Effect of microwave radiation on Fe/ZSM-5 for catalytic conversion of methanol to hydrocarbons (MTH)

by

TAU SILVESTER NTELANE

submitted in accordance with the requirements for
the degree of

MAGISTER TECHNOLOGIAE

in the subject

ENGINEERING: CHEMICAL

at the

UNIVERSITY OF SOUTH AFRICA

SUPERVISOR: PROF M S SCURRELL

CO-SUPERVISOR: PROF C M MASUKU

MARCH 2018
DECLARATION

I Tau Silvester Ntelane declare that this is my own work and that all the sources that I have used or quoted have been indicated and acknowledged by means of complete references.

I further declare that I have submitted the thesis chapters to originality checking software.

I further declare that I have not previously submitted this work, or part of it, for examination at University of South Africa for another qualification or at any other higher education institution.

……………………

TS NTELANE (58521623)

……………………day of………………………2018
ACKNOWLEDGEMENTS

♦ First and foremost, I will like to thank God, the Almighty for giving me the courage and strength to complete this work. Without God’s grace, this journey would have been impossible.

♦ I would like to express my genuine gratitude to my supervisors Prof. MS Scurrell and Prof. CM Masuku for their continuous guidance, encouragement, and support during the course of this work. Their supervision gave me hope in life and forever I will remain thankful.

♦ Also, I would like to thank Dr. Themba Tshabalala and Mr. Charles Noakes (from Poretech) for helping me to understand the concepts of using AutoChem II 2920 equipment.

♦ Equally important, many thanks to my colleagues in CREATE (Catalytic REaction Technology And Transformation of Energy) Research Flagship – UNISA. You guys were amazing especially; Tumelo Seadira, Sibusiso Dubaza and Thabelo Nelushi.

♦ A very special thanks to my guardian Mrs. ‘Nyane Mzamo, my elder sister Tsèpiso Ntelane, little sister Lemohang Ntelane and my niece Karabo Ntelane. To my late parents, thank you for everything.

“...I consider that our present sufferings are not worth comparing with the glory that will be revealed in us...” Romans 8:18
PRESENTATIONS AND PUBLICATIONS

Conference Presentations:

♦ 10th World Congress of Chemical Engineering (WCCE 10) 2017 conference, Barcelona, Spain, 1st-5th October 2017. Poster presentation tilted: Temperature-Programmed Surface Reaction (TPSR) study: Effect of Microwave radiation on Fe/ZSM-5 for catalytic conversion of Methanol to Hydrocarbons (MTH).


Publications:

♦ Manuscript titled, “Temperature-Programmed Surface Reaction (TPSR) study: Effect of Microwave radiation on Fe/ZSM-5 for catalytic conversion of Methanol to Hydrocarbons (MTH)” submitted to Microporous and Mesoporous Materials journal.
ABSTRACT

The effect of microwave radiation on the prepared 0.5Fe/ZSM-5 catalysts as a post-synthesis modification step was studied in the methanol-to-hydrocarbons process using the temperature-programmed surface reaction (TPSR) technique. This was achieved by preparing a series of 0.5Fe/ZSM-5 based catalysts under varying microwave power levels (0–700 W) and over a 10 s period, after iron impregnating the HZSM-5 zeolite (Si/Al = 30 and 80). Physicochemical properties were determined by XRD, SEM, BET, FT-IR, C_{3}H_{9}N-TPSR, and TGA techniques. It was found that microwave radiation induced few changes in the bulk properties of the 0.5Fe/ZSM-5 catalysts, but their surface and catalytic behavior were distinctly changed. Microwave radiation enhanced crystallinity and mesoporous growth, decreased coke and methane formation, decreased the concentration of Brønsted acidic sites, and decreased surface area and micropore volume as the microwave power level was increased from 0 to 700 W. From the TPSR profiles, it was observed that microwave radiation affects the peak intensities of the produced hydrocarbons. Application of microwave radiation shifted the desorption temperatures of the MTH process products over the HZSM-5(30) and HZSM-5(80) based catalysts to lower and higher values respectively. The MeOH-TPSR profiles showed that methanol was converted to DME and subsequently converted to aliphatic and aromatic hydrocarbons. It is reasonable to suggest that microwave radiation would be an essential post-synthesis modification step to mitigate coke formation and methane formation and increase catalyst activity and selectivity.

**Keywords:** Methanol-To-Hydrocarbons (MTH); Microwave radiation; Post-synthesis modification step; Temperature Programmed Surface Reaction; 0.5Fe/ZSM-5 catalysts; Coke deposition; Methane formation; Multi-mode microwave oven; Catalyst deactivation; Bed shape; ZSM-5 zeolite.
# TABLE OF CONTENTS

DECLARATION ........................................................................................................... ii  
ACKNOWLEDGEMENTS ........................................................................................... iii  
PRESENTATIONS AND PUBLICATIONS ..................................................................... iv  
ABSTRACT ................................................................................................................ v  
TABLE OF CONTENTS ............................................................................................... vi  
LIST OF FIGURES ..................................................................................................... ix  
LIST OF TABLES ......................................................................................................... xi  
LIST OF SCHEMES ................................................................................................... xii  
LIST OF ABBREVIATIONS ....................................................................................... xiii  
CHAPTER 1  ................................................................................................................ 1  
1.1 Introduction ......................................................................................................... 1  

**Figure 1.1:** Methanol to hydrocarbons (MTH) process (Baliban et al., 2012) ........ 2  
1.2 Problem Statement ............................................................................................ 3  
1.3 Aims and Objectives ........................................................................................... 4  
1.3.1 Aim .................................................................................................................. 4  
1.3.2 Objectives ....................................................................................................... 4  
1.3.3 Thesis Statement ............................................................................................. 5  
1.3 Structure of Thesis .............................................................................................. 5  
References .................................................................................................................. 6  
CHAPTER 2 ................................................................................................................ 9  
2.1 Methanol Economy ............................................................................................. 9  
2.2 MTH Process ..................................................................................................... 14  
2.3 Commercialized MTH Processes ....................................................................... 15  
  2.3.1 Commercialized MTG Processes .................................................................. 16  
  2.3.2 Commercialized MTO Processes .................................................................. 17  
  2.3.3 Commercialized MTP Processes .................................................................. 18  
2.4 ZSM-5 Zeolite ................................................................................................... 20  
2.5 Reaction Mechanisms ....................................................................................... 22  
  2.5.1 Olefin Methylation ......................................................................................... 24  
  2.5.2 Olefin Cracking ............................................................................................. 26  
  2.5.3 Hydrogen Transfer ......................................................................................... 27  
  2.5.4 Cyclization .................................................................................................... 27  
  2.5.5 Aromatic Methylation .................................................................................... 28
Catalysts characterization

Introduction

Experimental Procedures and Instruments used

Reagents used

Microwave Radiation

Studies to Mitigate Coke Formation

Factors Influencing Selectivity towards MTH Products

Microwave oven and Bed shape

Microwave heating of ZSM-5 zeolite

Influence of modifying ZSM-5 with elements

Influence of contact time

Influence of Partial Pressure and Co-feeding water

Influence of reaction temperature

Influence of Si/Al ratio

Influence of modifying ZSM-5 with elements

Microwave heating

Direct heating and Selective heating

Heterogeneous catalysts and Microwave absorption

Microwave oven and Bed shape

Application of Microwave Radiation in Catalysis

Mechanisms and types of Microwave heating

Microwave post-synthesis modification of catalysts

Catalysts testing (MeOH-TPSR experiments)

References

CHAPTER 3

Introduction

Reagents used

Experimental Procedures and Instruments used

Catalysts preparation and post-synthesis modification

Microwave post-synthesis modification of catalysts

Catalysts Characterization

Nitrogen Adsorption-desorption Analysis

Powder X-Ray Diffraction (p-XRD) analysis

Thermogravimetric analysis (TGA)

Scanning electron microscopy (SEM) analysis

Fourier Transform Infrared (FT-IR) Spectroscopy

Propylamine-Temperature programmed surface reaction (C₃H₇N-TPSR)

References

CHAPTER 4

Introduction

Catalysts characterization
4.2.1 X-ray diffraction analysis ................................................................. 74
4.2.2 Nitrogen adsorption-desorption analysis ........................................ 76
4.2.3 Thermogravimetric analysis .............................................................. 80
4.2.4 Scanning electron microscopy (SEM) analysis .................................... 81
4.2.5 Fourier Transform Infrared (FT-IR) Spectroscopy ............................. 84
4.2.6 C₃H₉N-TPSR for acidic sites determination ....................................... 87
4.3 Catalysts Testing (MeOH-TPSR experiments) ....................................... 90
  4.3.1 MeOH-TPSR ................................................................................. 90
References .................................................................................................. 101
CHAPTER 5 ............................................................................................... 105
5.1 Conclusions ........................................................................................ 105
5.2 Recommendations ................................................................................ 107
APPENDIX A ............................................................................................. 108
LIST OF FIGURES

Figure 1.1: Methanol to hydrocarbons (MTH) process. ..............................................................2
Figure 2.1: Methanol production processes operating worldwide.................................................10
Figure 2.2: Global Methanol demand by end use (a) 2011 demand = 55.4 Million Metric tons (b) 2016 demand forecast = 92.3 Million Metric Tons.........................................................12
Figure 2.3: 2021 Global Methanol Demand by end use, 2021 Demand = 95.2 Million Metric Tons: The Importance of MTO – 1 in 5 tons of methanol.........................................................13
Figure 2.4: ExxonMobil photo of Mobil’s commercial MTG plant in New Zealand in the 1990s. .................................................................................................................................17
Figure 2.5: (a) Skeletal diagram of the (100) face of ZSM-5 zeolite (10-membered ring openings), and (b) 3D channel structure of ZSM-5 zeolite. .........................................................22
Figure 2.6: Published areas in which microwave radiation has been applied. .........................41
Figure 2.7: Electromagnetic spectrum. ............................................................................................41
Figure 2.8: Types of microwave heating. .........................................................................................43
Figure 2.9: Multi-mode microwave oven schematic diagram..........................................................48
Figure 3.1: Experimental set-up for post-synthesis modification step. ............................................70
Figure 4.1: XRD patterns for the parent zeolites (HZSM-5) and microwave-untreated and treated catalysts: (a) 0.5FeZ10/0-700 and (b) 0.5FeX10/0-700.................................................................75
Figure 4.2: N$_2$ adsorption-desorption isotherms of microwave-treated and untreated catalysts at -196 °C: (a) 0.5FeZ10/0-700 and (b) 0.5FeX10/0-700 catalysts.................................................................77
Figure 4.3: SEM micrographs of microwave-treated and untreated catalysts..................................83
Figure 4.4: FT-IR spectra for the parent zeolites (HZSM-5) and microwave-untreated and treated catalysts: (a) 0.5FeZ10/0-700 and (b) 0.5FeX10/0-700 catalysts .................................................................84
Figure 4.5: C$_3$H$_9$N-TPSR data profiles for n-propylamine decomposition to propylene and ammonia..............................................................................................................................87
Figure 4.6: Propylene profiles obtained from the C$_3$H$_9$N-TPSR experiments over varying Si/Al ratio; 30 (a) and 80 (b) for determining the concentrations of Brønsted acidic sites (c$_B$). ......88
Figure 4.7: MeOH-TPSR data profiles for methanol conversion to C$_1$–C$_5$ aliphatic and C$_6$–C$_8$ aromatic hydrocarbons.................................................................................................................91
Figure 4.8: C$_1$ Alkane (Methane) profiles obtained from the MeOH-TPSR experiments over varying Si/Al ratio; 30 (a) and 80 (b)..................................................................
Figure 4.9: C₂ Aliphatic hydrocarbons (Ethane and Ethylene) profiles obtained from the MeOH-TPSR experiments over varying Si/Al ratio; 30 (a) and 80 (b).

Figure 4.10: C₃ Alkane (Propane) profiles obtained from the MeOH-TPSR experiments over varying Si/Al ratio; 30 (a) and 80 (b).

Figure 4.11: C₃-C₄ Alkenes (Propylene and Butene) profiles obtained from the MeOH-TPSR experiments over varying Si/Al ratio; 30 (a) and 80 (b).

Figure 4.12: C₆ Aromatic hydrocarbon (benzene) profiles obtained from the MeOH-TPSR experiments over varying Si/Al ratio; 30 (a) and 80 (b).

Figure 4.13: C₇-C₈ Aromatics (Xylene and Toluene) profiles obtained from the MeOH-TPSR experiments over varying Si/Al ratio; 30 (a) and 80 (b).

Figure 4.14: Increasing power level against maximum peak temperature for MTH process over 0.5FeZ₁₀₁₀₋₇₀₀ catalysts (a) and 0.5FeX₁₀₁₀₋₇₀₀ catalysts (b).

Figure A1: SEM micrographs of microwave-treated catalysts.

Figure A2: C₅ Alkene (Pentene) profiles obtained from the MeOH-TPSR experiments over varying Si/Al ratio; 30 (a) and 80 (b).

