Terminal Oxidation of *n*-Octane over ZSM-5 and Silicalite Catalysts in the Liquid Phase

By

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As the candidate's supervisor I have approved this dissertation for submission

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ABSTRACT

Three types of zeolites namely ion-exchanged ZSM-5 (Si/Al ratio of 47), framework substituted ZSM-5, and silicalite were synthesized. The synthesis of zeolite ZSM-5 was conducted using sol-gel method and modified using ionic exchange method to yield Fe-ZSM-5(47,IE), V-ZSM-5(47,IE), Cr-ZSM-5(47,IE) and Mn-ZSM-5(47,IE). In addition, 1.1Fe0.8V-ZSM-5(IE) and 0.4Fe1.2V-ZSM-5(IE) catalysts were synthesized to evaluate the activity of a bimetallic catalyst. Furthermore, the synthesis of Fe-ZSM-5(62), 1.6Fe-silicalite, 1.8V-silicalite, 0.9Fe0.8V-silicalite and 0.3Fe1.3V-silicalite was carried out by an isomorphic substitution. The numbers represent the metal Wt%, while the number in bracket represents Si/metal ratios. Powder XRD results showed that only the ZSM-5 phase was obtained for all the prepared catalysts and the optical density ratio of all the catalysts was above 0.7 confirming the catalysts' crystalline nature. All synthesized catalysts were tested in the oxidation of *n*-octane with H_2O_2 as the oxidant in MeCN at 80 °C for 8 hours. Fe-ZSM-5(47,IE), V-ZSM-5(47,IE), Cr-ZSM-5(47,IE), Mn-ZSM-5(47,IE), 1.1Fe0.8V-ZSM-5(IE) and 0.4Fe1.2V-ZSM-5(IE) produced selectivities of 38, 12, 10, 6, 21 and 17 % respectively to terminal products. Furthermore, 1.6Fe-silicalite, 1.8V-silicalite, 0.9Fe0.8V-silicalite and 0.3Fe1.3V-silicalite achieved terminal selectivities of 17, 12, 16 and 22 % respectively while Fe-ZSM-5(62) showed 20 % terminal selectivity. The terminal selectivities were found to increase with the decrease in the amount of vanadium used in ZSM-5 while the opposite was true for silicalite catalysts.

PREFACE

All the experimental work described in this thesis was performed at University of KwaZulu-Natal in the School of Chemistry & Physics, Westville Campus, Durban. The experimental work was done from May 2014 to November 2015 under the supervision of Prof. H. B. Friedrich and mentorship of Dr. M. N. Cele.

The work presented in this thesis represents original work by the author that has not been done or published elsewhere by others. The work of others that has been used in this work is fully acknowledged.

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HON (UKZN)

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DECLARATION - PLAGIARISM

I, ____ declare that

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3. This thesis does not contain other persons' data, pictures, graphs or other information, unless specifically acknowledged as being sourced from other person.
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CONFERENCE CONTRIBUTIONS

The following conferences have been attended where part of this work was presented:

CATSA Conference 2014, Pretoria, presented a poster entitled "**Oxidative activation of *n*-octane over V-ZSM-5 catalyst promoted with Fe, Cr, Mn, Co, or Ni**"

CATSA Conference 2015, Western Cape, presented a poster entitled " **Catalytic oxidation of *n*-octane over zeolite catalysts: Investigation of active metal, bimetallic catalysts, as well as the effects of different synthesis methods**"

College of Agriculture, Engineering and Science Conference 2015, Pietermaritzburg (UKZN), presented a poster entitled "**Oxidative activation of *n*-octane over ZSM-5 catalysts: Investigation of an active metal and bimetallic catalyst**"

ABBREVIATIONS

ATR = Attenuated Total Reflectance
BET = Brunauer-Emmet-Teller (surface area measurement technique)
CVD = Chemical Vapor Deposition
EDS = Energy Dispersive Spectroscopy
Evac = Evacuation
FT-IR = Fourier Tranform-Infrared
g = Gram
GC = Gas Chromatography
ICP-OES = Inductively Coupled Plasma-Optical Emission Spectroscopy
L = Litre
M = Molar (mole/litre)
MFI = Mordenite Framework Inverted
mg = Milligrams
Min = Minutes
mL = Millilitre
mm = Millimeter
SEM = Scanning Electron Microscopy
TEM = Transmission Electron Microscopy
Ti-MCM-41 = Titanium Mobil Composition of Matter 41
Ti-MMM-1 = Titanium Microporous Mesoporous Material 1
XRD = X-Ray Diffraction
ZSM-5 = Zeolite Socony Mobil number 5

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CHAPTER 1
INTRODUCTION

1.1. Definition of catalyst and catalytic cycle

Over the years the world has shown an enormous industrial growth that induces pressure for chemical products. Products are now needed at shorter time intervals due to the structure of supply chain industries. To meet the balance, substrates that can enhance the speed of products production are developed in the industrial market. Among such materials that are employed are catalysts.

Catalysis is one of the major important fields in chemistry and is the key approach to sustainability [1]. Catalysis involves speeding up the rate of reaction, hence leading to faster yields of products. Using a catalyst in a chemical reaction can also suppress some undesirable side reactions and decrease the activation energy of the reaction, hence increasing the thermodynamically favoured route. It is believed that the catalyst goes through a series of uninterrupted elementary steps during the chemical reaction (**Figure 1.1**). At the end of the reaction, the catalyst is reproduced as it was in the beginning of the reaction [2]. Therefore, a catalyst can be defined as the material that takes an indirect part in the production of products without it being consumed in any way during the reaction. In theory, what is shown by **Figure 1.1** is true, but the reality is, as the catalyst goes through the series of catalytic reaction cycles, it loses its activity and this phenomenon is called catalyst deactivation. One can characterise a catalyst by looking at its activity, selectivity and stability [3].

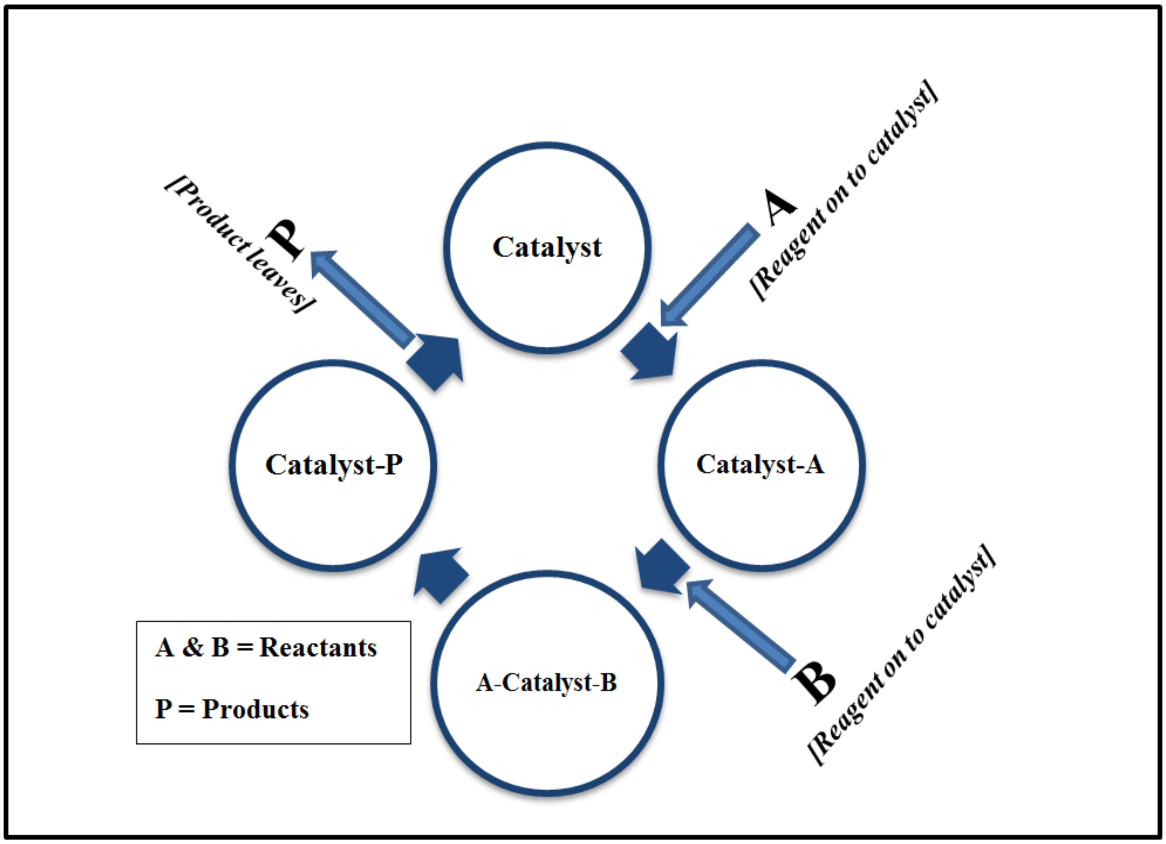


Figure 1.1: A Simple Catalytic Cycle

1.2. Categories of catalysis

Catalysis can be separated into two distinct common categories. One is homogeneous catalysis in which the catalyst and the reactants exist in a single phase which often leads to higher catalyst activity and reduced selectivity [4]. The phases could be a gaseous or liquid, with the liquid phase being most common. In a liquid phase, both the catalyst and the reactant molecules are reacted in a specific solvent. In this type of catalysis, most catalysts contain transition metals that are mostly stabilized by the ligand, which is normally an organic molecule that coordinates with the metal atom. The properties of the catalyst are easily tuned by either changing the metal or the ligand. Changing these two components can either reduce or improve the catalyst selectivity, activity, as well as stability. The major drawbacks in homogenous catalysis are the difficulty in product and catalyst separation and recycle after use. This is the reason why more than 80 % of industrial catalytic applications are carried out using heterogeneous catalysis [1, 4, 5].

In heterogeneous catalysis, the reactants and the catalyst are in different phases. These could be solid, liquid, gas or immiscible liquids. The different phases in heterogeneous catalysis lead to easy separation of products and also the catalyst can be used in more than one cycle in a catalytic reaction.

Catalytic selective oxidation plays a key role in industrial chemicals and intermediates manufacturing. Catalysis is the sector that dominates the global chemical industrial technology, with more than 80 % of all chemical products being synthesized using catalytic routes [8]. More than 60 % of the industrial chemical products are oxidation products [8]. According to the National Institute of Standards and Technology, the American chemical industry produces products worth $375 billion per year [9]. These figures imply that catalysis is one of the most important processes in the world.

1.3. Oxidations of alkanes to more valuable products

Alkanes are saturated hydrocarbons and this means that they are stable compounds and also they have no specific region of attack with no preferred reaction site. This limits their applications in the chemical industry, but makes them very economical and environmentally friendly substances. Saturated hydrocarbons often give more energy and less carbon dioxide compared to burning of unsaturated hydrocarbons. The main sources of alkanes are natural gas and petroleum, but a large amount is also produced from carbon monoxide and hydrogen by the Fischer-Tropsch process [6]. To make alkanes reactive species, one must cleave the C-C or the C-H bonds. Thereafter they can undergo reactions such as dehydrogenation, substitution, oxidative dehydrogenation and chain cleavage. Catalytically, functionalizing the terminal carbon of long linear alkanes still remains a challenge owing to the difficulty of controlling regioselectivity, as mentioned above. The secondary carbon-hydrogen bond dissociation energy of linear alkanes is 94.6 kcal mol^{-1}, while for the primary carbon it is 104 kcal mol^{-1}. These energies explain why the secondary carbons react faster than the primary carbons [7]. Because the internal positions of long linear alkanes, such as *n*-octane, react faster (secondary carbons are more reactive than primary carbons), the oxidation products will be a mixture of internal alcohols and ketones.

The spontaneous reaction of oxygen with alkanes is called autoxidation. This is another challenge that needs to be overcome when working in the liquid phase. Autoxidation selectivity also follows the trend set by the energy of the C-H bond dissociation. Therefore it also favors the oxidation of the internal positions in long linear alkanes [7].

1.4. Production of long linear alcohols in industry

Industrial production of long linear alcohols is carried out using Ziegler and oxo processes. These are both multistep processes which use alkenes as their feed. The Ziegler processes (**Figure 1.2**) is a five step process and uses ethylene as the starting material. At the end of the process, the alcohols are formed with aluminium hydroxide. This process is not a catalytic process, since Al_2O_3 is not recycled to $Al(Et)_3$ but converted to aluminium hydroxide instead [10, 11].

The oxo-process (**Scheme 1.1**), which is a term used instead of hydroformylation, also uses ethylene as the feed for the reaction with a H_2/ CO gas mixture in the presence of the catalyst. The reaction yields both linear and branched aldehydes [11].

$$\boxed{2R\text{-}RH{=}RH_2 + 2CO + 2H_2 \xrightarrow{HCo(CO)_4} R\text{-}CH_2\text{-}CH_2\text{-}CHO + R\text{-}CH\ (CH_3)\text{-}CHO}$$

Scheme 1.1: The oxo-Process

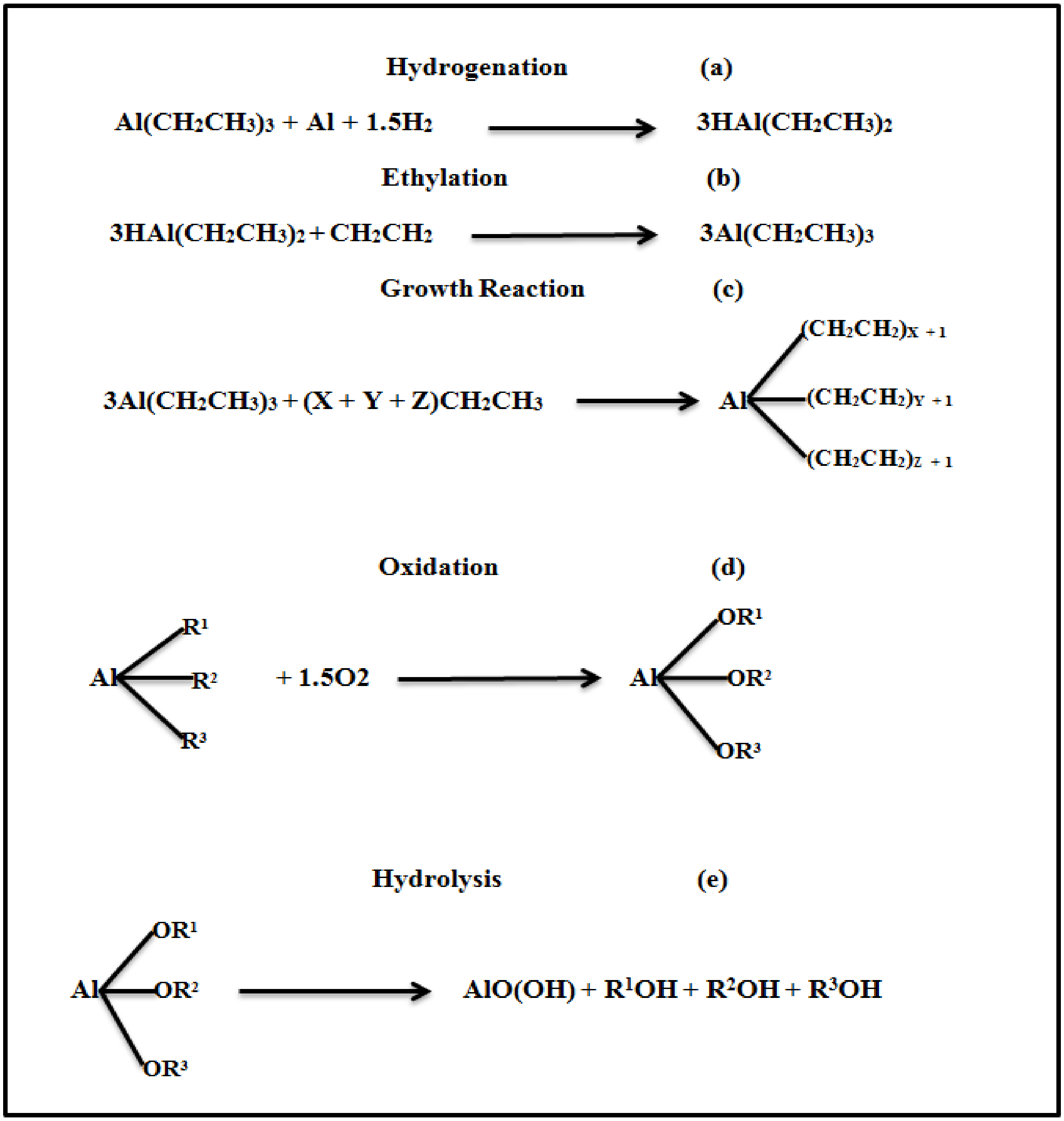


Figure 1.2: A concise scheme of the Ziegler process

1.5. Use of terminal long linear alcohols

Terminal alcohols can be incorporated with other groups to give a vast variety of useful derivatives. These could be aldehydes, ketones or carboxylic acids. **Figure 1.3** shows some industrial alcohol derivatives. These derivatives are very important in different industries. Different properties of alcohols make them suitable for a variety of applications. The use of alcohols as surfactants results from their amphiphilic character. This property, to a lesser extent, allows them to be used in cosmetics as well. Alcohols are also used as detergents because they aggregate at the interphase between two phases to form micelles, which have properties that dissolve organic compounds in water. Other uses are in plastic and cement compositions [11].

Terminal linear alcohols + Oxygen ⇒ Aldehyde, Carboxylic Acid
+ Alkali Melt ⇒ Carboxylic Acids
+ Alkali ⇒ Dimeric Alcohol
+ Proton ⇒ Ether, Olefin
+ Alkyne ⇒ Vinyl Ether
+ Carboxylic Acid ⇒ Ester
+ Hydrogen Halide ⇒ Alkyl Halides
+ Ammonia / Amine ⇒ Amines
+ Aldehyde / Ketone ⇒ Acetals
+ Sulfide ⇒ Thiols
+ Alcoholate / H_2S ⇒ Xanthates
+ Metals ⇒ Metal Alkoxides
+ Ethylenoxide / SO_3 ⇒ Ethoxilates/Ethersulfates

Figure 1.3: Example of reactions of the terminal hydroxyl group of an alcohol [11]

1.6. Different Catalysts investigated

1.6.1. Zeolites

1.6.1.1. Composition and structure

Zeolite discovery dates back to the middle of the eighteenth century when Baron Cronstadt heated crystals of certain minerals and they appeared to melt and boil at the same temperature by a phenomenon called intumescence. The name zeolite, given to the materials that intumesce, is from the Greek “zeo” to boil and “lithos” stone [12].

The building blocks of zeolites are the pores and channels of the 3D-aluminosilicate framework which makes up a crystalline microporous material. Zeolites find their main industrial importance in petroleum processing. They are used as adsorbents or desiccants, as ion-exchangers and as catalysts. The crystal structure of the zeolite is known. Zeolites bring an advantage that they can contain well defined pores in which the catalytically active sites are embedded [13-16]. The metal in the zeolite can be contained within the cages of its framework, which leads to reduced leaching probability [17].

Zeolites can be synthesized or be found in nature. At present more than 600 zeolites are known, with the conformation of SiO_4 and AlO_4 arranged differently to give the different zeolites. Many zeolites are commercialized for use in industry. The properties of some industrially important zeolites are defined in **Table 1.1**.

Table 1.1: Properties of some industrially important synthetic zeolites [13-16].

Name	**Structure type**	**Window**	**Dimensionality of pore system**	**Pore aperture (nm)**	**SiO_2/Al_2O_3**
A	LTA	8-ring	3	0.41	2.0 – 6.8
P	GIS	8-ring	3	0.31 x 0.45 0.28 x 0.48	2.0 – 5.0
ZSM-5	MFI	10-ring 10-ring	3	0.53 x 0.56 0.51 x 0.55	20 – ∞
X	FAU	12-ring	3	0.74	2.0 – 3.0
Y	FAU	12-ring	3	0.74	3.0 – 6.0
Mordenite	MOR	12-ring 8-ring	2	0.65 x 0.70 0.26 x 0.57	9.0 – 35

From **Table 1.1**, the zeolites channel windows range from eight to twelve oxygen atom rings, the pore diameters range from 0.41 nm to about 0.74 nm, which are similar to the diameter of the n-alkane of interest (**Figure 1.4**). These are the factors that lead to the selectivity of zeolites. The silica to aluminium ratios tell more about the acidity that enables the zeolites to be used as shape-selective catalysts in industrial applications and also tells us about the ionic exchange capacity of the zeolite material [18].

Zeolites have been used in many applications, which include the synthesis of ethylbenzene, the isomerisation of xylene and the disproportionation of toluene [19, 20].

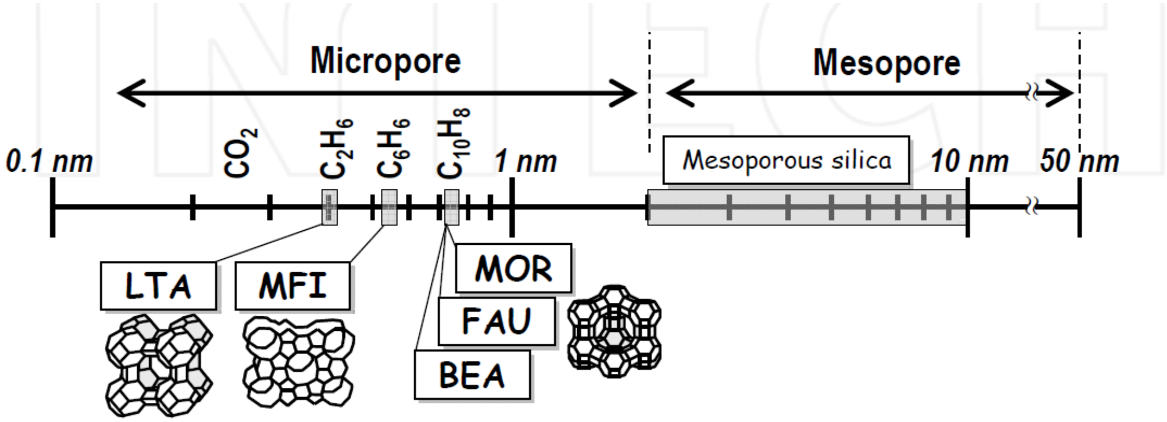
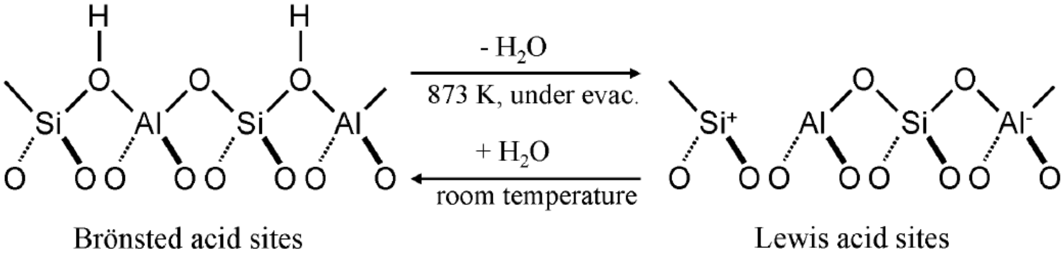


Figure 1.4: Zeolite structure, pore size and molecular diameter of hydrocarbons [20]

The features of ZSM-5 make it a suitable zeolite to be used as a catalyst in the oxidation of paraffins such as *n*-octane. Zeolite ZSM-5 is classified by its high silica content and this is the origin of its properties. Zeolite ZSM-5 belongs to the pentasil group, which is a group of zeolites that contains five membered rings. The rings of the pentasil groups are composed of Al and Si with oxygen bonding to both the elements in the lattice. The bonding of the aluminium and silicon in the lattice of the zeolite is based on Lowenstein’s rule that rejects the linkage of Al-O-Al in the zeolite framework. This means that for every one aluminate tetrahedral, there must be four silicate tetrahedra [21]. The resulting unit cell of the zeolite contains 96 silicate tetrahedral units that give rise to four straight channel sections and four zigzag channel intersections.

The tetrahedron in ZSM-5 or any other MFI zeolite can either have a neutral overall charge or a formal charge of -1. The difference is brought about by the composition of the zeolite framework. When only a Si-O tetrahedron is present in the lattice, the zeolite will be neutral, but if some of the Si^{4+} is replaced by the Al^{3+} ions, the charge changes to -1 and the introduction of a cation balances the charge and can induce acid sites. The negatively charged tetrahedron corresponds to a base [22]. Zeolites can have both Brønsted acid sites and Lewis acid sites (**Scheme 1.2**).



