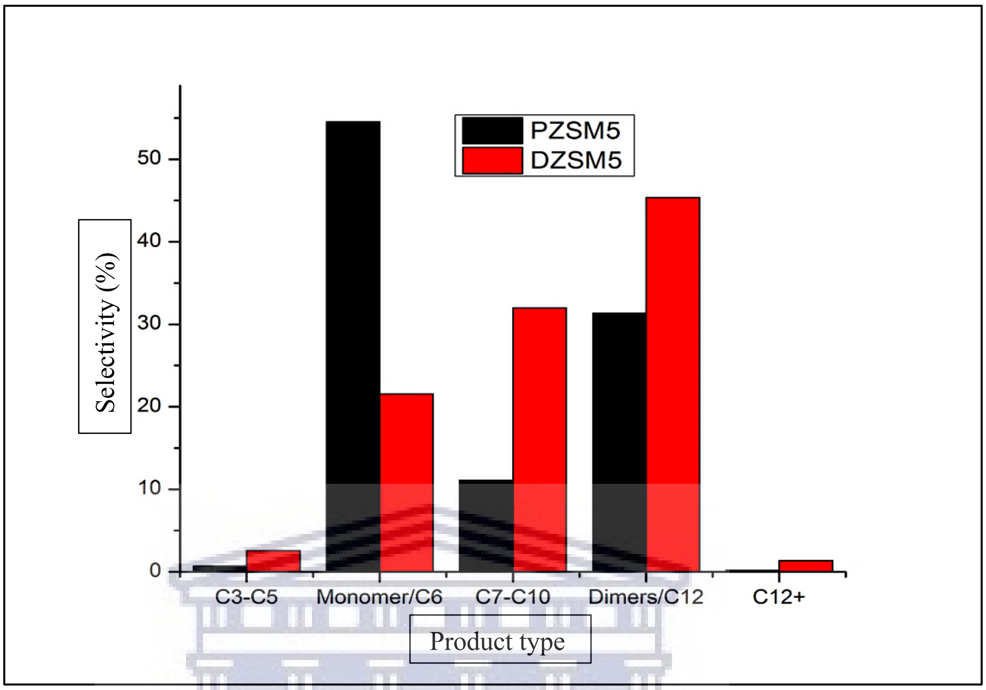


Figure 4.8: Bar graph representation of the product selectivity at the 48th hour in a 1-hexene over pristine and desilicated ZSM-5.

The product profile for both the pristine ZSM-5 and the desilicated ZSM-5 is shown in Figure 4.8 above. The products range from C_3 product to C_{12+} which is telling of different types of reactions taking place such as isomerization, cracking and oligomerization. The pristine ZSM-5 has approximately 55 % percent of C_6 products, roughly 30% of dimers (C_{12}), 10 % of C_7 to C_{10} products and at most 5 % of C_3 to C_5 products. Isomerization seems to be the dominating reaction for the pristine ZSM-5. The desilicated ZSM-5 on the other hand has a greater selectively towards dimers as compared to the pristine ZSM-5 which accounts for 45% percent, the C_6 products are about 20 % and 30 % of the C_7-C_{10} products and the 5 % comprises of C_3-C_5 products and a small amount of C_{12+} products. The main reaction in the desilicated ZSM-5 is oligomerization under these conditions. Furthermore, a high selectivity to diesel range (C_{10+}) products is obtained *i.e.,* greater than 50 %. This selectivity of the desilicated catalyst is enhanced as compared to the typical 60:40 gasoline: diesel ratio observed under industrial oligomerization processes conditions.

The difference in the product profile and product selectivity may be attributed to the different pore system however the effects of acidity cannot be excluded. The microporous system of the pristine ZSM-5 may limit the accessibility of reactant molecules to the active acid sites as well as hinder the formation of longer chain and branched hydrocarbons. In contrast, the desilicated ZSM-5 is a bimodal system with higher diffusion and accessibility of the acid site. This may increase activity and allow for branched and longer chained hydrocarbon molecules to diffuse out without undergoing secondary cracking reactions.

The differences in the product profile as well as the conversion of 1-hexene over the pristine and desilicated ZSM-5 elucidate the importance of enhanced textural properties such as porosity and the importance of the acidity. The NH_3-TPD and BET results have proven that the amount of weak Lewis and strong Bronsted Acid sites varies between the pristine ZSM-5 and the desilicated ZSM-5. The BET surface area changes as well as the pore dimensions. The desilicated ZSM-5 offer more diffusion of reactants and products to and from the active acid site compare to the pristine ZSM-5. With an increase in the accessibility to the acid site, so there is an increase in the catalyst activity of the catalyst. This may lead to more dimerization of 1-hexene hence the formation of heavier diesel range products. Due to the larger pores present on the desilicated ZSM-5 it is possible that the larger hydrocarbon molecules diffuse out of the zeolite without undergoing secondary reactions such as cracking. Hence an increase in selectivity to towards longer chain hydrocarbons is observed[47], [60], [68].

4.2 Monometallic doped ZSM-5

4.2.1 Characterization of monometallic ZSM-5

One percent of nickel, cobalt, chromium and zinc were added to the desilicated ZSM-5 using the incipient wetness impregnation method described in Chapter 2 (experimental). The catalysts are characterized using XRD, NH_3-TPD, SEM, TEM, and BET to study its physicochemical properties. These four catalysts were evaluated in the oligomerization of 1-hexene, using the previously established reaction conditions used in section 3.1.

4.2.1.1 X-ray diffraction (XRD) pattern analysis

A phase analysis of the metal doped desilicated ZSM-5 catalysts was determined by XRD. From Figure 4.9 (below) it is visible that after impregnation of the metals onto ZSM-5 the crystallinity of the desilicated ZSM-5 is not affected as sharp intense peaks are observed.

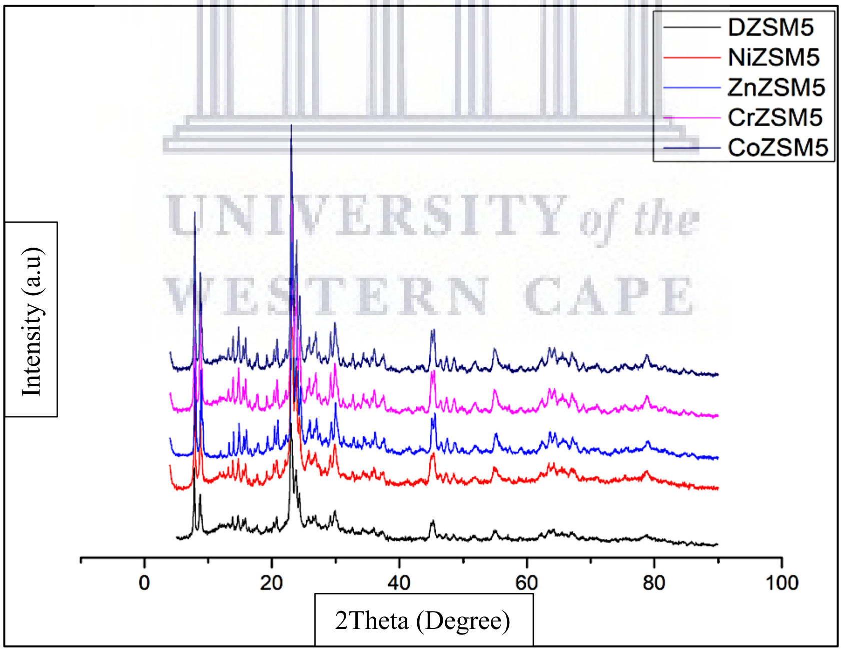


Figure 4.9: Display of the XRD-patterns for the monometallic catalysts with Desilicated ZSM-5

XRD patterns were recorded using BRUKER AXS D8 advance in a range 0f 2θ, 5° -90° (Cu-Kα radiation λKα1 = 1.5406 Angstrom) 40 kV. The monometallic doped ZSM-5 catalysts exhibit the typical MFI peaks at approximately 8° and 23° theta. The metals are introduced using the incipient wetness impregnation method. They are introduced in the salt form (*i.e.* nickel nitrate, zinc nitrate, cobalt nitrate and chromium nitrate). Hence the oxide form of the metal in deposited on the surface and internal space of the desilicated ZSM-5 after calcination [44], [46]. The presence of the metal oxide (Ni(O), Cr(O), Zn(O), and Co(O)) could not be observed by XRD analysis. This may be due to the small content added on the ZSM-5 which may result in crystals that are well dispersed and too small to be observed by XRD [70]. However, the peaks intensities corresponding to ZSM-5 seem to have increased after metal doping

This confirms that the introduction of the metals did not damage the crystalline structure of the desilicated ZSM-5. The crystallinity of all the catalysts was calculated using the intensity of the peaks in the range 5°-10° 2 theta and 20° - 27° 2theta. The chromium doped ZSM-5 has the most intense peaks of all the catalysts. The desilicated ZSM-5 was used as a reference and the crystallinity taken as 100 %. The relative crystallinities of the metal-doped ZSM-5 show that the chromium has a crystallinity of 112 %, 1 % Zn-ZSM-5 has a crystallinity of 110 %. The 1 % Ni-ZSM-5 and 1 % Co-ZSM-5 have a similar crystallinity of 96 % compared to that of the desilicated ZSM-5. The increased crystallinity after doping with Cr and Zn may suggest that the metals may be introduced into the framework structure of the zeolite[63][57].

4.2.1.2 B.E. T and NH3-TPD Results analysis

Table 4.2 depicts the textural and acid site densities of the four mono-metal-doped and desilicated ZSM-5. After metal doping, a decrease in the BET surface areas for all monometallic ZSM-5 samples is observed.

Table 4.2: Tabulation of the B.E.T and NH3-TPD Results

Catalysts	**S_{BET} *(m^2/g)***	**M, Area *(m^2/g)***	**E, S_{area} (m^2/g)**	**M, V *(cm^3/g)***	**P, V *(cm^3/g)***	**T_{min} *(^oC)***	**T_{max} *(℃)***	**Q_{min} *(µmol/g)***	**Q_{max} *(µmol/g)***
1%Co-ZSM-5	317	197	120	0.092	0.222	215	532	1598	247
1%Zn-ZSM-5	353	215	138	0.099	0.250	192	388	450	0
1%Ni-	280	170	110	0.079	0.355	197	362	875	1.8

ZSM-5									
1%Cr-ZSM-5	355	203	150	0.095	0.239	191	362	309	23
Desilicated-ZSM-5	425	274	151	0.160	0.115	196	394	537	48

S_{BET} = BET surface area
M, Area = Micropore Area
E, S_{area} = External Surface Area
M, V = Micro-Volume
P, V = Pore-Volume
T_{min} = Minimum Temperature (NH_3-TPD)
T_{max} = Maximum Temperature (NH_3-TPD)
Q_{min} = Acid site quantity minimum temperature (NH_3-TPD)
Q_{max} = Acid site quantity maximum temperature (NH_3-TPD)

Table 4.2 summarizes the textural properties and acidity of the monometallic ZSM-5 catalysts. The BET surface decreases from 425 m^2/g on the desilicated ZSM-5 to an average of 326 m^2/g on the monometallic ZSM-5. The pore volume decreases from 0.160 cm^3/g (desilicated ZSM-5) to an average of 0.091 cm^3/g on the monometallic ZMS-5. The external surface and micropore area for nickel and cobalt doped ZSM-5 decreases, suggesting the possibility of the metal particles being present in both the micropores and mesopores. However, for the zinc and chromium the decrease is minimal on the external surface, while there is a decrease in the micropore surface area. The zinc and chromium doped ZSM-5 have the biggest decrease in strong acid sites, suggesting that the particles maybe present in the micropores and interact with the strong Bronsted acid sites [67].