Figure A3: C₄-C₅ Alkanes (butane and Pentane) profiles obtained from the MeOH-TPSR experiments over varying Si/Al ratio; 30 (a) and 80 (b).
LIST OF TABLES

Table 3.1: List of reagents used together with their suppliers. ......................................................... 68
Table 4.1: Physicochemical properties of microwave-untreated and treated catalysts (0.5FeX_{1000-700} and 0.5FeZ_{1000-700}). ........................................................................................................ 79
Table 4.2: Coke quantity for Methanol-To-hydrocarbons conversion over microwave-treated and untreated catalysts (0.5FeX_{1000-700} and 0.5FeZ_{1000-700}). .............................................................. 81
Table 4.3: Effect of Fe loading, and microwave post-modification on the ratio of the band intensities of the FT-IR spectra and relative crystallinity estimated from FT-IR spectra. ...... 86
Table 4.4: Determination of Brønsted acidic sites from C_3H_7N-TPSR. ........................................... 90
Table A1: Maximum desorption peak temperatures (T_{max} values) from MeOH-TPSR data for adsorbed methanol over microwave untreated (0.5FeX_{1000} & 0.5FeZ_{1000}) and treat (0.5FeX_{10119-700} & 0.5FeZ_{10119-700}) catalysts. ......................................................................................................................................... 109
LIST OF SCHEMES

Scheme 2.1: Dual-cycle mechanism for Methanol to Hydrocarbons over H-ZSM-5. ........24
Scheme 2.2: Two proposed olefin methylation mechanisms; Co-adsorbed mechanism and Surface methoxide mechanism. ........................................................................................................26
Scheme 2.3: Two proposed aromatic methylation mechanisms; top (direct mechanism) and bottom (stepwise mechanism)..................................................................................................................29
## LIST OF ABBREVIATIONS

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>BET</td>
<td>Brunauer-Emmett-Teller</td>
</tr>
<tr>
<td>BTX</td>
<td>Benzene, Toluene, and Xylene</td>
</tr>
<tr>
<td>CTAB</td>
<td>Cetyltrimethylammonium Bromide</td>
</tr>
<tr>
<td>DICP</td>
<td>Dalian Institute of Chemical Physics</td>
</tr>
<tr>
<td>DMTO</td>
<td>Dimethyl ether or Methanol-To-Olefin</td>
</tr>
<tr>
<td>DMTP</td>
<td>Dimethyl ether or Methanol-To-Propylene</td>
</tr>
<tr>
<td>FCC</td>
<td>Fluid Catalytic Cracking)</td>
</tr>
<tr>
<td>FMTP</td>
<td>Fluidized-bed Methanol-To-Propylene</td>
</tr>
<tr>
<td>FT-IR</td>
<td>Fourier Transform Infrared Spectroscopy</td>
</tr>
<tr>
<td>GHG</td>
<td>Greenhouse gas</td>
</tr>
<tr>
<td>GHz</td>
<td>Gigahertz</td>
</tr>
<tr>
<td>IUPAC</td>
<td>International Union of Pure and Applied Chemistry</td>
</tr>
<tr>
<td>KTA</td>
<td>Kilo Tons per Annum</td>
</tr>
<tr>
<td>LHSV</td>
<td>Liquid Hourly Space Velocity</td>
</tr>
<tr>
<td>MGC</td>
<td>Mitsubishi Gas Chemical</td>
</tr>
<tr>
<td>MTA</td>
<td>Mega Tons per Annum</td>
</tr>
<tr>
<td>MTBE</td>
<td>Methyl-tert-butyl ether</td>
</tr>
<tr>
<td>MTG</td>
<td>Methanol-To-Gasoline</td>
</tr>
<tr>
<td>MTH</td>
<td>Methanol-To-Hydrocarbons</td>
</tr>
<tr>
<td>MTO</td>
<td>Methanol-To-Olefins</td>
</tr>
<tr>
<td>MTP</td>
<td>Methanol-To-Propylene</td>
</tr>
<tr>
<td>OGD</td>
<td>Olefin-to-Gasoline/Distillate</td>
</tr>
<tr>
<td>PDH</td>
<td>Propane Dehydrogenation</td>
</tr>
<tr>
<td>SAPO-34</td>
<td>Silicoaluminophosphate-34</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscopy</td>
</tr>
<tr>
<td>SMTO</td>
<td>SRIPT Methanol-To-Olefins</td>
</tr>
<tr>
<td>SMTP</td>
<td>SRIPT Methanol-To-Propylene</td>
</tr>
<tr>
<td>SRIPT</td>
<td>Shanghai Research Institute of Petrochemical Technology</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermogravimetric Analysis</td>
</tr>
<tr>
<td>TIGAS</td>
<td>Topsøe’s improved gasoline synthesis</td>
</tr>
<tr>
<td>TPSR</td>
<td>Temperature Programmed Surface Reaction</td>
</tr>
<tr>
<td>wt.%</td>
<td>Weight percent</td>
</tr>
<tr>
<td>-------</td>
<td>----------------</td>
</tr>
<tr>
<td>XRD</td>
<td>X-Ray Diffraction</td>
</tr>
<tr>
<td>ZSM-5</td>
<td>Zeolite Socony Mobil-5</td>
</tr>
</tbody>
</table>
1.1 Introduction

In recent years, research and development of alternative processes for clean fuel sources to replace petroleum energy sources has attracted tremendous attention. This is due to the challenges facing the transport sector which heavily relies on petroleum as the primary energy source in countries like South Africa (Singh, 2006), and the ever-growing propylene gap amongst others (Plotkin, 2014). These challenges include; greenhouse gas (GHG) emissions which are the results of fossil fuels consumption to meet the energy demands like in South Africa (Escobar et al., 2009; Pone et al., 2007). These emissions cause many harmful effects such as climate change, rise in sea level, receding of glaciers, loss of biodiversity, etc. (Gullison et al., 2007). Moreover, uncertainty over the future price of crude oil, caused by political instability in the crude oil exporting countries (Nkomo, 2017), and the rising exhaustion of fossil fuel resources (Escobar et al., 2009), are also driving forces to search for alternative fuel sources and petrochemical derivatives. There is a need to develop alternative, sustainable, renewable, efficient and cost-effective energy sources which result in lower or zero emissions.

Various alternative energy resources that have been explored so far to produce fuels include biomass, biogas (Murphy and McCarthy, 2005), alcohols, vegetable oils (Agarwal, 2007), natural gas and coal (Han and Chang, 2000). Due to its physical and chemical properties, methanol has been considered and verified as an eye-catching cleaner fuel to produce liquid fuel (high octave gasoline) and petrochemicals from methanol derivatives. Methanol-to-hydrocarbons (MTH) and Fischer–Tropsch (F-T) processes have been used as alternative routes to petroleum refineries (Baliban et al., 2012).

Methanol is converted to hydrocarbons (gasoline and olefins) using acidic zeolites or zeotypes as catalyst. The commercially used zeolites are ZSM-5 and SAPO-34 (Amghizar et al., 2017; Keil, 1999). In the MTH process, methanol is converted to the mixture of hydrocarbons in the range, C₂ to C₁₀ which includes; paraffins, olefins and aromatics. Since diesel or jet fuel fractions are not produced in this process, Mobil developed another route which is abbreviated
as MOGD. MOGD is the combination of methanol-to-olefins (MTO) and Mobil olefin-to-gasoline/distillate (OGD) processes. The distillate that is produced, is also hydrotreated to form diesel or kerosene (Figure 1.1) (Baliban et al., 2012; Keil, 1999).

![Methanol to hydrocarbons (MTH) process](image)

**Figure 1.1:** Methanol to hydrocarbons (MTH) process (Baliban et al., 2012).

The ZSM-5 zeolite is mainly used as a catalyst to produce a high yield of hydrocarbons due to its catalytic properties (Keil, 1999). However, in the MTH process, catalyst deactivation by coke deposition is the main challenge. Using other conventional commercial catalysts, coke deposition is even increased. Coke deposition is attributed to diffusion limitation of larger molecules within the zeolite pore cavity which then hinders the contact between the reactant and product species with zeolite active sites. Coke deposition decreases the catalyst activity and selectivity (Benito et al., 1996; Liu et al., 2016; Tian et al., 2015; Ye et al., 2015).

Much interest has been paid in the preparation of nanoporous, mesoporous or hierarchical ZSM-5 from microporous ZSM-5 zeolite to overcome diffusional limitations. Hierarchical or mesopores in zeolites can be created during synthesis directly using templating techniques or in a post-synthesis modification step. Post-synthesis modification involves the dealumination.
or desilication of part of the zeolite using a chemical leaching approach. As it can be observed from the literature, several attempts have been conducted to increase the accessibility of the catalyst active sites in order to overcome catalyst deactivation due to coke deposition in the MTH process (Ahmadpour and Taghizadeh, 2015; Chen et al., 2016; Wang et al., 2014; Wei et al., 2015).

However, all the studied techniques to overcome coke deposition have some drawbacks and are covered in detail in the literature review in this present work. For example, the chemical leaching approach involves multiple steps to create the hierarchical or mesoporous zeolites, and an undesired Si/Al ratio is sometimes attained. The templating approach involves the use of expensive templates, and it is complicated to use templates as there is phase separation between micro and mesoporous phases when using surfactants as templates. Moreover, creating nano-sized ZSM-5 zeolite also has difficulties, as it is difficult to separate the seeding particles and the nano-sized ZSM-5 zeolite aggregates (Bjørgen et al., 2008; Majano et al., 2009; Meng et al., 2016; Meng et al., 2009; Shen et al., 2014). In this present study, we seek to use microwave radiation as post-synthesis modification step to overcome coke deposition and methane production in the MTH process by either creating the hierarchical or mesoporous catalysts.

1.2 Problem Statement

Despite the superior results of ZSM-5 in the MTH process, which include high selectivity towards desired hydrocarbons, resistance to deactivation due to coke deposition as compared to other zeolites, etc. (Chen et al., 2017; Mokrani and Scurrell, 2009; Wu et al., 2013; Zhang et al., 2017), the microporous characteristic of ZSM-5 zeolite significantly influences mass transfer of the reactants and products to/from the active sites, and as a result, ZSM-5 still suffers from diffusion limitations of larger molecules resulting in restrictions in the catalyst activity and lifetime (Bjørgen et al., 2008; Hu et al., 2014). Due to ZSM-5’s unique pore structure, only gasoline range hydrocarbons are allowed to diffuse out, and larger molecules than those found in this range are responsible for ZSM-5 zeolite deactivation. Catalyst deactivation due to coke deposition is still a significant challenge which needs to be solved.
In this study, we investigate the possibility of using microwave radiation to modify metal impregnated ZSM-5 by creating either mesopores or hierarchical structures in ZSM-5 zeolite in order to overcome catalyst deactivation which is associated with high methane production in the MTH process. Microwave ovens are cheap and readily available for industrial, domestic and laboratory use. Already exploited modification steps like chemical leaching, templating, etc. have some drawbacks which limits their wider application.

1.3 Aims and Objectives

1.3.1 Aim
The aim of this work is to create mesoporous or hierarchal iron-impregnated ZSM-5 (Fe/ZSM-5) catalysts using microwave radiation as post-synthesis modification step to overcome catalyst deactivation in MTH process.

1.3.2 Objectives
The objectives set to achieve the aim of this work are:

(i) To prepare HZSM-5 from NaZSM-5 zeolite by varying Si/Al ratio; a low value of 30 and a high value of 80 was used.
(ii) To prepare 0.5Fe/ZSM-5 catalysts using the incipient wetness impregnation (IWI) method from HZSM-5 parent zeolite and iron(III) nitrate nonahydrate.
(iii) To modify the prepared 0.5Fe/ZSM-5 catalysts using microwave radiation under varying microwave power levels (0-700 Watts) and over a 10 s duration.
(iv) To characterize the microwave treated and untreated catalysts prepared above using: nitrogen adsorption-desorption analysis, powder x-ray diffraction (p-XRD) analysis, thermogravimetric analysis (TGA), scanning electron microscopy (SEM) analysis, Fourier transform infrared spectroscopy (FT-IR), and propylamine-temperature programmed surface reaction (C₃H₅N-TPSR).
To study the effect of microwave radiation on the product distribution in the MTH process using methanol-temperature programmed surface reaction (MeOH-TPSR) technique.

1.3.3 Thesis Statement

Microwave radiation is an effective post-synthesis modification step to overcome catalyst deactivation due to coke deposition in MTH process.

1.3 Structure of Thesis

This thesis is divided into five chapters:

- Chapter 1: this chapter presents the introduction, problem statement, research aim and objectives, and the thesis statement.
- Chapter 2: this chapter presents a literature review of this research giving the details on methanol economy, methanol to hydrocarbons, ZSM-5 zeolite, catalyst deactivation, studies to mitigate coke deposition and their limitations, and microwave radiation.
- Chapter 3: this chapter presents the general experimental procedures followed, list of reagents used, and list of characterization techniques used.
- Chapter 4: this chapter presents the Results and Discussion obtained.
- Chapter 5: this chapter presents the conclusions and recommendations necessary for future work.
References


2.1 Methanol Economy

Thanks to the Nobel Laureate George Olah and coworkers, and some researchers before him for advocating for the use of methanol and its derivatives as alternative fuel sources. The aim was to replace the petroleum-based chemicals and fuels in order to use methanol and its derivatives as a route to sustainable development in the future (Olah, 2005; Yang and Jackson, 2012). This advocacy is a result of the recognized rapid population growth and expanding economies which causes increasing global energy demand. To meet this energy demand, petroleum-based fuels have been and are still being used as primary energy sources. The bottlenecks for using these petroleum-based fuels are fluctuating petroleum prices, greenhouse gas emissions which constantly possess threats to the environment, and the depletion of world fossil resources (Riaz et al., 2013). This has augmented the search and use of environmentally friendly alternative fuels.