Scheme 1.2: Formation of Brønsted and Lewis sites in zeolites [23]

According to **Scheme 1.2**, the Brønsted acid sites arise from bridging hydroxyl groups within the pore structure of zeolites. An increase in temperature causes the protons to move and at 600 °C under evacuation they can be lost as water molecules which results in the formation of Lewis acid sites. This can be reversed at room temperature to obtain Brønsted acid sites [23].

The Si/Al ratio controls the hydrophilicity of the zeolites, in which ZSM-5 tends to be moderately hydrophilic to highly hydrophobic. Other zeolites with low silica content, such as types A, X, and Y, are very hydrophilic [24]. The high stability of zeolites to thermal treatment and acidity makes it possible for them to be tuned without any structural defects.

1.6.1.2. Shape selectivity

Zeolites have a narrow range of pore sizes because of their crystallinity, which results in better selectivity than non-crystalline or amorphous materials. From **Figure 1.5**, reactant selectivity is the phenomenon whereby the zeolite discriminates the reactants in terms of their size. The bulky molecules are excluded from entering the intra-crystalline channel-structure, while the smaller molecules are allowed to enter. Product selectivity refers to the diffusivities of the reaction products formed in terms of microporous pore design and crystal size of the catalyst particles. This takes into account the steric hindrance of the products. The more sterically hindered products stay longer in the zeolite cavities, while the less sterically hindered ones are released faster [22].

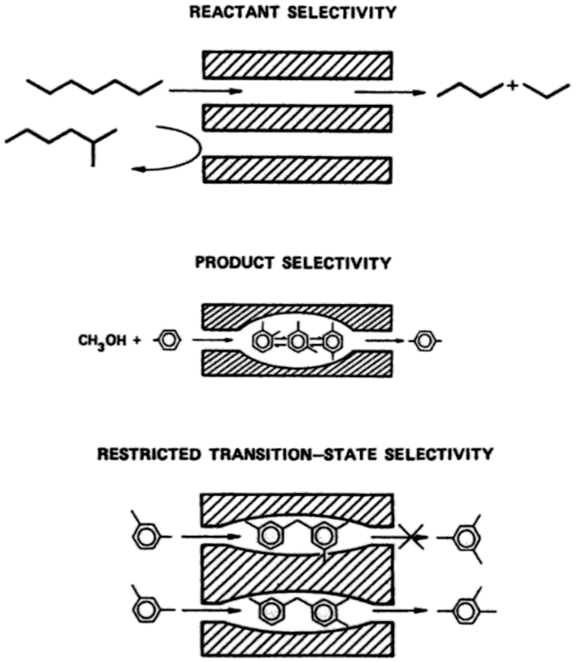


Figure 1.5: Examples of how zeolite pores affects the selectivity of reactions [22]

1.6.2. Silicalites

Zeolites can be modified to get specific surface areas, pore volumes and more specific features depending on the reaction to be carried out. The modification of ZSM-5 to silicalite is also possible and has been carried out by many scientists. Silicalites are defined as compounds containing anionic silicon, i.e. SiO_4^{4-}. Substitution of framework aluminium ions by a different metal result in structures that are no longer called a zeolite, but are now called silicalites. Thus, there are metallosilicalites with a ZSM-5 structure and these can also be used in catalysis. The best known silicalites are titanium based, and they are named TS-1. This silicalite has been used and studied more than any other silicalites [25, 26].

1.6.3 Literature review for the terminal functionalization of linear alkanes

Functionalising the terminal carbon of saturated hydrocarbons remains one of the interesting and challenging topics in the chemical industry. This is even more difficult to carry out with alkanes with long chains (hence much research is done on lower alkanes), and this is because of the regioselectivity issues associated with these substances.

1.6.3.1. Selective alkane oxidation using heterogeneous catalysts in solution

Alkane oxidation has been explored using three broad and commonly known types of catalysis, i.e. homogeneous, heterogeneous and bio-catalysis. The work contained in this thesis is based on the heterogeneous part of catalysis; therefore most of the literature review focuses on this. This is because the chemical industry sees more advantages in heterogeneous catalysts. Hence, as mentioned before in Section **1.2**, more that 80 % of industrial applications are carried out via heterogeneous catalysis. However, bio-catalysis is a promising part of catalysis now. Biocatalysts have properties that make them highly selective catalysts under mild reaction conditions and can also offer ease of separation [27, 28]. Some of the broadly used and known biocatalysts are methane monooxygenase, alkane hydroxylase and cytochrome P450. These are very good catalysts for the activation of alkanes to their corresponding alcohols. The major drawback with these enzyme/whole cell based catalysts is that they have very limited regions of operation [27].

Homogeneous catalysis is known for its ability to give high conversions. A disadvantage is the difficulty in the product separation at the end of the reaction and also the product contamination with catalyst is greatest in homogeneous catalysis [4]. What follows is a review on the oxidation of *n*-octane by heterogeneous catalysts.

Singh and Selvam reported on *n*-octane oxidation using chromium and vanadium silicate-1 (CrS-1 and VS-1 respectively) with *tert*-butyl hydroperoxide as an oxidant. In this work, conversions of 7.7 and 8.7 % and terminal selectivities of 1.0 and 0.2 % for the two catalysts respectively were reported. The major drawback of these catalysts is the poor terminal selectivity [29].

In other work carried out [30], no terminal selectivity was reported using Ti-MMM-1, TS-1 and Ti-MCM-41 as catalysts and hydrogen peroxide as the oxidant. This work reported conversions as high as 19.8 % and selectivities up to 80 % to the 2-, 3-, and 4-alcohols. While alcohols are important in industry, terminal oxidation gives even more useful alcohols and therefore it is better to have a catalyst system that is capable of achieving that.

Other work on *n*-octane oxidation reported conversions of 2.9 and 1.8 % and total terminal selectivities of 8.8 and 13 % using Fe-NaY and FeTPP-NaY respectively [31]. This work was done in a liquid phase system using hydrogen peroxide as the oxidant. Setbacks of this system are relatively poor terminal product selectivities and relatively low conversions.

In another recent study, the oxidation of *n*-octane was carried out using three catalysts based on Fe-MOF-5. These catalysts were named Fe_4-MOF-5, Fe_2–Zn_2-MOF-5 and $Fe_{0.9}$–$Zn_{3.1}$-MOF-5. The results showed that the terminal selectivity increased with a decrease in Fe content and increase in the Zn content of the catalysts. The conversions showed the opposite trend [32]. The highest terminal selectivity obtained was 19.8 %.

In the previous summarized reports [29-32], the oxidation of *n*-octane gave the corresponding C-8 oxygenated products, such as octanol, octanones, octanal and no octanoic acid, which is the kind of systems that the work contained in this thesis is based on. The scope of *n*-octane oxidation is much larger than this, because in other studies (gas phase) the oxidation of *n*-octane gave a mixture of products including octenes, aromatics, cracked products, COx and short chain oxygenates. In one system, vanadium based catalysts were used at higher temperatures and a conversion of 16 % was achieved with selectivity of 51 % towards heptenes, 14 % aromatics and 15 % oxygenates for a total value added products selectivity of 80 % [33].

In another similar study as the above, a similar product distribution was reported with much improved selectivity to oxygenated products. The catalysts in this study were based on cerium. The selectivity to terminal oxidation was poor, as it was below 5 % at a conversion of around 30 % [34].

One study that was carried out using a similar system of catalyst as the one used in this study was on the activation of hexane over vanadium modified zeolite ZSM-5. The Na-

V-ZSM-5 catalyst for this study was prepared via solid state ion-exchange with one weight percent metal loading. This was a gas phase study which activated hexane to a range spectrum of products such as alcohols, ketones, alkenes and aromatic compounds. The conversions obtained in this study were very high with poor terminal selectivity. The highest conversion obtained was 39 % with selectivities to 1-hexanol and hexanoic acid of 1.6 and 2.1 % respectively [35]. High temperature, poor terminal selectivity and COx formation were the major drawbacks of the study, because this can reduce the life time of the catalyst.

The reaction between alkanes and oxygen species proceeds via different pathways, and there is competition between parallel and consecutive reactions [7]. The literature explored shows that a variety of products can form from one reaction and, therefore, product selectivity in this branch of catalysis still remains the challenge. The goal remains to develop a catalyst system that is selective to the desired product at decent conversion.

1.7. Aim and motivation of this Project

Medium to long linear alkanes have multiple reaction sites; hence the functionalization of the terminal carbon remains a major challenge because it is very difficult to control regioselectivity. Therefore, the aim of this project is to investigate liquid phase medium linear *n*-alkane terminal activation using the selective oxidation of *n*-octane (as the model *n*-alkane) to 1-octanol and octanal over ZSM-5 and silicalite zeolite catalysts in acetonitrile as a solvent and H_2O_2 as the oxidant (**Figure 1.6**).

Liquid phase catalysis can be applied in both heterogeneous and homogeneous catalysis. In heterogeneous systems it brings a lot of advantages, such as the possibility of using clean oxidants such as hydrogen peroxide. The catalyst can also be regenerated and be used in more than one cycle [1]. However there are potential disadvantages of reactions carried out in liquid phase systems when compared to gas phase systems. Separation and purification of the products is laborious and intensive mixing of the compounds requires mechanically stable catalysts in liquid phase system offers.

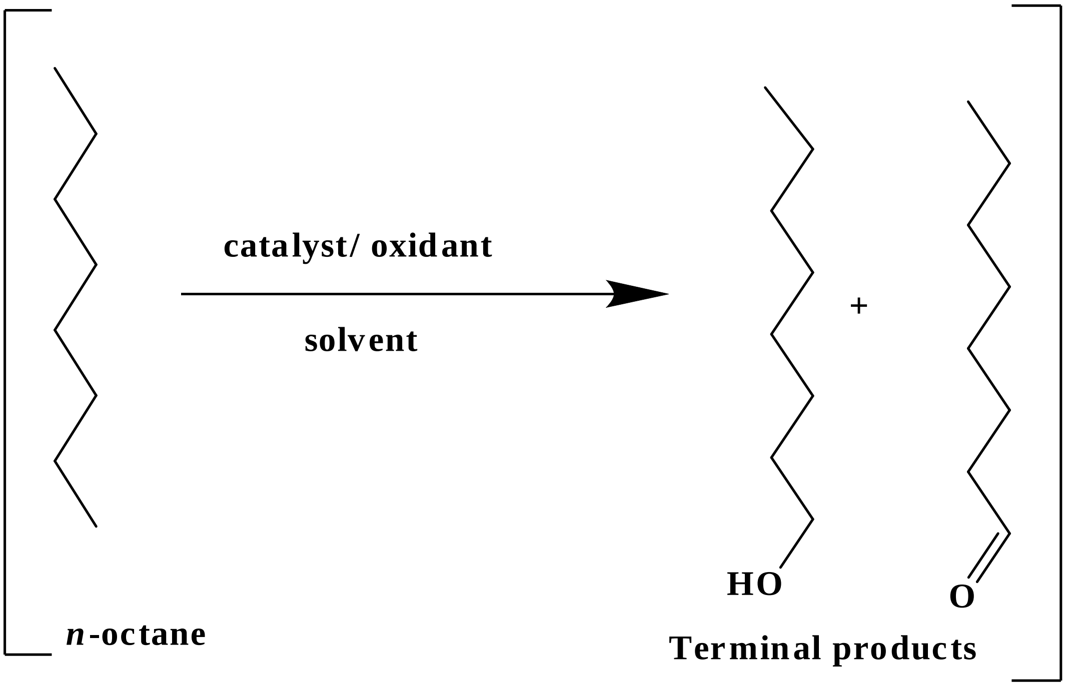


Figure 1.6: Aim of this thesis

All the prepared catalysts will be tested using a liquid phase system, taking advantage of the mild conditions that this system offers. This work was supported and funded by c*change under the supervision of Professor H. Friedrich and the mentorship of Dr M. Cele of the University of KwaZulu-Natal.

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Chapter two
Experimental Techniques

2.1. Introduction

In this chapter, the details of the catalysts synthesis, the characterisation techniques used to define the prepared catalysts, the catalytic experimental conditions used for the reactions carried out and also the products analyses and quantification at the end of the reaction are discussed.

2.2. Catalyst preparation

2.2.1. Preparation of Na-ZSM-5 zeolite by a sol-gel method

The zeolite used for all the catalysts syntheses was prepared using a Teflon lined Parr reactor set up which was the hot plate and oil bath. The prepared ZSM-5 had a Si/Al ratio of 47:1 and contained the following oxide mole compositions: SiO_2 = 0.325523 mol and Al_2O_3 = 0.0065105 mol.

In a Teflon beaker, 2.442 g of aluminium nitrate salt [$Al(NO_3)_3.9H_2O$] was dissolved in 100 mL of deionised water, which was previously acidified by three drops of perchloric acid. After the salt has dissolved, 3.5 mL of perchloric acid was added to the solution. This solution was labelled solution 1.

In a second Teflon beaker, 25 g of sodium silicate [Na_2O_3Si] solution was added to 141 mL of deionised water. This was labelled solution 2. Both the solutions were kept in the fridge overnight.

While still cold, solution 2 was added drop wise to solution 1 with vigorous stirring until the pH was at 4.5 (using pH paper). About 14.8 mL of 40 % colloidal silica was added into the remainder of solution 2, which was then followed by the addition of sodium chloride (2 g) and 6.7 g tetrapropylammonium bromide [TPA] to the slurry that resulted. This was then added to solution 1 and the resultant pH of the creamy slurry was 10.5. The slurry was then transferred to a Teflon lined autoclave and allowed to crystallize at 160 °C for 3 days without agitation.

After crystallization, solids were filtered under vacuum, washed with hot water and dried at 110 °C overnight. The Na-ZSM-5 obtained was then calcined under air at 500 °C for 16 h [1].

2.2.2. Preparation of monometallic Na-ZSM-5 catalyst by wet ionic exchange

Four catalysts were prepared using the same ionic exchange procedure. The catalysts were ion-exchanged with iron (Fe), vanadium (V), chromium (Cr) and manganese (Mn).

The required amounts of metal salts (**Table 2.1**) were dissolved in 20 mL of deionised water, and 2 g of the parent ZSM-5 was mixed into the solution under constant stirring for 3 h. Thereafter the mixture was transferred to a 50 mL round bottom flask, and then connected with a condenser. The mixture was then left to reflux overnight at a temperature of 100 °C [2]. The mixture was then filtered under vacuum and the filtrate dried at 110 °C overnight. The resulting catalyst was calcined under air at 500 °C for 16 h [1].

Table 2.1 shows the mass and type of metal salt used for the preparation of the different M-ZSM-5 catalysts prepared by the wet ion exchange method (where M = metal). The number 47 and the IE in the parenthesis denote the Si/Al ratio and ionic exchange method respectively.

Table 2.1: Mass of metal salts used for each catalyst.

Catalyst prepared	Metal salt used	Mass of metal salt/ g
Cr-ZSM-5(47,IE)	$Cr(NO_3)_3.9H_2O$	1.581
Fe-ZSM-5(47,IE)	$Fe(NO_3)_3.9H_2O$	2.683
Mn-ZSM-5(47,IE)	$C_6H_9MnO_6.2H_2O$	1.780
V-ZSM-5(47,IE)	VCl_3	1.045

2.2.3. Preparation of a Fe-ZSM-5 catalyst by framework substitution.

An iron containing zeolite was prepared using frame-work substitution, using the previously mentioned procedure (**2.2.1**), with the iron [Fe] metal incorporated together with the aluminium salt during the synthesis in solution 1. The mass of iron nitrate [$Fe(NO_3)_3.9H_2O$] dissolved was 2.683 g to make up a 2 wt% composition of the metal [1]. The reason for making a Fe catalyst of this nature was to compare it with the Fe-Silicalite.

2.2.4. Preparation of bimetallic ZSM-5 catalysts by ionic exchange

Bimetallic catalysts containing varying amounts of Fe and V were prepared by wet ionic exchange following the same procedure as in Section **2.2.2**. The catalysts were named after their metal contents, i.e. 1.1Fe0.8V-ZSM-5 contains 1.1 wt% and 0.8 wt% of Fe and V respectively. **Table 2.2** shows the details of the prepared bimetallic catalysts [2].

Table 2.2: Mass of metal salt used for each catalyst.

Catalyst	**Metal loading/ g**		**Overall metal loading**
	$Fe(NO_3)_3.9H_2O$	**VCl_3**	
1.1Fe0.8V-ZSM-5(IE)	1.341	0.522	2 %
0.4Fe1.2V-ZSM-5(IE)	0.671	0.783	2 %

2.2.5. Preparation of silicalite catalysts by a sol-gel method

Silicalite catalysts contained ~2 wt% overall of Fe and V were prepared. The composition and the method of preparation were kept similar to the preparation of Na-ZSM-5 in section **2.2.1** for comparison purposes. The only difference in the two syntheses is that the silicalites are aluminium free. Solution 1 is made up of the metal salt of interest. Everything else is the same as shown in Section **2.2.1** [1]. The prepared catalysts were 1.6Fe-silicalite, 0.9Fe0.8V-silicalite, 0.3Fe1.3V-silicalite and 1.8V-silicalite. Again, the naming of the catalysts is based on the metal content they contain.

2.3. Catalysts characterisation

2.3.1. Inductively coupled plasma-optical emission spectroscopy (ICP-OES)

Catalyst dissolution was performed using 10 mL of hydrofluoric acid to 0.2 g of sample. Multi element standards were prepared and the elemental content was determined by means of a Perkin Elmer, Optima 5300 DV ICP-OES [3].

2.3.2. Fourier transform infrared (FT-IR) spectroscopy

The Fourier transform infrared spectra were collected on a Perkin Elmer attenuated total reflectance (ATR) spectrometer, Spectrum 100 FT-IR, with 4 scans at a resolution of 4

cm^{-1} and scan speed of 0.2 cm^{-1} s^{-1} [4]. Pyridine adsorption for the catalysts was performed at room temperature until saturation. The saturation period was one hour [9].

2.3.3. X-ray diffraction (XRD)

The X-ray diffraction was carried out using a Bruker AXS D8 Advance diffractometer using Cu Kα radiation. The data was collected between 5 and 60° (2θ) at the rate of 1° min^{-1} with a 0.02 scanning step size [4, 5].

2.3.4. Braunauer Emmet Teller (BET surface area) and porosity measurements

Nitrogen–BET surface area and porosity measurements were performed using a Micromeretics Gemini 2375 instrument. Samples weighing from 0.06 to 0.075 g were degassed from room temperature to 200 °C at an initial step rate of 1°C/min overnight before carrying out the measurements. The surface area measurements were performed at a temperature of -196 °C [6-7].

2.3.5. Transmission electron microscopy (TEM)

Transmission Electron Microscope (TEM) images were obtained from a JEOL JEM 1010. Sample preparation was done by taking a small amount of the sample into a small vial and adding methanol. Before analysis, the samples are put under sonication for about 10 minutes. Thereafter the copper grid is dipped into the sample using a small clipper to hold the grid and then put under a light to dry the sample on the grid.

2.3.6. Scanning electron microscopy (SEM)

Samples were mounted on an aluminium stub using double sided carbon tape and were subsequently coated with a Au sputter coat using a Bio-Rad E5200 Auto sputter coater.

The coated samples were then analysed using a Zeiss ULTRA 55 FEGSEM. The instrument has a field emission tungsten hairpin filament with a ZrO reserve, as an electron source [8].

2.4. Gas Chromatographs

The reaction products were analysed by a PerkinElmer Auto System GC equipped with Flame Ionisation Detector using a Pona 50 × 0.20mm× 0.5 µm column [4] and results quantification analysis was carried out by using internal response factors. The internal response factor (K) of each product was calculated by finding the ratio of a known amount of product over a constant amount of 1,2-dichlorobenzene (internal standard) using the following equation.

K = [(Area IS) * (Amount SC)] / [(Amount IS * area SC)]

K = Internal Response Factor

IS = Internal Standard

SC = Specific compound of interest

Detailed products quantification calculations are in the Appendix.

2.5. Chemicals and reagents

The *n*-octane used as the feed during catalytic testing was of ≥ 99.0 % purity and acquired from Fluka. The gas chromatograph standards (1-octanol, 2-octanol, 3-octanol, 4-octanol, octanal, 2-octanone, 3-octanone, 4-octanone, 1,2-dichlorobenzene) used to determine response factors were supplied by Sigma-Aldrich and were also of high purity. For ICP-OES all standards (Fe, Si, Al, Mn, Co, V, and Na) were 1000 ppm and obtained from Polychem Supplies. Hydrofluoric acid (40 %) was obtained from Riedel-de-Haën and used for digestion of the precursors and catalysts.

The metal salts used in the catalytic synthesis were obtained from Merck and the minimum purity of the salts was ≥ 97 %. The precursors (40 % colloidal silica, tetrapropylammoniumbromide and sodium chloride) used for all the zeolite and sillicalites synthesis were supplied by Sigma-Aldrich. The sodium silica solution was obtained from UniTEK chemical suppliers, with a SiO_2 purity of ≥ 50 %.

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Chapter Three

Activation of *n*-octane using different transition metals in ZSM-5

3.1. Introduction

The chemistry of metals in the periodic table differs according to the group and the period they belong to. The metals that provided the most interesting properties in catalysis over the years are the transition metals. These metals are known as the d-group elements and they have one outermost orbital filled with electrons next to the partially filled d-orbitals. The partially filled d-orbitals are filled as you go across from left to right of the periodic table and thus the stability of the metal increases. Properties of these metals differ from one to the next. The ability of these metals to have multiple oxidation states makes them suitable materials for catalysis. Transition metals are able to accept electrons (oxidising agents) and also donate electrons (reducing agents). Therefore the oxidising ability of transition metals is expected to decrease across from left to right of the table, with some irregularities when it comes to chromium, and copper as their outer *s* orbital is only filled with one electron [1-3].

Previous studies have been carried out to show the different properties of different transition metals used in a same application. Anipsitakis and Dionysiou tested nine transition metals for the activation of different oxidants and radical generation. From this study they postulated that the redox behaviour of metals in solutions relies on the size, charge, metal hydrolysis and also complexation with other counter-ions present in the reaction media [3].

Stein et al. studied the active metals in the oxidation of different hydrocarbons. These ranged from straight chain hydrocarbons to branched and cyclic. They used many oxides of different metals, such as oxides of cobalt, chromium, iron, manganese, nickel, cerium, thorium, aluminium, titanium, lead, vanadium, magnesium, copper, zinc, tungsten, silicon, and zirconium. When oxidizing pentane and heptane they found that cobalt was the most active metal, followed by chromium, iron, manganese and nickel respectively. Other metals were found to be moderately active and vanadium was found to be the least active. One other interesting finding was that the reactivity increased with molecular weight in a given homologous series [4]. The products of these reactions were the alkenes together with some cracked products.

The aim of this study is to obtain oxygenated products. A question is whether the trend of reactivity differs with the type of reaction products one forms?

3.1.1 Synopsis of this chapter

The aim of the work reported in this chapter is to identify the transition metals that will give best catalysts in terms of selectivity and conversion. In this case, the selectivity refers to the terminal oxygenated products. Thereafter, the metals that give the best results will be taken further to synthesise another set of catalysts, such as bimetallic catalysts of ZSM-5 and silicalite.

3.2. Experimental

3.2.1. Catalyst synthesis and characterisation

Na-ZSM-5 was prepared as described in Section **2.2.1** and Fe-ZSM-5, V-ZSM-5, Cr-ZSM-5 and Mn-ZSM-5 catalysts were prepared as described in Section **2.2.2** [18]. Catalysts characterization is described in Section **2.3**.

3.2.2 Catalyst testing

All the reactions carried out were under nitrogen atmosphere. In a typical test run, 13 mL of acetonitrile was added into a two-neck round bottom flask (50 mL) fitted with a stopper and a condenser. This was followed by the consecutive addition of 1.8 mmol of *n*-octane, 16 mmol of H_2O_2 (30 wt% in water) and 0.1 g catalyst. The reactions were conducted at 80 °C for 8 hours. The products of the reaction were analysed and quantified by Perkin Elmer Auto System GC equipped with a Flame Ionisation Detector using a Pona 50 x 0.20 mm x 0.5 μm column, (See Appendix for calculations). The residual H_2O_2 was quantified by titrating 3 mL of the reaction solution acidified with 0.2 M H_2SO_4 with 0.02 M $KMnO_4$ [5, 6]. Chlorobenzene was used as an internal standard.