The acidity of the metal-doped desilicated ZSM-5 was studied by NH_3-TPD. Table 4.2 presents the amount of acidity and Figure 4.10 displays the acid strength distribution of the monometallic zeolites. Typically, there are two NH_3 desorption peak ranges for the ZSM-5 zeolite. They occur at approximately 200 °C (low temperature) and at approximately 400°C to 500°C (high temperature) and correspond to the presence of weak and strong acid sites respectively. [57][40], [71].

Desilication is a process in which silica is selectively removed from the zeolite framework structure. However, this may also cause the removal of Al atoms from the framework resulting in extra-framework Al^{3+} species which form weak Lewis acid sites. The introduction of metal further increases the amount of weak acid sites for Ni and Co doping. Similar results have been reported in the literature [72].The reason for this effect can be attributed to the metal oxide species (*i.e.* NiO) that are now present in the desilicated ZSM-5. Previous studies have shown that impregnation with 1 *wt%* Ni, apart from the formation of

Ni^{2+} compensation cations, at loadings above 0.4 *wt%* small NiO particles exist as well as NiO oligomeric species. These species may be responsible for the increase in weak acid sites. Furthermore, the presence of these particles may also explain why the Ni-ZSM-5 has the lowest BET surface area i.e. that both Ni^{2+} ions and small NiO particles may be present in an outside the micropore channels[27].

The Chromium and Zinc doped ZSM-5 show a decrease in both strong and weak acid sites. It suggested that the species $[Zn(OH)]^+$ which is the reactive species instead of ZnO , is located in the Bronsted site which could explain the decrease in strong acid site. However the ZnO species may be present on the surface of ZSM-5, and when activated to the $[Zn(OH)]^+$ they are transported from the surface to the channels of ZSM-5. The activation is done by hydrogen treatment or self-activation during a catalytic reaction. The observed decrease in micropore area and unchanging external surfaces of both the zinc and chromium may be due to the ions transported from the surface to the channels of ZSM-5 where they interact with framework aluminium resulting in decreased strong acidity [41]. [41]. The species Cr^{3+} is the species that is hypothesized to be present in a form of Cr_2O_3 [41], [73].

The exception is the cobalt catalyst which has a higher quantity of strong acid site compared to the other metal doped desilicated ZSM-5. The peak at the lower temperature occurs at approximately 250 °C and the peak at higher temperature at approximately 550 °C. Cobalt contains 1598 µmol/g and 247 µmol/g amount of weak and strong acid sites respectively. This may be due to the presence of Co^{2+} species which may act as strong Lewis acids.

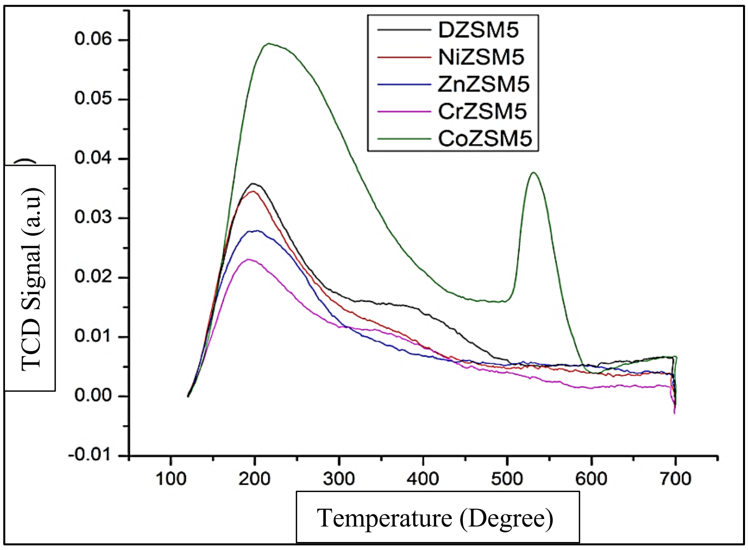


Figure 4.10: NH3-TPD profile of the monometallic ZSM-5 catalysts

4.2.1.3 SEM and TEM analysis

The morphology of the mono-metal-doped ZSM-5 was obtained by using scanning and transmitting electron microscopy. There is no apparent difference observed in the morphology of the ZSM-5 crystals before and after metal doping from the SEM micrographs.

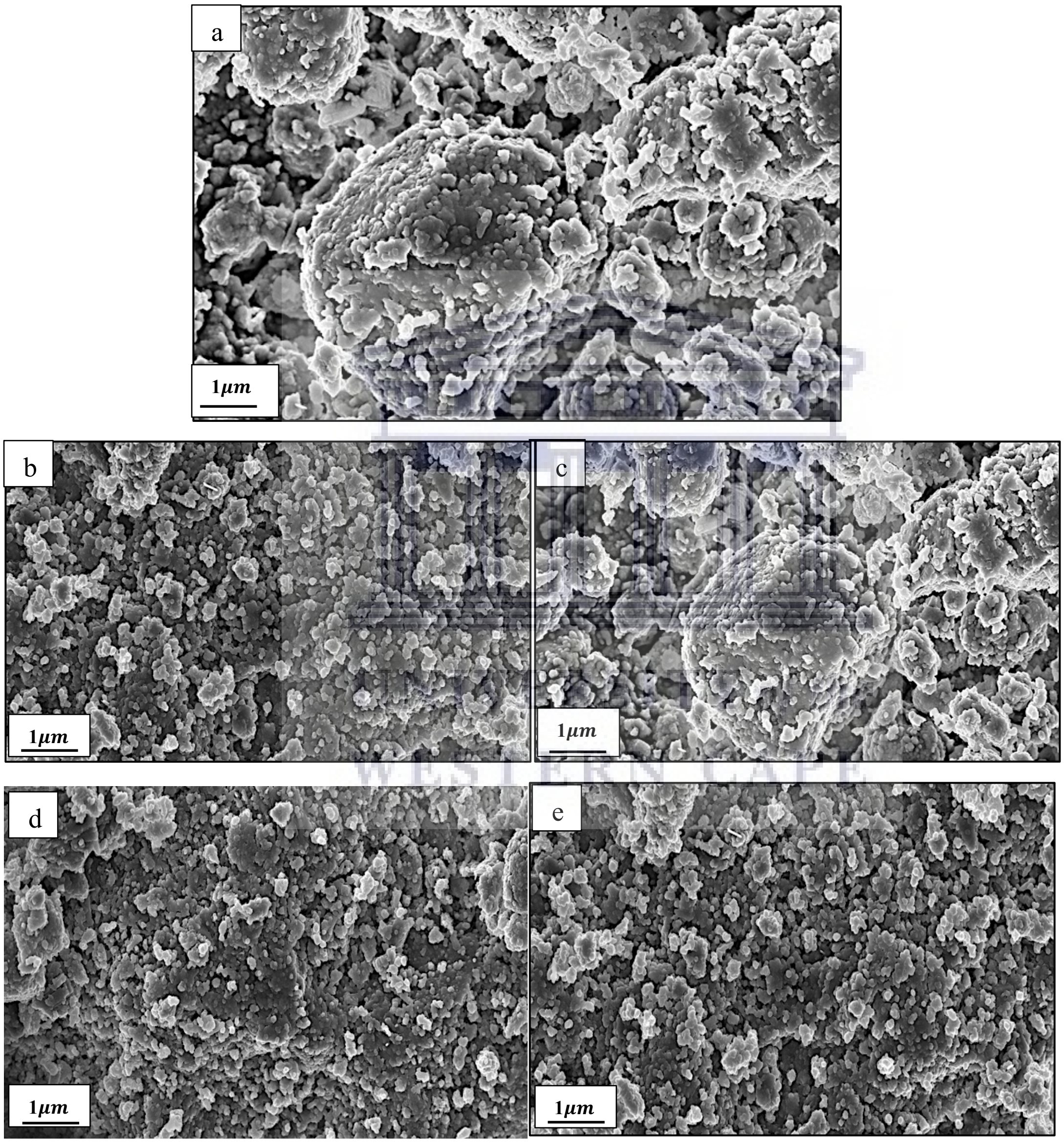


Figure 4.11: Imaging of the SEM micrographs of (a) Desilicated ZSM-5, (b) 1%Ni-ZSM-5, (c) 1%Cr-ZSM-5, (d) 1%Zn-ZSM-5 and (e) 1%Co-ZSM-5

The SEM images of the desilicated and metal doped ZSM-5 are shown in Figure 4.11 (above). The SEM images show particles that have a spheroidal shape with an average size of 4 μm. The large spheroids seems to be aggregates of smaller crystals. The morphology of the metal doped ZSM-5 is similar to the one of the desilicated ZSM-5. These observations indicate that the zeolite MFI structure remains intact even after the addition of the metals. This is in agreement with literature [71], [72], [74].