A few promising alternative energies being studied so far include hydrogen energy, nuclear energy, bio energy, solar energy, hydro energy and wind energy. However, due to the extreme importance of petroleum-based fuels and chemicals, the latter which serve as raw materials in various chemical industries, the use of petroleum-based fuels will not completely leave the history stage. For that matter, methanol is a promising alternative fuel as it is also a vital raw material in chemical industries, and because of its use in the transportation sector (Su et al., 2013), hence the so called term, “methanol economy”.

Besides the methanol economy, the hydrogen economy as an alternative, is an option also being studied worldwide (Seadira et al., 2018). However, as pointed out by Olah (2005), hydrogen generation and its utilization as a clean fuel have some drawbacks. Its use as a fuel is not convenient, and its transportation possesses some safety concerns. Moreover, the needed infrastructure is not available for a hydrogen economy although it may eventually be developed, and the hydrogen volumetric power density is also a drawback. A methanol economy can serve as a feasible and realistic means of storing hydrogen energy by producing methanol from syngas. Methanol is easy to handle and to transport essentially using already
existing infrastructure, and it can be used conveniently as a fuel and a raw material for manmade hydrocarbons and their products (Olah, 2005). Moreover, processes used for methanol production have cleaner production with some challenges related to catalyst deactivation (Riaz et al., 2013).

Methanol is produced starting from multiple sources either traditionally or renewably from coal, natural gas, biomass, landfill gas and recycling captured carbon dioxide (CO₂) from power plant/industrial emissions and atmospheric CO₂ (Bozzano and Manenti, 2016; Pérez-Fortes et al., 2016). The latter has recently been receiving great interest as a green-methanol synthesis pathway as this will alleviate the main manmade cause of global warming (Olah, 2005; Pérez-Fortes et al., 2016). Despite that, mature technologies are available for natural gas conversion to syngas in order to produce methanol and are widely used in chemical process industries. Producing methanol from natural gas still dominates the industry (Amigun et al., 2010; Riaz et al., 2013). Figure 2.1 depicts methanol production processes currently operating worldwide under the following operating conditions; pressures of 50-100 atm and temperatures of 200-300 °C (Bozzano and Manenti, 2016).

![Figure 2.1](image-url): Methanol production processes operating worldwide (Bozzano and Manenti, 2016).
Methanol plays a vital role as a major chemical intermediate and its transformation into very important products and commodities drive and span our daily life (Riaz et al., 2013). Methanol and its derivatives are utilized for the following: fuels, medicines, pesticides (Yang and Jackson, 2012), plastics, resins, adhesives, paints, antifreeze, silicones, polymers, single-cell proteins (Bozzano and Manenti, 2016), as a hydrogen carrier for fuel cells, wastewater denitrification, electricity generation, transesterification of vegetables oils for biodiesel production (Riaz et al., 2013), and so on. Among the methanol derivatives, the most important include: formaldehyde, methyl-tert-butyl ether (MTBE), acetic acid and dimethyl ether (Bozzano and Manenti, 2016). Figure 2.2–2.3 shows a summary of methanol demand by end use for 2011 and projected demand forecast for 2016 and 2021.
Figure 2.2: Global Methanol demand by end use (a) 2011 demand = 55.4 Million Metric tons (b) 2016 demand forecast = 92.3 Million Metric Tons (Riaz et al., 2013).
Figure 2.3: 2021 Global Methanol Demand by end use, 2021 Demand = 95.2 Million Metric Tons: The Importance of MTO – 1 in 5 tons of methanol (Alvarado, 2005).

As shown in Figure 2.2-2.3, in 2011, formaldehyde production was the largest methanol consumer accounting for almost 32.0% of methanol demand worldwide, and with the 2016 and 2021 methanol demand forecast, formaldehyde production become the second largest after falling to 25.0% and 26.9% and the gasoline/fuel applications becoming the largest methanol demanding sector rising to 31.0% and 28.5% respectively as anticipated. Compared to 2011 end use demand (6.0%), the methanol-to-olefins/propylene (MTO/MTP) demand is anticipated to become a high growing sector, rising to 22.0% and 19.3% by 2016 and 2021. With some methanol derivatives declining, such as formaldehyde, while others are strongly increasing such as MTO/MTP, and biodiesel for example, the methanol market is in a changing state with overall world methanol demand anticipated to grow to 95.2 million metric tons by 2021 (Alvarado, 2005). This shows that there is an increasing interest in methanol and its derivatives (synthetic gasoline, diesel, olefins, and some wide-ranging chemical products). Ensuring novel ways to design the catalysts to overcome catalyst deactivation by coke, green-methanol synthesis pathways, further technology development and increasing practical application, a methanol economy is a realistic and feasible alternative to replace petroleum-based fuels and mitigate greenhouse emissions and atmospheric CO₂.
2.2 MTH Process

Out of two teams of Mobil scientists working on different projects, one team was attempting to convert methanol to ethylene oxide over ZSM-5 zeolite at Mobil Chemical Edison, New Jersey, while the other team was attempting to methylate isobutene with methanol using ZSM-5 at Mobil Oil’s Central Research Laboratory in Princeton; this led to the discovery of methanol-to-hydrocarbons (MTH) by coincidence as neither of the aforementioned reactions proceeded according to their expectations (Keil, 1999; Mokrani and Scurrell, 2009). This gave rise to a large number of detailed investigations on the reaction mechanisms involved and catalyst optimization.

The discovery of methanol into value-added hydrocarbons (gasoline with high octane number) over solid acidic zeolite in the 1970s, and the first and second oil catastrophes in 1973 and 1978 respectively, triggered immense interest for industrial development of the reaction and the search for alternatives to petroleum (Chang, 1983; Keil, 1999). Since methanol can be produced from various carbon sources by proven technology, the discovery by Mobil offered a new alternative source for petroleum and classical synthetic fuel processes like Fischer-Tropsch (Chang, 1983).

This led to the demonstration and development of the first Mobil pilot plant (4 barrels per day) using fixed-bed reactor to check the feasibility of the MTG process in response to the New Zealand government request (Keil, 1999; Ye et al., 2015). In addition to the fixed-bed MTG process, a 4 barrels per day MTG pilot plant using a fluidized-bed technology which surpassed fixed-bed reactor technology in terms of excellent heat transfer properties, high octane numbers, and continuous catalyst regeneration (Keil, 1999); this was developed in Paulsboro, New Jersey and later on, scaled-up to a demonstration plant (100 barrels per day) in Wesseling, Germany during 1981-1984 (Ye et al., 2015). This plant successfully demonstrated the performance of the fluidized-bed reactor system for MTG and methanol-to-olefins (MTO) technology (Keil, 1999). In 1985, the first Mobil MTG commercial plant was implemented in New Zealand with a gasoline capacity of 14,500 barrels per day based on natural gas converted into methanol through syngas (Ye et al., 2015).

After Mobil’s discovery about the synthetic shape-selective ZSM-5 zeolite in MTG process, Union Carbide reported the successful synthesis of silicoaluminophosphate (SAPO) catalyst
and developed the MTO process in 1986 using SAPO with the olefins yield exceeding 90%. They reported that by modifying the process, about 60% selectivity towards ethylene and propylene can be attained (Keil, 1999). In the Mobil’s MTG process, the hydrocarbons produced spin from $C_1$ to $C_{11}$ with roughly 80% selectivity towards $C_{5+}$ (benzene fraction) hydrocarbons (Ye et al., 2015). This boils down to a conclusion that the zeolite topology and the operating conditions used determine classes of hydrocarbons produced from methanol over acidic zeolites or zeotypes (Ilias and Bhan, 2012).

As the oil prices dropped again in the 1980s, further developments of commercial processes were forced to stop. However, this never thwarted the investigations on the bench scale and submissions of the patent applications (Keil, 1999). Recently, much interest has been paid into the MTH processes especially in catalyst synthesis, reaction mechanism, reaction kinetics, process development and reactor scale-up. This is driven by roaring high energy demand, global warming, search for petrochemicals from non-petroleum based sources, and depleting fossil fuels which resulted in a search for alternatives for fossil fuels. Many researchers, for example Stöcker have reviewed the catalyst details and reaction mechanisms for MTH processes especially MTO/MTP, MTG and Mobil’s olefin-to-gasoline and distillate (MOGD) (Stöcker, 1999). Therefore, understanding the reaction mechanism and shape selectivity of the targeted products over relevant zeolite catalyst is very important.

2.3 Commercialized MTH Processes

Owing to enormous demands of petrochemicals which drive and span our daily life which can be derived alternatively from methanol and its derivatives, especially propylene, ethylene, and high octane gasoline. Numerous companies and institutions have put more effort in the research and development of the MTH process since it was first discovered by Mobil Corporation. Major progress has been accomplished regarding catalyst synthesis, the reaction mechanisms involved, and process research and development (Stöcker, 1999). Several MTH processes have either been commercialized or are ready to be commercialized.
2.3.1 Commercialized MTG Processes

In October 1985, the world’s first commercial MTG plant using a fixed-bed system was set into operation in New Zealand (Allum and Williams, 1988). The plant was designed to produce 14,450 barrels per day of high octane gasoline, and for 1986 as a whole, 584,780 tons of gasoline were produced which was equivalent to nearly 35% of New Zealand’s premium gasoline consumption (Maiden, 1988). Several parallel reactors were used in the commercial MTG unit in New Zealand, and alternating catalyst regeneration was done to maintain the continuous operation, as the ZSM-5 was slowly deactivated by coke deposition even though it was shown as a feasible catalyst of choice for the MTG process (Ye et al., 2015).

Mobil corporation currently held by ExxonMobil, continued further improving the MTG process and started to license the improved MTG process. In 2010 the first MTG unit was started up in Shanxi, China with a production capacity of 100 kilo tons of gasoline per annum using the improved ExxonMobil MTG technology (Ye et al., 2015). Figure 2.4 shows the ExxonMobil photo of Mobil’s commercial MTG plant in New Zealand in the 1990s (Hindman, 2017). Besides the Mobil Oil methanol-to-gasoline (MTG) process, the Haldor-Topsøe TIGAS (Topsøe’s improved gasoline synthesis) process was also commercialized (Losch et al., 2015).
Some improved ExxonMobil MTG fixed-bed licenses issued are listed below (Hindman, 2017):

(i) 2006, Shanxi, China, 100 KTA  
(ii) 2007. Wyoming, U.S., 600 KTA  
(iii) 2011, Shanxi, China, 1 MTA  
(iv) 2012, Louisiana, U.S., 1.6 KTA  
(v) 2012, Louisiana, U.S., 500 KTA  
(vi) 2014, U.S., 640 KTA

### 2.3.2 Commercialized MTO Processes

For more than 30 years, the DICP (Dalian Institute of Chemical Physics) has been keen on the research and development of the MTO process, with the aim of developing a commercially available MTO process. In the 1990s, DICP scientists successfully upgraded the MTO technology to DMTO (dimethyl ether or methanol-to-olefin) technology after completing an MTO pilot test in 1991. In late 2010, China witnessed a couple of milestone developments of its own MTO technology based on DMTO technology. The world’s first commercial MTO
process was started up successfully in its first trial run with production capacity of 600,000 tons of light olefins (ethylene and propylene) per annum in Baotou, China (Ling, 2011).

Later on in October 2010, the first licencing agreement on DMTO-II was signed with the production capacity of 670,000 tons of light olefins per annum (Ling, 2011). So far, twelve commercial units applying DICP’s DMTO technology have been realized in China with annual production capacity of 6.5 million tons of light olefins (Liu, 2017). Several MTO processes have either been commercialized or are ready for commercialization; these include in addition to the DMTO process, the MTO process by Norsk Hydro/UOP, and the SINOPEC’s MTO (SMTO) process by SINOPEC (Bleken et al., 2012; Ye et al., 2015).

2.3.3 Commercialized MTP Processes

Propylene is the second largest olefin feedstock, and it is produced traditionally as a by-product of the steam cracking process for ethylene production, and from FCC (fluid catalytic cracking) units (Wei et al., 2011). Since it is produced as a by-product, its production volume is determined by ethylene and gasoline production, respectively. The above mentioned traditional two propylene sources are now facing a down-turn as stream crackers in North America and the Middle East are now shifting to ethane feedstocks resulting in a decrease in propylene production volume, and the propylene demand continuously growing and outpacing the growth of new steam crackers and new FCC units. With the 2015 forecast, about 80% of propylene demand was supplied by the traditional refineries and steam crackers, and 20% was projected to be met by alternative processes (Ding. and Hua, 2013). However, crude oil cracking to produce light olefins is expected to be in a short supply in the foreseeable future (Zhang et al., 2014). Therefore, new processes with high propylene yield are required to avoid a continuously growing propylene gap.