3.3. Results and Discussion

3.3.1 Catalyst characterisation

Looking at all the FT-IR spectra (**Figure 3.1**) of the prepared samples, they all show the same pattern of peaks. These peaks were assigned according to the Flanigen-Khatami-Szymanski correlation [7]. The absorptions around 1060, 790 and 430 cm^{-1} are assigned to Si and AlO_4 tetrahedra internal and external symmetric vibrations. The presence of double rings of tetrahedra in the framework gives rise to the band around 650 – 540 cm^{-1}.

Bands appearing around 1220 cm^{-1} are attributed to an external asymmetrical stretching vibration of SiO_2 and also indicate the formation of ZSM-5 with 3D channel morphology [7, 8, 9]. There are no bands near 1600 cm^{-1} which could be assigned to the bending of molecular adsorbed water, which confirms the presence of BrØnsted acid sites on the zeolite catalysts [10, 11].

The FT-IR spectra also agree with the XRD data on the purity and the crystallinity of the catalysts prepared (see Section **2.2.2**). By taking the ratios of the bands at about 430 and 540, one can characterize the presence of the zeolite framework. The ratio of these two peaks (optical density ratio) is reported to be close to 0.7-0.8 [7]. The value is less than 0.7 for materials with amorphous silica. All the catalysts prepared showed an optical density ratio of greater than 0.7.

The powder XRD diffractograms of all the prepared catalysts showed the pure phase ZSM-5 pattern (**Figure 3.2**) [19]. The peaks at 6-9, 22-24 and 45º confirm the presence of an MFI structure [19]. The intensity of the peaks confirms that the prepared zeolite catalysts are crystalline and pure. This is further confirmed by the FT-IR optical density ratio (**Figure 3.1**) [12]. Another observable feature of the diffractograms are the similarities between the parent Na-ZSM-5 and the ionic exchange modified zeolites. This confirms the structural stability of the ZSM-5 materials, hence no observable change is seen when modified under different conditions and methods. No peaks are seen at 38.7 and 41.6° 2θ values for the Fe-ZSM-5(47,IE) catalysts. The absence of these peaks suggests the absence of the iron haematite phase [13, 14].

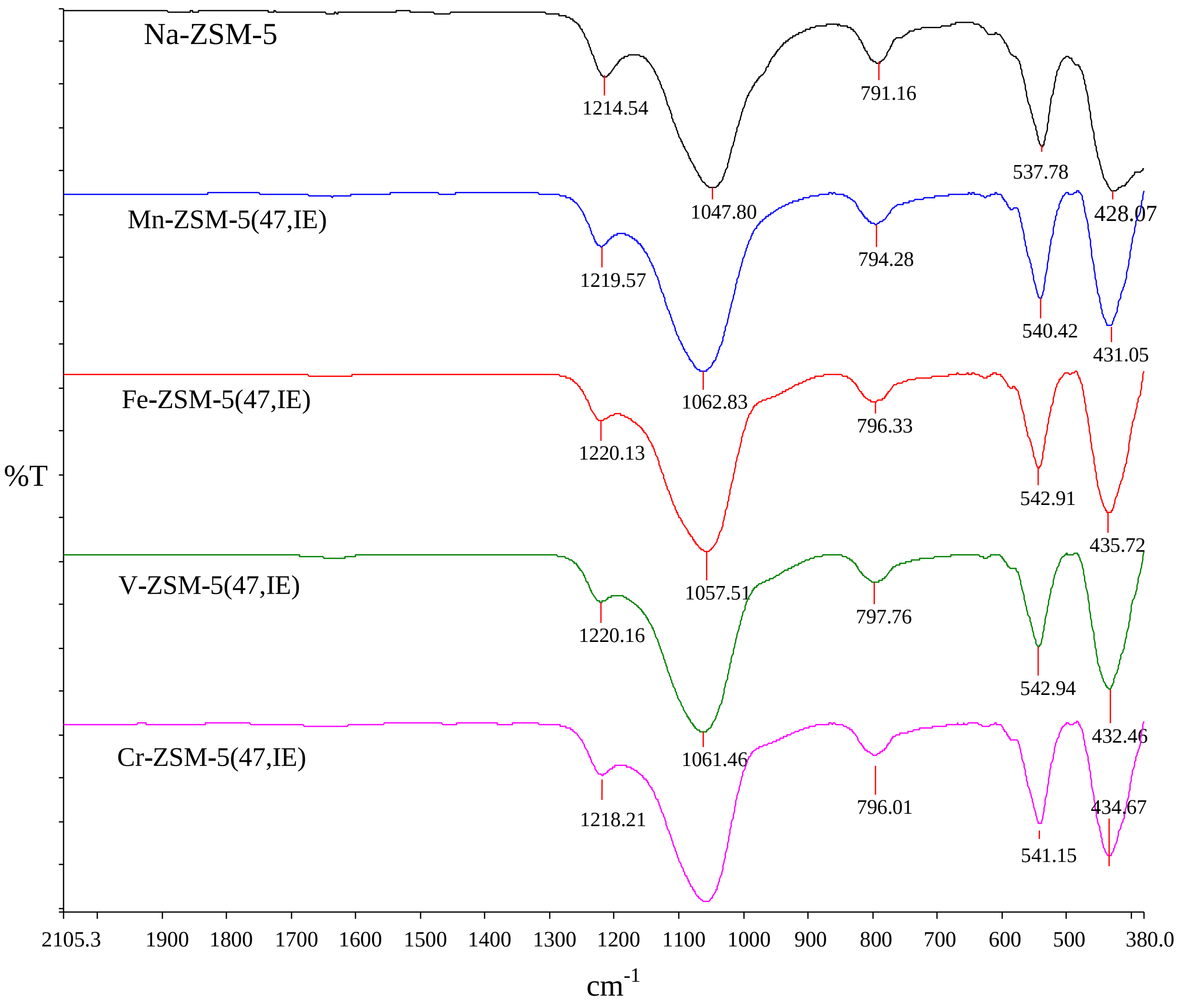

Figure 3.1: Infrared spectra of the fresh zeolite ZSM-5 and the ZSM-5 catalysts prepared by ion exchange

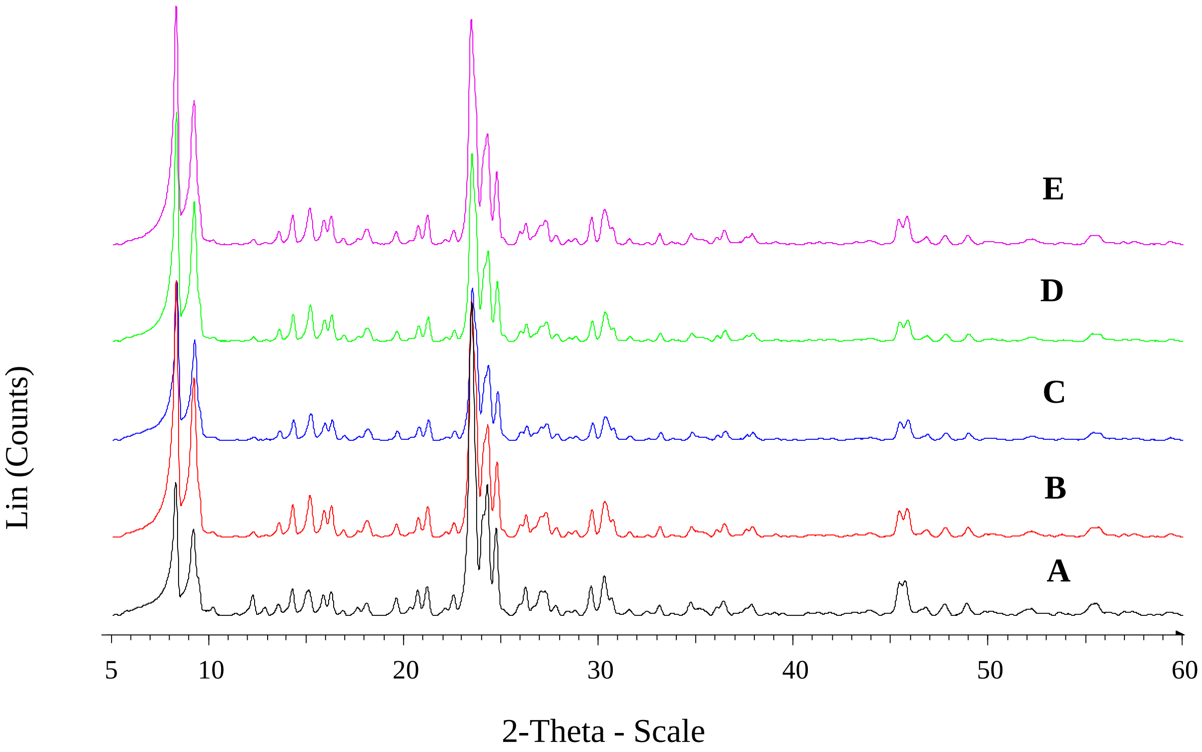

Figure 3.2: p-XRD diffractogram of (A) Na-ZSM-5, (B) Fe-ZSM-5(47,IE), (C) Mn-ZSM-5(47,IE), (D) V-ZSM-5(47,IE), (E) Cr-ZSM-5(47,IE)

Adsorption and porosity characteristics of the parent and for the ion exchanged zeolites derived from nitrogen adsorption-desorption isotherms are given in **Table 3.1**. The BET surface area differed with the metal loaded on the zeolite. The iron exchanged zeolite showed higher surface area compared to all the other catalysts.

There is no observable trend from the chemical properties of the metals that explains the different surface areas obtained for the catalysts.

Table 3.1: Surface properties and ICP results.

Catalysts	BET m^2/g	Pore Volume cm^3/g	ICP / %Wt.
Na-ZSM-5	326.7	0.18	-
Fe-ZSM-5(47,IE)	413.2	0.20	1.6
Mn-ZSM-5(47,IE)	310.8	0.18	1.7
Cr-ZSM-5(47,IE)	329.9	0.21	1.6
V-ZSM-5(47,IE)	354.1	0.19	1.7

There was a small change observed for the pore volumes of the ion-exchanged zeolites compared to the parent zeolites for all the ion exchanged zeolites. This suggests that there is no pore blocking effect of the exchanged metals. These results can also be supported by the powder XRD data which confirms the absence of other phases apart from the ZSM-5 phase [14]. Metal loading on the zeolite did not change the structure of the parent ZSM-5, this is further confirmed by the FT-IR and p-XRD data.

According to the SEM analysis (**Figure 3.3**), the synthesized ZSM-5 catalysts have similar morphology to one another. The catalysts have the MFI-typical morphology which is the lath-shape [15]. Depending on the template used to prepare the zeolite, the morphology may differ, and this is because different templates have different tendencies in filling in the channels, hence leading to different crystal growth orientation [15]. The other most common morphologies of zeolites are hexagonal-like shape and ellipsoidal shaped crystals [15]. Some spheroidal crystals are observed for the catalysts as a result of the presence of Na^+ [15].

TEM analysis also compliments the results of the SEM analysis, the images clearly show the spherical shape of the zeolite catalysts (**Figure 3.4**).

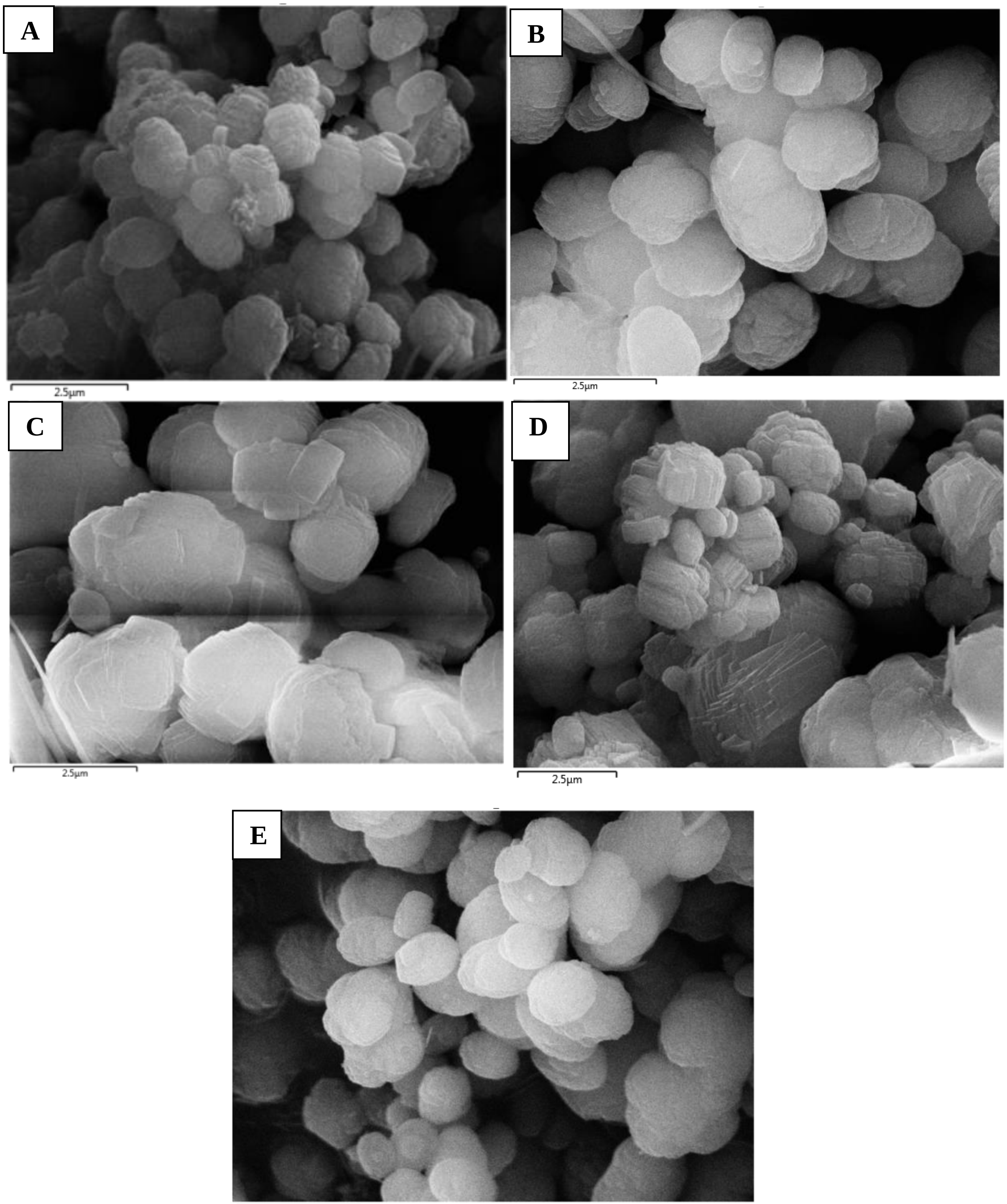

Figure 3.3: SEM images of (A) Na-ZSM-5, (B) Mn-ZSM-5(47,IE), (C) Fe-ZSM-5(47,IE), (D) V-ZSM-5(47,IE), (E) Cr-ZSZSM-5(47,IE)

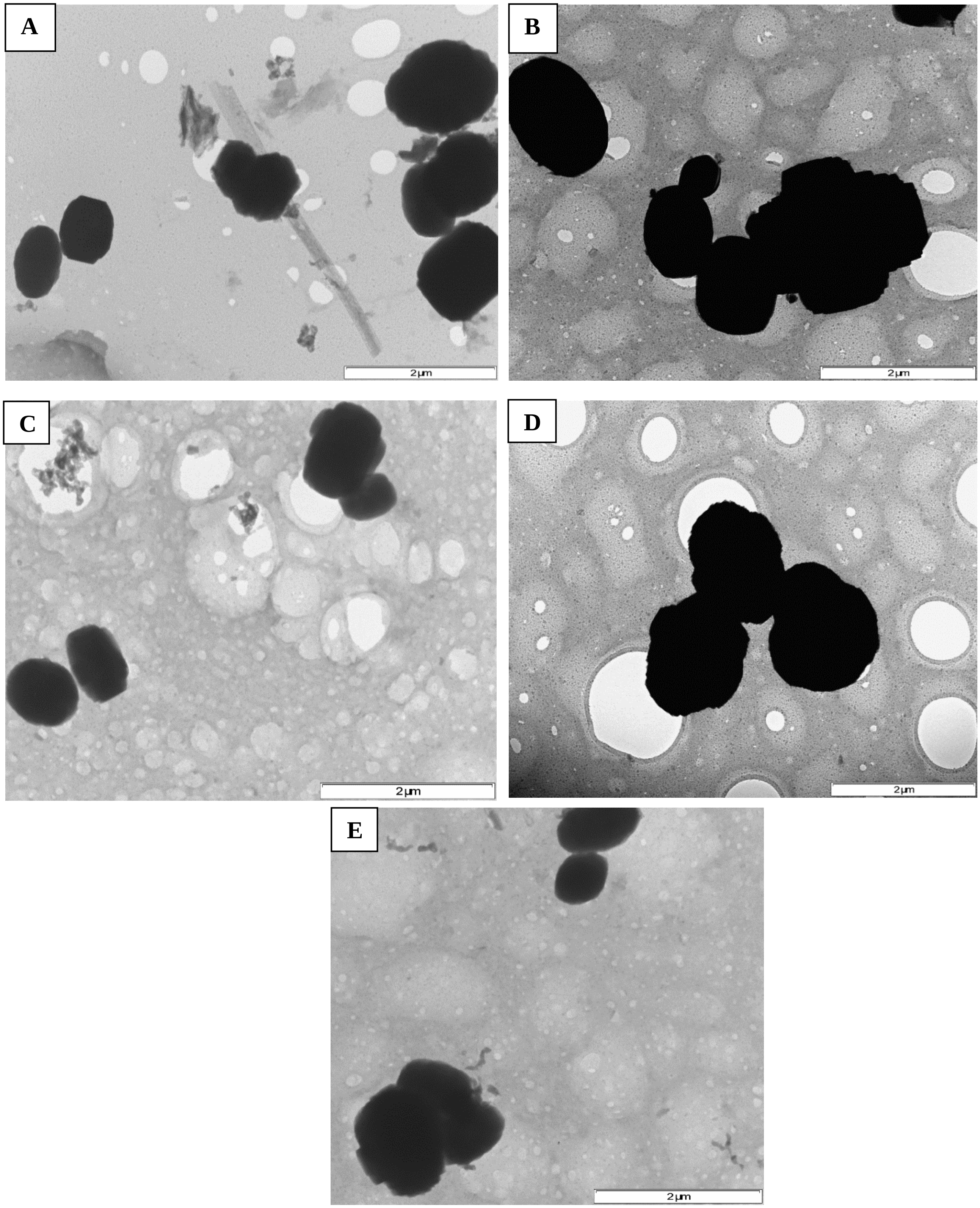

Figure 3.4: TEM images of (A) Na-ZSM-5, (B) Mn-ZSM-5(47,IE), (C) Fe-ZSM-5(47,IE), (D) V-ZSM-5(47,IE), (E) Cr-ZSZSM-5(47,IE)

3.3.2 Catalyst testing

After fully characterizing the prepared catalysts, Fe-ZSM-5(47,IE) was chosen to perform some reaction condition optimisation studies for this part of the work. This catalyst was used to carry out reactions to find the optimum oxidant (H_2O_2) ratio for the reaction. The catalyst was also used to obtain the optimum reaction time for the oxidation of *n*-octane to terminal oxygenated products. The temperature to carry out these reactions was chosen to be 80 °C because previous work has shown that this is the optimum temperature for related compounds [16-17]. Also, this is the boiling point of acetonitrile.

The data in **Figure 3.5** shows that in the presence of H_2O_2, the overall conversion of octane to the corresponding oxygenates gradually increases with time. The rate of increase in conversion is dependent to the amount of oxidant used in the reaction. When more oxidant was added to the reaction there were more products produced as a function of time. This is shown by the slopes of the graphs in **Figure 3.5**, which become steeper when more oxidant is used. It is also seen in the figure that excess oxidant does not lead to even faster rates. The slopes when 2 mL or 3 mL of oxidant are added are essentially the same. This may be due to limited active sites on the catalyst. Using 2 or 3 mL of oxidant thus gives similar conversions, and the highest conversion obtained was about 3 %. The generally low conversions may be due to the rate of diffusion of products from the ZSM-5 structure channels and pores. This is known to be a limiting factor in similar reactions [16]. The reaction mechanism using peroxide oxidants is believed to follow the radical reaction which results in the formation of radicals which then react with the organic molecule to produce alcohols, aldehyde and ketones as follows:

$$M^{3+} + H_2O_2 \longrightarrow M^{2+} + HOO^{\bullet} + H^{+}$$

$$M^{2+} + H_2O_2 \longrightarrow M^{2+} + 2OH^{\bullet}$$

$$OH^{\bullet} + R\text{-}H \longrightarrow R\text{-}OH + H^{\bullet}$$

Where M = metal

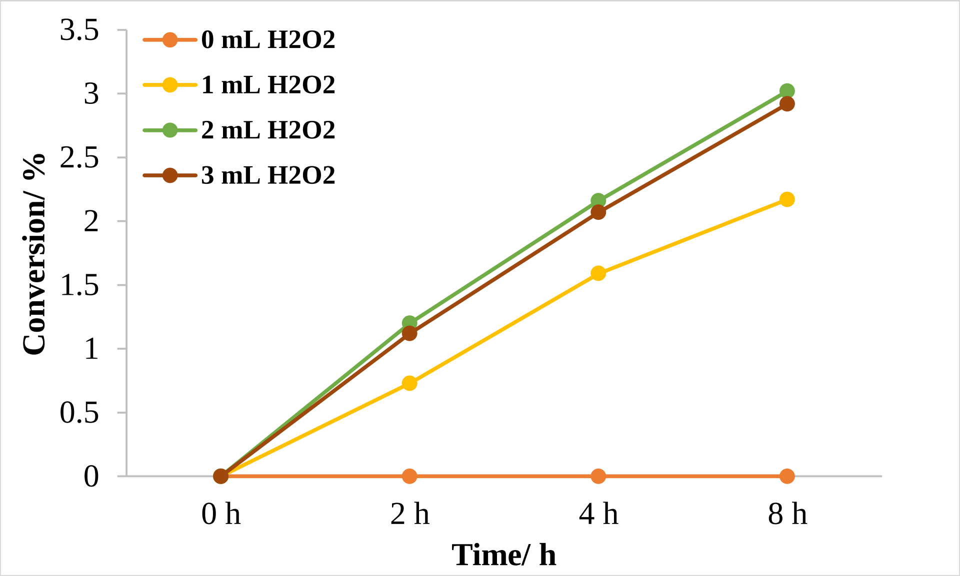

Figure 3.5: oxidation of *n*-octane to C8 oxygenates as the function of oxidant and reaction time for Fe-ZSM-5(47, IE)

Only octanols and octanones were observed as the products of the reaction. The octanol to octanone ratio changed with time for the reactions carried out. Taking the reaction where 1.0 mL oxidant was used, after the first two hours the octanol/octanones ratio was 2:1. However, after eight hours of reaction the ratio was over 3:1, and this shows that after some time the hydrogen peroxide is nearly used up and further oxidation of alcohols to ketones is less. However, when using 2 mL of oxidant the ratio after two hours is about 3:1, while after eight hours it drops to 2:1, suggesting that further oxidation of alcohol was prominent as the hydrogen peroxide was not used up. Data in **Figure 3.6** shows the selectivity to terminal oxygenates is affected by both the reaction time and amount of oxidant. The figure shows that most terminal activation takes place during the first two hours of the reaction. After that time the other sites of the alkanes oxidise more rapidly than the terminal sites of the alkane. During the first two hours, 1-octanol and octanal selectivity reached 39, 38 and 35 % for reactions carried out with 1 mL, 2 mL and 3 mL oxidant respectively. It is also seen that more oxidant leads to less terminal oxidation, because the secondary and tertiary carbons are more favoured.

Figure 3.7 shows that conversion increases with time and then after 8 h it levels off. This may be attributed to the very low desorption rate of the products from the catalyst pores [16]. The conversion after 8 h was 2.2 % and after 12 h, it did not effectively show any change, as the conversion was determined as 2.3 %.