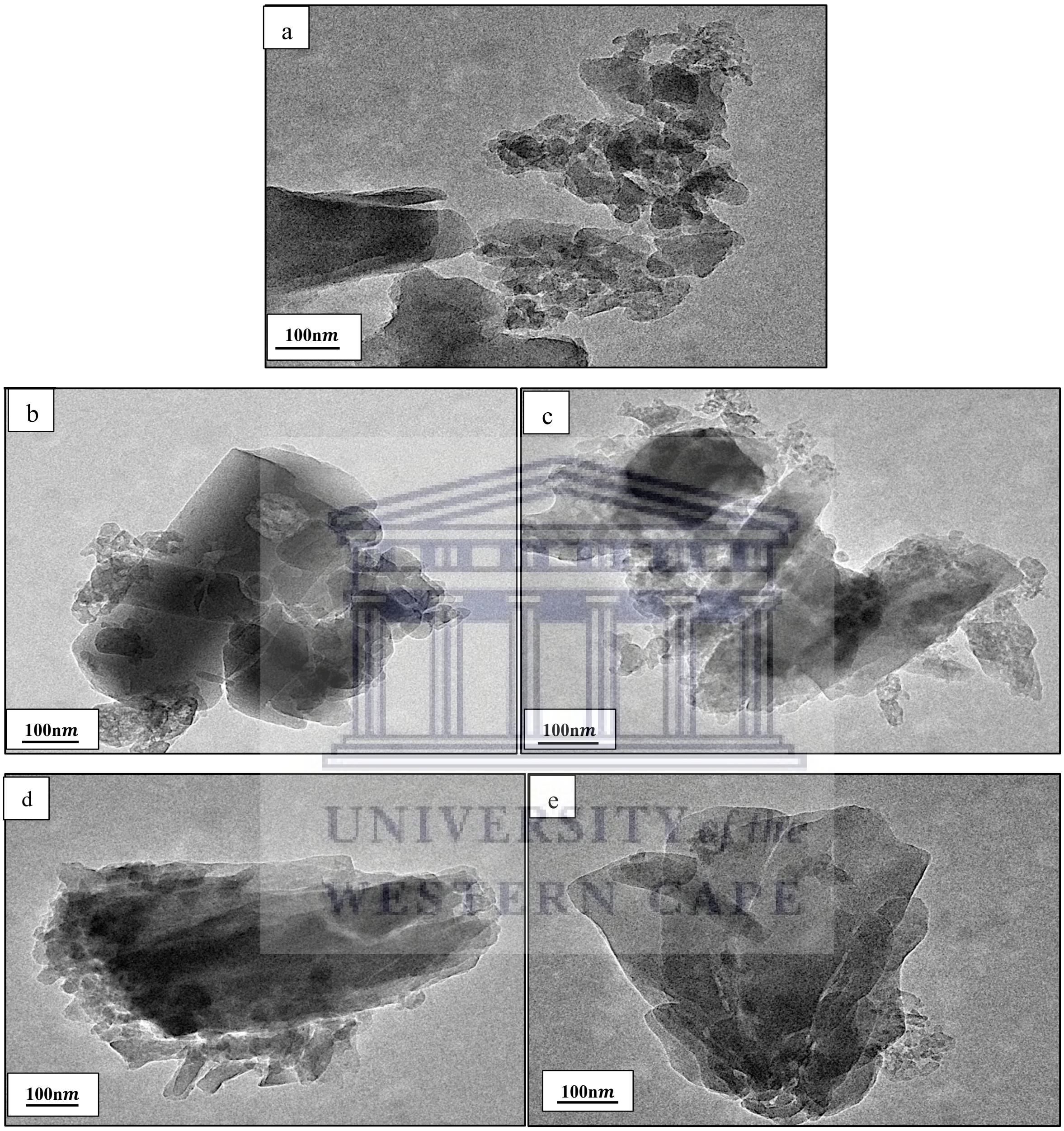
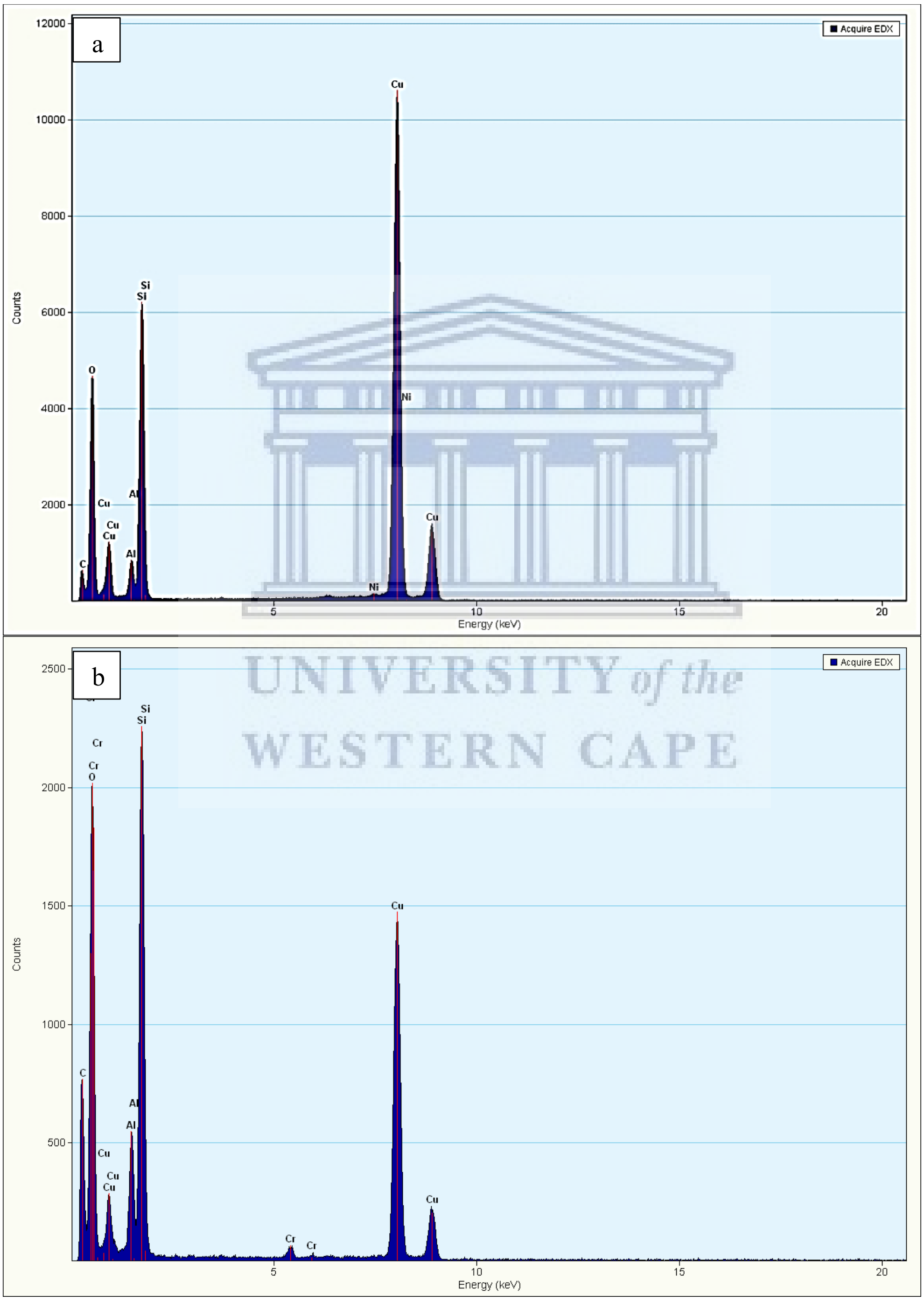


Figure 4.12: Imaging of the TEM micrographs of (a)Desilicated-ZSM-5, (b) 1%Ni-ZSM-5, (c) 1%Cr-ZSM-5, (d) 1%Zn-ZSM-5 and (e) 1%Co-ZSM-5.

Figure 4.12 (above) illustrates the TEM micrographs of the desilicated and metal doped desilicated ZSM-5. It is difficult to determine the presence of metals using both SEM and TEM analysis due to the small amount loaded which may result in the metals present mostly as cation or very small well dispersed particles, However, EDS analysis confirms that the presence of metals on the ZSM-5 zeolite. The EDS spectra are shown in Figure 4.13. The loadings as determined by EDS are 0.66 % Nickel in the Ni-ZSM-5 present,0.99 % Chromium in Cr-ZSM-5, 0.91 Zinc in Zn-ZSM-5, and 0.86 % Cobalt in the Co-ZSM-5 which are close to the theoretical 1 *wt%* loadings. Therefore the EDS spectra confirm that ZSM-5 with a 1 *wt%* metal-loading was successfully synthesized.

4.2.1.4 EDS results



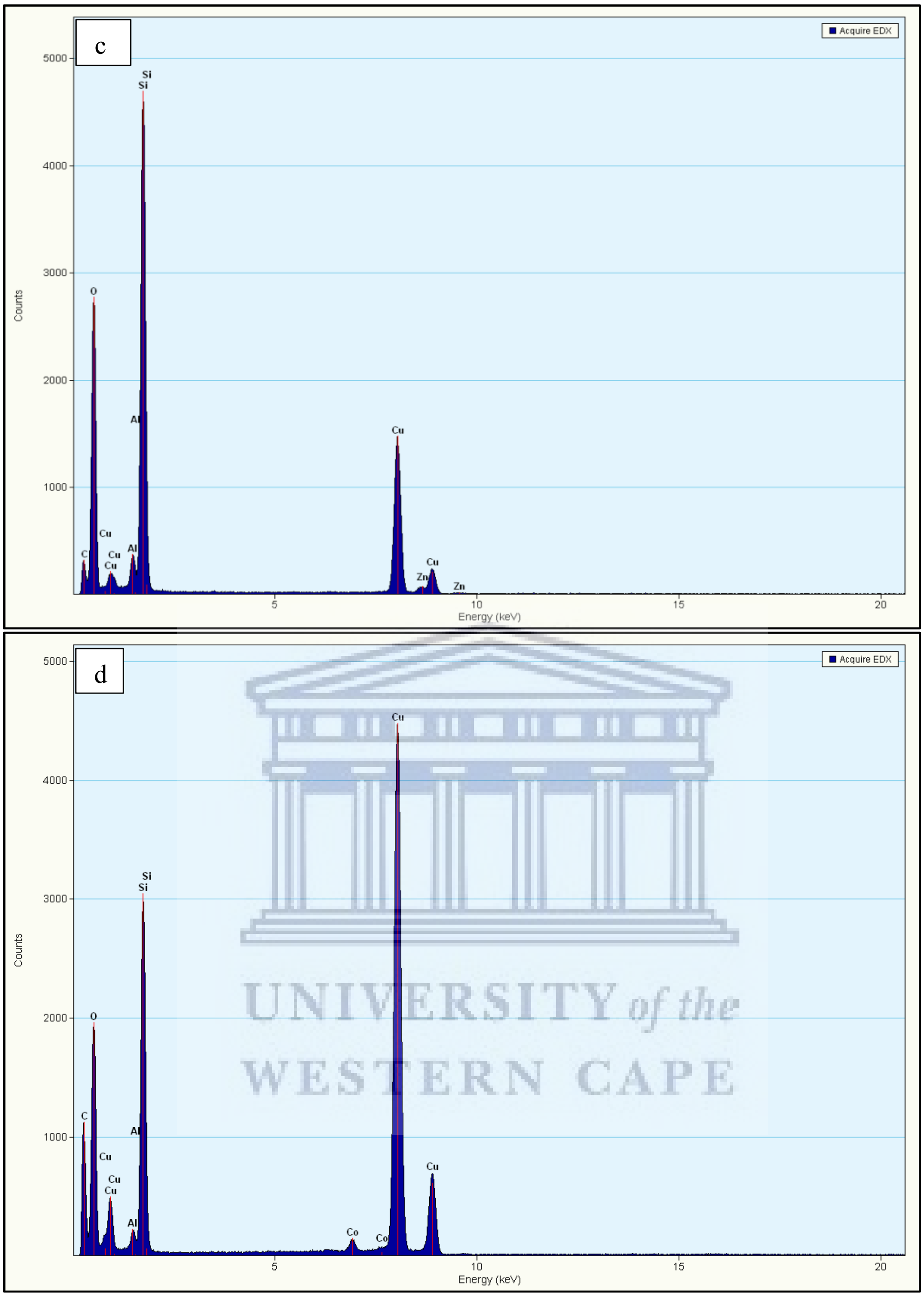


Figure 4.13: Images of the EDS micrography of (a) 1%Ni-ZSM-5, (b) 1%Cr-ZSM-5, (c) 1%Zn-ZSM-5 and (d) 1%Co-ZSM-5.

4.2.2 Monometallic Catalysts Evaluation

The catalysts were evaluated in the oligomerization reaction using 1-hexene as the feed. The reaction conditions (Temperature = 220 °C, Pressure = 40 bars and WHSV = 1.5) used were similar to the one used in the evaluation of the pristine and desilicated ZSM-5 in section 4.1. The reaction was run for 72 hours. The conversion of 1-hexene over the monometallic doped ZSM-5 catalysts as a function of time is plotted in Figure 4.14 (below).