High demands for propylene derivatives and propylene scarcity are the driving forces for propylene prices overshooting the projected 2015 forecast. Therefore, the research and development of alternatives for traditional propylene sources and propylene derivatives has been extensively pursued. These alternatives include; propane dehydrogenation (PDH), olefin metathesis, propylene derivatives from non-propylene feedstocks, and methanol-olefin/propylene especially in the countries where naphtha and natural gas are very scarce like China (Ding and Hua, 2013).
However, there are a few limitations that can be pointed out for each of the following alternative process; even though PDH has received much attention, few feedstock sources are available to sustain the process in the near future as fossil fuels used to produce propane are depleting unlike the MTH process where methanol has diversified carbon sources. Thus, MTH process can be regarded as the most promising option because of methanol on its own and various petrochemicals obtained from methanol derivatives (Bozzano and Manenti, 2016; Riaz et al., 2013; Su et al., 2013; Yang and Jackson, 2012). Even though olefin metathesis is a well-developed technology, the lucrativeness of the metathesis process is determined by the price difference between ethylene, butane, and propylene. Olefin metathesis units also need access to large C₄ streams that are free of isobutylene and butadiene (Ding and Hua, 2013).

The non-propylene feedstocks that have been proven to produce propylene derivatives include, butanol, acrylic acid, propylene glycol, epichlorohydrin, and 1,3-propanediol processes. These processes are at or close to the commercialization stage. These no-propylene feedstocks are produced using bio and fossil-based routes but there are also some limitations towards vast implementation of each one of them. For example, the cost of the fermentation process, the price of purchased propylene and ethylene, the price of biomass, the cost of producing ethylene oxide from ethylene, the cost and number of catalysts used to produce 1,3-propanediol, the cost of chlorine as a raw material for producing glycerin, the cost of alcohols to produce biodiesel and by-product (glycerin) (Ding and Hua, 2013), and the price of vegetable oils used to produce biodiesel which surpasses the price of crude oil (Kennedy, 2017). These aforementioned limitations are very crucial in determining whether the process will be competitive in the market or not compared to other commercially available propylene producing processes. This is not to say that they are not feasible alternatives for producing propylene and its derivatives apart from the MTH process.

Propylene with high yield can be obtained from the MTP process. The MTP process was first put into the commercialization stage in 2010 in China by the Lurgi company using a fixed-bed reactor and a high-silica nanosized HZSM-5 zeolite as a catalyst (Ahmadpour and Taghizadeh, 2015; Zhang et al., 2017). In 2011, two MTP processes were successfully started up in Ningxia Autonomous Region, and in Duoteng, Inner Mongolia Autonomous Region, China by Shenhua Ningxia Coal Chemical, and Datang International Power Generation Company Ltd. respectively (Ding and Hua, 2013). The JGC/Mitsubishi DTP (dimethyl ether-to-propylene)
process and Lurgi MTP process are major processes based on MTP technology. Several MTP technologies were also developed, including: the SMTP technology, FMTP (fluidized-bed methanol-to-propylene) technology, and the DMTP technology developed by Shanghai Research Institute of Petrochemical Technology, Tsinghua University, and the DICP based on their DMTO process, respectively (Ding and Hua, 2013).

2.4 ZSM-5 Zeolite

Numerous types of catalysts with different topologies, compositions, morphologies, and under different reaction conditions have been examined extensively in the MTH process before (Chang, 1983), and even after the discovery of the MTH process over acidic ZSM-5 zeolite in the 1970s by Mobil Corporation (Rostamizadeh and Yaripour, 2016; Yaripour et al., 2015; Yaripour et al., 2015; Zhang et al., 2017). Molten ZnCl₂, P₂O₅, Al₂O₃, silica gel, silica-alumina, activated Al₂O₃ or Type-C Al₂O₃, amorphous silica-alumina, and metal molybdate catalyst modified with nickel chromite were used in the MTH process prior to ZSM-5 zeolite. Some of the products obtained were light alkanes, mostly methane, hexamethylbenzenes, isobutene, dimethyl ether, carbon monoxide and carbon dioxide (Chang, 1983).

For the last four decades, a comprehensive screening of a large variety of catalysts characterized by different compositions (distribution and number of acidic sites), topologies (cavity/channels networks and dimensions), and morphologies (micro and mesoporosity, crystal dimensions) has been made (Olsbye et al., 2012). The aims were to increase selectivity towards light olefins, gasoline range hydrocarbons, and to find a catalyst which is resistant to deactivation by coke deposition (Mokrani and Scurrell, 2009). The MTH process has been assessed over a range of catalysts starting from small-pore zeolites (SAPO-34, ZSM-58, Sigma-1, HFU-1, etc.), medium-pore zeolites (EU-2, ZSM-5, etc.), and large-pore zeolites (CON, modified Y zeolites, Ba/dealuminated mordenite, Mn/ZSM-12, etc) (Mikkelsen and Kolboe, 1999; Yaripour et al., 2015; Yaripour et al., 2015; Zhang et al., 2017).

Among all the catalysts studied, Zeolite Socony Mobil-5 (ZSM-5) was recognized to be a remarkably effective catalyst for the MTH process in an industrial application owing to its
inherent advantages: high octane number gasoline produced (Mokrani and Scurrell, 2009), high selectivity towards propylene (Zhang et al., 2017), strong resistance to catalyst deactivation caused by coke deposition which permits reasonable cycle lengths to be attained without extreme catalyst requirements (Wu et al., 2013; Yurchak, 1988), a 10-ring interconnected channel system with high/adjustable Si/Al ratio, high thermal/hydrothermal stability, and high catalytic activity (Chen et al., 2017; Yaripour et al., 2015). The appropriate choice of the catalyst is very critical as it plays a major role in the success of the process.

Beside medium-pore ZSM-5 zeolite, SAPO-34 zeolite with small-pores is used as a catalyst in industrial MTH processes for high selective production of light olefins (Howe et al., 2016). Despite the fact of high selectivity towards ethylene, SAPO-34 is deactivated by coke deposition quicker than ZSM-5 zeolite. Thus, fluidized-bed technology is the best choice for any MTH processes using SAPO-34 zeolite as a catalyst (Ye et al., 2015). The high selectivity towards light olefins is still a challenge and there is still ample opportunity for research to design novel catalysts for the selective production of light olefins. ZSM-5 zeolite as a catalyst is still a subject of interest owing to its properties towards deactivation by coke deposition.

ZSM-5 zeolite is a porous aluminosilicate framework composed of AlO₄ and SiO₄ tetrahedra (Fathi et al., 2014). ZSM-5 zeolite has 10-membered ring openings, and three-dimensional (3D) pore structure consisting of straight channels intersecting with sinusoidal channels. Figure 2.5(a) demonstrates the skeletal diagram of the face of ZSM-5, where the 10-membered ring openings are the entrances to the sinusoidal channels. Figure 2.5(b) demonstrates two channel structures in ZSM-5 zeolite; straight channels (0.53 nm × 0.56 nm), and sinusoidal channels (0.51 nm × 0.55 nm) which create the 3D network responsible for ZSM-5 zeolite’s high selectivity and stability (Omojola et al., 2018).
2.5 Reaction Mechanisms

There has been lively debate surrounding the MTH process since it was discovered regarding the following two aspects: the origin of the first C–C bond from the C₁ units, that is methanol.
or DME, and the mechanism by which MTH proceeds. Theoretical and experimental work indicated that direct coupling of two methanol molecules does not occur (Lesthaeghe et al., 2006; Lesthaeghe et al., 2007; Marcus et al., 2006). Early work postulated that the MTH reaction is autocatalytic in the sense that the small amounts of hydrocarbons greatly enhance the rate of C\textsubscript{1} units conversion until a steady-state is reached, and with an observable catalytic induction period (Ono and Mori, 1981). It has been shown that by co-feeding methanol with higher hydrocarbons (C\textsubscript{2+}), the catalyst induction period is significantly reduced, and this shows that both olefins and C\textsubscript{2+} species play a critical role in the MTH process (Langner, 1982; Ono and Mori, 1981).

Dahl and Kolboe, (1996) proposed the hydrocarbon pool mechanism in which the pool of (CH\textsubscript{2})\textsubscript{n} species within the zeolite pores is formed by methanol to produce light olefins, alkanes, and aromatics. They showed that high hydrocarbons are not formed by successive methylations of ethylene. In recent years, it is widely accepted that the MTH process proceeds through a dominating indirect route called “hydrocarbon pool mechanism” (Ilias and Bhan, 2012). Mole et al., (1983) indicated that \textsuperscript{12}C-atoms of ethylene matched exactly the \textsuperscript{12}C-atoms of toluene when co-feeding \textsuperscript{13}C-methanol with \textsuperscript{12}C-toluene over ZSM-5, and this shows that ethylene was formed by dealkylaion of methylbenzenes, not by direct C-C coupling of C\textsubscript{1} units.

Bjørgeno et al., (2007) assessed the reactivity of the organics residing in the zeolite pores during the MTH reaction over ZSM-5 using transient \textsuperscript{12}C/\textsuperscript{13}C methanol-switching experiments. It was observed that \textsuperscript{13}C content and evolution of ethylene resembled exactly the ones for p/m-xylene and trimethylbenzenes, indicating that ethylene was formed predominantly from the lower methylbenzenes. In contrast to ethylene, the \textsuperscript{13}C content incorporation of C\textsubscript{3+} olefins matched each other, indicating that propylene and higher alkenes are formed to a considerable extent from alkene methylations and interconversions (e.g., cracking reactions) not from ethylene methylation.

It has been shown that two catalytic cycles run simultaneously during the MTH reaction over H-ZSM-5 namely: ethylene formation from the lower methylbenzenes followed by remethylation-aromatics carbon pool cycle, and a methylation/cracking cycle involving only the C\textsubscript{3+} alkenes–olefin carbon cycle (Scheme 2.1) (Bjørgen et al., 2007; Svelle et al., 2006).
These two catalytic cycles co-exist in the MTH reaction over ZSM-5; as a result, the aromatics/ethylene carbon pool cycle cannot run without the olefin-carbon pool cycle.

Scheme 2.1: Dual-cycle mechanism for Methanol to Hydrocarbons over H-ZSM-5 (Ilias and Bhan, 2012).

Ilias and Bhan, (2012) proposed six major chemistries that occur within the dual cycle mechanism for the MTH process over ZMS-5 zeolite namely, (i) olefin methylation, (ii) olefin cracking, (iii) hydrogen transfer, (iv) cyclization, (v) aromatic methylation, and (vi) aromatic dealkylation.

2.5.1 Olefin Methylation

Scheme 2.1 indicates that olefin homologation (methylation of the olefin carbon double bond) exists and is one route by which methyls are incorporated into hydrocarbon products (Ilias and Bhan, 2012). Tau and Davis, (1993) indicated that olefin methylation reactions exist over ZSM-5 zeolite using isotopic tracer studies. Several researchers have also shown that the olefin methylation route overwhelm in some one-dimensional 10-membered ring zeolites (ZSM-22, and ZSM-23) as these zeolites hinder both the hydrocarbon pool mechanism and secondary
reactions (Cui et al., 2008; Teketel et al., 2011). These catalysts (ZSM-22, ZSM-23, and ZSM-48) gave high selectivity towards hydrocarbon products rich in C$_5^+$ aliphatic hydrocarbons (Teketel et al., 2011).

Ilias and Bhan, (2012) indicated that for all feed compositions that were tested using $^{13}$C-labelled co-feeds (propylene and toluene), the C$_5$-C$_7$ olefins all had very similar fractions of isotopomers containing three $^{13}$C atoms as expected based on methylation of the $(n - 1)$ olefins, showing that these olefins were formed primarily from olefin homologation reactions. In contrast, the expected $^{13}$C atoms of propylene based on ethylene homologation did not match the observed $^{13}$C distribution of propylene for any of the feed compositions tested, showing that ethylene homologation is not a significant route for propylene formation, and ethylene does not play any significant role in any olefin-based catalytic cycle. The contributions of olefin methylation are hard to be accessed due to some difficulties to separate the olefin methylation reactions from the reactions caused by the hydrocarbon pool mechanism and secondary reactions overwhelm the primary reactions over ZSM-5 or SAPO-34 as catalysts (Song et al., 2000).

Two mechanisms for olefin methylation by methanol and dimethyl ether have been proposed namely (Scheme 2.2): (1) coadsorbed mechanism in which methanol/DME and an olefin are adsorbed on a single acid site and react in a single, associative/concerted step without formation of a surface methoxide intermediate; and (2) a surface methoxide mechanism in which protonation of methanol or DME by the zeolite acidic site protonate to form a surface methoxide that desorbs upon reacting with an olefin with lower carbon content (ethylene) to form higher carbon content olefin (propylene) (Ilias and Bhan, 2012; Maihom et al., 2009).
Scheme 2.2: Two proposed olefin methylation mechanisms; co-adsorbed mechanism and surface methoxide mechanism (Ilias and Bhan, 2012).