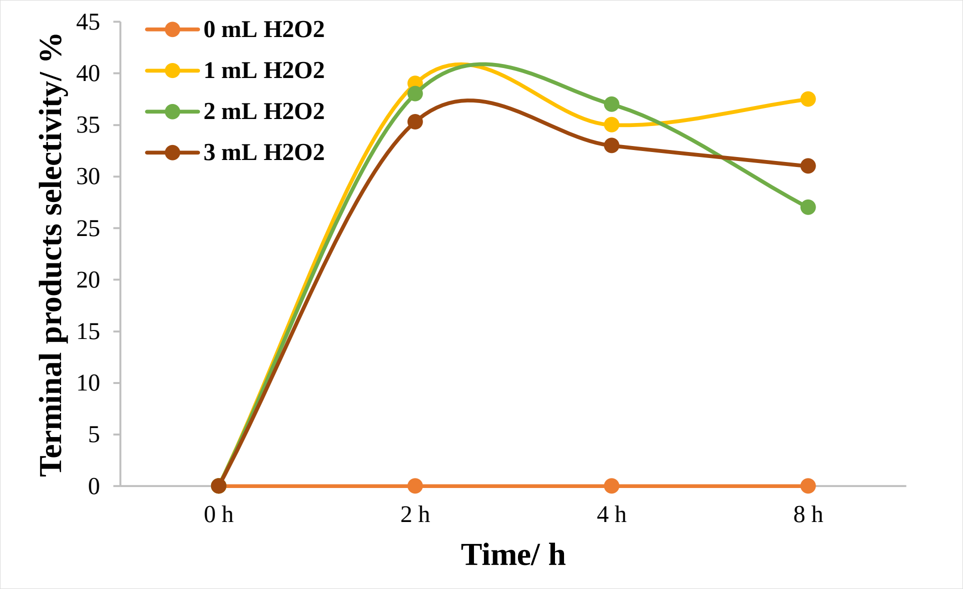

Figure 3.6: Terminal selectivity of *n*-octane oxidation as the function of time using different amounts of oxidant for Fe-ZSM-5(47, IE)

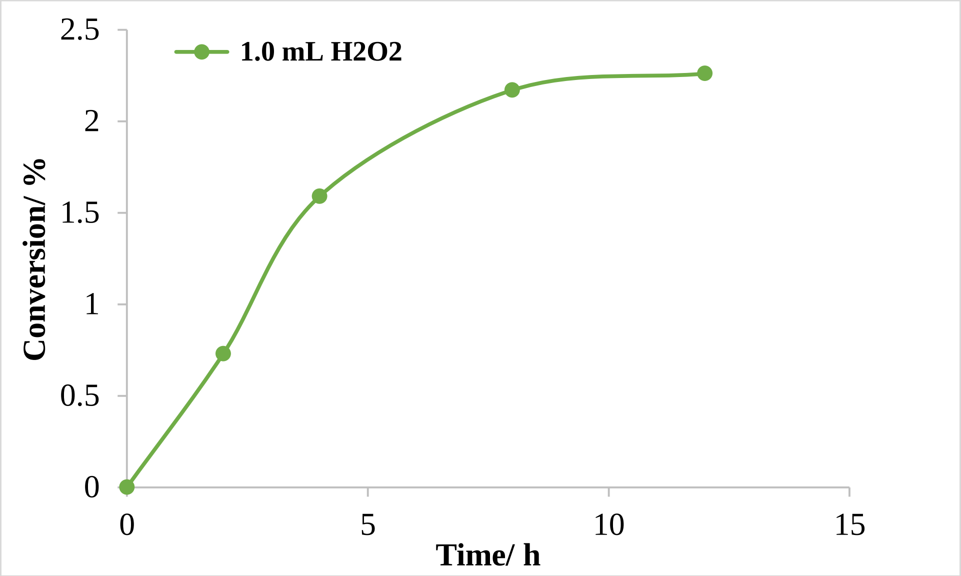

Figure 3.7: oxidation of *n*-octane to C8 oxygenates as the function of reaction time for Fe-ZSM-5(47, IE)

Thus, the conversion was found to be stationery after 8 hours of reaction. Therefore, the combination of 8 hours reaction time and 1 mL oxidant at 80 °C was used to carry out further tests to establish the scope of the catalytic process for the Fe-ZSM-5(47,IE), V-ZSM-5(47,IE), Cr-ZSM-5(47,IE) and Mn-ZSM-5(47,IE) catalysts. The conversion and selectivities of the catalysts were compared as shown in **Figure 3.8**. It was observed that Fe-ZSM-5(47,IE) showed better selectivity (37 %) to terminal products compared to the other three catalysts at a conversion of 2.2 %. The Cr-ZSM-5(47,IE), V-ZSM-5(47,IE) and Mn-ZSM-5(47,IE) showed 10, 12 and 6 % selectivity to terminal products at conversions of 5.1, 6.6 and 3.3 % respectively.

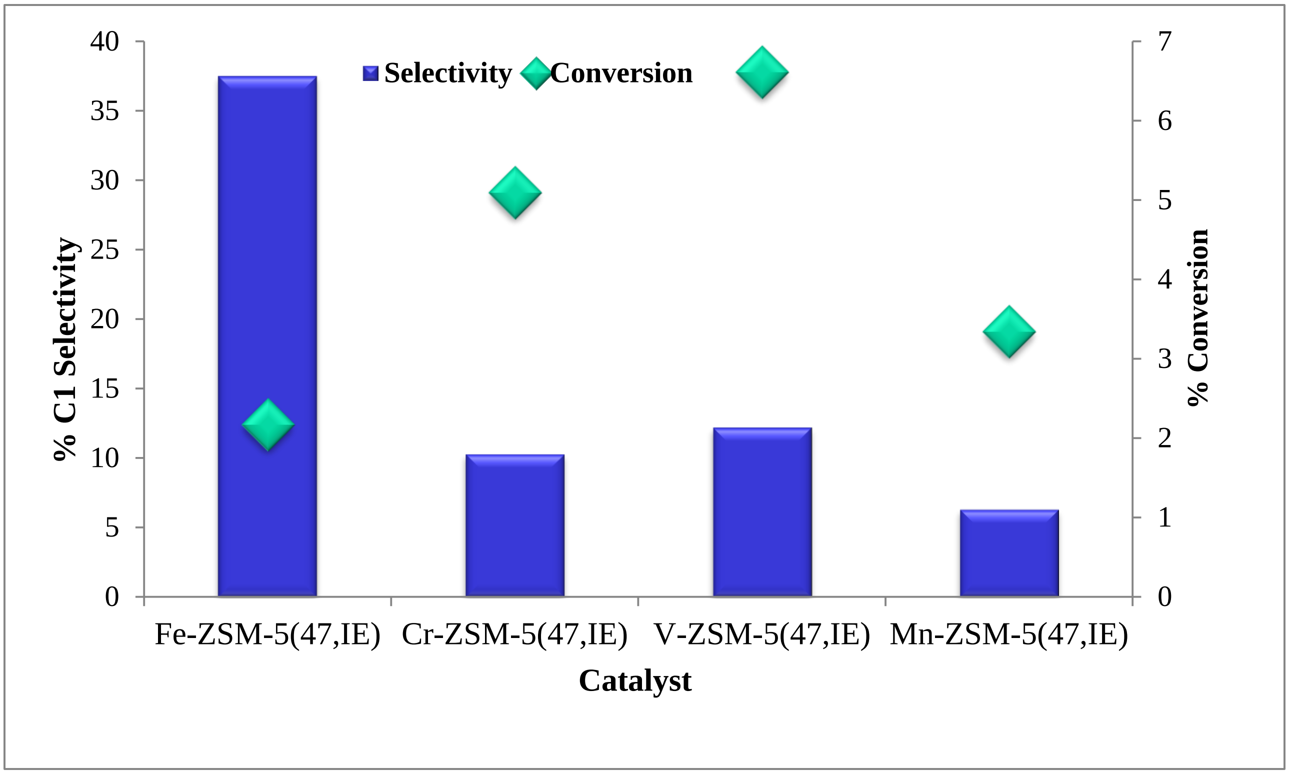

Figure 3.8: Catalytic results of *n*-octane oxidation over different ZSM-5 catalysts

Figure 3.9 shows the reaction products distribution over the tested catalysts. Nearly all the catalysts show a similar trend of products, with higher selectivities to over oxidation products. Fe-ZSM-5 was the only exception to this trend, where alcohols were more dominant than ketones. This means that the Fe-ZSM-5(47,IE) catalyst inhibits the overoxidation of the primary products. This may be attributed to the low activity possesed by Fe-ZSM-5(47,IE). No cracking products were observed for any catalysts under any of the conditions employed [16].

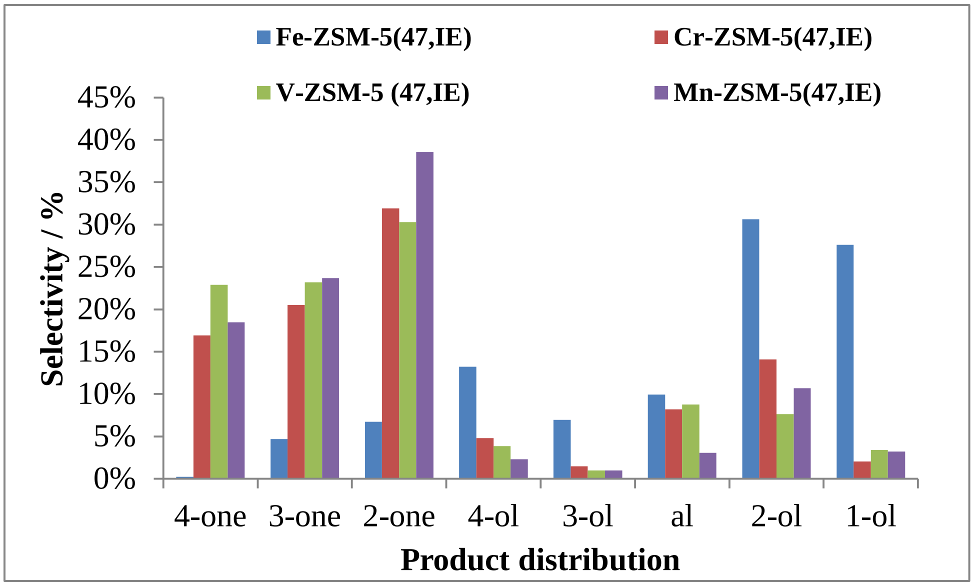

Figure 3.9: Product distribution of *n*-octane oxidation over different ZSM-5 catalysts

Based on these results, Fe-ZSM-5(47,IE) and V-ZSM-5(47,IE) were chosen as the catalysts to use as a basis for preparing bimetallic catalysts, since Fe in ZSM-5 showed good selectivity to desired products (terminal oxygenates), while V in ZSM-5 gave higher conversion. It has hoped that combining the two metals (Fe and V) in one system may give good selectivity at improved conversion.

The catalyst Fe-ZSM-5(47,IE) was used to carry out catalyst stability tests at the optimum temperature of 80 °C. Three cycles were carried out using the same catalyst. No change in ZSM-5 structure was observed for the used catalyst as confirmed by XRD, FT-IR and SEM analysis (Appendix). It was observed that the catalyst maintained constant conversion of about 2 % with no noticable change in product distribution, implying that the ZSM-5 catalyst is efficiently recyclable (Appendix).

3.4. Conclusions

Analysis of the catalysts by *p*-XRD and FT-IR showed that there were no additional phases other than ZSM-5. Also, the optical density ratio obtained proved that the zeolites were crystalline. Introduction of transition metals to the Na-ZSM-5 by ionic exchange does not alter the overall structure of the zeolite. The oxidation of *n*-octane to their corresponding oxygenates increased as a function of time until eight hours, after which it starts to levels off. When different oxidant amounts were used, the conversion correlated to the amount of oxidant used, up to a conversion of about 3 %. Using more oxidant lead to over oxidation of primary products (alcohols) to secondary products (ketones), hence the reaction with 1.0 mL oxidant showed a ratio of more than 3:1 to alcohols/ ketones while using more oxidant gave a ratio of 2:1. Furthermore, using 1 mL of oxidant gave higher selectivity towards 1-octanol and octanal.

Reactions carried out using the Fe-ZSM-5(47,IE) catalyst gave a conversion of 2.2 %, with selectivity to terminal oxygenates of 37 %, which was higher than those of the other three catalysts used for the same reaction under the same conditions. The vanadium catalyst gave a conversion of 6.6 %. The Fe-ZSM-5 catalyst prepared was stable under optimum reaction conditions and was used for three cycles without losing any of its activity.

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Chapter Four

Preparation of the bimetallic zeolite catalysts for the oxidation of *n*-octane to terminal oxygenates

4.1. Introduction

Different metals have different catalytic properties. Some metals are not active for certain catalytic processes when they are not supported by other metals, and some work well individually and get retarded when they are mixed with other metals in the same catalytic reaction. However, it is generally true that most metals can enhance catalysts in one or two ways. Metals either enhance a catalyst to be highly selective with low conversion, or a highly active catalyst (gives good conversion but with poor selectivity) [1]. To tackle this challenge, chemists and engineers have investigated ways to using more than one metal per catalyst to try and improve the skewed catalytic performance.

For the purpose of this work, the focus was on previous work that was carried out using zeolites, more especially ZSM-5, since this is a good basis for this work, which also deals with ZSM-5 type zeolite catalysts. However, it should be mentioned that lot of work has been reported using non-zeolite bimetallic catalysts for the oxidation of different substrates.

From the work reported by Jodaei et al. [2], H-ZSM-5 based bimetallic catalysts were used to oxidize ethyl acetate. For this work, Ag was used as the primary metal of the catalysts and three other transition metals were used in order to promote the catalytic activity. The catalysts were prepared by ion exchange and the metals employed were Fe, Mn and Co. The results of the reactions showed that the activity of the bimetallic system was higher than that of the individual components. The activities of the catalysts with respect to transition metals were observed to follow the sequence: Fe > Co > Mn [2].

Forde et al. reported work on the oxidation of methane using a Cu-Fe-ZSM-5 catalyst prepared by chemical vapour decomposition. For this work hydrogen peroxide was employed as the oxidant. The results of the work showed that when Fe-ZSM-5 was used as a catalyst, an activity of 15.8 mol product kg (cat) $^{-1}$ h^{-1} could be achieved and when a bimetallic catalyst was employed, activity of 11.4 mol product kg (cat) $^{-1}$ h^{-1} was obtained. The work also showed that upon the introduction of the second metal, such as Cu, the selectivity of alcohol increases, while that of formic acid decreases. The selectivity to methanol was 12 and 78 mol% when Fe-ZSM-5 and Cu-Fe-ZSM-5 were used respectively [1].

No previous work was found reporting the oxidation of *n*-octane to oxygenates for bimetallic ZSM-5 zeolites and silicalites. Most previous work reported on the use of bimetallic ZSM-5 zeolites and silicalites focuses on dehydrogenation reactions and also on the oxidation of volatile organic compounds (VOCs) and the reduction of NOx [3-9].

The the aim of this work was to explore the oxidation of *n*-octane using ZSM-5 bimetallic systems prepared from vanadium and iron. This work continues from the work discussed in the previous chapter, and it is looking at integrating the two metals in one catalyst in the hope that they will synergistically work together to give a catalyst that is more active with good selectivity towards terminal oxygenates.

For this part of the work, a total of eight catalysts were prepared and tested to see the effect of adding vanadium into Fe-ZSM-5 with a Si/Al ratio of 46 and Fe-Silicalite catalysts in the oxidation of n-octane. For both the ZSM-5 and the silicalite, different ratios of Fe and V were used to study any effect. The intention was to discover if the introduction of vanadium to the Fe based zeolite catalysts will have any effect on the conversion and selectivity of the reaction. The catalysts prepared for this part of the work were 1.6Fe-ZSM-5(IE), 1.7V-ZSM-5(IE), 1.1Fe0.8V-ZSM-5(IE), 0.4Fe1.2V-ZSM-5(IE), 1.6Fe-Silicalite, 1.8V-Silicalite, 0.9Fe0.8V-Silicalite, and 0.3Fe1.3V-Silicalite. The numbers in the catalyst name correspond to the metal weight percent in the catalyst, IE refers to ion exchange.

4.2. Experimental

4.2.1. Catalyst synthesis and characterisation

The 1.6Fe-ZSM-5(IE) and 1.7V-ZSM-5(IE) catalysts were prepared as previously described in Section **2.2.2**. The 1.1Fe0.8V-ZSM-5(IE) and 0.4Fe1.2V-ZSM-5(IE) catalysts were prepared as described in Section **2.2.4** and the silicalite catalysts preparation method is described in Section **2.2.5**. Catalysts characterization is described in Section **2.3**.

4.2.2 Catalyst testing

As reported in the previous chapter, the reactions were carried out under nitrogen atmosphere. Due to the low activities shown by the silicalite catalysts, the testing conditions were modified. Thus 18 mL of acetonitrile was added into a two-neck round bottom flask (50 mL) fitted with a stopper and a condenser. This was followed by the consecutive addition of 1.8 mmol of *n*-octane, 0.25 g catalyst and 16 mmol of H_2O_2 (30 wt% in water). The reaction temperature and time were kept constant at 80 °C and 8 hours respectively. The products of the reaction were analysed by a Perkin Elmer Auto System GC equipped with a Flame Ionisation Detector using a Pona 50 x 0.20 mm x 0.5 µm column. The internal standard was kept as chlorobenzene.

4.3. Results and Discussion

4.3.1 Catalyst characterisation

Figure 4.1 and **Figure 4.2** show the FT-IR spectra of the two different systems of catalysts prepared. **Figure 4.1** shows the spectra of the ZSM-5 zeolite catalysts and the **Figure 4.2** shows the silicalite catalysts' spectra. Both the catalysts belong to the MFI family of porous solids. The difference in the two types of materials is in the synthesis method. In the synthesis of the ZSM-5 catalysts, aluminium is included as one of the framework constituents, while for the silicalite, there is no aluminium in the framework, but instead there is the metal of interest.

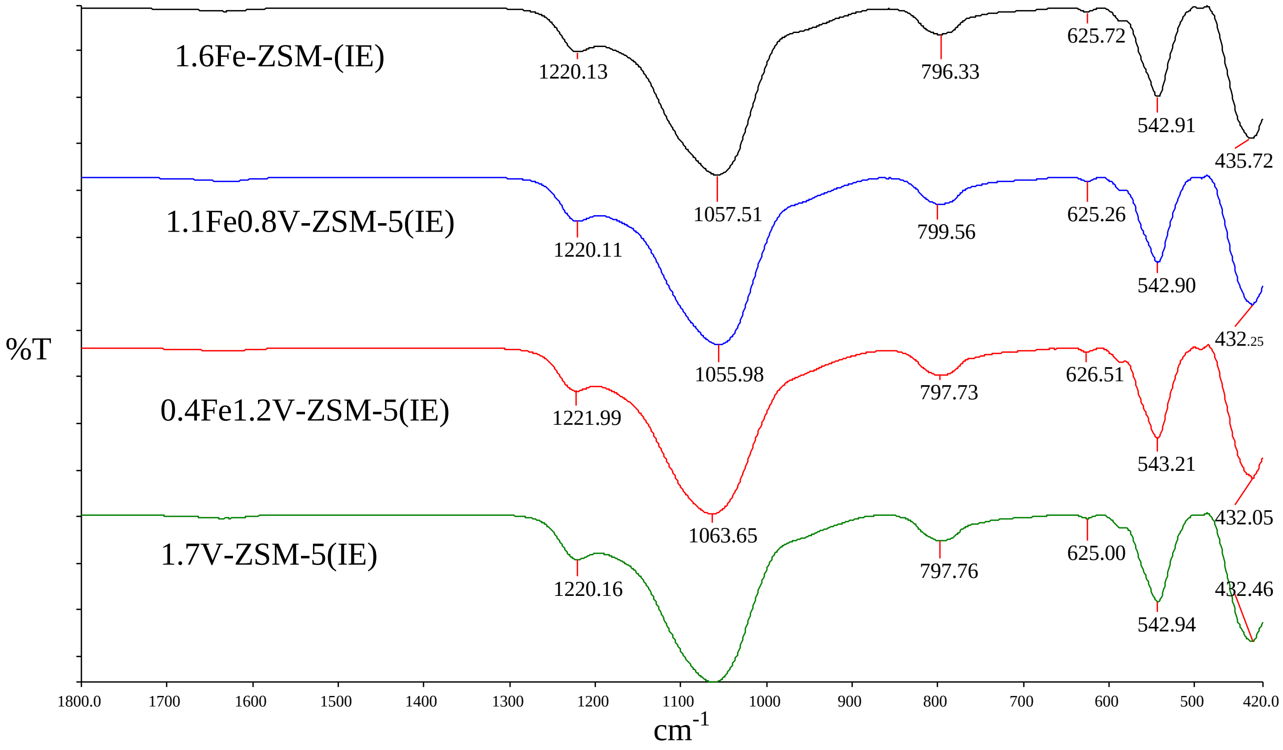

Figure 4.1: Infrared spectra of the mono/bimetallic ZSM-5 catalysts prepared by ion exchange

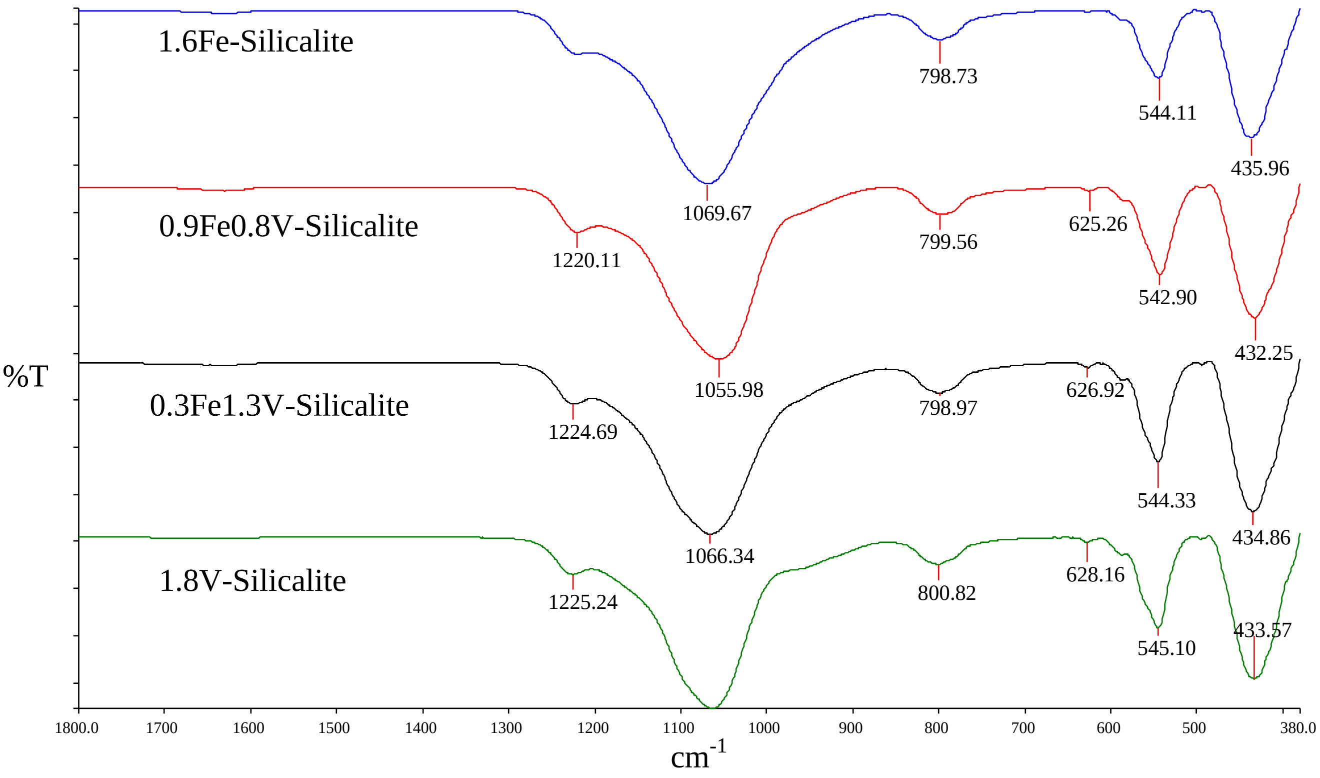

Figure 4.2: Infrared spectra of the mono/bimetallic silicalite catalysts prepared by ion exchange

The two types of catalysts show the same FT-IR absorption bands, proving that they belong to the same MFI family. Absorptions for Si and AlO_4/MO_4 tetrahedra internal (where M = metal) and external symmetric vibrations are found at around 1060, 790 and 430 cm^{-1}. The bands at around 650-540 cm^{-1} are assigned to the double rings of tetrahedra in the framework. The external asymmetrical stretching vibration of SiO_2 is always shown by a strong band around 1220 cm^{-1}. This is the band that confirms the ZSM-5 structure with 3D channel morphology [10-14]. The purity and crystallinity of the prepared catalysts was confirmed by the optical density ratios which agree with the literature [10]. All the catalysts show a value greater than 0.7 for the optical density ratio [10].