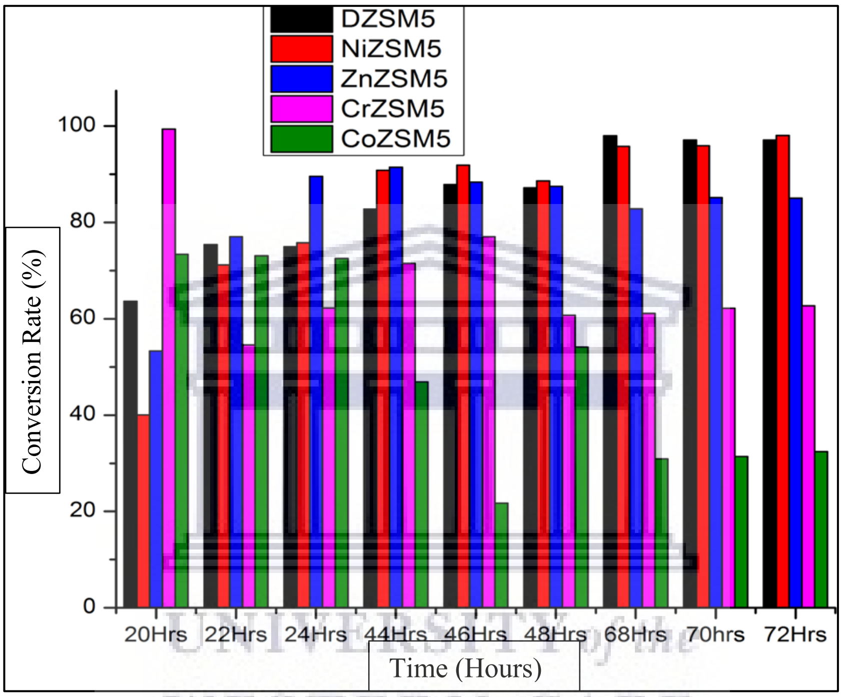


Figure 4.14: Bar graph representation of the conversion of 1-hexene over different acid catalyst in an oligomerization process.

The initial conversion amongst the 4 catalysts varies greatly. Initially the Cr-doped ZSM-5 has the highest conversion whereas Nickel doped ZSM-5 has the lowest. After the first 20 hours, the 1 % Cr-ZSM-5 has a conversion of 99 %. Then it fluctuates between 54 % and 77 % before it reaches what is seems to be a steady-state in the 48th hrs. The conversion of the 1-hexene on the 1 % Cr-ZSM-5 seems to remain stable beyond 48 hrs for the duration of the reaction at 62 %.

The cobalt doped ZSM-5 has the second highest conversion after 20 hrs. It seems to have reached a steady-state from the 20th hrs with a conversion of 73 % until the 24th hour. After the 24th hrs the conversion decreases to 21 % and has the lowest conversion thereafter compared to the other catalysts. The cobalt may de- active faster because of its greater acidity. The larger amount and strength of acid sites may lead to high initial activity. This may also cause many more secondary reactions which can cause the formation of carbonaceous deposits that block acid sites leading to a quicker rate of deactivation. However, further studies on the amount of coke formation will be performed in future for confirmation.

Interestingly, over the 1 % Zn-ZSM-5 and 1 % Ni/ZSM-5 catalysts the conversion increases gradually as the reaction proceeds. the initial conversion of the Zinc doped ZSM-5 is around 55 % at the 20th hour and reaches the steady state at the 24th hour and remains fairly constant throughout the reaction, maintaining a conversion of approximately 80 %. The nickel on the other hand seems to reach a steady state at a slightly later stage approximately on the 44th hour and then maintains a high conversion of at least 90 % which is the highest of all the metal doped catalysts.

The factors that affects the conversion, selectivity and stability of a catalyst in an oligomerization process, are vast from the nature and distribution of acidity to reaction conditions. The mono-metallic catalysts were evaluated in similar reaction conditions. Hence the difference in performance can be attributed to difference in their catalyst nature in terms of acidity as well as the porosity. The Nickel doped ZSM-5 showed the highest conversion compared to other metal doped ZSM-5. It has the lowest external surface area, but relatively high strong acid site compared to the zinc and chromium doped ZSM-5 similar to that of the desilicated ZSM-5. These observations could explain the higher conversion as the Ni doped and undoped ZSM-5 had similar conversion and similar amount of strong acid sites.

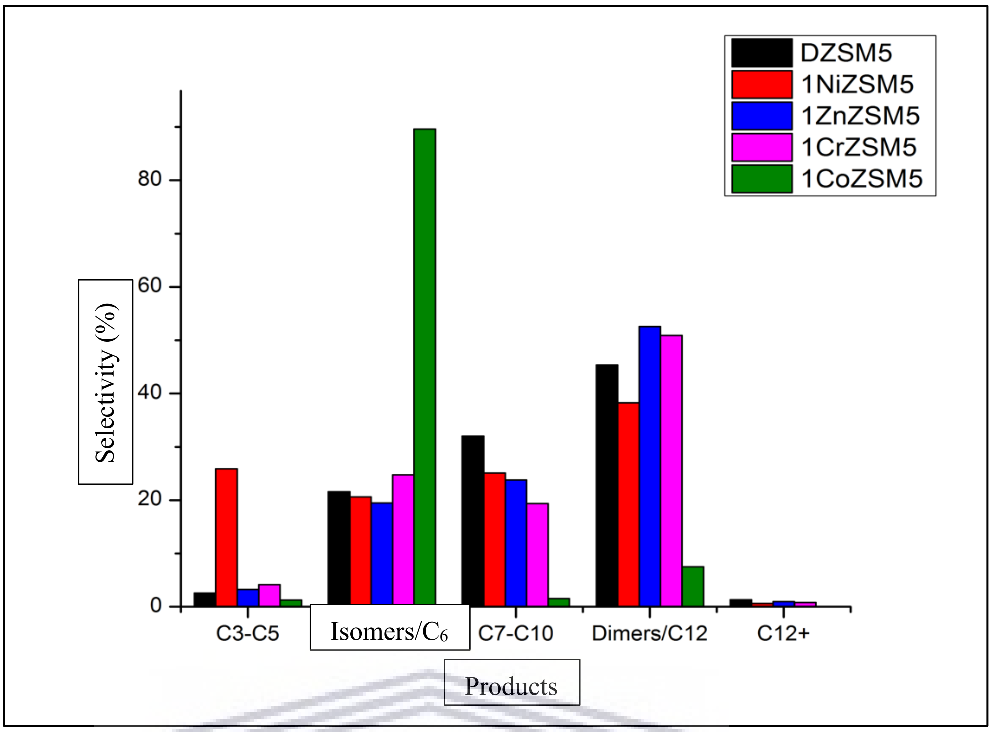


Figure 4.15: Bar graph representation of the product selectivity at the 48th hour in a 1-hexene oligomerization in different mono-metal

Figure 4.15 (above) shows the selectivity of the four different catalysts. The catalysts show a wide product distribution due to many reactions occurring such as oligomerization, cracking, isomerization and hydrogen transfer. The 1 % Zn-ZSM-5, 1 % Ni-ZSM-5, 1 % Cr-ZSM-,5 and the desilicated ZSM-5 are highly selective towards the dimers products with 55 %, 38 %, 52 %, and 45 % respectively indicating the catalysts were successful for the oligomerization of hexene.

The pore size and diffusion properties play a crucial role in the promotional effects of chromium. It was shown by A. de klerk when he looked at the oligomerization of 1-hexene and 1-octane over solid acid catalysts and showed that when chromium is supported on pore size and diffusion restricted catalyst such as pristine ZSM-5, it does show an improvement as it promotes the formation of heavier olefins. However when it is supported on a catalyst with larger pores and better diffusion properties it shows an improvement in producing dimers and trimers. This could explain the good selectivity it shown in producing dimers when added to the desilicated ZSM-5, such that it out performed nickel doped ZSM-5 and the desilicated ZSM-5.

The cobalt doped catalyst (1%Co-ZSM-5) has a product profile that is dominated by isomers. A high selectivity to isomerization products approximately 90 % is obtained. Other products include 8 % dimers, 1 % of C_7-C_{10} products, and 1 % of C_3-C_5 products. Cobalt doped zeolite have shown a high selectivity towards branched products in an n-hexene/n-hexene reactions[57], [70]. It is well known that oligomerization requires strong acid sites. However, competing reactions such cracking and skeletal isomerization of C_{5+} olefins require similar conditions. Skeletal isomerization of 1-hexene will require the presence of weak acid site, which could explain the presence of the C_6 isomers in all the catalyst and why the cobalt doped ZSM-5 was selective towards C_6 products since it has the most amount of weak acid sites compared to the rest of the catalysts. It is also possible that isomerization occurs on strong Lewis acid sites which may be present in the cobalt doped ZSM-5 as noticed from the increase in strong acid sites in NH_3-TPD analysis [7]. The results below show the selectivity of the catalysts evaluated.

The nickel doped catalyst has a product profile that is comprised of 38 % of Oligomerization products, 24 % of C_7-C_{10} products, and 20 % of C_6 isomerization and about 18 % of C_3-C_5 cracking products. While the zinc dope ZSM-5 has 54 % of Oligomerization, 21 % of C_7-C_{10} cracking products, 19 % isomerization products, and 3 % of C_3-C_5 cracking products. The Zinc doped catalyst has a higher selectivity towards oligomer products when compared to the nickel doped catalyst and all other catalysts. It also shows an almost 10 % increase in selectivity compared to the desilicated ZSM-5 which suggests that impregnation with Zn may improve oligomerization selectivity to heavier hydrocarbons.

These catalyst properties are enhanced because of improved acid properties [57], [70]. From the NH_3-TPD profile, the zinc and the nickel doped catalysts show an increase in weak Lewis acid sites compared to the chromium doped but contain less than the cobalt doped ZSM-5. However they have a higher conversion rate, better selectivity towards oligomers and more stable compare to the cobalt and chromium. Therefore the results may suggest that the amount and strength of Lewis acid sites may be important in promoting oligomerization as it is noticed that a much greater amount of both weak and strong Lewis acid sites on the cobalt doped ZSM-5 begins to favour isomerization over oligomerization. In previous studies, nickel is shown to promote the oligomerization reaction when it is supported on a ZSM-5 catalyst [8], [41], [75]. However further studies on the interaction of Zn and Ni with the zeolite acid sites and understanding the mechanism of promotion is needed.

The research octane numbers (RON) have been determined using the DHA software for all the catalysts. The results are presented in Table 4.3.

Table 4.3: Tabulation of the Research octane number (RON) for the mono-metallic

Catalyst	**RON @20hr**	**RON @22hr**	**RON @24hr**	**RON @44hr**	**RON@ 46hrs**	**RON @48hr**	**RON @68hr**	**RON @70hr**	**RON @72hr**	**AVG RON**
1%Ni/ZSM-5	111	106	106	95	80	85	85	83	82	93
1%Zn/ZSM-5	109	103	100	88	78	77	90	93	92	92
1%Cr/ZSM-5	105	106	103	81	85	72	77.6	74.2	72.7	86
1%Co/ZSM-5	115	114	112	132	144	138	143	141	139	131

The RON numbers obtained for the four monometallic catalysts ranges from 72-139. The average RON for the 1 % Zn/ZSM-5, 1 % Co-Zn/ZSM-5, 1 % Ni/ZSM-5 and 1 % Cr/ZSM-5 catalysts are 92, 131, 93 and 86 respectively. These results indicate that all catalysts produce good quality octane gasoline. Low RON numbers of less than 80 were only obtained for the 1 % Cr/ZSM-5 catalyst. These observations are line with literature that the oligomerization products formed from a Cr supported catalyst have less branches as compare to the ones of nickel [7],[55].