2.5.2 Olefin Cracking

Olefin cracking is the important route used commercially in Lurgi’s methanol-to-propylene (MTP) process to increase the production of propylene using highly siliceous ZSM-5 catalyst (Olsbye et al., 2012). Ilias and Bhan, (2012) showed that there was a high content of $^{12}$C atoms from $^{13}$C-DME in propylene when a 4 kPa partial pressure of $^{13}$C-propylene was co-reacted with a 70 kPa partial pressure of $^{12}$C-DME, showing that propylene was formed by cracking of larger olefins.

The olefin cracking mechanism requires an olefin to be protonated to form an alkoxide intermediate, followed by $\beta$-scission of the alkoxide to form a smaller alkoxide and smaller olefin. Subsequently, the smaller alkoxide desorbs to form another olefin and leaves behind a proton to regenerate the acid site of the zeolite. Speciation of olefin isomers is critical in determining the product selectivity for the MTH process. For example, if olefin cracking is considerably faster than olefin methylation, then the product distribution should be rich in light olefins. In contrast, if olefin cracking is slower than olefin methylation, then the product
distribution may be rich in larger olefins, which may cyclize to eventually form aromatics (Ilias and Bhan, 2012).

### 2.5.3 Hydrogen Transfer

Hydrogen transfer is a bimolecular reaction which involves transfer of a hydrogen atom between an adsorbed surface alkoxide and a cyclic or acyclic alkane or alkene. The identity of species that can undergo hydrogen transfer is changing with conversion, and as a result, the rate of hydrogen transfer varies with conversion (Ilias and Bhan, 2012).

Hydrogen transfer involves the abstraction of a hydrogen atom and is mediated by carbocationic transition states. As compared to linear alkanes, branched alkanes are facile hydrogen donors because the resulting carbocationic transition states are more stable as inferred by density functional theory (Boronat et al., 2000). Alkenes with tertiary allylic C−H bonds are even more reactive hydrogen donors than branched alkanes because they delocalize positive charge more effectively, which leads, in turn, to more stable carbocations (Ilias and Bhan, 2012).

### 2.5.4 Cyclization

As shown in Scheme 2.1, the olefin- and aromatic-based cycles are not independent of one another and “communicate” through cyclization and aromatic dealkylation steps. Cyclization is related to aromatization in that cycloalkanes and cycloolefins are not stable products of MTH and are quickly dehydrogenated to form aromatics. There are two possible generalized routes to olefin cyclization and aromatization. One involves dehydrogenation of olefins to form dienes and trienes that undergo cyclization to aromatics. In the second route, olefins first form cycloalkanes and are subsequently dehydrogenated to form aromatics. In both of these routes, dehydrogenation occurs through hydrogen transfer reactions in which olefins or cycloalkanes donate hydrogen to other hydrocarbons that act as hydrogen acceptors (Ilias and Bhan, 2012).

Dass and Odell, (1988) studied the conversion of C₁-C₇ alkanes, methanol, and co-feeding benzene over ZSM-5 zeolite as catalyst. They found that the gasoline produced from n-heptane at reaction temperature > 400 °C, is comparable to that one produced from methanol, at 370 °C and 410 °C reaction temperatures; the main products of n-heptane conversion were mainly
alkanes presumably from \textit{n}-heptane cracking, and gasoline range products at elevated temperatures, respectively. By co-feeding benzene, they found that the yields to ethylbenzene are higher for \textit{n}-heptane than for methanol. Moreover, they found that toluene is also a significant product of \textit{n}-heptane and its yield is not attributed to adding benzene. They suggested that toluene is probably produced by ring closure of the heptane ring. The formation of these large aromatics shows dehydrogenation through hydrogen transfer, cyclization and side reactions of cyclization, such as olefin oligomerization and alkylation of aromatics. The question of whether cyclization occurs prior to olefin dehydrogenation or vice versa still needs to be addressed.

2.5.5 \textbf{Aromatic Methylation}

Aromatics, specifically polymethylbenzenes, play a critical part in MTH catalysis in that these species, along with olefins, act as scaffolds for methylation reactions. The isotopic labeling studies of co-feeding methanol with aromatic benzene or toluene show that $^{13}$C atoms from methanol were situated in the aromatic ring as well as in the methyls groups – an excess of $^{13}$C was most pronounced in tri- and tetramethylbenzenes over ZSM-5 catalyst. This shows that aromatic methylation involves sequential methylation and it is the main reaction taking place over ZSM-5 catalysts (Mikkelsen \textit{et al.}, 2000).

However, Ilias and Bhan, (2012) showed that aromatic methylation is not the only route for producing other methylbenzenes. From their $^{12}$C/$^{13}$C isotopomer distributions, \textit{o}-xylene and \textit{p}-xylene containing seven $^{13}$C atoms were formed from $^{13}$C-toluene methylation, but when the feed composition was varied using $^{13}$C-toluene and $^{12}$C-DME and/or $^{12}$C-propylene, the isotopic distribution of \textit{o}-xylene closely matched the expected isotopic distribution, indicating that \textit{o}-xylene comes from toluene methylation entirely, whereas the observed $^{13}$C content for \textit{p}-xylene and larger polymethylbenzenes differ from the expected $^{13}$C content by methylation of the (\textit{n} - 1) methylbenzene, showing that these aromatics are not exclusively formed from methylation reactions instead cyclization reactions occur predominantly for C$_8$, aliphatics to form \textit{p}-xylene and larger aromatics.

There are two proposed distinct mechanisms for aromatic methylation like in olefin methylation: A stepwise, (consecutive, or dissociative) mechanism and a direct (concerted, or associative) mechanism (Martinez-Espin \textit{et al.}, 2017; Svelle \textit{et al.}, 2012), and are shown in
Scheme 2.3. The primary difference between the two, is that the stepwise mechanism involves
the formation of the covalently bonded surface methoxy group as a reaction intermediate, while
in the direct mechanism, there is no such reaction intermediate formed.

In the stepwise mechanism, methanol or DME is physisorbed unimolecularly on the Brønsted
acid site through hydrogen bonding and subsequent Brønsted proton transfer to form water and
methoxy intermediate. The formed methoxy group is then attached to the species to be
methylated resulting in a cationic species, which is assumed to be quickly re-oriented and
deprotonated to regenerate the original Brønsted acid site of the zeolite and the neutral
methylated product. In the direct mechanism, methanol or DME reacts directly with the species
to be methylated in a concerted fashion resulting in a protonated methylated product. Then,
quick re-orientation and back protonation of the zeolite occur which result in the neutral
methylated product and water or methanol, respectively (Svelle et al., 2011).

Scheme 2.3: Two proposed aromatic methylation mechanisms; top (direct mechanism) and
bottom (stepwise mechanism) (Martinez-Espin et al., 2017).
2.5.6 Aromatic Dealkylation

At the commercial scale, SAPO-34 zeolite is used as a catalyst to produce light olefins almost exclusively through aromatic dealkylation (Olsbye et al., 2012); this shows the vital role played by this chemistry route to olefin production. Experimental evidence has clearly shown that methylbenzenes and their protonated counterparts (or other related cyclic species) are central reaction intermediates for alkene formation in the MTH reaction (Olsbye et al., 2012).

Two distinct reaction mechanisms have been proposed on how these alkenes are formed from these species (mechanisms for aromatic dealkylation) namely: the paring, and the side-chain methylation mechanism. In the paring mechanism, the gem-methylation of a methylbenzene results in ring contraction. Subsequently, an alkyl substituent is formed which then cracks to produce light olefins. The side-chain methylation mechanism is also commenced by gem-methylation of a methylbenzene species which results in the removal of a methyl hydrogen, thus forming an exocyclic double bond, which can undergo side chain methylation. This side chain can then crack to form ethylene or propylene. The starting point for both aforementioned mechanisms is the gem-methylation step in which the aromaticity is broken down and the charged species is formed due to aromatic ring being doubly methylated. The key intermediate of the side-chain methylation mechanism that distinguishes it from the paring mechanism is the formation of methylbenzenes that also have ethyl, propyl, or other alkyl groups. The paring mechanism provides the mechanism that results in the ring carbon of methylbenzene being incorporated into the olefin formed, and also methyl group carbons on the aromatic to become incorporated into the benzene ring (Ilias and Bhan, 2012).

Ilias and Bhan, (2014) using isotopic labeling studies indicated that at 250–450 °C and low conversions (< 10 C%) with varying isotopic feed compositions of $^{13}$C/$^{12}$C over ZSM-5 zeolite, the $^{13}$C-content of ethylene and propylene from tetramethylbenzene most closely match the experimentally observed $^{13}$C-contents of ethylene and propylene. This shows that aromatic dealkylation to form ethylene and propylene occurs through the paring mechanism and that tetramethylbenzene is the predominant aromatic precursor for light olefin formation for MTO conversion over ZSM-5 zeolite. Understanding the communication between olefin- and aromatic-based cycles is a critical step in controlling selectivity of the MTH process over ZSM-5, since both cycles are not isolated from one another. Current interest in the MTH process has shifted to the production of olefins.
2.6 Factors Influencing Selectivity towards MTH Products

From the dual cycle mechanism over ZSM-5 zeolite, it has been shown that these two cycles namely – namely, the olefin-carbon cycle and aromatic-carbon cycle mechanism - communicate and are not independent of one another. Thus, to enhance the selectivity towards either light olefins or gasoline range hydrocarbons, one cycle must be suppressed and the other enhanced. Therefore, understanding this dual cycle is crucial. As an example, in order to enhance selectivity towards light olefins, it is essential to inhibit their conversion to aromatics. Numerous approaches that influence high selectivity towards either light olefins or gasoline over ZSM-5 have been investigated comprehensively. These approaches include: modifying the reaction condition (co-feeding water and/or varying methanol partial pressures, varying reaction temperature, varying contact time, etc.), varying Si/Al ratio of ZSM-5, varying ZSM-5 crystal size, modifying ZSM-5 with elements, etc. (Chang et al., 1984; Chang and Silvestri, 1977; Khanmohammadi et al., 2016; Chang, 1984; Luk'yanov, 1992; Mokrani and Scurrell, 2009; Stöcker, 1999; Spivey et al., 1992).

2.6.1 Influence of Si/Al ratio

As it has been shown here, the MTH process has been assessed over a range of catalysts starting from small-pore zeolites, medium-pore zeolites, and large-pore zeolites under different reaction conditions (Mikkelsen and Kolboe, 1999; Yaripour et al., 2015; Yaripour et al., 2015; Zhang et al., 2017). Most of the open literature deals with either SAPO-34 or ZSM-5 catalyst in the MTH process. SAPO-34 shows high selectivity towards ethylene production in the MTO process due to its small pore openings and moderate acid strength (Behbahani et al., 2014); however, high rate of catalyst deactivation due to coke deposition is observed on SAPO-34 (Álvaro-Muñoz et al., 2014; Chen et al., 1999). For that matter, ZSM-5 zeolite is a very promising candidate for MTO as a catalyst owing to its inherent advantages outlined in the previous sections, and it has been used at large MTO scale (e.g. Lurgi’s methanol-to-propylene (MTP) process) (Olsbye et al., 2012). However, the selectivity towards light olefins in the MTO over ZSM-5 catalyst is relatively low (Behbahani and Mehr, 2014). ZSM-5 zeolite has also been used in the MTG process to produce high octane gasoline.

ZSM-5 zeolite is a porous aluminosilicate framework composed of AlO₄ and SiO₄ tetrahedra (Fathi et al., 2014). The framework is negatively charged, and this is attributed to the partial
substitution of Si in the framework by Al. The charge of the unit cells is usually localized by the extra-framework cations (usually Na⁺), and these cations are exchangeable. Therefore, protonated zeolite can be derived by exchanging the cations with ammonium ones first, followed by thermally decomposing exchanged ammonium cations providing strong acid sites which give ZSM-5 zeolite high catalytic activity. As inferred above, the strength and density of acidic sites, more precisely the number of accessible Brønsted acid sites per unit cell are vital in determining the activity of the ZSM-5 zeolite and product distribution in MTH process. Zeolite acid sites may be related to tetrahedrally coordinated Al content (Benito et al., 1996; Primo and Garcia, 2014); thus, Si/Al ratio plays a vital role in determining the life span and activity of the ZSM-5 catalyst. ZSM-5 zeolite with low Si/Al ratio (i.e., high Al content) generally has a high density of acidic sites, and therefore high activity which lead to fast catalyst deactivation by rapid coke formation (Wan et al., 2016). Increasing Si/Al ratio of the zeolite can enhance the selectivity towards light olefin in the MTH process (Chang et al., 1984; Prinz and Riekert, 1988).

Wan et al., (2016) studied the effect of varying Si/Al ratio (23-411) of ZSM-5 zeolite in the MTG process. It was observed that decreasing the Si/Al ratio facilitated higher methanol conversion, and also decreased the catalytic activity which can be increased by increasing the Si/Al ratio; C₂-C₄ alkenes decreased, C₁-C₄ alkanes increased, a low gasoline yield was produced, and the rate of the aromatization increased reaction, which led to formation of coke precursors. As a result, rapid catalyst deactivation occured. The ZSM-5 zeolite with Si/Al ratio of 217 indicated 100% methanol conversion, low coke formation and high gasoline yield under studied reaction conditions.