The p-XRD patterns of the two sets of catalysts (**Figure 4.3 and Figure 4.4**) are similar, showing the true fingerprint of the MFI material. The intensity of the peaks agrees with the FT-IR results, showing the crystalline nature of the catalysts. Importantly, for the Fe based catalysts, no haematite phase lines are observed at 38.7 and 41.6° 2θ [15, 16].

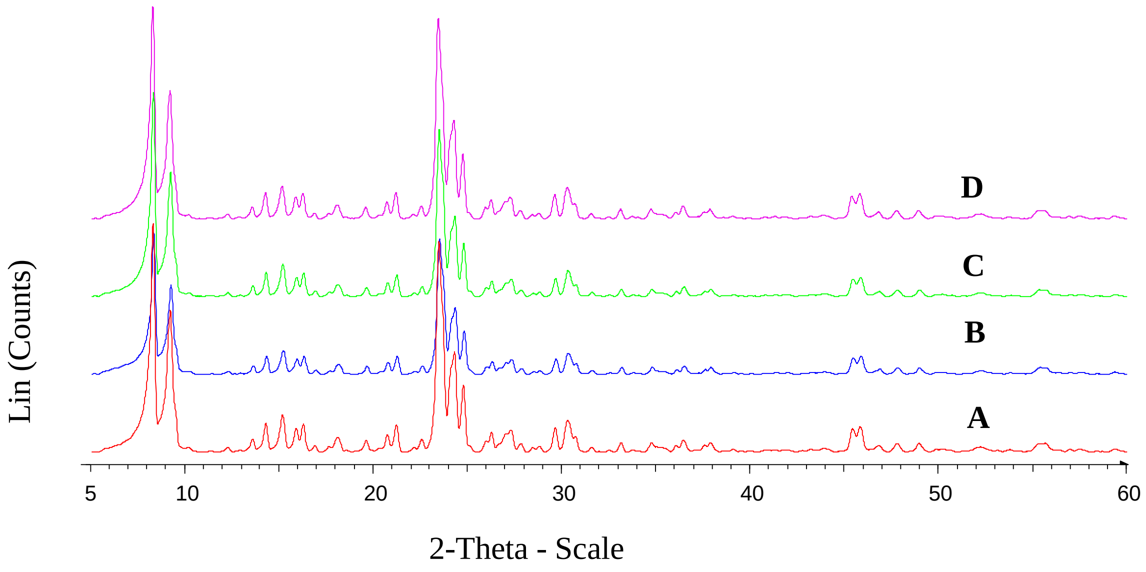

Figure 4.3: p-XRD diffractogram of (A) 1.6Fe-ZSM-5(IE), (B) 1.1Fe0.8V-ZSM-5(IE), (C) 0.4Fe1.2V-ZSM-5(IE), (D) 1.7V-ZSM-5(IE)

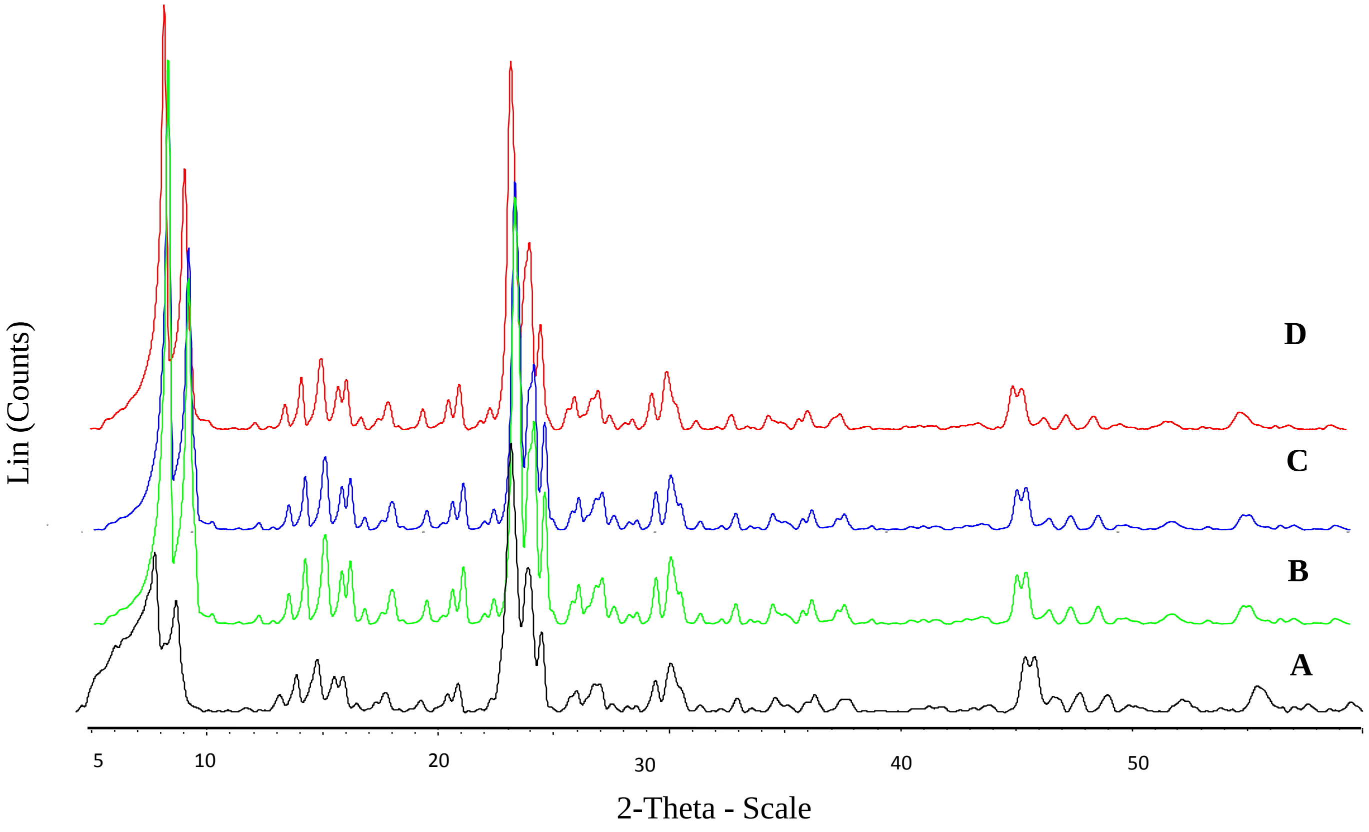

Figure 4.4: p-XRD diffractogram of (A) 1.6Fe-Silicalite, (B) 0.9Fe0.8V-Silicalite, (C) 0.3Fe1.3V-Silicalite, (D) 1.8V-Silicalite

The FT-IR and the p-XRD results clearly show that incorporation of the metal into the frame work of the zeolite does not alter the overall structure of the zeolite material. This is true for both the silicalite and the ZSM-5 zeolite. What makes these results even more interesting is that the two types of catalysts (silicalite and ZSM-5) have the active metals situated differently with respect to the frame-work of the material, because of the different synthesis procedures. Therefore this shows that the structure of the zeolite is retained whether the metal is within the framework or in an extra-framework position of the zeolite.

Table 4.1 shows the BET surface area measurements and the micropore volumes, and the ICP-OES results of all the prepared catalysts. For all the catalysts, the targeted weight percent loading of the metals was two percent. The ICP results show the exact percentage of metal that was successfully loaded into the catalyst.

Table 4.1: Surface properties and ICP results of the ZSM-5 and silicalites catalysts.

Catalysts	BET (m^2/g)	Pore Volume (cm^3/g)	Pore Size (nm)	ICP (wt%.)
1.6-Fe-ZSM-5(IE)	413.2	0.20	20.9	1.6
1.1Fe0.8V-ZSM-5(IE)	379.9	0.21	22.0	1.1 Fe, 0.8 V
0.4Fe1.2V-ZSM-5(IE)	363.7	0.21	22.7	0.4 Fe, 1.2 V
1.7V-ZSM-5(IE)	354.1	0.19	21.2	1.7

Catalysts	BET (m^2/g)	Pore Volume (cm^3/g)	Pore Size (nm)	ICP (wt%.)
1.6Fe-Silicalite	391.8	0.11	24.0	1.6
0.9Fe0.8V-Silicalite	383.2	0.20	21.2	0.9 Fe, 0.8 V
0.3Fe1.3V-Silicalite	390.9	0.21	21.5	0.3 Fe, 1.3 V
1.8V-Silicalite	344.5	0.19	22.2	1.8

The lowest metal loading was 1.6 % on 0.4Fe1.2V-ZSM-5(IE) and the highest loading was 1.9 % on the 1.1Fe0.8V-ZSM-5(IE) catalyst. For the ZSM-5 catalysts, the surface area seemed to decrease with increasing the amount of vanadium in the extra-framework region of the zeolite. The decrease in the surface area of the catalysts may be due to vanadium dispersed on the outer surface of the zeolite [17]. The constant pore volumes for all the catalysts confirm that no major pore blockage took place from the introduction of vanadium to the Fe-ZSM-5 catalyst. These results are further supported by the *p*-XRD results which showed that only the MFI phase was obtained during the synthesis and modification of the catalysts.

Table 4.1 also shows the BET surface area measurement and the micropore volumes for the silicalites catalysts. The surface area of the catalysts did not show a constant trend with the metal loaded, but again the catalyst with the lowest surface area was the 1.8V-Silicalite. The pore volumes of the three catalysts with vanadium loading were similar to one another, while the pore volume for Fe-Silicalite was very low compared to the other three catalysts. The decrease in the pore volume of the Fe-Silicalite may be due to possible pore reaction resulting from the size of the atomic radii of iron which is relatively higher than that of vanadium. This may be possible since the metal is in the framework of the catalyst in this case.

From the SEM analysis (**Figure 4.5**) of the different sets of catalysts, it is clear that all catalysts have similar shapes. The Zeolite ZSM-5 catalysts have a more lath-like shape than the silicalite catalysts. This could be attributed to the different crystallinities that the catalysts have. According to Sang et al., a high Si/Al ratio improves crystallinity of the catalysts [18]. Hence, the silicalites with the higher Si/M ratio will have higher crystallinity as well as less lath-like shape. The overall shape of all the catalysts is the same and that is of the typical MFI material (hexagonal). Another factor that can explain the difference in crystallinity is that for low silica zeolite samples, the crystallisation time in the reactor was 36 hours and for the high silica zeolite samples it was 48 to 60 hours. The difference in times was because, as the molar ratio of SiO_2/Al_2O_3 increases, the induction period becomes longer. The presence of Na^+ gives rise to the spheroidal crystals observed in the catalysts images [18].

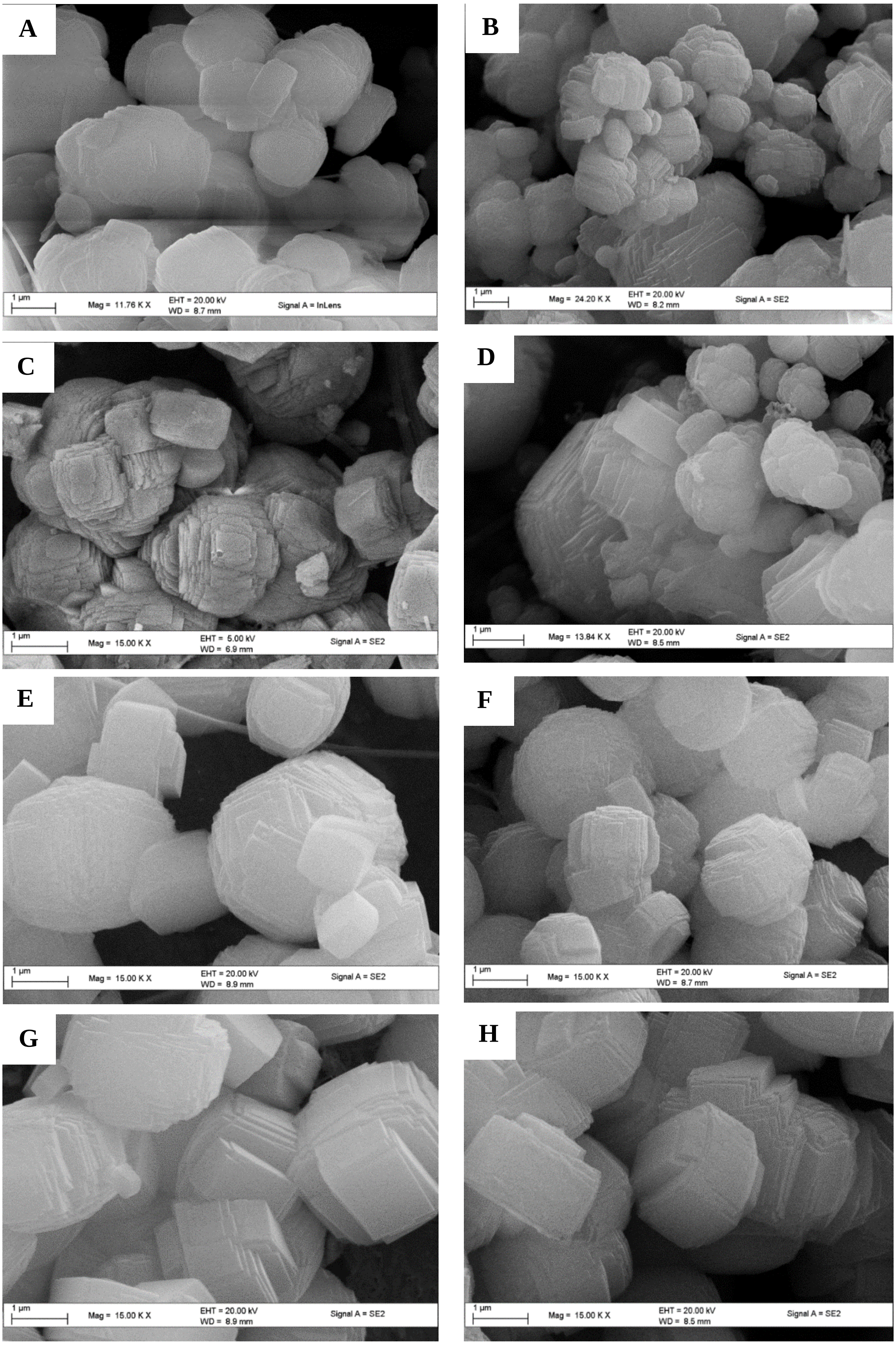

Figure 4.5: SEM images of (A) 1.6Fe-ZSM-5(IE), (B) 1.1Fe0.8V-ZSM-5(IE), (C) 0.4Fe1.2V-ZSM-5(IE), (D) 1.7V-ZSM-5(IE), (E) 1.6Fe-Silicalite, (F) 0.9Fe0.8V-Silicalite, (G) 0.3Fe1.3V-Silicalite, (H) 1.8V-Silicalite

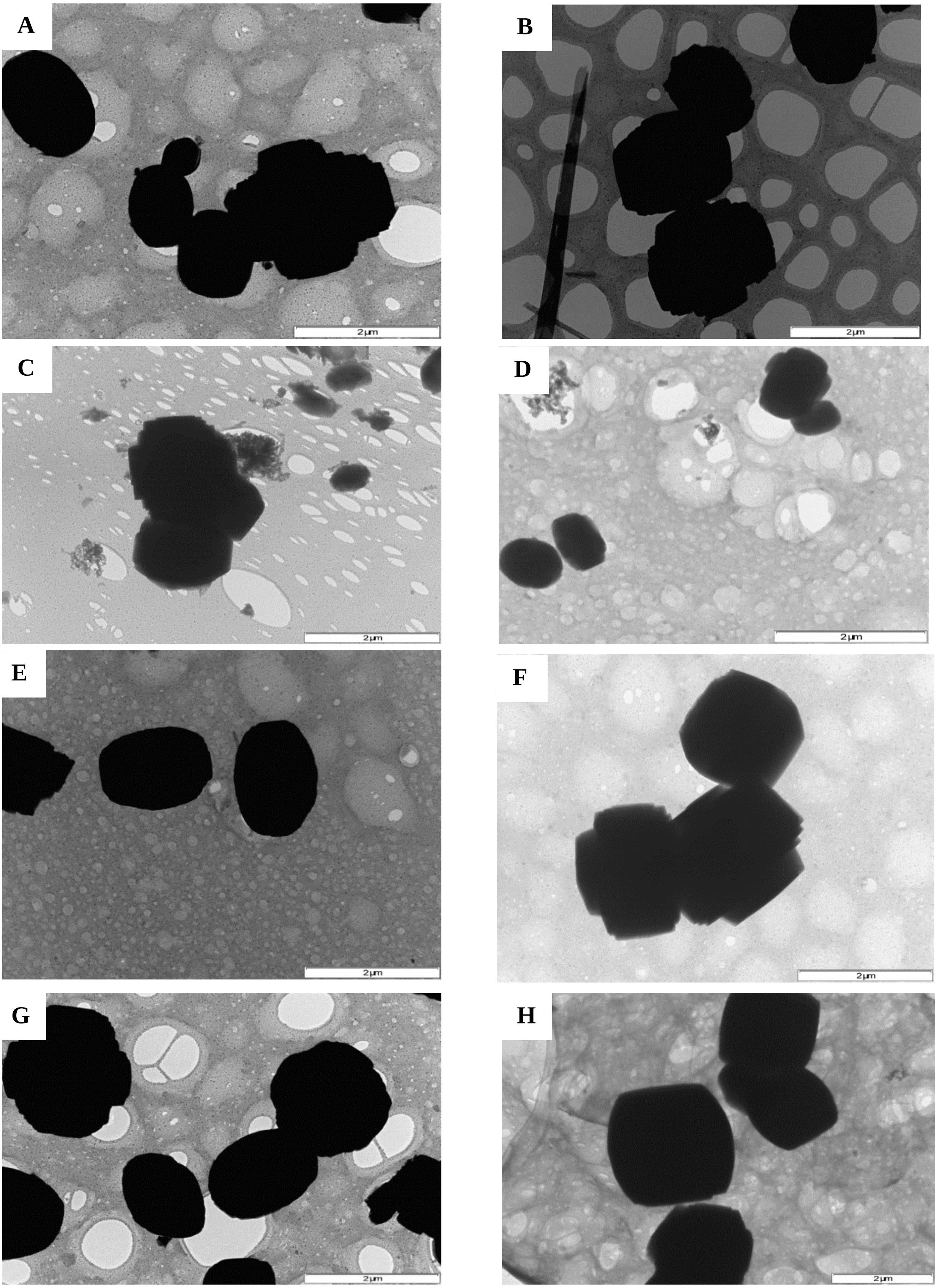

Figure 4.6: TEM images of (A) 1.6Fe-ZSM-5(IE), (B) 1.1Fe0.8V-ZSM-5(IE), (C) 0.4Fe1.2V-ZSM-5(IE), (D) 1.7V-ZSM-5(IE), (E) 1.6Fe-Silicalite, (F) 0.9Fe0.8V-Silicalite, (G) 0.3Fe1.3V-Silicalite, (H) 1.8V-Silicalite

The TEM analysis (**Figure 4.6)** was also carried out to confirm the SEM results, which shows the hexagonal shapes of the MFI material for all the catalysts.

4.3.2 Catalyst testing

After characterization, the catalysts were all tested under the conditions cited in Section 4.2.2. The results in **Figure 4.7** show how the introduction of vanadium as the second metal to Fe-ZSM-5 influences the conversion as well as the selectivity to terminal oxygenated products (1-octanol and octanal). It is clear from the figure that introduction of vanadium to the Fe-ZSM-5 catalyst via wet ion exchange enhanced the conversion, while the terminal selectivity is reduced. In the monometallic Fe-ZSM-5, the conversion was about 1.8 % and the terminal selectivity was about 31 %. Upon the introduction of vanadium, the conversion and selectivity changes to about 3 % and 21 % respectively for 1.1Fe0.8V-ZSM-5(IE). The conversion further improved when vanadium loading increased to 1.5 wt% and iron loading decreased to 0.5 wt%. The monometallic V-ZSM-5 showed a very poor terminal selectivity but relatively high conversion.

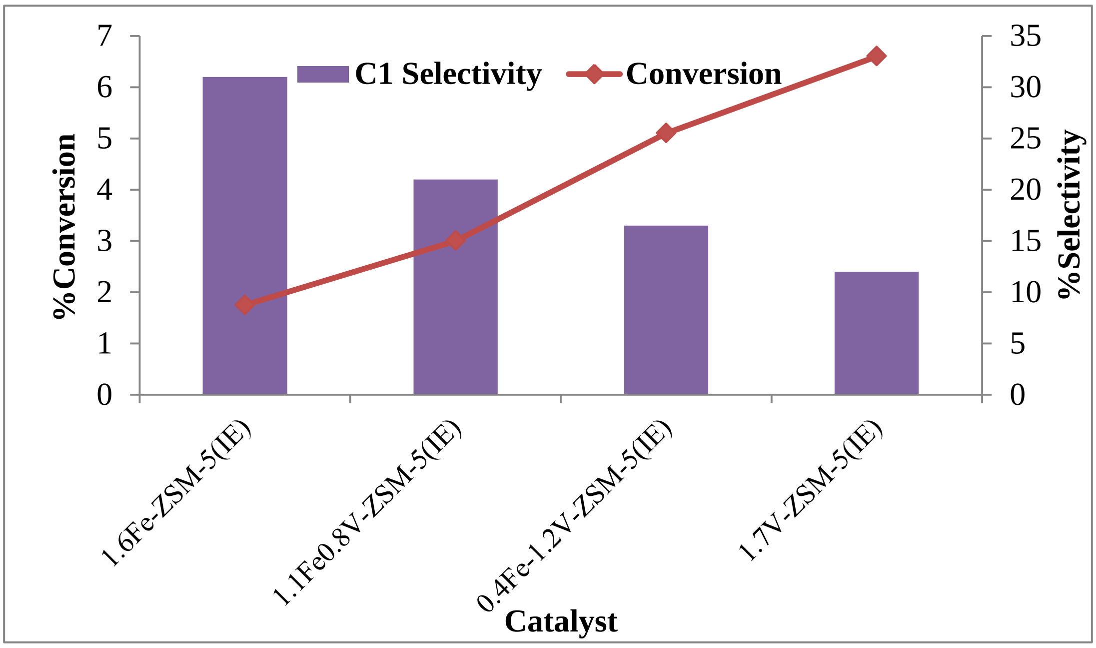

Figure 4.7: Catalytic results of *n*-octane oxidation over different ZSM-5 catalysts

Due to the introduction of vanadium, a significant change in octanone(s)/octanol(s) ratio was observed, with higher amounts of octanones observed at the higher vanadium concentrations used and, hence, higher conversions as shown in **Table 4.2**, for all the catalysts.

Table 4.2: Selectivity to terminal products, conversion and octanone(s)/octanol(s) ratio.

Catalysts	Selectivity (%)	Conversion (%)	octanone(s)/octanol(s) ratio
1.6Fe-ZSM-5(IE)	31	1.75	0.9
1.1Fe0.8V-ZSM-5(IE)	21	3.00	1.4
0.4Fe1.2V-ZSM-5(IE)	17	5.10	3.0
1.7V-ZSM-5(IE)	12	6.60	5.7

Rection conditions: catalyst = 0.25 g, octane/H_2O_2 = 8.9 (molar ratio),
acetonitrile (18 ml), reaction time = 8 hours at 80 °C
Octanones(s) = octanone(s) + octanal

The trend in terms of selectivity for the above discussed catalysts still holds even when the iso-conversion reactions were carried out (**Figure 4.8**).