On the other hand the Cobalt doped ZSM-5 produced the highest RON, meaning the products produced from 1 % Co are highly branched as the average number is 131 which is the highest amongst all the monometallic catalyst. The Zinc and Nickel doped ZSM-5 have a similar average in RON numbers, suggesting that they are producing more or less similar products.

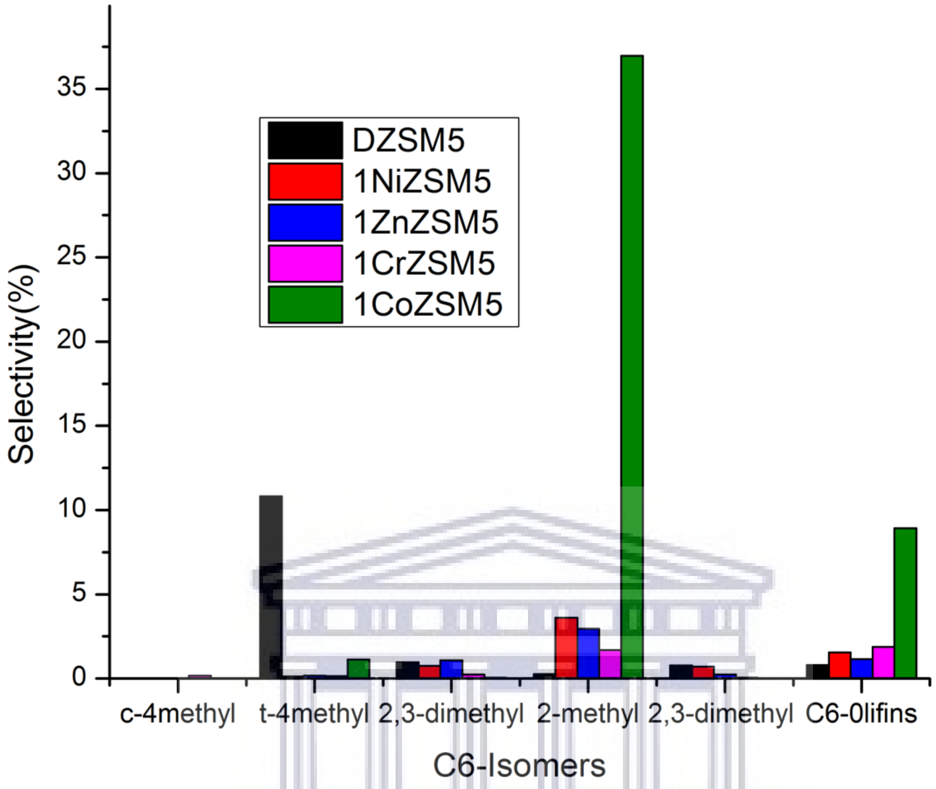


Figure 4.16: Bar graph representation of C6 isomers selectivity over different catalysts on the 48th hour in a 1-hexene oligomerization.

c-4methyl-2-2-pentene = c-4methyl
t-4methyl-pentene = t-4methyl
2,3-dimethyl-1butene = 2,3 -dimethyl
2-methyl-1petene = 2-methyl
2,3-dimethylbutane = 2,3-dimethyl
C6-olefins = C_6-Olefins
1-hexene oligomerization

Figure 3.16 above presents the selectivity to C_6 isomers that were identified using DHA software for the different metal doped catalysts at the 48th hour of the reaction. Among the five catalysts, the cobalt modified ZSM-5 had the highest selectivity to C_6 isomers (total) indicating the isomerization reaction was promoted instead of oligomerization. Among the produced C_6 isomers the cobalt catalyst was selective towards mono and di-branched alpha and internal olefins. It is most selective towards the 2-methyl-1petene isomer, followed by the C_6 olefins which are a combination of C_6 iso-olefins that could not accurately be identified in the database of the GC. The desilicated catalysts was selective towards the t-4methyl-pentene, while the other catalysts shows no apparent favourite isomers but produced little or next to zero of the C_6 isomers.

The zinc doped ZSM-5, is the best-performing catalyst in terms of selectivity to diesel range hydrocarbons. However, the cobalt doped ZSM-5 is highly selective to branched C_6 isomers which will result in gasoline with a high octane number. With these observations, the best-suited metals for a bimetallic catalyst are zinc and the cobalt. A bi-metallic catalyst is envisaged which can promote both selectivity to longer chain hydrocarbons as well as high octane gasoline. Therefore bimetallic Zn/Co-ZSM-5 catalysts with different Zn:Co ratios were prepared to investigate its effect on selectivity to gasoline and diesel range products.

4.3 Bimetallic doped ZSM-5

4.3.1 Characterization of Bimetallic ZSM-5

Section 4.3 discusses the characterization of bimetallic doped desilicated ZSM-5. The following characterization techniques were used: XRD for the crystallinity, TEM for the morphology of the catalyst, BET and NH3-TPD for the pore structure and acidity of the catalysts respectively. The catalysts were evaluated in the oligomerization of 1-hexene. Amongst the monometallic catalyst investigated, cobalt promoted the most isomerization, while zinc promoted the most oligomerization. The two were combined to synthesize a bimetallic catalyst Co-Zn-ZSM-5 to investigate whether it would produce a catalyst selective to both high octane gasoline as well as diesel range products. Three variations were synthesized 0.3% Co-0.7%Zn /ZSM-5, 0.5% Co-0.5%Zn /ZSM-5, 0.7%Co -0.3%Zn /ZSM-5. The sum of the metal loading equals 1 *wt%*, as it is compared to the performance of the monometallic loaded, pristine, and the desilicated ZSM-5.

4.3.1.1 X-ray diffraction (XRD) pattern analysis

XRD was used to determine the phase purity and relative crystallinity of the materials. The XRD patterns of the bimetallic catalysts are shown in Figure 4.17. The XRD pattern illustrates that bimetallic doped ZSM-5 has the typical MFI zeolite pattern. The introduction of the two metal species does not alter the zeolite framework structure.

In the XRD patterns of 0.3 Co-0.7 Zn/ZSM-5, 0.5Co-0.5Zn/ZSM-,5 and 0.7 Co-0.3 Zn/ZSM-5 only the typical ZSM-5 peaks at approximately 8°-10° and 22-25° 2 theta are observed. There are no visible peaks corresponding to the presence of the loaded metals in either separate phases for the cobalt oxide and zinc oxide nor a solid solution of the two. This is most likely due to the low metal loading.

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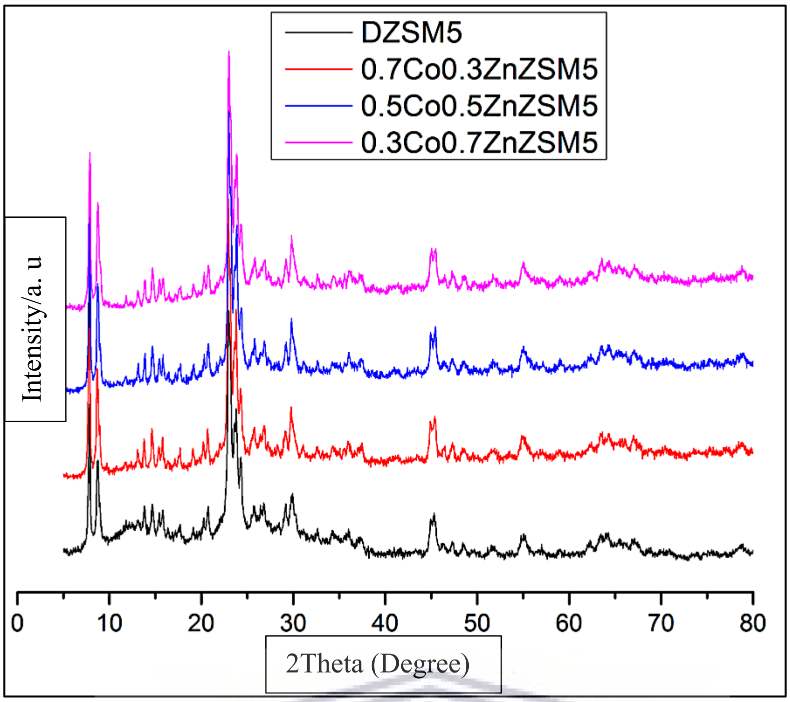

Figure 4.17: Graphical representation of the XRD pattern of the bimetallic doped desilicated ZSM-5

4.3.1.2 B.E.T and NH$_3$-TPD Results analysis

XRD patterns were recorded using BRUKER AXS D8 advance in a range 0f 2θ, 5° -90° (Cu-Kα radiation λKα1 = 1.5406 Angstrom) 40 kV. The surface, textural and acidity properties were obtained using BET and the NH3-TPD analysis. Table 4.4 displays the bimetallic (0.3 Co-0.7Zn /ZSM-5, 0.5 Co-0.5 Zn/ZSM-5, and 0.7 Co-0.3 Zn/ZSM-5) catalysts surface areas, pore volumes, and the amount of acidity determined from integration of the desorption profiles.

Table 4.4: Tabulation of the B.E.T and NH3-TPD Results

Catalyst	**S_{BET} (m^2/g)**	**M, Area (m^2/g)**	**E, S$_{area}$ (m^2/g)**	**M, V (cm^3/g)**	**P, V (cm^3/g)**	**T$_{min}$ (°C)**	**T$_{max}$ (°C)**	**Q$_{min}$ (μmol/g)**	**Q$_{max}$ (μmol/g)**
0.5Co-0.5Zn/ZSM-5	366	233	133	0.084	0.28	238	501	5158	197
0.3Co-0.7Zn/ZSM-5	363	236	126	0.095	0.22	238	496	5542	306
0.7Co-0.3Zn/ZSM-5	360	229	131	0.090	0.25	244	515	5504	0.49
Desilicated-ZSM-5	425	274	151	0.160	0.29	196	394	537	48

S_{BET} = BET surface area

M, Area = Micropore Area
E, S_{area} = External Surface Area
M, V = MicroVolume
P, V = PoreVolume
T_{min} = Minimum Temperature (NH_3-TPD)
T_{max} = Maximum Temperature (NH_3-TPD)
Q_{min} = Acid site quantity minimum temperature (NH_3-TPD)
Q_{max} = Acid site quantity maximum temperature (NH_3-TPD)

Table 4.4 shows a summary of the textural and acidity properties of the bimetallic (desilicated ZSM-5). The BET surface area decreases from 425 m2/g to a surface area of approximately 360 m2/g and the micropore volume decreases from 0.160cm^3/g to 0.09 cm^3/g after the bimetallic loading with a total of 1 *wt%*. The surface areas are the same for the catalysts with different Zn:Co ratios. These changes may be due to the metal particles covering the surface and internal space of the desilicated ZSM-5. Similar alterations are illustrated on the monometallic desilicated ZSM-5 with the same weight loading indicating that they have similar textural properties.