Benito et al., (1996) showed that the greater proportion of higher molecular olefins was observed as Si/Al ratio increases. Moreover, the ratio of Brønsted/Lewis acid site increases, and total acidity decreases as the Si/Al ratio increases. This was explained using the mechanism of propagation of oxonium ions. From small scale to larger scale in MTP process, high-silica ZSM-5 zeolite normally with Si/Al ratio greater than 170 is being used as a suitable catalyst due to its inherent advantages to give high propylene selectivity and catalytic stability (Ahmadpour and Taghizadeh, 2015; Hu et al., 2012; Khanmohammadi et al., 2016; Rostamizadeh and Taeb, 2015). For the MTG process, ZSM-5 zeolite with Si/Al ratio in the range of 30-70 is used as a suitable catalyst with better catalytic activity and life span (Chang
et al., 1984; Chang and Grover, 1977; Bjørgen et al., 2008; Wan et al., 2014; Zaidi and Pant, 2004). The choice of suitable Si/Al ratio is very crucial to ensure high catalytic activity and long life span.

2.6.2 Influence of reaction temperature

The reaction temperature for the MTH (MTG and MTO) process has an effect on the product distribution. It was shown that at high reaction temperature (>500 °C), lower selectivity towards light olefins was observed accompanied by the formation of increasing number of carbon oxide molecules over ZSM-5 catalyst (Chang and Silvestri, 1977; Zhang et al., 2014); however, as the reaction temperature was decreased (≤ 500 °C), the selectivity towards the light olefins was enhanced (Chang et al., 1984; Chang and Silvestri, 1977; Zhang et al., 2014). Generally, the optimum reaction temperature used to harvest high yield of olefins especially propylene, ranges from 450°C to 500 °C (Chang et al., 1984; Wu et al., 2013; Zhang et al., 2014). It was also shown that reaction temperature has an effect on the aromatic selectivity, and as the reaction temperature was increased, the selectivity towards aromatics also increased (Di et al., 2013; Inoue et al., 1995). For example, Di et al., (2013) showed that when the MTG reaction temperature was increased from 340 to 420 °C, the aromatics increased from 70.8 wt.% to 84.3 wt.%, respectively.

2.6.3 Influence of Partial Pressure and Co-feeding water

Olefin selectivity is greatly enhanced by conversion at subatomospheric methanol partial pressures. Chang et al., (1984) indicated that when the methanol partial pressure was increased from 1 atm to 6 atm using pure methanol as feed, C₂–C₅ olefins decreased from 58 wt.% to 41 wt.%, and aromatics increased from 13 wt.% to 20 wt.%. In another set of experiments, when methanol partial pressure was decreased from 1 atm to 0.4 atm by co-feeding water and keeping the total pressure constant at 3 atm, C₂–C₅ olefins increased from 65 wt.% to 77 wt.%, and aromatics decreased from 12 wt.% to 7 wt.%. This indicated that subatomospheric and/or atmospheric methanol partial pressures (Wu et al., 2013), and partial pressures greater than atmospheric (Di et al., 2013; Wan et al., 2014) enhance olefin, and aromatic selectivity, respectively. Moreover, this indicates the effect of water in the feed stream on the hydrocarbons distribution from methanol conversion over ZSM-5 catalyst. The presence of water in the feed
stream slows down the catalyst deactivation (Ghavipour et al., 2013), and increase the ethylene, and propylene selectivity (Wu et al., 2013).

2.6.4 Influence of contact time

Several authors have shown the influence of varying contact time on the MTH product distribution over zeolites (ZSM-5) (Chang, 1984; Chang et al, 1984; Chang and Silvestri, 1977; Inoue et al., 1995; Luk'yanov, 1992; Stöcker, 1999), and the trade-offs between the contact time and the catalyst Brønsted acidity (Chang, 1984; Chang et al., 1984). Chang and Silvestri, (1977) performed experiments on methanol conversion at 371 °C and liquid hourly space velocity (LHSV) equal to 1080, 108, and 1. At lowest contact time (LHSV = 1080), the dehydration of methanol to dimethyl ether and C2-C4 alkenes formation dominated, and as the contact time was increased to LHSV of 1, aromatics and paraffins dominated. This indicated that as the contact time was increased, the yield of light olefins increased, and reached the maximum at the expense of decreasing oxygenates concentration. As the contact time further increased, the yield of light olefins decreased while the yield of aromatics and paraffins increased indicating that those alkenes were intermediates to aromatics.

It is clear that the selectivity of olefins can be enhanced by decreasing contact time, and alternatively to reducing contact time, decreasing the Brønsted acidity of the zeolite also plays a significant role. Decreasing the Brønsted acidity can be achieved by either increasing the Si/Al ratio during the crystallization process for zeolites like ZSM-5 or by partially neutralizing the acidic sites. These two approaches have been found to give corresponding selectivity for olefin formation from methanol conversion over zeolites when compared on the same basis of proton concentration. From the plots of selectivity vs Si/Al ratio, and selectivity vs contact space time, similar trajectory was observed (Chang, 1984). When the contact time was adjusted to achieve complete conversion in the high Si/Al ratio region, significant aromatization occurred indicating the trade-off between contact time and catalyst Brønsted acidity (Chang, 1984; Chang et al., 1984).

2.6.5 Influence of modifying ZSM-5 with elements

The effect of modifying the zeolites with certain elements (e.g. metals, nonmetals, etc.) to increase product selectivity in the MTH process has been reported and dealt with extensively
Cha[35ter 2: Literature Review

(Froment et al., 1992; Khanmohammadi et al., 2016; Mokrani and Scurrell, 2009). The zeolite’s inner pore system is the catalytically active surface, and its structure depends on the zeolite topology, composition and the extra-framework cations in the interior space channels (Khanmohammadi et al., 2016). As mentioned above, these cations are sources of positive charge for compensating the negative charge of the framework, and they can be exchanged using other cations. These cations play a very critical role in determining the catalytic activity of the zeolite via their interaction with the Brønsted acid sites. Even the nonmetallic elements such as phosphorus also interact with the Brønsted acid sites, thereby affecting the catalytic activity of the zeolite. To introduce the elements into the zeolites, several modification procedures have been applied, and these includes: ion exchange, incorporation, and impregnation. Many attempts have been made using various elements across the periodic table ranging from alkali metal, alkaline earth metal, transition metal, nonmetal elements, etc. to improve the selectivity towards the hydrocarbons (gasoline and olefins) from methanol conversion using zeolites.

Elements such as phosphorus, Cs, Ca, Fe, Co, Pt, La, Zr, Mn, etc. have been used to modify ZSM-5 zeolite and studied in the conversion of methanol to hydrocarbons process. The results indicated that in all cases, modification increased the shape-selectivity to light olefins (Hajimirzaee et al., 2015; Inui et al., 1986; Rostamizadeh and Taeb, 2015; Zarei et al., 2017; Zhang et al., 2014; Zhao et al., 2006). Liu et al., (2009) reported the modification of ZMS-5 zeolite (Si/Al = 220) using a large variety of promoter elements such as P, Ce, W, Fe, Mn, Gr, Mo, Ga, V, and Ni. P was found to have improved the propylene selectivity, 55.6% in comparison with 46.4% in H‐ZSM‐5 zeolite. The rank order of propylene selectivity over different promoters was P > Ce > W > Mn > Fe > Gr > Mo > Ga > V > Ni.

Zaidi and Pant, (2004) used Zn and Cu to modify ZSM-5 zeolites (Si/Al = 45) in the MTH process, and the results indicated that the selectivity towards gasoline range hydrocarbons was increased for modified ZSM-5 more than for parent ZSM-5 zeolite alone. Ga was also used to modify the ZSM-5 zeolite, and the addition of Ga to the ZSM-5 zeolite noticeably increased the selectivity towards the aromatic hydrocarbons at the expense of C2–C4 alkenes, without affecting the overall conversion (Freeman et al., 2002). Moreover, Dai et al., (2018) modified ZSM-5 zeolite (Si/Al = 25) with varying Ga metal loadings (1-5 wt.%), they reported that with increasing Ga contents, the selectivity towards gasoline range hydrocarbons increased from
28% to 66.7% for the parent ZSM-5 zeolite and 5%Ga/ZSM-5 catalyst, respectively. However, the catalyst lifetime gradually decreases with increasing Ga content, and dropped down to 15 h compared to ~ 30 hours for the parent zeolite. The reason for this drop can be better explained using the dual cycle mechanism in the MTH process. The Ga species promoted the olefin cycle to aromatics cycle, accompanied by rapid accumulation of coke deposits. This shows that introducing some elements into the ZSM-5 zeolite is an efficient way to modify the acidity of the zeolite, thereby enhancing the selectivity towards the desired hydrocarbons from methanol conversion.

2.7 Catalyst Deactivation due to Coke Formation

Zeolites, especially ZSM-5, are widely employed in the MTH process. Despite the superior results of ZSM-5 in the MTH process, which include high selectivity towards desired hydrocarbons, resistance to deactivation due to coke deposition as compared to other zeolites, etc. (Chen et al., 2017; Wu et al., 2013; Zhang et al., 2017), the microporous characteristic of ZSM-5 zeolite significantly influences mass transfer of the reactants and products to/from the active sites, and as a result, ZSM-5 still suffers from diffusion limitations of larger molecules resulting in restrictions in the catalyst activity and lifetime (Bjørgen et al., 2008; Hu et al., 2014). Due to ZSM-5’s unique pore structure, only gasoline range hydrocarbons are allowed to diffuse out, and large molecules than those found in this range, are responsible for ZSM-5 zeolite deactivation.

In principle, there are two main causes of zeolite deactivation, namely dealumination and coking. Dealumination involves the removal of the tetrahedrally coordinated aluminium framework which is compulsory for generating Brønsted acid sites, by so doing breaking down the acidic structure of the zeolite catalyst (De Lucas et al., 1997; Gayubo et al., 2003). Coking involves the blockage of the active sites, pore mouths, and intersections of the zeolite by polycondensed aromatics formed from adsorbed carbocation intermediates on the strong acidic sites of the zeolite (Guisnet and Magnoux, 2001; Guisnet et al., 2009; Ilias and Bhan, 2012; Schulz, 2010). Catalyst deactivation due to dealumination is irreversible unlike deactivation caused by coking which is reversible by burning off the residual carbon deposits or washing in
industrial applications. However, the initial catalyst activity and lifetime cannot be achieved again (Gayubo et al., 2001; Gayubo et al., 2003).

The location, composition of coke, and the rate of coke formation are determined by the zeolite properties (channels, pores, cavities, active sites, Si/Al ratio, crystal size, etc.), reaction conditions (temperature, pressure, etc.), and the features of the reaction system (characteristics of the reactor, shape and size of reactant and product molecules, etc.) (Guisnet, 2002; Guisnet et al., 2009; Guisnet and Magnoux, 2001; Schulz, 2010; Ye et al., 2015). Catalyst deactivation by coke deposition still remains the challenging topic for economic use of ZSM-5 zeolite in the MTH process. Thus, knowledge about the catalyst deactivation is very important for catalyst and process development.

2.8 Studies to Mitigate Coke Formation

Catalyst deactivation remains a challenging topic in the MTH process, and numerous methods (morphological modification, varying amount of acid sites, etc.) have been tried to mitigate the rapid deactivation of ZSM-5 catalyst caused by coke deposition in the MTH process in order to improve diffusivity of the reactants and products to and from the active sites, and subsequently increase catalyst lifetime. Morphological modification involves the preparation of either nano-sized, mesopore or hierarchical ZSM-5 zeolites from microporous ZSM-5 zeolites (Liu et al., 2014; Meng et al., 2017; Meng et al., 2017; Pan et al., 2014; Shen et al., 2014; Wang et al., 2014).

Crystal size also influences greatly the ZSM-5 catalyst performance, and recently more efforts have been put into reducing the crystal size to the nanoscale in order to overcome diffusion limitations encountered by the ZSM-5 zeolites in the MTH process which subsequently leads to catalyst deactivation (Pan et al., 2014; Shen et al., 2014). The crystal size reduction has been successfully achieved via hydrothermal crystallization to synthesize nanocrystalline ZSM-5 (Mintova et al., 2013; Mohamed et al., 2005). The advantage of synthesizing nanocrystalline ZSM-5 includes increased external surface area which provides more accessibility of active sites to the reactants, and more importantly, crystal size reduction shortens the diffusion path
length resulting in significantly enhanced mass transfer of both reactant and product species in or out. Nanocrystalline ZSM-5 show better performance than their micro-sized ZSM-5 counterparts (Choi et al., 2009; Rownaghi and Hedlund, 2011; Shen et al., 2014). For example, Shen et al., (2014) showed that Zn/ZSM-5-AP60 exhibits aromatics selectivity above 62% over 42 h time on stream, the coke formation rate was about 4.41 mg g\textsuperscript{-1}h\textsuperscript{-1} compared with its counterpart conventional Zn/ZSM-5 catalyst with aromatics selectivity below 54% over 3.6 h time on stream, and the coke formation rate was 26.33 mg g\textsuperscript{-1}h\textsuperscript{-1}. Moreover, Zn/ZSM-5-AP60 exhibits lower selectivity towards overall total olefin compared to Zn/ZSM-5 catalyst, possibly due to enhanced hydrogen transfer ability to harvest more aromatics. The greater catalytic performance of Zn/ZSM-5-AP60 catalyst may be attributed to the size of nanocrystalline ZSM-5 which favors diffusion of both reactant and product species, and thus inhibiting coke deposition.