To achieve iso-thermal iso-conversion, the reactions were carried out under similar conditions as cited in Section **4.2.2**, only the reaction times were varied between the catalysts and the results are shown in **Figure 4.8**. The high terminal selectivity shown by the presence of Fe in the catalysts may be as the results of the size of the iron compared to vanadium. The high surface area of the catalyst also means that this could result in having the *n*-octane approaching the active site with the primary carbon and, hence, the activation of primary carbon is favored. Also the Fe may occupy sites favourable to primary oxidation, while the vanadium counter ions are accessible to the secondary carbon atoms of *n*-octane.

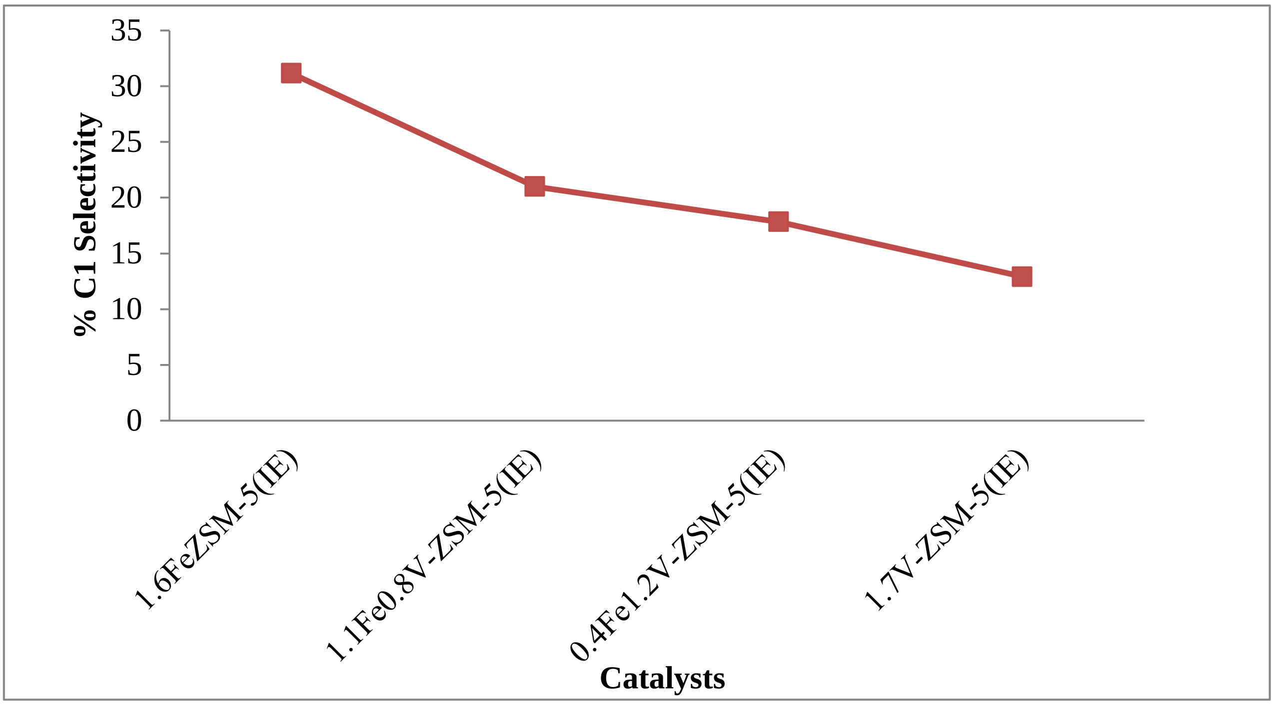

Figure 4.8: Selectivity to C-1 product over different ZSM-5 catalysts at iso-conversion of 2.7 %

When comparing the catalytic results for the zeolites in **Figure 4.7**, with the results for the silicalites in **Figure 4.9**, the results proved to be completely different from one another. Both the sets of catalysts (**Figure 4.7 and 4.9**) were tested under similar conditions and quantified by the same procedure. For the silicalite catalysts, there was no constant relationship observed between the introduction of the vanadium to Fe-silicalite and the terminal selectivity, except that the monometallic catalysts showed better terminal selectivity compared to the bimetallic silicalites. The 1.6Fe-silicalite showed terminal selectivity of 17 % and then the selectivity dropped for the two bimetallic catalysts. The 1.8V-silicalite gave the highest terminal selectivity of 21 %.

The irregularities in the selectivity of the catalysts may suggest that the two metals in the bimetallic catalysts (0.9Fe0.8V-silicalite and 0.3Fe1.3V-silicalite) are working individually and there is no synergy between the two metals. The conversion between the catalysts also showed that there is little synergy between vanadium and iron in the silicalite catalysts. 1.6Fe-silicalite gave the highest conversion of 2.9 %, and decreasing the iron content in the catalysts and introducing vanadium lowered the conversion of the reaction. 0.3Fe1.3V-silicalite and 1.8V-silicalite gave the lowest conversion of about 1.5 ± 0.1 %.

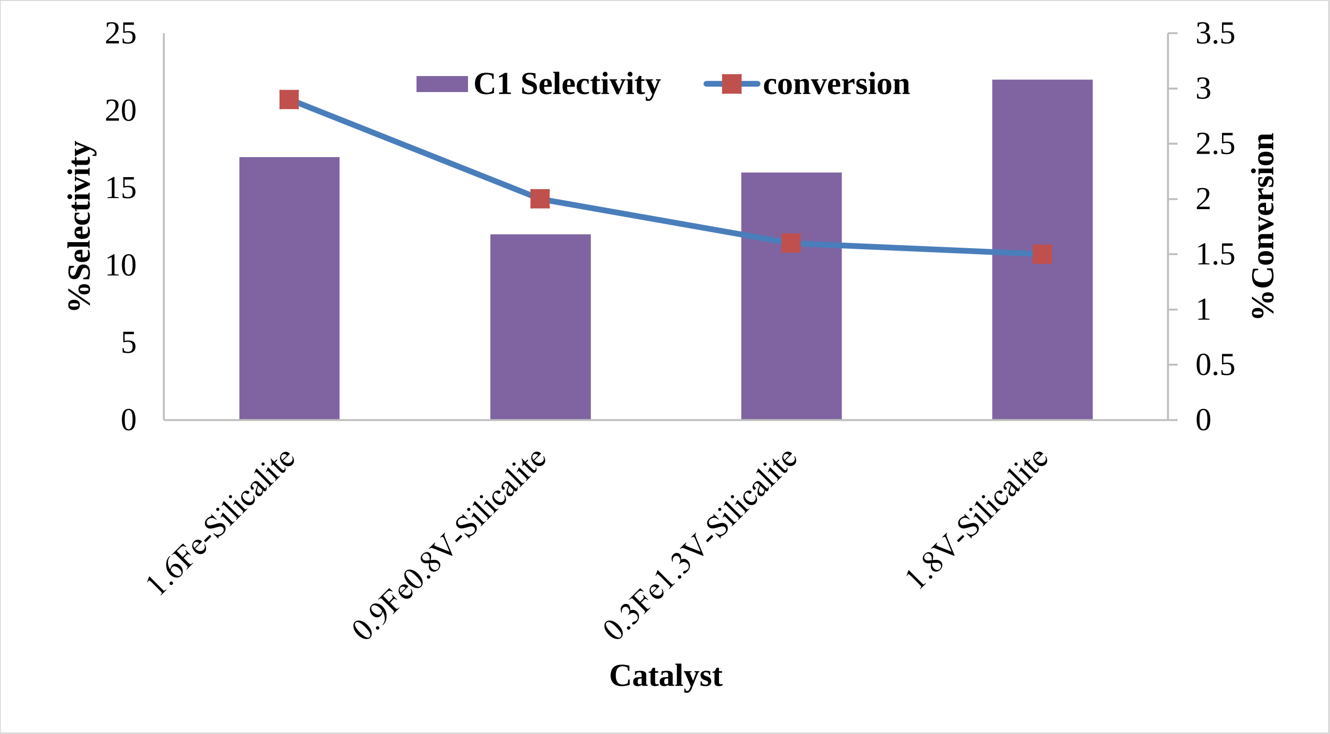

Figure 4.9: Catalytic results of *n*-octane oxidation over different silicalite catalysts

When the relative concentration of vanadium was increased in the Fe-silicalite catalysts (**Table 4.3**) and using similar reaction conditions as before, the conversion was observed to decrease. Vanadium introduction to Fe-silicalite also showed a significant change in octanone(s)/octanol(s) ratio, with higher amounts of octanones observed at the lower or zero vanadium concentrations. These results also suggest that the catalyst first produces octanols and then octanones (conversion effect). The differences observed from the catalysis results obtained from zeolite ZSM-5 and the silicalite catalysts may be due to the different environments that the transition metals are in within the two systems of catalysts. For the zeolite ZSM-5, the metal ion is in extra-framework positions, while for the silicalite, the active metal (Fe) is contained inside the frame-work of the catalyst. These differences can lead to different chemistry.

Table 4.3: Selectivity to terminal products, conversion and octanone(s)/octanol(s) ratio

Catalysts	Selectivity (%)	Conversion (%)	octanone(s)/octanol(s) ratio
1.6Fe-silicalite	17	2.90	2.2
0.9Fe0.8V-silicalite	12	2.00	1.6
0.3Fe1.3V-silicalite	16	1.6	1.3
1.8V-silicalite	22	1.5	0.9

Rection conditions: catalyst = 0.25 g, octane/H_2O_2 = 8.9 (molar ratio),
acetonitrile (18 ml), reaction time = 8 hours at 80 °C
Octanones(s) = octanone(s) + octanal

The C-1 selectivity trend on the silicalite catalysts was also maintained at iso-conversion of 1.7 % (**Figure 4.10**) using the average conversion of four repeat reactions carried out.

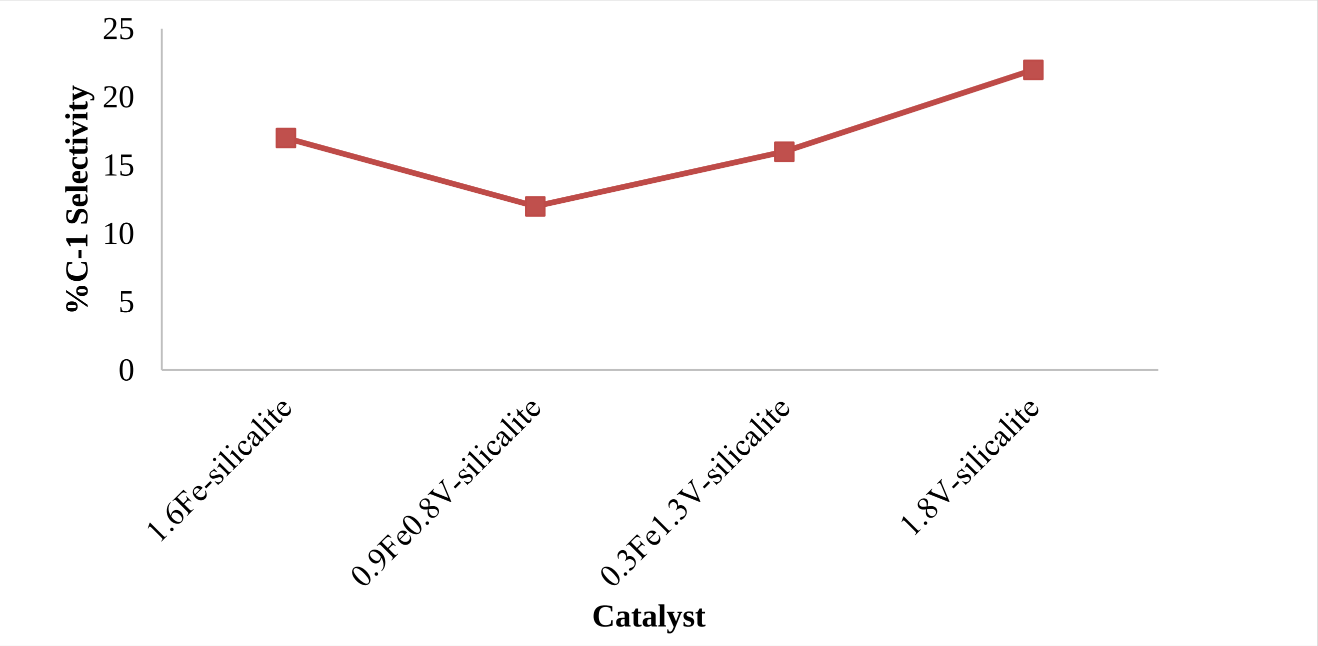

Figure 4.10: Selectivity to C-1 product over different silicalite catalysts at iso-conversion of 1.7 %

4.3.3 Catalyst stability test

Catalyst 0.9Fe0.8V-silicalite was used to carry out catalyst stability tests at the optimum temperature of 80 °C. Three cycles were carried out using the same catalyst. No change in silicalite structure was observed for the used catalyst as confirmed by XRD, FT-IR and SEM analysis (Appendix). It was observed that the catalyst maintained constant conversion of about 1.9 % with no noticeable change in product distribution, implying that the silicalite catalyst is efficiently recyclable (**Figure 4.11**).

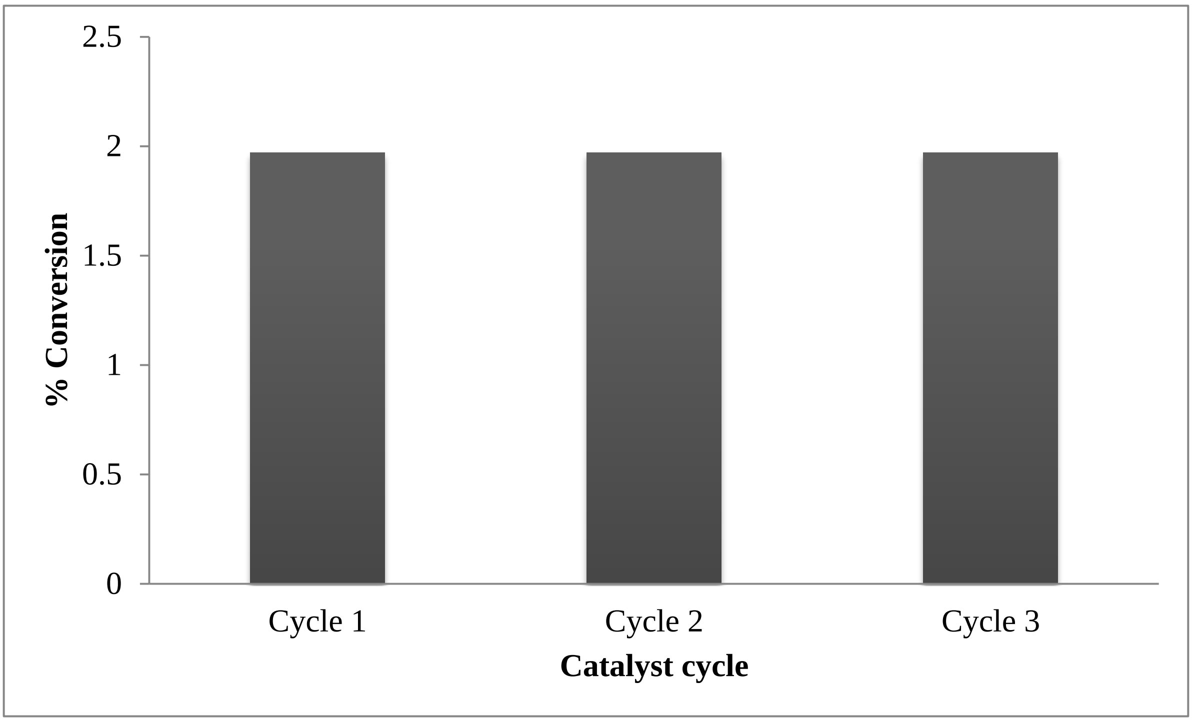

Figure 4.11: Conversion data after three reaction cycles using recycled 0.9Fe0.8V-silicalite under optimum conditions

4.4. Conclusions

Successful syntheses of the ZSM-5 zeolite and silicalite monometallic and bimetallic catalysts were confirmed by p-XRD and FT-IR. ZSM-5 zeolite catalysts were prepared by ionic exchange and silicalite catalysts were prepared by isomorphic substitution. The ICP-OES showed that all catalysts contained the active metals at reported values. The BET surface areas for the zeolite catalysts decreased with the introduction of vanadium, while the pore volumes remained constant, suggesting little or no pore blocking by the metals. Reducing the concentration of Fe and introducing vanadium into the zeolite ZSM-5 catalysts improved the conversion, while reducing the selectivity to primary oxygenated products (octanal and 1-octanol).

When using the silicalite catalysts, there was no correlation between the concentration of Fe and V in the catalysts with respect to the selectivity to terminal oxygenates, but reducing the Fe content lead to a decrease in the conversion of the reaction. For both catalysts, the octanone(s)/octanol(s) ratio had the same relationship with the conversion. For higher conversions more ketones were forming compared to alcohols, suggesting that ketones are a result of secondary oxidation. 0.9Fe0.8V-Silicalite gave a conversion of 2.0 % with octanone(s)/octanol(s) ratio of 1.6, while 1.1Fe0.8V-ZSM-5(IE) gave 3.0 % conversion and a ratio of 1.4. The recyclability of 0.9Fe0.8V-Silicalite was explored and it also proved to be stable over three cycles under optimum conditions.

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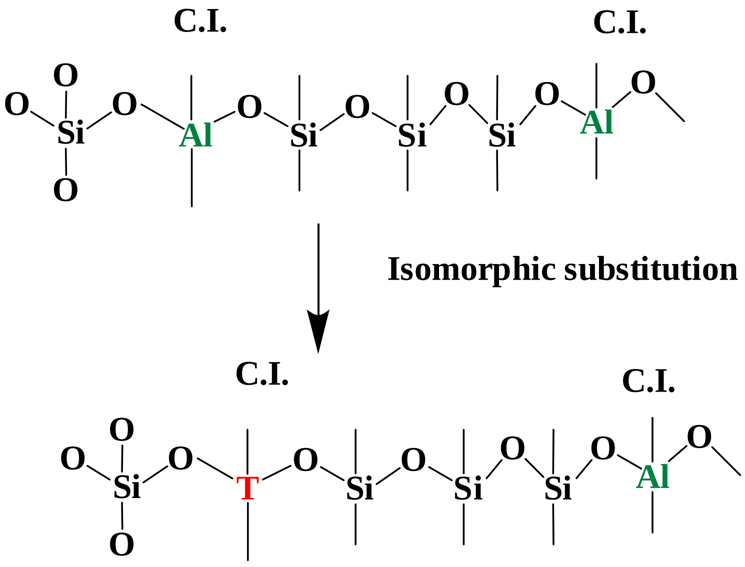
Chapter Five

Oxidation of *n*-octane to terminal oxygenates using Fe-ZSM-5 and silicalite catalysts

5.1. Introduction

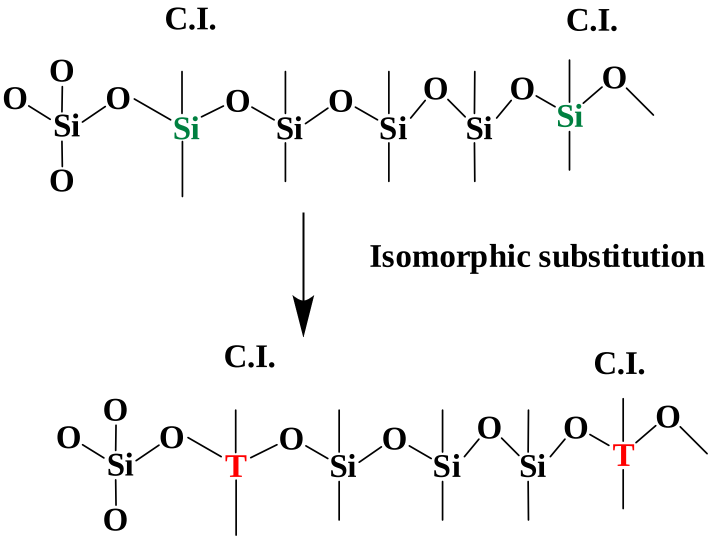
In catalysis, the chemistry of transition metals depends on their environment and the support they are on. For zeolites, transition metals can be incorporated into the framework using different techniques and this leads to different chemistry of the catalysts. The commonly known methods of incorporating transition metals into the zeolite are isomorphic substitution, vapor deposition (CVD) and ionic exchange [1, 2]. Different methods result in different catalytic environments, i.e. ionic exchange results in the transition metal in the extra-framework positions of the zeolite, while isomorphic substitution puts the metal into the framework of the zeolite. Apart from that, with isomorphic substitution one can also tune the zeolite catalyst further. From this method, two catalysts can be prepared having similar MFI structures, but different constituents, i.e. zeolite ZSM-5 contains aluminium in its framework and silicalite does not have aluminium. **Scheme 5.1** and **Scheme 5.2** show how the metal occupies the frame-work of the zeolite ZSM-5 and silicalite prepared by isomorphic substitution respectively.

Previous studies have shown that silicalites can be used in the oxidation of paraffins to terminal oxygenates [3-5]. **Table 5.1** shows that different silicalite catalysts can be used for this type of reaction, but it also shows that these catalysts give very low selectivities to primary oxidation products. The exception, Fe-silicalite-1, gave 93 % C-1 selectivity only because methane was the substrate for this reaction.



C.I. : Counterion (H^+, Na^+, Ca^{2+})
T: V^{3+}, Fe^{3+}, etc.

Scheme 5.1: An illustration of isomorphic substitution for ZSM-5 catalyst



C.I. : Counterion (H^+, Na^+, Ca^{2+})
T: V^{3+}, Fe^{3+}, etc.

Scheme 5.2: An illustration of isomorphic substitution for silicalite catalyst

Table 5.1: Previous studies for the oxidation of paraffins using silicalites catalysts.

Catalyst	Substrate	Solvent	Oxidant	C-1 Selectivity	Reaction temp. (°C)
VS-1	octane	MeCN	TBHP	0.2	100 [3]
TS-2	hexane	MeCN	H_2O_2	0	80 [4]
VS-2	hexane	MeCN	H_2O_2	3.7	80 [4]
Fe-silicalite-1	methane	-	H_2O_2	93	80 [5]

On the other hand ZSM-5 catalysts prepared by isomorphic substitutions have previously been used in different chemical reactions other than the oxidation of paraffins to terminal oxygenates. Pérez-Ramírez et al. prepared isomorphously substituted iron zeolites and tested them in direct N_2O decomposition and N_2O reduction by CO [6]. In another study by Phu et al., Fe-ZSM-5 catalysts with Si/Fe ratios of 43 to 203 were prepared and used for the total oxidation of phenol in aqueous solution [7]. Not much work has been done in the catalysis of paraffins using framework substituted ZSM-5 catalysts.

In this work, Fe-ZSM-5 catalysts and Fe-silicalite catalysts, both prepared by isomorphic substitution, were tested in the oxidation of *n*-octane in liquid phase reactions to give terminal oxygenates, such as 1-octanol and octanal. For this part of the work, vanadium catalysts were not included, since it was shown that Fe gives a more terminally selective catalyst compared to vanadium. The prepared catalysts have a Si/Fe ratio of 62.

5.2. Experimental

5.2.1. Catalyst synthesis and characterisation

The framework substituted Fe-ZSM-5(62) and the Fe-silicalite(62) catalysts' preparation is described in Section **2.2.3** and **2.2.5** respectively. The characterization of both catalysts is described in Section **2.3**.

5.2.2 Catalyst testing

The procedure for catalyst testing is the same as described in the previous chapter (**Chapter 4**). The reactions were carried out under nitrogen. The reactions for the two catalysts were carried out in 18 mL of acetonitrile in a two-necked round bottomed flask (50 mL), fitted with a stopper and a condenser. This was followed by the consecutive addition of 1.8 mmol of *n*-octane, 0.25 g catalyst and 16 mmol of H_2O_2 (30 wt% in water). The reaction temperature and time were kept constant at 80 °C and 8 hours. The products of the reaction were analysed by a Perkin Elmer Auto System GC equipped with a Flame Ionisation Detector (FID) using a Pona 50 x 0.20 mm x 0.5 μm column. The internal standard for the reaction was chlorobenzene (0.04 g).

In order to test for active metal leaching, the solution was filtered off at the reaction temperature in order to prevent any soluble metal from readsorbing onto the catalyst surface on cooling [15]. The filtrate was put back in the reaction flask to react further with any soluble metal present in the reaction solution. After removal of the catalyst by filtration after 3 h or 4 h, the filtrate was allowed to react for 8 h or 9 h respectively, which allowed a comparison of conversion to a run with a catalyst.