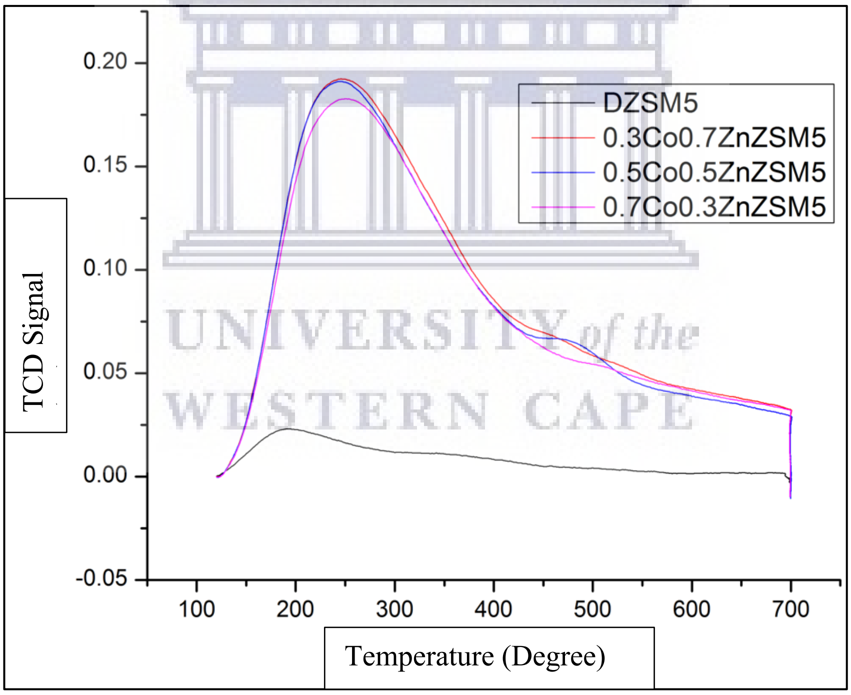

Figure 4.18: Graphical representation of the NH3-TPD profile of the Bimetallic ZSM-5 (Desilicated)

The NH_3-TPD profiles of the bimetallic catalysts are shown in Figure 4.18. The three catalysts namely: 0.3 Co-0.7 Zn/ZSM-5, 0.5Co-0.5Zn/ZSM-5, and 0.7 Co-0.3 Zn/ZSM-5 have a similar amount of weak acid sites represented by the peak at approximately 250 °C albeit, the values have considerably increased when compared to the desilicated catalyst. The number of weak acid changes from 394 mol/g(desilicated) to an average of 808 mol/g on the monometallic and an average of 5401 mol/g on the bimetallic. The noted increase may be a result of the cation species present on the surface of the ZSM-5. Cation species such as Zn^{2+}, Co^{2+} may act as Lewis acids and increase overall acid site density.

4.3.1.3 Transmission Electron Microscopy (TEM) analysis

The morphology of the bimetallic-doped ZSM-5 was obtained by using the transmission electron microscopy. The TEM micrographs in Figure 4.19 show no apparent differences in the morphology of the desilicated and the bimetallic doped ZSM-5 (Desilicated). The TEM images contain dark spots. The dark spots that are present on the metal-doped and are also present on the desilicated ZSM-5. These observations are however inconclusive as to whether the dark spots are due to presence of metals as the metal loadings are very low and no clear morphology of particles is distinguished. An X-ray mapping is needed to elucidate the presence of the metals. However the decrease in BET surface area does prove that the metals are present on the desilicated ZSM-5. The structure of the ZSM-5 remaining intact is evident on the TEM micrographs, for all three different catalysts. The results are supported by literature and as well as the XRD and BET results [53], [66], [76].

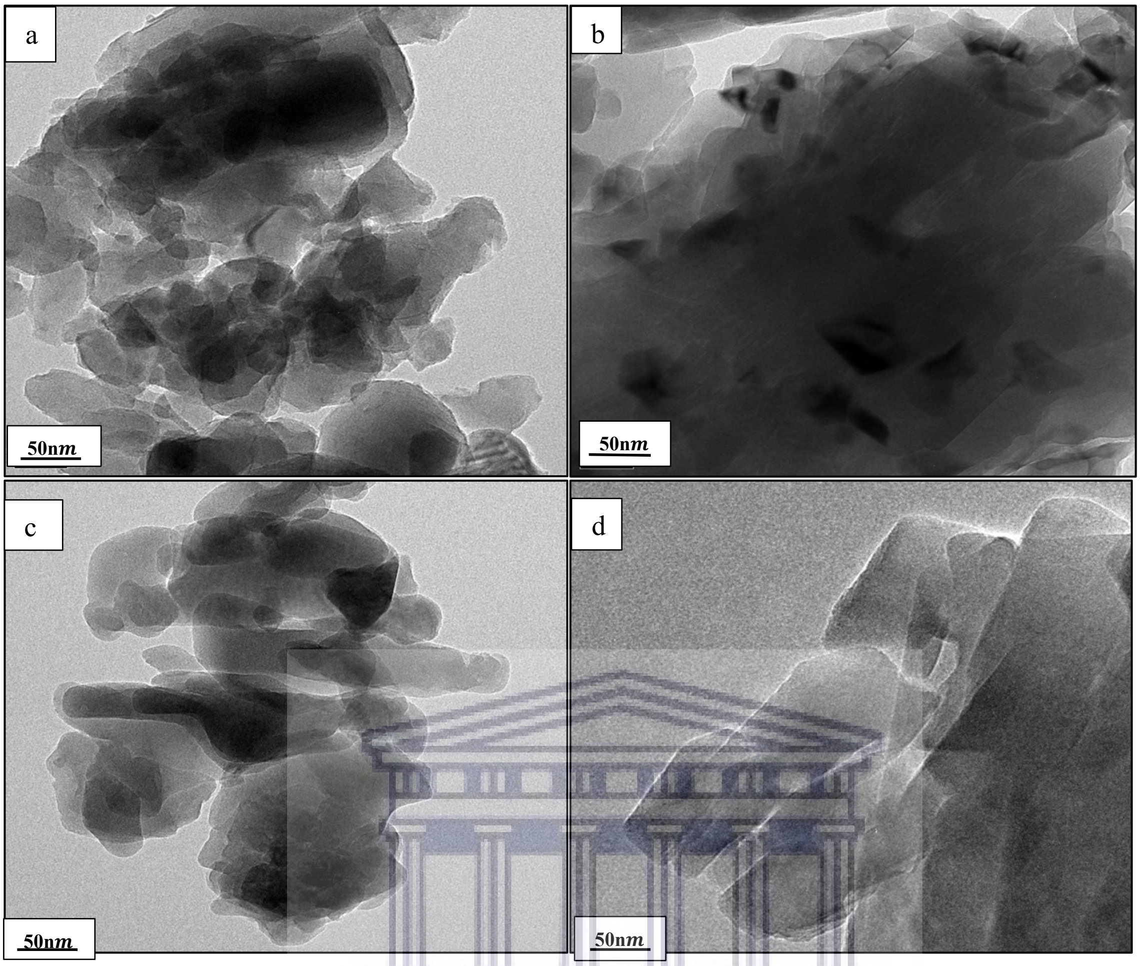

Figure 4.19: Imaging of the TEM micrographs of the bimetallic doped ZSM-5(desilicated) namely (a) 0.3Co-0.7Zn/ZSM-5, (b) 0.5Co-0.5Zn/ZSM-5, (c) 0.7Co-0.3Zn/ZSM-5 and (d) Desilicated ZSM-5 (D-ZSM-5).

4.3.2 Bimetallic Catalyst Evaluation

The bimetallic catalysts were assessed in the oligomerization of 1-hexene. The reaction conditions used were similar to the ones described in sections 4.1 and 4.2 (T = 220 °C, P = 40 bar, WHV = 1.5). The results presented in Figure 4.20 (below) show that the bimetallic ratios of the metals loaded on ZSM-5 with a total of 1 *wt%* gives different catalytic activity, selectivity, and stability when the catalyst performances are compared to each other.

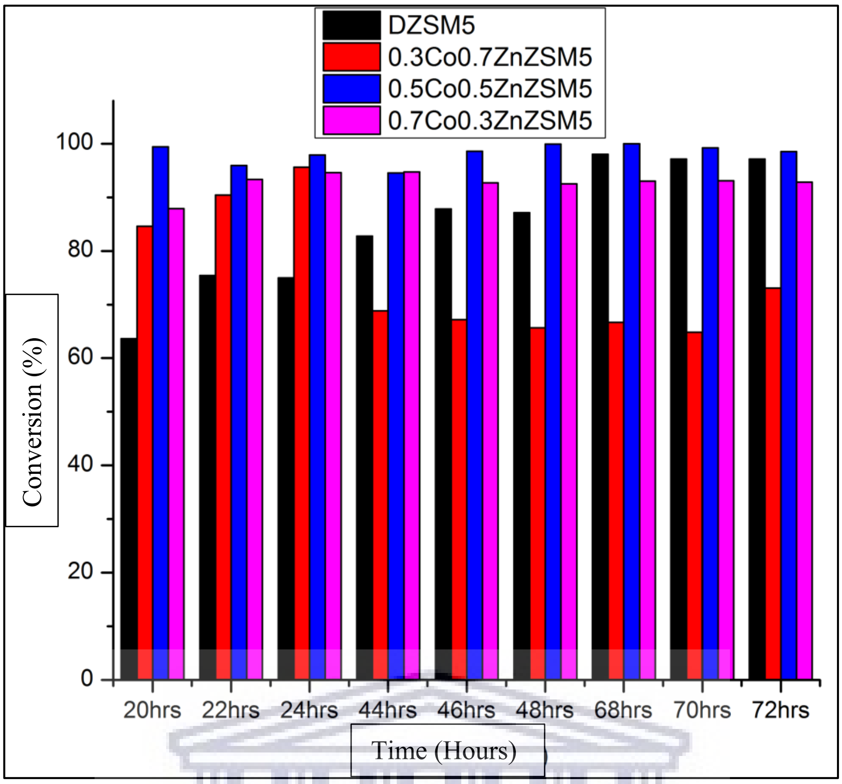

Figure 4.20: Bar Graph representation the conversion of three bimetallic catalysts as a function of time on stream

Within the initial 24 hrs, the conversions of the three bimetallic catalysts are above 90 %. The activity of catalyst 0.3 Co-0.7 Zn/ZSM-5 declines until the 48th hr, after which it reaches a steady-state with a conversion of at least 65 %. On the other hand, the 0.5 Co-0.5 Zn/ZSM-5 and 0.7 Co-0.3 Zn/ZSM-5 catalysts reached a steady-state at an earlier stage compared to 0.3Co-0.7Zn/ZSM-5. The steady-state is indicated around the 25th hour and both have a higher conversion of at least 90 % for the duration of the reaction. It is still unclear as to why there is a decrease in conversion for the 0.3 Co-0.7 Zn/ZSM-5 as it would be expected that as the cobalt loading increases it may lead to a lower conversion as the 1 *wt%* Co monometallic catalyst had the lowest activity. Therefore further investigations are still required. Furthermore, it is shown that the desilicated as well as metal modified catalysts had good stability as the activity of all four catalysts appears stable until the 72-hr mark.