However, nano-sized zeolites might be thermodynamically unstable because of high surface energy and enormous amounts of surface defects. Nanocrystals are difficult to handle and have low yields during synthesis, in which the majority of the building units are left unused in the mother liquid. This limits the application of the nanocrystalline zeolites in the industrial sector (Zhu et al., 2011). An alternative approach (seed-induced method) to synthesize nanocrystalline ZSM-5 have been developed with the following advantages; fast crystallization of ZSM-5, and low consumption of templates (Majano et al., 2009; Xue et al., 2012). However, crystal intergrowth and secondary growth typically occurs leading to compact aggregates with larger crystal sizes formed with respect to the seed particles, and separation is a problem (Majano et al., 2009).

Many methods to synthesize nanocrystals ZSM-5 have been extensively reported in the literature, for example; seed crystallization (Majano et al., 2009; Ren et al., 2010), using organosilanes (Gao et al., 2016), surfactants (Chen et al., 2017; Frunz et al., 2006; Goncalves et al., 2008), growth in confined space (Frisch et al., 2009; Yoo et al., 2008), using large amounts of templates under autogenous pressure (Kalita and Talukdar, 2009; Reding et al., 2003) and, etc. However, separation of the nanocrystals from the reaction mixture remains a big challenge, and the use of expensive surfactants and organosilanes, and large amounts of templates restricts the application of these methods in the industrial sector.
Another particular promising approach in morphological zeolite modification to overcome ZSM-5 deactivation due to coke deposition, is to synthesize mesoporous or hierarchical zeolite catalysts (Ahmadpour and Taghizadeh, 2015; Bleken et al., 2013; Wan et al., 2014; Zhang et al., 2014). The term, “hierarchical” refers to the presence of at least two porosity types in the ZSM-5 zeolite, namely; micropores and mesopores size range (Wan et al., 2014). As a result, hierarchical ZSM-5 takes both the advantage of microporous and mesoporous materials, thus showing superior catalytic performance. Numerous methods to prepare mesoporous or hierarchical ZSM-5 zeolite have been developed, these methods include; chemical leaching, synthesis using templates, surfactants, and etc. (Čejka and Mintova, 2007; Egeblad et al., 2007; Mintova and Čejka, 2007; Van Donk et al., 2003; Verboekend and Pérez-Ramírez, 2011).

Much concentration has been paid in preparing mesoporous or hierarchical ZSM-5 using chemical leaching (dealumination and desilication) approaches (Behbahani and Mehr, 2014; Triantafillidis et al., 2001; Wei et al., 2015), as well as steaming (Jia et al., 2018; Wei et al., 2017; Xing et al., 2017). However, for the past few years, the use of soft and/or hard template (Ahmadpour and Taghizadeh, 2015; Kim et al., 2010; Meng et al., 2009; Tao et al., 2006; Wang et al., 2014; Xue et al., 2012; Zhu et al., 2011) to create mesoporous or hierarchical ZSM-5 with high efficiency has been drawing growing attention because there is better control of the pore size, and the mesoporous or hierarchical structure can be achieved without crystallinity being lost. Nevertheless, the use of templates has some drawbacks, as these templates are expensive, complicated and energy-intensive to be used during synthesis and/or to be prepared, and produce large amounts of aqueous pollutants, thus limiting their industrial applications (Ahmadpour and Taghizadeh, 2015; Wang et al., 2017; Zhang et al., 2014). Moreover, the use of conventional cationic surfactants (e.g. cetyltrimethylammonium bromide (CTAB)) remains a significant challenge due to phase separation between mesoporous and microporous-phase when preparing mesoporous or hierarchical ZSM-5 zeolite (Zhang et al., 2014; Zhu et al., 2011). Chemical leaching approaches to create hierarchical structures may be seen as relatively cheap and easy to carry out, but treating zeolites with chemicals frequently results in major losses of zeolites because of chemical dissolution, and frequently undesired changes to the zeolite Si/Al ratio.
2.9 Microwave Radiation

It was not until 1946, at the end stage period of World War II when Dr. Percy Spencer with the Raytheon Corporation noticed something unusual – the candy bar melted in the pocket while standing in front of an active radar set. Dr. Spencer was the first to examine this incident, and he later on carried out an experiment on popcorons and subsequently, on an egg (Pradhan et al., 2012; Rana and Rana, 2014). This gave birth to the development and commercialization of microwave ovens in 1947-1978, and in 1971, Liu and Wightman reported the decomposition of alcohols, ethers and ketones using microwave radiation (Liu and Wightman, 1971). Following that, in 1986 two important papers were published regarding successful application of microwave radiation in organic synthesis (Gedye et al., 1986; Giguere et al., 1986). Figure 2.6 summarizes published areas in which microwave radiation has been applied. It is obvious that the use of microwave radiation has shifted from food processing to processing advanced materials (Mishra and Sharma, 2016).
Microwaves are regarded as electromagnetic waves lying in between the infra-red and radio frequencies, with wavelengths between 0.01-1m (corresponding to frequencies of 30 - 0.3 GHz) in the electromagnetic spectrum as shown in Figure 2.7 (Rana and Rana, 2014). Most domestic microwave ovens are authorized to operate in the 2.45 GHz. The 0.915 GHz and $2.172 \times 10^{-5}$ GHz radio frequencies are frequently used for industrial electromagnetic heating to avoid interfering with telecommunication and radar frequencies (Zlotorzynski, 1995).

2.9.1 Application of Microwave Radiation in Catalysis

Among the areas (environmental, nuclear chemistry, engineering, and etc.) in which microwave technology has been used (Zlotorzynski, 1995), in catalysis microwave technology offers many advantages in chemical reactions (microwave-assisted synthesis) as compared to traditionally used methods, such as conventional heating. These advantages include: increased rates of reaction, save time, offers fast and relatively low-cost access to very high temperatures.
and pressures, clean and higher yields, etc. (Caddick and Fitzmaurice, 2009; Gedye et al., 1986; Menéndez et al., 2010; Rana and Rana, 2014; Zhang and Hayward, 2006).

In recent years, the application of microwave radiation in heterogeneous catalysis has received great interest due to the nature of microwave radiation’s ability to quickly, widely, uniformly and internally heat the material (Ohgushi et al., 2009). Microwave radiation has been applied widely in the synthesis (Anuwattana et al., 2008; Somani et al., 2003; Arafat et al., 1993; Li and Yang, 2008), ion exchange (Kuroda et al., 2002; Romero et al., 2007), modification (Hasan et al., 2015), and reactivation of zeolites (Ohgushi and Nagae, 2003; Polaert et al., 2010).

Anuwattana et al., (2008) synthesized ZSM-5 zeolite using both conventional and microwave heating from cupola slag waste. As compared to conventional heating, microwave heating increased the rate of ZSM-5 formation by 4 times at 150 °C, and produced smaller ZSM-5 particles with 0.3 µm in size, and 3 µm obtained by using conventional heating. Moreover, Katsuki et al., (2005) also reported that the rate of ZSM-5 formation increased by 3-4 times at 150 °C, and produced smaller ZSM-5 particles with 0.3-5 µm when using microwave heating. It is clear that, synthesizing zeolites from microwave heating provides many advantages such as, narrow particle size distribution, and fast crystallization.

Modern domestic microwave ovens are readily available for academic and industrial applications due to their relatively low-cost. Alkylation, aromatic and nucleophilic substitution, condensation, oxidation, reduction reaction, and etc. have been successfully carried out via microwave-assisted synthesis. Several useful reactions can be carried out using domestic microwave ovens using different microwave-assisted procedures, including non-solid state reaction and solid state reaction (Pradhan et al., 2012).

2.9.2 Mechanisms and types of Microwave heating

Microwave heating occurs through two distinct mechanisms, which are dipolar polarization and conduction. The heating primarily results from the interaction of charged particles in the material and/or magnetic dipoles with the electric field. In dipolar polarization, the electric field of the microwave induces motion on the dipoles until they align themselves with the
alternating field and this is significant in water and other polar fluids. In conduction, the electric field of the microwave gives rise to a current traveling in phase with the field and causing resistive heating. This mechanism is common in solid materials with mobile charge carriers (Kitchen et al., 2013).

Figure 2.8 shows the types that characterize and distinguish microwave heating from conventional heating both in theory and in practice. These are the types that offer microwave heating outstanding advantages over the conventional heating method. As shown, these types of microwave heating can be classified into: (a) direct heating, (b) selective heating, and (c) hybrid heating. In direct heating, the material is directly exposed to the microwave radiation, for example, when heating food. In selective heating, the material is still directly exposed to the microwave radiation. However, the specific region is heated while the other is not as a result a desired part of the material is heated without disturbing the rest of the volume properties. Hybrid heating combines the direct and selective heating properties as shown below (Mishra and Sharma, 2016).

**Figure 2.8:** Types of microwave heating (Mishra and Sharma, 2016).

**2.9.2.1 Direct heating and Selective heating**

Selective heating offers the most obvious advantage of heating the catalyst in heterogeneously catalyzed reaction whereas in homogeneously catalyzed reaction, both the catalyst and the medium are heated to the temperature needed to start the reaction (Stiegman, 2015). Selective heating allows the generation of high temperatures on specific regions of the material while others remain at lower temperatures and this is generally used in heating specific active sites in supported metal catalysts (Zhang et al., 2003). Similarly, direct heating allows selective heating of specific reactants that interact with the microwave radiation to be heated more strongly than others (Kitchen et al., 2013). Some zeolites when are directly subjected to
microwave radiation without solution or solvent; they are easily and effectively heated to a
glowing (melting) temperature (Whittington and Milestone, 1992; Ohgushi and Nagae, 2003;
Ohgushi et al., 2001). This melting of certain zeolites is related to sufficient absorption of
microwave radiation caused by prolonged microwave treatment and further lead to possibly
the migration of cations into the large cavities of the zeolite (Whittington and Milestone, 1992).

2.9.3 Heterogeneous catalysts and Microwave absorption

The absorption of microwave power in a material is influenced by the electromagnetic
properties of the material and most significantly, the penetration depth. As a result, microwave
radiation penetrates inside different materials in different ways. Thus, under the same
conditions of microwave heating, some materials are capable of absorbing more microwave
radiation than others. For nonmetallic materials, microwave penetration is defined in terms of
Penetration Depth (D_p), and it is expressed mathematically as (Chandrasekaran et al., 2012;
Rattanadecho, 2006):

\[
D_p = \frac{1}{\alpha} = \frac{1}{2\pi f} \left( \frac{2}{\mu' \mu_0 \varepsilon_0 \kappa'} \right)^{1/2} \left[ \left( 1 + \tan^2 \delta \right)^{1/2} - 1 \right]^{-1/2}
\]  

(2.1)

Where;
\[\alpha = \text{attenuation factor}\]
\[\varepsilon_0 = \text{permittivity of free space}\]
\[f = \text{frequency}\]
\[\mu' = \text{magnetic permeability}\]
\[\mu_0 = \text{permeability of free space}\]
\[\kappa' = \text{relative dielectric constant}\]

For metallic materials, microwave penetration is defined in terms of Skin Depth (D_s), and it is
expressed mathematically as (Mishra and Sharma, 2016):

\[
D_s = \frac{1}{\sqrt{\pi \mu_0 \sigma}} = 0.029 (\rho \lambda_0)^{0.5}
\]  

(2.2)
Different materials possess different microwave absorption characteristics due to their differences in magnetic and electric field strengths during microwave irradiation. This leads to their classification into different groups, as: microwave transparent, absorber, opaque and mixed absorbers (Mishra and Sharma, 2016). Heterogeneous catalyst materials are classified into different groups and each exhibits different microwave absorption characteristics, namely (Stiegman, 2015):

(i) Solid oxide catalysts: in this category we have any bulk oxide employed as catalysts. For example, simple binary oxides like Al₂O₃, ZrO₂, SiO₂ and TiO₂, ternary oxides like perovskites and spinels, and porous aluminosilicates and silicates like templated mesoporous sieves and zeolites.

(ii) Metals: in this category, we have metals used as catalysts in chemical reactions like Ag, Ni, Cu and etc.

(iii) Support catalysts: in this category, we have an active site like metal particle or transition metal or complex deposited on an oxide support surface performing part or all of the catalytic function.

All these catalysts respond to microwave radiation in different ways and as a result affect the chemical reactions differently.