5.3. Results and Discussion

5.3.1 Catalyst characterisation

Fe-silicalite(62) is the same catalysts as 1.6Fe-Silicalite. For the purpose of this chapter, the nomenclature was changed to Fe-silicalite(62) since for this chapter, the Si/Fe ratio in both the catalysts is being compared instead of the Si/Al ratio. The number in the parenthesis denotes the Si/Fe ratio.

The FT-IR characterization (**Figure 5.1**) for Fe-silicalite(62) was previously discussed in Section **4.3.1**. It was shown that it was indeed an MFI material. The results were further supported by the p-XRD (**Figure 5.2**), which also showed that the synthesized material had an MFI finger print and the intensity of the peaks showed the crystalline nature of the catalyst [12]. The crystallinity of the material was further supported by the optical density ratio, which was found to be above 0.7 [8-11].

The isomorphously substituted Fe-ZSM-5 FT-IR data, shown in **Figure 5.1,** corresponded to those of typical MFI materials. The band around 550 cm^{-1} of the Fe-ZSM-5(62) is assigned to the 5-membered rings in the MFI lattice [9]. The other characteristic bands are the same as for the Fe-silicalite(62) and they were discussed in Section **4.3.1**.

The p-XRD pattern for the Fe-ZSM-5(62) is similar to the patterns of all the previously prepared catalysts. All peak positions matched those reported for the MFI-structure [12] and no-impurity phase was observed. The low background and high intensity of the peaks in the prepared catalysts also indicates the high crystallinity of the material [7].

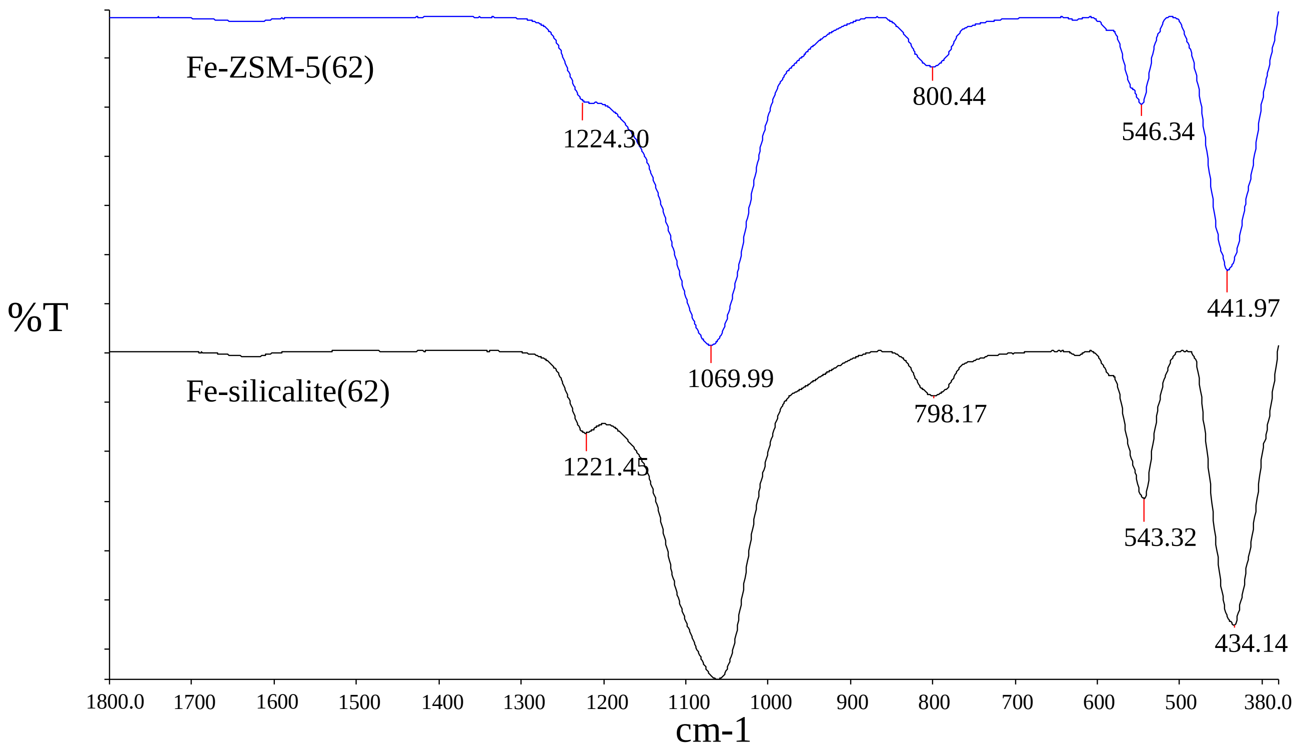


Figure 5.1: Infrared spectra of the Fe-silicalite(62) and Fe-ZSM-5(62) catalysts prepared by isomorphic substitution

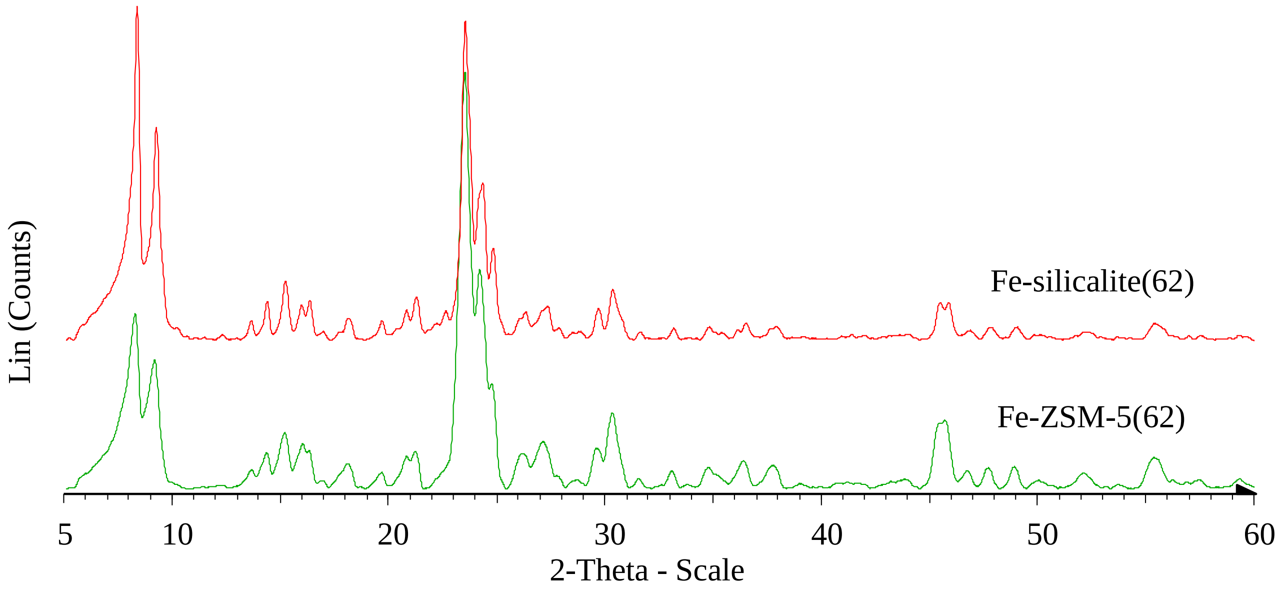


Figure 5.2: p-XRD of the Fe-silicalite(62) and Fe-ZSM-5(62) catalysts prepared by isomorphic substitution

The BET surface area measurements and the micropore volumes (**Table 5.1**) show that despite having almost similar metal loadings (1.4 % and 1.6 %), the two different catalysts have different surface area and also different pore volumes. Fe-ZSM-5(62), which contains Al in its framework, has a smaller surface area and larger pore volume compared to Fe-silicalite(62), which does not contain Al in its framework, The small surface area of the ZSM-5 may be due to aluminium species inside the zeolite pores and channels which may also widen the pores of the zeolite [13]. The absence of aluminium in the framework of silicalites results in relatively small pore volumes. If four metal atoms are present in the framework (Al, Si, Fe and O) the increase in the pore volume will be anticipated [14]. Silicalites have only three metal atoms (Si, Fe and O), hence the pore volume is different from that of the Fe-ZSM-5(62).

Table 5.2: Surface properties and ICP results of the ZSM-5 and silicalite catalysts.

Catalysts	BET (m^2/g)	Pore Volume (cm^3/g)	Pore Size (nm)	ICP (%Wt.)
Fe-ZSM-5(62)	359	0.19	20.9	1.4
Fe-Silicalite(62)	392	0.11	24.9	1.6

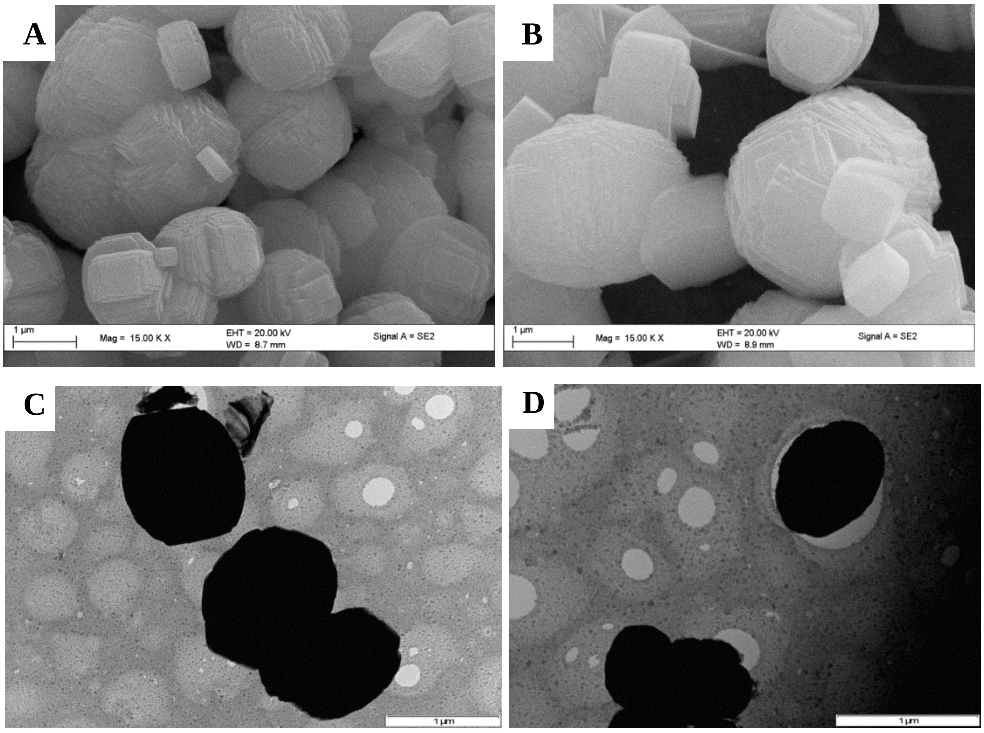


Figure 5.3: (A) SEM image of Fe-ZSM-5(62), (B) SEM image of Fe-silicalite(62), (C) TEM image of Fe-ZSM-5(62), and (D) TEM image of Fe-silicalite(62)

The SEM results of Fe-silicalite(62) and Fe-ZSM-5(62) show that there is no significant difference in morphology of the catalysts (**Figure 5.3**). The morphology of the MFI type catalysts was showen to be independent of the framework constituents. The shape for both the catalysts is of the typical MFI materials shape, which is hexagonal. The only difference observed for the catalysts is the crystallinity, which makes the SEM images appear slightly different, but the TEM images confirm the similar shapes of the catalysts.

5.3.2 Catalyst testing

Both the catalysts were tested under the conditions cited in Section 5.2.2. The catalytic data in **Figure 5.4** shows that Fe-ZSM-5(62) gave a low conversion but good selectivity to terminal oxygenates compared to Fe-Silicalite. Fe-ZSM-5(62) gave a conversion of 1.8 % and terminal selectivity of 20 %, while the Fe-Silcalite(62) catalyst gave 2.9 % conversion and a terminal selectivity of 17 %.

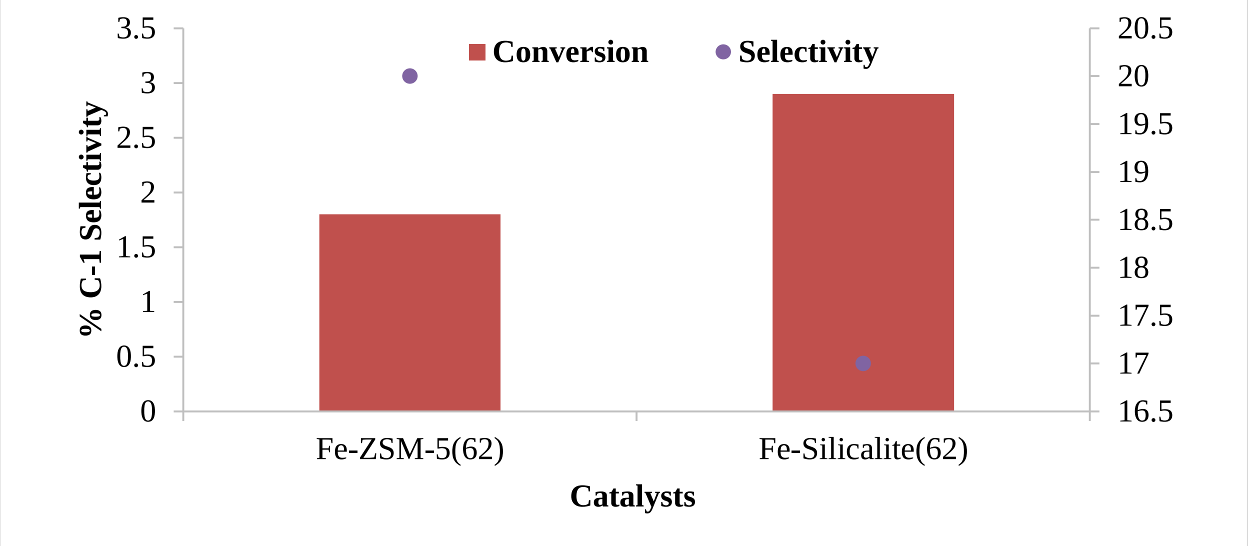


Figure 5.4: Catalytic results of *n*-octane oxidation over different catalysts systems

Previous studies showed that the silicalite catalysts gave very low terminal oxidation selectivity in paraffins oxidation [3,4]. This may be because silicalite does not have Al in the framework, which induces acidic sites of the zeolite catalyst which may play a role in the selectivity of the catalyst. The presence of the Fe in the framework of the silicalite improves the ability of the silicalite to activate the primary carbon. This ability depends on the Si/Fe ratio used in the catalysis.

The octanone(s)/octanol(s) ratio (**Table 5.3**) was higher over the Fe-silicalite(62) catalyst. This means that further oxidation of alcohols to ketones was higher for the silicalite catalyst, which matches the higher conversion obtained on the silicalite catalyst. These results also suggest that the catalyst first produces alcohols and then ketones. The results also agree with results from the previous chapter, in that ZSM-5 zeolite catalysts produce less ketones than the silicalite catalysts.

Table 5.3: Selectivity to terminal products, conversion and octanone(s)/octanol(s) ratio.

Catalysts	Selectivity (%)	Conversion (%)	octanone(s)/octanol(s) ratio
Fe-ZSM-5(62)	20	1.8	1.7
Fe-silicalite(62)	17	2.9	2.2

Rection conditions: catalyst = 0.25 g, octane/H_2O_2 = 8.9 (molar ratio),
acetonitrile (18 ml), reaction time = 8 hours at 80 °C
Octanones(s) = octanone(s) + octanal

Iso-conversion reactions (**Figure 5.5**) were carried out for the two catalysts and the results also agreed with the results in **Figure 5.4**, in that Fe-ZSM-5(62) is more selective towards the desired products compared to Fe-silicalite(62).

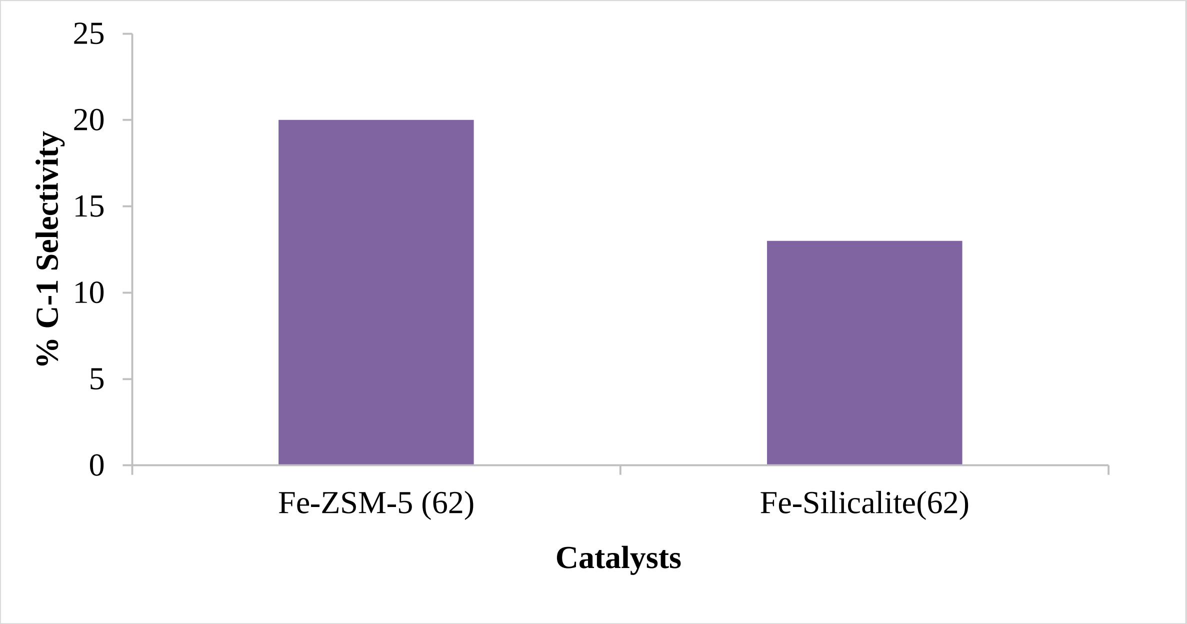


Figure 5.5: Selectivity to C-1 product over different catalyst systems catalysts at iso-conversion of 1.7 %

5.3.3 Catalyst recyclability and leaching tests

Both the catalysts were used to carry out catalyst recyclability stability tests at the optimum temperature of 80 °C. Three cycles were carried out using the same catalyst. No change in both the silicalite and ZSM-5 zeolite structure was observed for the used catalysts as confirmed by XRD, FT-IR and SEM analysis (Appendix). It was observed that the silicalite catalyst maintained constant conversion of about 1.6 % with no noticeable change in product distribution, implying that the silicalite catalyst is efficiently recyclable. The Fe-ZSM-5(62) did not maintain constant conversion for the three cycles. The product distribution was maintained by the catalyst while the selectivity to alcohols and ketones was not constant with each cycle. The alcohols increased with the decrease in conversion.

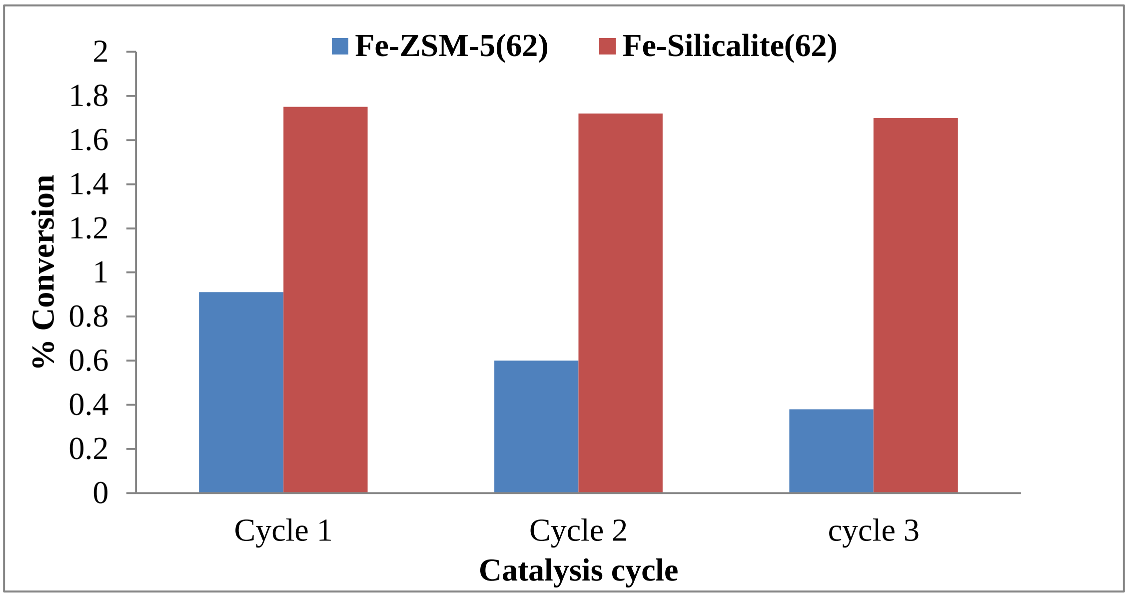


Figure 5.6: Conversion data after three reaction cycles using recycled catalysts at optimum conditions

To look at the possibility of leaching from the catalysts, reactions were carried out and the leaching test was done using a hot filtration technique and the results, in **Table 5.4**, show that for Fe-ZSM-5(62), the active metal might have been leaching and the conversion was continuing after hot filtration. This was not the case when looking at the results of using Fe-silicalite(62).

Table 5.4: Recyclability test by hot filtration.

Catalyst	Conversion after 8h with a catalyst/ %	Conversion after 3-4 h with a catalyst/ %	Conversion after catalyst filtration (8h)/ %
Fe-ZSM-5(62)	1.8 ± 0.03	0.33 ± 0.02	0.49 ± 0.02
Fe-silicalite(62)	2.9 ± 0.04	1.62 ± 0.03	1.75 ± 0.05

5.4. Conclusions

p-XRD and FT-IR confirmed the synthesis of both the Fe-ZSM-5(62) and Fe-Silicalite(62) by isomorphic substitution. The prepared catalysts had a Si/Fe ratio of 62, as confirmed by ICP-OES. The presence of Al in the Fe-ZSM-5(62) decreased the BET surface area of the catalyst. SEM and TEM analyses showed that the morphology of the two catalysts was similar, and showed the expected hexagonal shape. The absence of Al in the framework of the Fe-Silicalite(62) decreased the pore volume of the catalyst. Fe-ZSM-5(62) was more selective to terminal oxidation of *n*-octane to oxygenates, such as octanol and octanal. The Fe-Silicalite gave a higher conversion of 2.9 % compared to 1.8 % over the Fe-ZSM-5(62). In both catalysts, the octanone(s)/octanol(s) ratio had the same relationship with the conversion. Thus, for higher conversions more ketones were formed compared to alcohols, implying that ketones are a result of secondary oxidation. The recyclability test showed that Fe-Silicalite(62) is stable up to at least three cycles under optimum conditions, while the Fe-ZSM-5(62) was not stable up to three cycles, with evidence of leaching.

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Chapter six

Summary and Conclusion

The syntheses of Fe-ZSM-5(47,IE), Cr-ZSM-5(47,IE), Mn-ZSM-5(47,IE) and V-ZSM-5(47,IE) were achieved using the ion-exchange method to incorporate the Fe into the extra-framework position of the zeolite. The XRD results revealed that only the ZSM-5 phase was obtained for all the synthesised catalysts even after modification. Studies on Fe-ZSM-5(47,IE) showed that terminal selectivity and conversion of *n*-octane was time and oxidant dependent. Furthermore, the results showed that the octanone(s)/octanol(s) ratio increases with the amount of oxidant suggesting that octanols are primary products which upon further oxidation resulted in octanones. Only C8 oxygenate products were obtained. The Fe-ZSM-5(47,IE) catalyst gave a conversion of 2.7 % with the highest terminal selectivity compared to Cr, Mn and V-ZSM-5(47,IE). V-ZSM-5 gave the highest conversion of 6.6 % and terminal selectivity of 12 % .The XRD, FT-IR and SEM results showed that the catalysts are stable. Fe-ZSM-5(47,IE) was used as the model catalyst for the recyclability study. It was found that the catalyst is recyclable and the conversion of recycled catalyst was found to be the same as of the fresh catalyst, with the same product distribution.