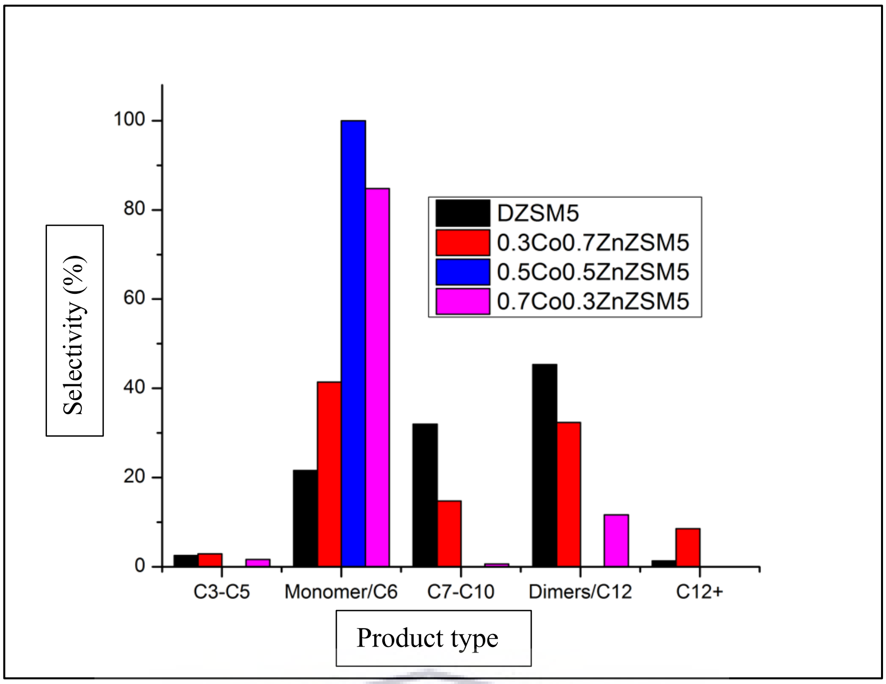

Figure 4.21: Depicts the selectivity profile of the three different bimetallic at 48 hours

Figure 4.21 (above) shows the selectivity of the bimetallic catalysts, along with the selectivity of the desilicated ZSM-5. A wide product distribution is observed for the D-ZSM-5 and 0.3 Co-0.7 Zn/ZSM-5 catalysts due to multiple reactions occurring in addition to oligomerization such as cracking, isomerization and hydrogen transfer. However the product distribution for the 0.5Co-0.5Zn/ZSM-5 and 0.7 Co-0.3 Zn/ZSM-5 are quite narrow as mostly isomerization products form *i.e.* greater than 80 % selectivity. Hence the selectivity of the catalysts are different when compared to each other. The 0.5Co-0.5Zn/ZSM-5 is highly selective towards C_6 products as no other hydrocarbon products are obtained. The cobalt played a vital role in obtained C_6 isomers, where we demonstrated that the cobalt doped ZSM-5 promotes isomerization, an observation that is supported by the literature [57] [70]. The 0.3 Co-0.7 Zn/ZSM-5 comprises roughly 40 % of C_6 products, 30 % of dimers products, 15 % of C_7-$C_{10,}$ approximately 3% of C_3-C_5 products and approximately 12 % of C_{12+}, thus making it the best performing catalyst in terms of producing dimers in the diesel range as well as selectivity to gasoline range products. In fact it produced more long range hydrocarbon *i.e.* C_{12}+ products than the D-ZSM-5 but has overall same selectivity to diesel range as the D-ZSM-5. This highlights in some way that oligomerization has been enhanced by this bimetallic system. The 0.7Co-0.3Zn/ZSM-5 has approximately 83% of C_6 products, 12% of dimers, 2 % of C_7-$C_{1,0}$ and 2 % of C_3-C_5 products which shows that mostly isomerization took place with very little oligomerization. Thus the effects of increasing cobalt doping leading to an enhancement in isomerization in the bimetallic system are clearly noticed.

These results suggest that the ratios in which the zinc and cobalt are combined to form a bimetallic promoter are highly significant. The promotional effects of both the metals are only maintained at the correct ratio. This ratio is one where there is more zinc in the system. At a 1:1 ratio and Co: Zn greater than 1, the Co is seen to be the dominant promoter and only isomerization products are formed with very little oligomerization. Thus it can be said that the effects of the zinc and cobalt were not complimentary with greater than 50 % Co content.). However, the catalysts 0.3Co-0.7Zn/ZSM-5 shown a lot of promise as its product profile contain C_7-C_{10} hydrocarbons, dimers and C_{12+} products falling into the gasoline, jet fuel and diesel ranges respectively. These observations suggest that the catalyst 0.3 Co-0.7 Zn /ZSM-5 has the potential to produce good quality gasoline and distillate products. Further studies with higher Zn:Co ratios will be conducted in future.

The research octane numbers (RON) obtained for the three catalysts at various times throughout the reaction are shown in Table 4.5.

Table 4.5: Tabulation of the Research octane number (RON) for the bimetallic

Catalyst	**RON @20hr**	**RON @22hr**	**RON @24hr**	**RON @44hr**	**RON@ 46hrs**	**RON @48hr**	**RON @68hr**	**RON @70hr**	**RON @72hr**	**AVG RON**
0.3Co-0.7Zn/ZSM-5	108.9	91.6	83.3	133.2	136.5	82.5	137.0	106.3	129.0	112
0.5Co-0.5Zn/ZSM-5	107.1	105.6	107.5	108.1	107.5	108.2	106.4	103.6	106.5	107
0.7Co-0.3Zn/ZSM-5	110.2	108.8	110.4	108.1	129.0	131.5	123.9	129.1	121.6	119

The higher the RON the more effective is the gasoline in the anti-knocking of the engine. Previous studies on the RON and Motor Octane Number (MON) have shown that High-quality gasoline normally has a high RON and MON which helps in the efficiency and economy of the engine [1]. The RON of the gasoline can be increased by increasing the degrees of branching in the hydrocarbons. Gasoline with a RON of a 100 can be considered a high octane fuel. The RON numbers obtained for the three bimetallic catalysts ranges from 82-137. The average RON for the 0.3 Co-0.7 Zn/ZSM-5, 0.5 Co-0.5 Zn/ZSM-5 and 0.7 Co-

0.3 Zn/ZSM-5 catalysts are 112, 107 and 119 respectively. These results indicate that all catalysts produce high octane gasoline. Low RON numbers of less than 85 were only obtained with the 0.3 Co-0.7 Zn/ZSM-5 catalyst. The 0.5 C0-0.5 Zn/ZSM-5 catalyst maintained the average RON of 107 throughout the reaction and the highest RONs were obtained for the 0.7Co-0.3Zn/ZSM-5 catalyst. The results indicate that as the Co loading is increased from 0.3 to 0.7 *wt%* the RON also increases. This may be due to the Co promoting the isomerization of C_6 hydrocarbons leading to more branched products and hence an increase in the RON. When the metals were loaded with a 1:1 ratio the RON was well maintained without increasing or decreasing as the reaction proceeded.

When the Zn loading was the highest in the system i.e. in the 0.3 Co-0.7 Zn/ZSM-5 catalyst, the relatively lower RONs obtained may be due to the oligomerization reaction been favoured as the hexenes are converted to dimers and hence selectivity to diesel range products are increased. Therefore the 0.3 Co-0.7 Zn/ZSM-5 catalyst seems to be the most promising as it produces the highest selectivity to diesel range hydrocarbons as well as high octane gasoline.

4.4 Comparison of the different Catalyst studied

This section looks at the comparison of the four different types of catalysts prepared and tested in this study *i.e.* a pristine ZSM-5, a desilicated ZSM-5, Zn modified desilicated ZSM-5 and a bimetallic Co-Zn desilicated ZSM-5. The activity, selectivity, and stability of these catalysts are compared and discussed. Figure 4.22 (below) shows the conversions of 1-hexene as a function of time on stream.

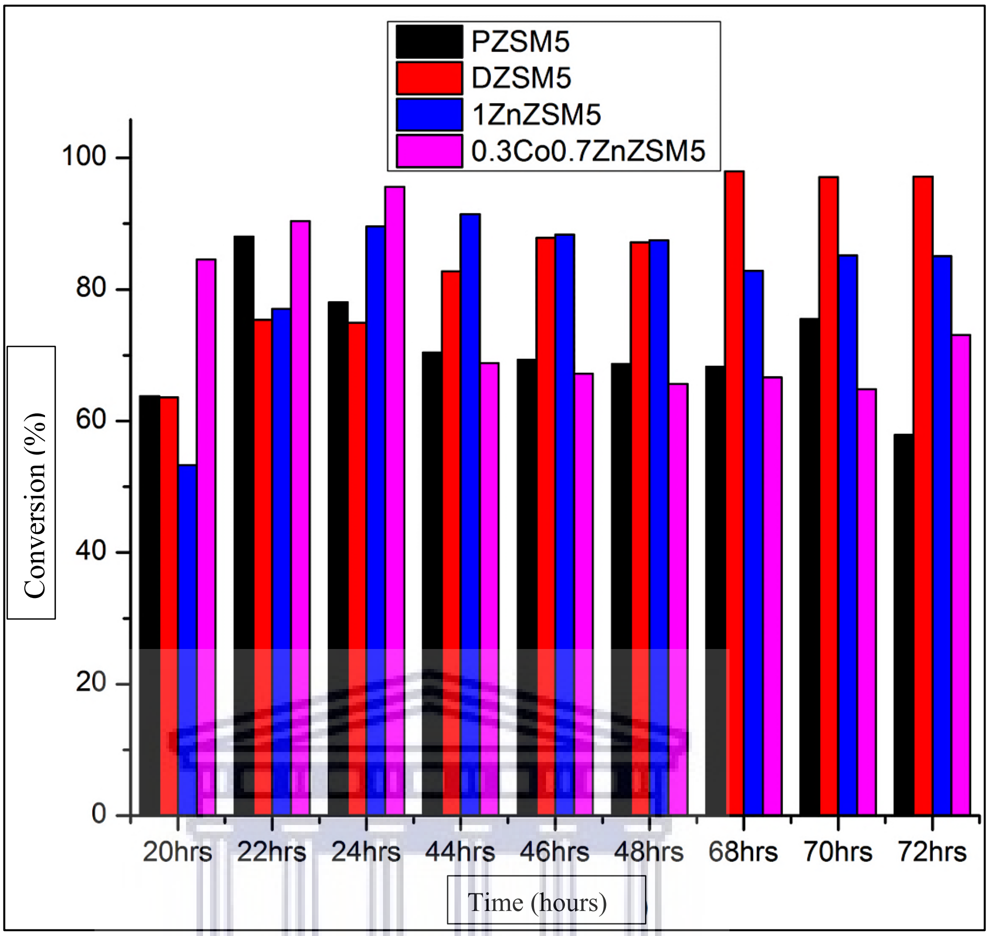

Figure 4.22: Bar Graph representation of the conversion rate Pristine-ZSM-5 (P-ZSM-5), Desilicated-ZSM-5 (D-ZSM-5), 1%Zn-ZSM-5 (1ZnZSM5) and 0.3Co-0.7Zn/ZSM-5 (0.3Co0.7ZnZSM5)

The conversions observed for the four different catalysts show that the D-ZSM-5 and 1%Zn-ZSM-5 have similar activity while the P-ZSM-5 and 0.3 Co- 0.7 Zn-ZSM-5 have similar activity throughout the reaction. The D-ZSM-5 and 1 % Zn-ZSM-5 catalysts have higher conversions percentage compared to the other two catalysts. This high conversion is maintained; it is at least 80 % after the 44-hr mark and is maintained throughout the reaction. The activities of P-ZSM-5 and 0.3Co-0.7Zn-ZSM-5 increases in the first 24 hours. It then decreases to approximately 65 % -70 % where it is maintained although P-ZSM-5 shows some deactivation in the last hours of the reaction.

Figure 4.23 below demonstrates the product profile of the four catalysts. The monometallic catalyst is highly selective toward dimers, as it contains 55% of dimers products, 20% C_6 isomers, 5 % C_3-C_5, 22 % C_7-C_{10} and 3 % C_{12}+. The desilicated ZSM-5 comprises 45 % dimers, 20 % of C_6 isomers, 2 % C_3-C_5, 30 % C_7-C_{10} and 3 % C_{12+}. The monometallic and the desilicated ZSM-5 selectivity towards the dimers may be the result of the enhanced diffusion properties and the promotional effects of zinc as compared to the pristine ZSM-5.

The 0.3 Co-0.7 Zn/ZSM-5 comprises roughly 40 % of C_6 products, 30 % of dimers products, 15 % of C_7-$C_{10,}$ 4 % of C_3-C_5 products and approximately 11 % of C_{12+}. Compare these results to the pristine one which contains 55 % of C_6 products, 13 % of C_7-C_{10}, 30 % of dimers and 2 % of C_3-C_5. These results are similar to one another with an exception of the C_{12}+ products in the bimetallic which is not present on the pristine and the lower selectivity to C_6 isomers in the bimetallic catalyst. As Co promotes isomerization and Zn oligomerization when combined it seems that they compete with each other and a wide product distribution is obtained that shows selectivity to isomers and dimers which is slightly enhanced compared to the pristine ZSM-5.

The difference between the effects of the monometallic and the bimetallic catalysts on the catalytic performance, the zinc had good selectivity towards dimers while the cobalt had as strong selectivity towards isomers, however when the two metals are combined in the bimetallic catalyst only a slight enhancement is observed. The cobalt in the bimetallic promotes isomerization and competes with the zinc which promotes oligomerization. It is yet not clear how zinc functions as a promoter, more work needs to be done to understand its effects on the acidity but we do see an improvement when comparing the desilicated to the monometallic catalysts. The results show that the 1 % Zn-ZSM-5 performance excelled in comparison to other catalysts when it came to producing dimers, while the bimetallic 0.3Co-0.7 Zn/ZSM-5 was selective towards C_6 isomers, it also contained a good amount of C_7-C_{10} products, dimers and C_{12+} products *i.e.* good selectivity to gasoline and diesel in a 60:40 ratio.

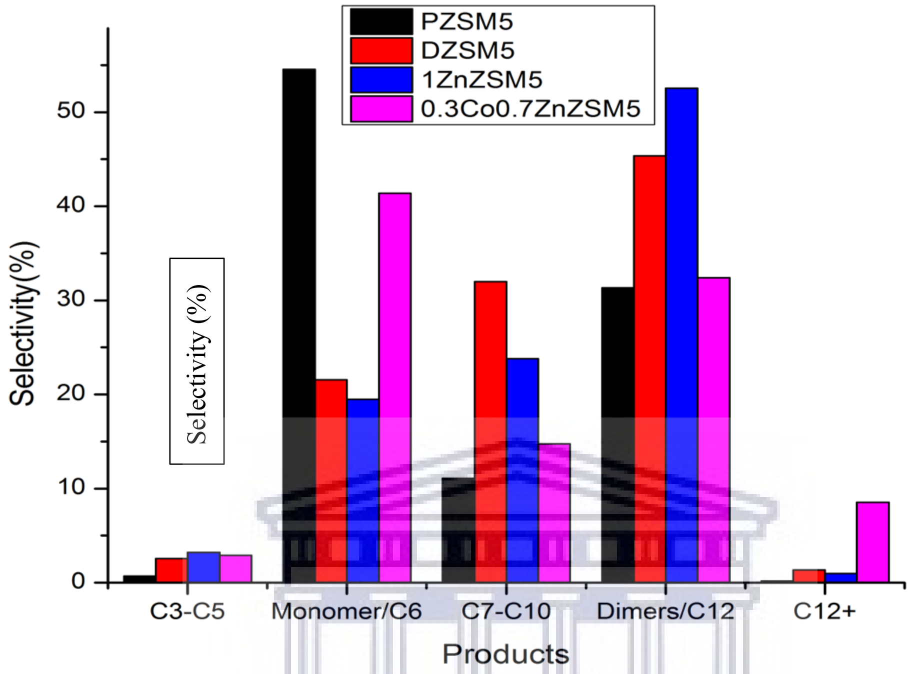

Figure 4.23: Bar Graph representation of the product-profile/selectivity percentage of Pristine-ZSM-5(PZSM5), Desilicated-ZSM-5(DZSM5), 1%Zn-ZSM-5(1ZnZSM5) and 0.3Co-0.7Zn/ZSM-5(0.3Co0.7ZnZSM5) at 48th hour

Table 4.6: Tabulation of the Research octane number (RON) for the four different types of catalysts prepared and evaluated.

Catalyst	**RON @20hr**	**RON @22hr**	**RON@ 24hr**	**RON @44hr**	**RON @46hr**	**RON@ 48hrs**	**RON@ 68hrs**	**RON@ 70hrs**	**RON@ 72hrs**	**AVG RON**
0.3Co-0.7Zn/ZSM-5	108	91	83	133	136	82	137	106	129	112
P-ZSM-5	135	98	103	101	101	100	104	100	121	107
D-ZSM-5	135	102	101	102	94	91	92	92	93	101
1%Zn/ZSM-5	109	103	100	88	78	77	90	93	92	92

Table 4.6 discusses the RON numbers obtained for the four different catalysts namely: 0.3 Co-0.7 Zn/ZSM-5, Pristine/ZSM-5, Desilicated/ZSM-5, and 1 % Zn/ZSM-5 which range from 77-137. The catalyst 0.3 Co-0.7 Zn/ZSM-5, Pristine/ZSM-5, Desilicated/ZSM-5,and 1% Zn/ZSM-5 average a RON of 112, 107, 101,and 92 respectively. The quality of gasoline is

directly related to the RON number. The higher the RON the higher quality of gasoline. These results suggest that the gasoline produced by the catalysts is of high quality.

RON lower than 80 were obtained on the 1 % Zn /ZSM-5 at the 46 and 48 hrs, this may be a result of oligomerization which is favoured compared to isomerization that has a directly proportional relationship with the RON number. The bimetallic catalyst is more selective to branched C_6 products compared to the monometallic. This may result from the cobalt effects as it promotes isomerization, the average RON number increases from 92 to 112 when cobalt is present which correlates with the results shown in Table 2 in section 4.3. which shows an increase in the RON numbers with an increase of cobalt loading moving from an average of 112 0.3Co-0.7Zn/ZSM-5 to 119 for 0.7 Co-0.3 Zn/ZSM-5. The selectivity to gasoline is similar when comparing the pristine and bimetallic doped ZSM-5(slightly higher in the pristine), the RONs is also quite similar with the bimetallic being slightly better (112) indicating that high octane gasoline is produced. However as they are very similar this may also suggest at this Co:Zn ratio only small promotional effects of each metal are noticed. It may be possible to achieve better selectivity to diesel while still maintaining a gasoline with RON above 100 by decreasing the percentage of Co in the bimetallic system for example in a 0.1 Co:0.9 Zn ratio. These tests will be investigated in future.

CHAPTER 5: CONCLUSION AND FUTURE WORK

The main purpose of this study was to synthesise and modify a hierarchical ZSM-5 zeolite for 1-hexene oligomerization. In chapter 4, the characterization and the performance of the synthesized catalysts were discussed.

ZSM-5 was successfully synthesized and modification *via* the desilication process was a success with the desilicated ZSM-5 indicating more efficient diffusion properties, which improves the mobility of reactant, products to and from the catalytic active site. The desilication process does not alter the framework of the zeolite, however, the amount of weak acid and strong acid site is altered. The desilicated ZSM-5 catalyst performed better than the pristine ZSM-5, it showed enhanced activity by approximately 20 %, increased selectivity towards dimers, more stable and active beyond the 72 hrs.

The effects of metal doped desilicated ZSM-5 were then studied. Four metals were investigated: cobalt, nickel, zinc, and chromium. The characterisation of these metal modified ZSM-5 showed that the framework of the MFI type zeolite was not changed after the doping process, but NH_3-TPD confirmed the amount of weak and strong acid sites was changed. BET analysis showed decreases in the micropore and external surface areas indicating the metals were well dispersed on the surface and in the pores of the desilicated ZSM-5. Among the four-metal modified ZSM-5 catalysts the zinc doped ZSM-5 indicated the best performance in terms of activity and selectivity comparison with the other three metal in the oligomerization reaction, while the cobalt exhibited enhanced performance in isomerization when compared to the other three catalysts.

One of the objectives of the study was to increase selectivity to diesel while also producing a high octane gasoline which led to the synthesis of a bimetallic catalyst. The bimetallic catalyst was a combination of zinc and cobalt which was found to promote oligomerization and isomerization respectively. The metals were combined with the aim that they will result in a synergetic relationship and produce highly branched gasoline and distillate products. Three catalysts with different ratios namely 0.3 Co-0.7 Zn/ZSM-5, 0.5 Co-0.5 Zn/ZSM-5, 0.7 Co-0.3 Zn/ZSM-5 were synthesized. The characterisation of the catalyst indicates that the zeolite framework is not altered, but the number of weak acid sites increased after the doping process. The catalyst's performance was evaluated in oligomerization of 1-hexene, the reaction condition used were similar to the ones in section 4.1-4.2 (T= 220 °C, P = 40 bar and WHSV = 1.5). Different catalytic activity, selectivity, and stability were observed. The catalyst 0.5 Co- 0.5 Co/ZSM-5 produced mainly C_6 isomers.. As the Co content in the bimetallic system was increased the selectivity to isomers increased and therefore the Co promotional effects dominated that of Zn. At higher Zn contents a higher selectivity to dimers and diesel range products was obtained as well as high octane gasoline confirmed by RONs above 100.

Section 4.4 showed that the desilication of a microporous (pristine) ZSM-5 does improve the diffusion properties and some acidic properties. Catalytic activity, selectivity, and stability were improved as well. The framework of the zeolite remains intact throughout the desilicated and doping process. The metal-doping of the desilicated ZSM-5 showed similar improvements. The cobalt doped ZSM-5 was exceptional in the isomerization of 1-hexene. However when the bimetallic system is compared to the activity and selectivity of the pristine ZSM-5 it was found that there is a slight enhancement in oligomerization as more C_{12}+ products were formed than any other catalyst. Furthermore, gasoline with high RONs were obtained but the selectivity to the overall gasoline and diesel ranges were similar to the pristine ZSM-5. This may suggest that at this ratio the effect of the metals seem to compete with each other. The bimetallic catalyst resulted in a wider product distribution with lower selectivity to distillates and was more selective towards C_6 products than the monometallic Zn doped and unmodified desilicated ZSM-5.

In conclusion, the aim our study was satisfied. However, concerning the limitation of the study, we noted that the quantity of the metal introduced may have been sub minimal (1% M/ZSM-5). Additional studies utilizing greater quantities of the metal may elucidate further interesting and novel findings. Furthermore, varying the Co : Zn ratio by further decreasing the Co content may be synthesized to investigate if higher diesel selectivity can be obtained while still producing high octane gasoline.

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