The syntheses of the ZSM-5 and silicalite bimetallic catalysts were successful, as only the ZSM-5 phase was observed (by p-XRD and FT-IR). There was no change observed in the pore volume of the bimetallic catalysts compared to the monometallic catalysts. The selectivity to terminal products was found to be influenced by the amount of Fe and V used in the catalysts. The introduction of V in Fe-ZSM-5 improved the conversion while decreasing the terminal selectivity. For the silicalite catalysts, terminal selectivity was improved by the introduction of V, while the conversion decreased. No clear trend for the terminal selectivity was seen over the catalysts.

A comparative study of framework substituted Fe-ZSM-5 and Fe-silicalite was conducted. The catalysts were prepared by isomorphic substitution and characterized by p-XRD, FT-IR, SEM, TEM, ICP-OES and BET surface measurements. The morphology of the catalysts was similar and showed the expected hexagonal shape. Fe-ZSM-5(62) catalysts showed higher terminal selectivity (20 %) and lower conversion compared to Fe-silicalite(62). Only C8 oxygenate products were observed in all *n*-octane oxidation reactions. The product distribution from Fe-ZSM-5(62) was found to be similar to the product distribution obtain from the use of Fe-silicalite(62) under similar oxidation reaction conditions.

In conclusion, this work has shown that Fe-zeolite type materials are effective in the oxidation of *n*-octane in the liquid phase and that good selectivity to terminal products can be achieved. It was also shown that selectivity and conversion of the *n*-octane could be controlled using bimetallic ZSM-5 catalysts.

APPENDIX

Supplemental information

Table of Content

Calculation of the conversion and selectivity

$$X_i = \frac{Y_i Z_i}{\sum_i Y_i Z_i} \text{X}100\%$$

Where Xi is the mole fraction of component i, Zi is the response factor of component i, and Yi is the peak area of component i. The conversion of octane is defined as the ratio of number of moles of octane consumed in the reaction to the total moles of octane initially added. The selectivity to i-octanol is defined as the ratio of number of moles of 1-octanol produced to the total number of moles of all products.

$$\text{Conversion of octane} = \frac{\text{moles of octane consumed}}{\text{moles of octane initially added}} \text{ X } 100\ \%$$

$$\text{Selectivity to 1-octanol} = \frac{\text{moles of 1-octanol produced}}{\text{moles of all products}} \text{ X } 100\ \%$$

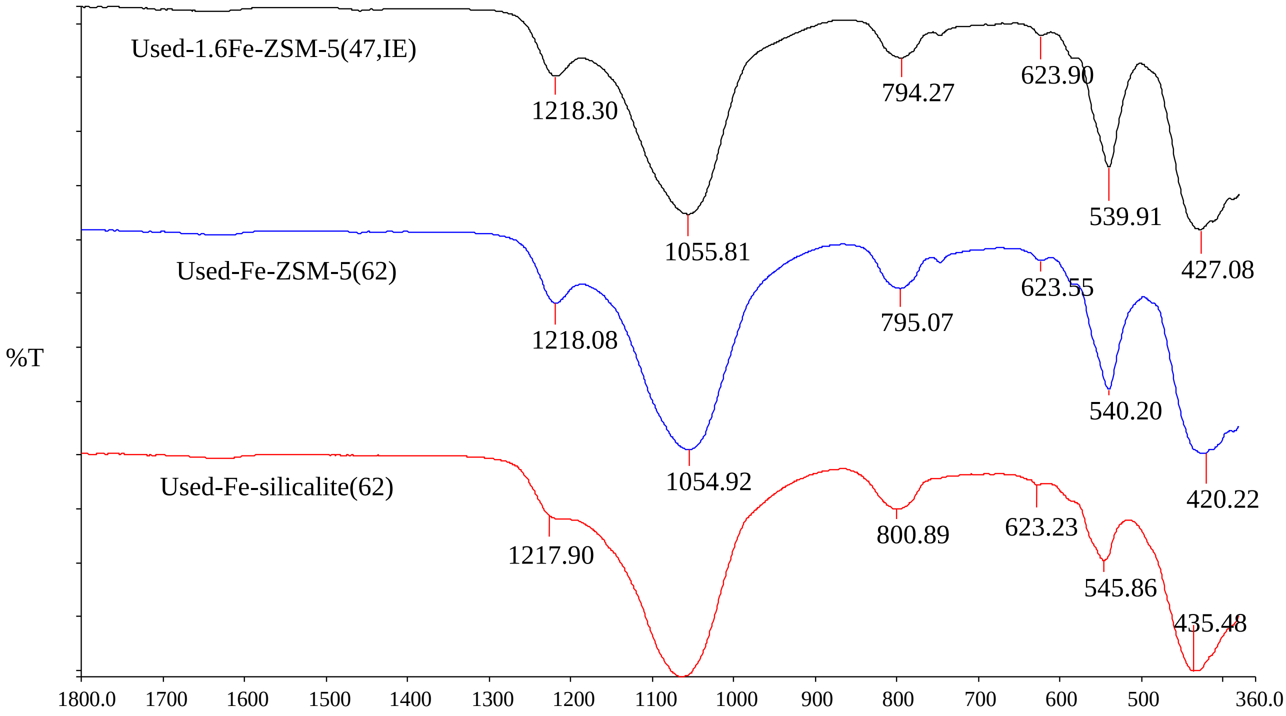

Figure A 2: FT-IR of used catalysts

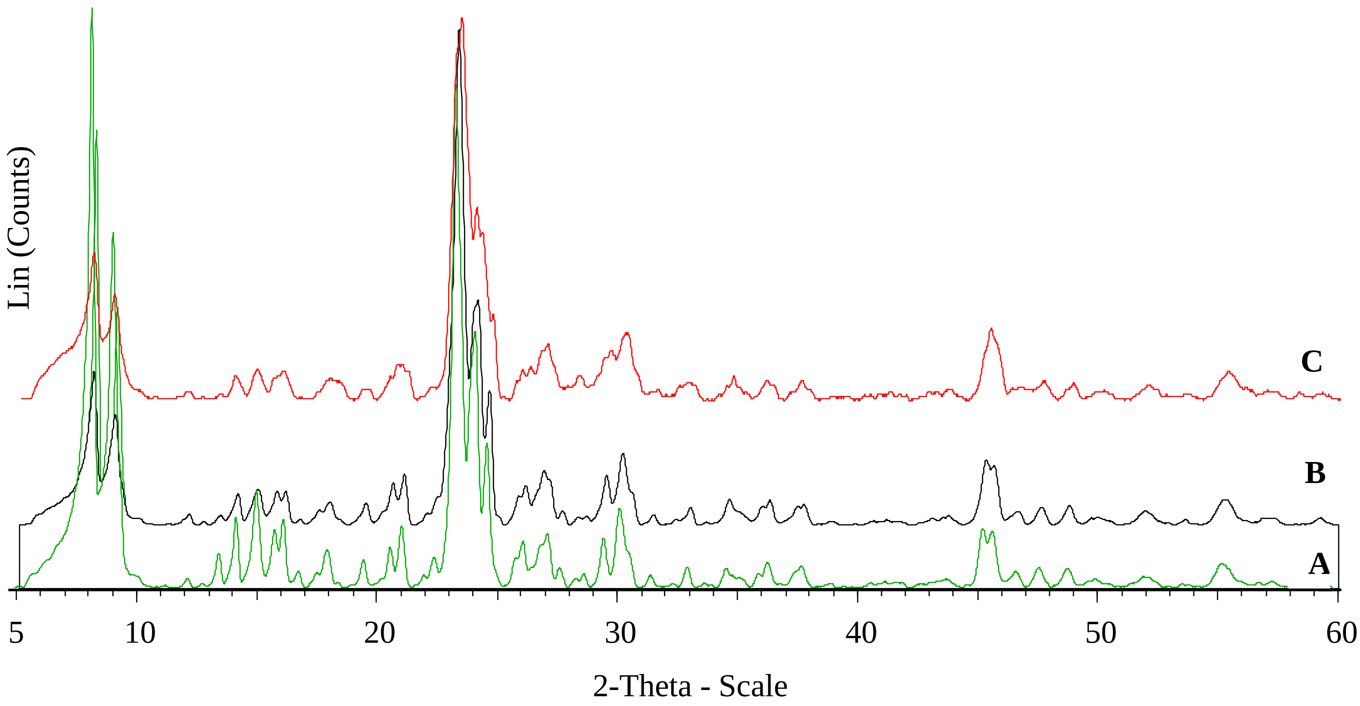

Figure A 2: p-XRD of (A) used Fe-silicalite (62), (B) used Fe-ZSM-5(47,IE), (C) used Fe-ZSM-5(62)

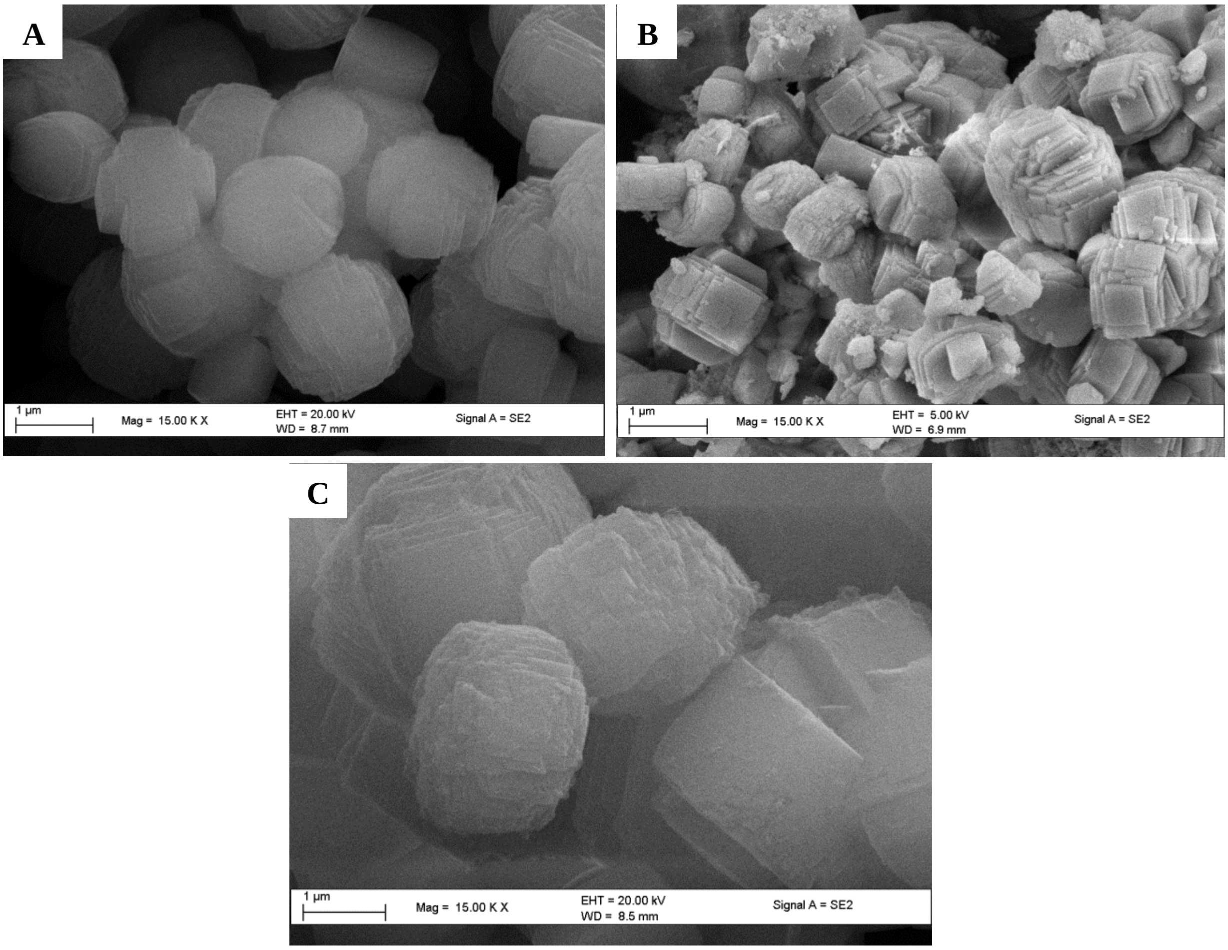

Figure A 3: SEM of (A) used Fe-silicalite (62), (B) used Fe-ZSM-5(47,IE), (C) used Fe-ZSM-5(62)

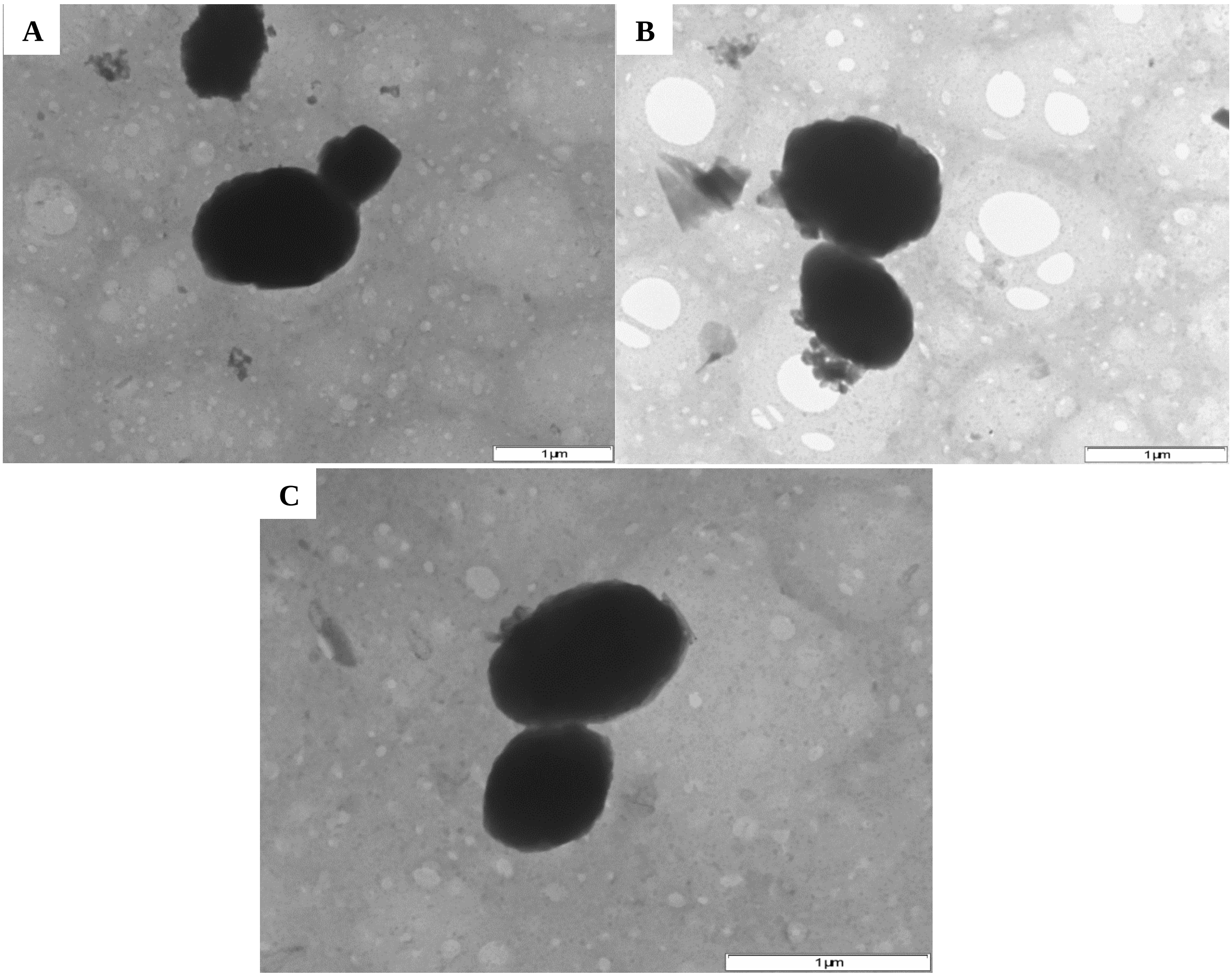

Figure A 4: SEM of (A) used Fe-silicalite (62), (B) used Fe-ZSM-5(47,IE), (C) used Fe-ZSM-5(62)

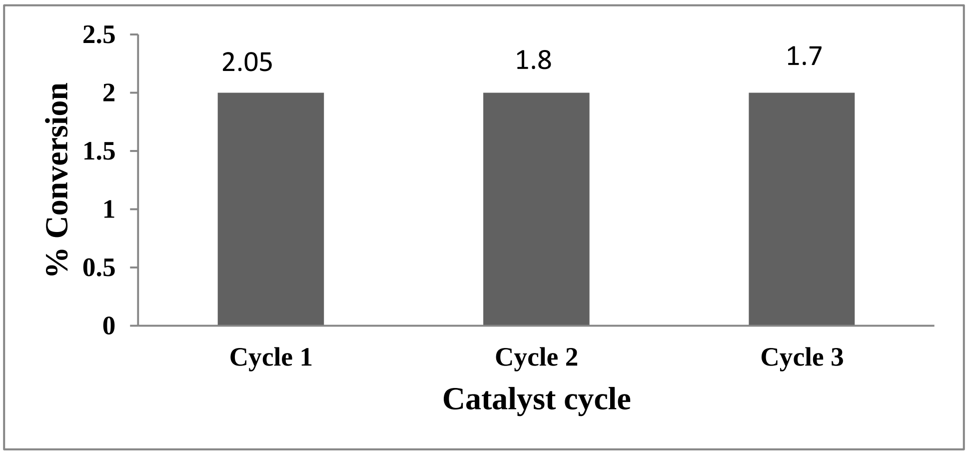

Figure A 5: Conversion data after three reaction cycles using Fe-ZSM-5(47,IE) at optimum conditions

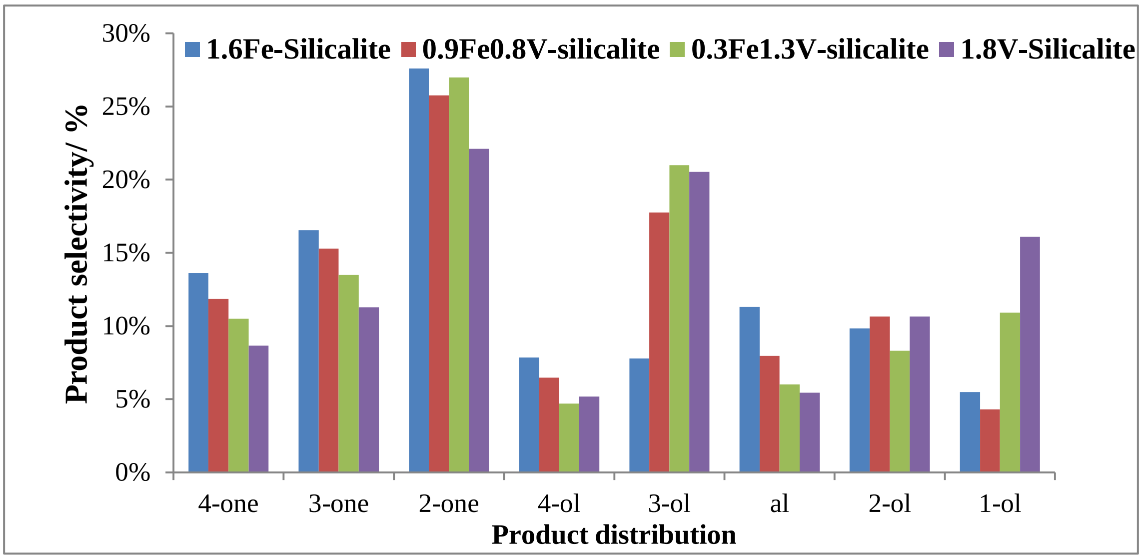

Figure A 6: Product distribution of *n*-octane oxidation over different silicalite catalysts

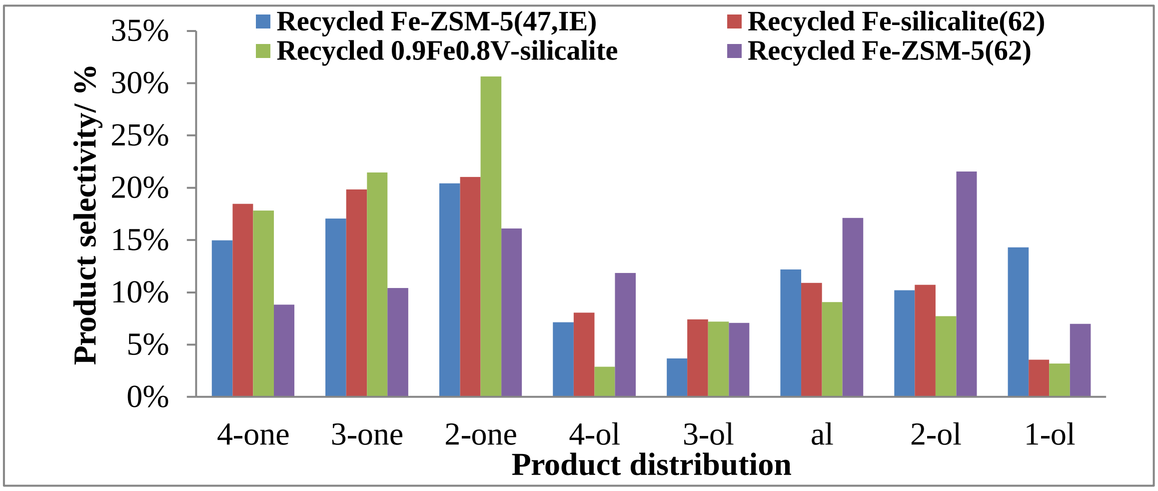

Figure A 7: Product distribution of *n*-octane oxidation over different recycled catalysts

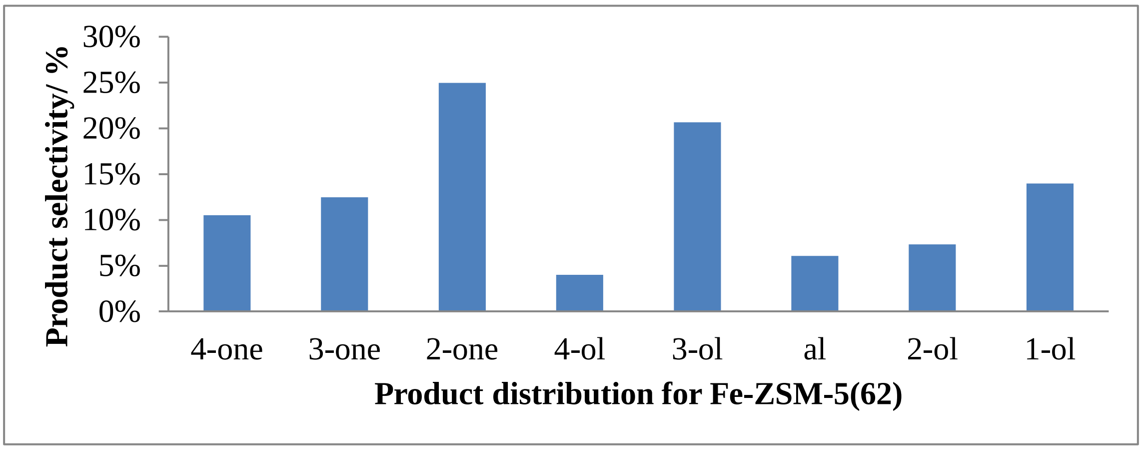

Figure A 8: Product distribution of *n*-octane oxidation over Fe-ZSM-5(62)

Table A 1: octanone(s)/octanol(s) ratio over different catalysts at iso-conversion of 2.7 % for ZSM-5 and 1.7 % for silicalite catalysts.

Catalysts	octanone(s)/octanol(s) ratio
1.6-Fe-ZSM-5(IE)	1.1
1.1Fe0.8V-ZSM-5(IE)	1.4
0.4Fe1.2V-ZSM-5(IE)	1.2
1.7V-ZSM-5(IE)	1.7
1.6Fe-silicalite	1.3
0.9Fe0.8V-silicalite	1.5
0.3Fe1.3V-silicalite	1.4
1.8V-silicalite	1.1

Table A 2: Surface properties of the ZSM-5 and silicalites catalysts.

Catalysts	BET (m^2/g)	Pore Volume (cm^3/g)	Pore Size (nm)
Na- ZSM-5	326.7	0.18	20.1
Na-silicalite	383.0	0.13	24.9