2.9.3.1 Microwave heating of ZSM-5 zeolite

The precise main mechanism of direct absorption of microwave energy, and consequently the transformation to heat depends on the temperature, the amount of water adsorbed and the structure (type, location and cluster of mobile cations between different sites in the zeolite framework). The reason being, the cations are accountable for neutralizing the charge of the primary building block of the zeolites (AlO₄ tetrahedrons) (Kraus et al., 2015). The number of cations per unit cell of the zeolite decreases with increasing Si/Al ratio and vice versa (Mentzen
et al., 2006; Simon and Flesch, 1999; Ohgushi and Kawanabe, 1994). For instance, Mentzen et al., (2006) showed that for Cs/ZSM-5 with Si/Al = 70, and for Cs/ZSM-5 with Si/Al = 10, there are 0.7 and 7.7 cesium cations per unit cell, respectively. As the increasing Si/Al ratio causes the decrease in the number of exchangeable cations per unit cell that provide an active site for water absorption, this increases the hydrophobicity of the zeolites as the weakly bonded cations are expelled by increasing Si/Al ratio (Ohgushi and Kawanabe, 1994). As a result, this reduces the ability of the zeolites to absorb energy under microwave irradiation (Whittington and Milestone, 1992), so in these materials, microwave irradiation is favorably based on a cation hopping mechanism (Gracia et al., 2013; Ohgushi et al., 2009; Whittington and Milestone, 1992).

Whittington and Milestone, (1992) reported that either hydrated or dehydrated Na/ZSM-5 or Na/USY do not undergo any large temperature increase under microwave irradiation and stated that this may be due to the low sodium content, but may be correlated to the cavity size of ZSM-5, and the fact that these zeolites are hydrophobic. Ohgushi and Kataoka, (1992) found that there exist two types of Na$^+$ ions (NaI and NaII) in Na/ZSM-5 with Si/Al ratio = 13. Also for Na/ZSM-5, there exist a single type of Na$^+$ ion (NaI) with Si/Al ratio = 685 (Ohgushi and Kawanabe, 1994). The differences between the two are due to the difference in binding strength of the Na$^+$ ion to the zeolite framework. The weakly bonded NaII are favourably expelled by increasing Si/Al ratio. NaI have higher activation energy for movement, less affinity for water molecules adsorbed and it is more strongly bonded to the zeolite framework than NaII (Ohgushi and Kawanabe, 1994). A stronger cation-zeolite framework interaction results in higher activation energy and a lower resonance frequency. With regards to microwave radiation, that material can be labelled as microwave-transparent.

2.9.4 Microwave oven and Bed shape

Microwave ovens are often classified into two categories, namely single-mode and multi-mode ovens. In a single-mode microwave oven, the targeted material being heated is positioned at the antinodal position of the standing electromagnetic field to ensure faster processing. The cavity size in single-mode microwave oven is equivalent to one wavelength, and only one
vessel can be irradiated at a time. Multi-mode microwave ovens have larger cavities due to larger dimensions than for single-mode microwave ovens, and they provide a more homogeneous electromagnetic field due to the rotation inside the cavity and stirrer (Figure 2.9). Multi-mode microwave ovens can accommodate a number of samples to be heated at the same time. Household microwave ovens fall under this category (Chandrasekaran et al., 2012; Mishra and Sharma, 2016; Rana and Rana, 2014).

Single-mode microwave ovens have been used in material processing with phase change, mineral and environmental processing, ceramic and metal sintering, and in continuous flow microwave processing. Multi-mode microwave ovens have been used in food processing, metallurgical, polymer and ceramic applications (Chandrasekaran et al., 2012). Recently, multi-mode microwave ovens have been used in heterogeneous catalysis because they are cheap, readily available, easy to operate, save time and provide better catalytic activity and selectivity in chemical reactions (Dlamini et al., 2016; Dlamini et al., 2015; Janjic and Scurrell, 2002; Mohiuddin et al., 2017; Linganiso and Scurrell, 2016).

However, heating several kilograms or more of the pure dry hydrophobic zeolites is difficult at the industrial scale (Kraus et al., 2015). By taking advantage of the findings on the effect of bed shape during microwave irradiation using multi-mode microwave oven (Linganiso and Scurrell, 2017), we further use the findings (uniformly and thinly spreading of material to be irradiated promotes better microwave absorption than having cone-shaped bed) to see the if microwave radiation can be used to post-modify metal impregnated ZSM-5 zeolite in the methanol-to-hydrocarbon process.
Summary of Chapter 2

The MTH process is a promising alternative process to replace the use of petroleum sources as primary energy resources. However, use of microporous metal-based ZSM-5 catalysts leads to diffusion limitations as larger molecules block the pore channels and cover the catalyst active sites. This diffusion limitation results in coke deposition which causes catalyst deactivation and high methane production. This is a significant challenge facing the MTH process. In this present study, we seek to investigate the use of microwave radiation as a post-synthesis modification step to create mesoporous or hierarchical metal-based ZSM-5 catalysts to overcome coke deposition. In order to achieve the set aim, the multi-mode microwave oven was used to carry out the post-synthesis modification step.
References


CHAPTER 3
Experimental Procedures and Reagents used

3.1 Introduction

In this chapter, the reagents and the instruments used are presented. The experimental procedures used for synthesizing and characterizing the microwave treated and untreated iron-containing HZSM-5 catalysts are described in detail. The following techniques were used to characterize the microwave treated and untreated catalysts to study the effect of microwave radiation as post-synthesis modification step: powder x-ray diffraction (p-XRD), thermogravimetric analysis (TGA), scanning electron microscopy (SEM), Fourier transform infrared (FT-IR) spectroscopy, nitrogen adsorption-desorption analysis, and n-propylamine-temperature programmed surface reaction (C₃H₉N-TPSR). The effect of microwave radiation on the product distribution in the methanol conversion to hydrocarbons (MTH) process was examined using methanol-temperature programmed surface reaction (MeOH-TPSR) technique.

3.2 Reagents used

The reagents used in this work were used as received without any purification, and are presented in Table 3.1.
Table 3.1: List of reagents used together with their suppliers.

<table>
<thead>
<tr>
<th>REAGENTS</th>
<th>SUPPLIERS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminium sulfate octadecahydrate, ≥97%</td>
<td>Sigma Aldrich</td>
</tr>
<tr>
<td>Ammonium nitrate, ≥99.0%</td>
<td>Sigma Aldrich</td>
</tr>
<tr>
<td>Iron(III) nitrate nonahydrate, ≥98%</td>
<td>Sigma Aldrich</td>
</tr>
<tr>
<td>Methanol, ≥99.9%</td>
<td>Sigma Aldrich</td>
</tr>
<tr>
<td>n-Propylamine, 98%</td>
<td>Sigma Aldrich</td>
</tr>
<tr>
<td>Silica, 99.8%</td>
<td>Sigma Aldrich</td>
</tr>
<tr>
<td>Sodium hydroxide, 99.99%</td>
<td>Sigma Aldrich</td>
</tr>
<tr>
<td>Tetrapropylammonium bromide, 98%</td>
<td>Sigma Aldrich</td>
</tr>
<tr>
<td>ZSM-5 (Si/Al = 30)</td>
<td>Zeolyst International</td>
</tr>
</tbody>
</table>

3.3 Experimental Procedures and Instruments used

This section presents the experimental procedures and instruments used.

3.3.1 Catalysts preparation and post-synthesis modification

0.5wt.% Fe/ZSM-5 with Si/Al ratio = 30 was prepared as follows. As received, 30.0 g ZSM-5 (Si/Al = 30 from Zeolyst International) in the ammonium form was calcined for 5 h at 550 °C to obtain the protonated form of the zeolite. The 0.5Fe/ZSM-5 catalyst was prepared using the incipient wetness impregnation method, whereby 0.95 g iron(III) nitrate nonahydrate (Fe(NO$_3$)$_3$·9H$_2$O) was dissolved in enough distilled water. 26.0 g HZSM-5 (on dry basis) was taken in its powdered form and to it, the iron nitrate solution was slowly added with constant stirring. The mixture was then kept at room temperature and allowed to equilibrate overnight. The mixture was then evaporated to dryness at 100 °C followed by calcination for 5 h at 550 °C.

0.5wt.% Fe/ZSM-5 with Si/Al ratio = 80 was prepared as follows using incipient wetness impregnation. The Na/ZSM-5 sample with Si/Al = 80 was synthesized under hydrothermal
conditions at 150 °C for 72 h following a procedure previously reported by Yu et al. (2013). The molar composition of the synthesis gel was: 9.0 Na$_2$O : 1.0 Al$_2$O$_3$ : 80 SiO$_2$ : 0.53 (TPA)$_2$O .1300 H$_2$O. The product was then dried in the oven at ~80 °C overnight, and subsequently calcined in a furnace at 500 °C for 5 h. 11.0 g of NaZSM-5 was refluxed in 110 mL 0.8M NH$_4$NO$_3$ solution at 80 °C for 5 h, the mixture was then filtered and washed with distilled water. This aforementioned step was repeated four times to obtain NH$_4$ZSM-5. The NH$_4$/ZSM-5 was dried overnight in an oven at 110 °C and then calcined at 550 °C for 5 h in a furnace to produce HZSM-5. To get 0.5Fe/ZSM-5 catalyst, 0.27 g iron(III) nitrate nonahydrate (Fe(NO$_3$)$_3$ 9H$_2$O) was dissolved in enough distilled water. 7.40 g HZSM-5 (on dry basis) was taken in its powdered form and to it, the iron nitrate solution was slowly added with constant stirring. The mixture was kept at room temperature and allowed to equilibrate overnight. The mixture was then evaporated to dryness at 100 °C followed by calcination for 5 h at 550 °C.

3.3.1.1 Microwave post-synthesis modification of catalysts

The 0.5Fe/ZSM-5 catalysts were modified using microwave irradiation as follows; ~1.00 g of 0.5Fe/ZSM-5 catalyst (on a dry basis for both Si/Al = 30 and 80) was placed and uniformly dispersed on a flat-bottomed domestic microwave oven plate (glass tray). The sample was then subjected to microwave radiation for 10 s on varying power level (0-700 W) using domestic microwave oven (DEFY, DM0368 MWM 2030M) (Figure 3.1). Microwave-treated samples were then denoted as 0.5FeZ$_{\text{time/power level}}$ for Si/Al = 30 and 0.5FeX$_{\text{time/power level}}$ for Si/Al = 80.
Chapter 3: Experimental Procedures and Reagents

3.3.2 Catalysts Characterization

3.3.2.1 Nitrogen Adsorption-desorption Analysis

The specific surface area ($S_{BET}$), micropore volume and total pore volume were analyzed by N$_2$ adsorption-desorption measured at -196 °C using Micromeritics TriStar II 3020 instrument. Prior to the analysis, about 0.20 g of the sample was degassed for 3 h at 400 °C.

3.3.2.2 Powder X-Ray Diffraction (p-XRD) analysis

The XRD analysis was performed on a Rigaku D/MAX – 1400 instrument with a Cu-Kα radiation, with a scan speed of 15°/min and a scan range of 10-90° at 40 kV and 40 mA.

3.3.2.3 Thermogravimetric analysis (TGA)

The TGA was applied to estimate the coke content deposited on microwave-treated and untreated catalysts after the methanol conversion to hydrocarbons tests. The analysis was conducted using Thermogravimetric Analyzers (Discovery TGA 5500) in the presence of air and the temperature range of 25–1000 °C with the heating ramp rate of 10 °C/min.
3.3.2.4 Scanning electron microscopy (SEM) analysis

JEOL JSM-6010PLUS/LA analytical scanning electron microscope (SEM) was used to determine material morphology. The samples were coated with a thin gold film prior to analysis.

3.3.2.5 Fourier Transform Infrared (FT-IR) Spectroscopy

The structural properties of the catalysts were analyzed using VERTEX 70 FT-IR spectrometer coupled with RAM II FT-Raman module with spectral resolution of 4 cm\(^{-1}\) in the range from 400-4000 cm\(^{-1}\) at room temperature.

3.3.2.6 Propylamine-Temperature programmed surface reaction (C\(_3\)H\(_9\)N-TPSR)

The effect of microwave radiation on the Brønsted acidic sites was determined using Propylamine-Temperature programmed surface reaction (C\(_3\)H\(_9\)N-TPSR) on the Micromeritics AutoChem II 2920 coupled with MKS Cirrus\textsuperscript{TM}2 Benchtop Atmospheric Pressure Gas Analysis System. The C\(_3\)H\(_9\)N-TPSR experiment was carried out as follows; the samples (0.5FeX\(_{\text{time/power level}}\) and 0.5FeZ\(_{\text{time/power level}}\)) about ~20 mg per trial each was pretreated \textit{in situ} at 500 °C for about an hour maximum under flowing helium gas (He) and then cooled to ambient temperature. n-Propylamine was chemisorbed at 120 °C by passing He as a carrier gas through a saturator containing n-propylamine. The sample was then purged for 120 minutes afterwards in flowing helium to remove any physically adsorbed n-propylamine to ensure 1 : 1 ratio of adsorbed n-propylamine to Brønsted acidic sites, and then the temperature was increased at a temperature ramp of 10 °C/min up to 500 °C.

For C\(_3\)H\(_9\)N-TPSR technique in the present study, the temperature of the sample (the microwave-treated and untreated catalysts) was increased linearly with time. The desorbing species were continuously monitored by their characteristic mass fragments (m/e): 17 (ammonia), 30 (n-propylamine), and 41 (propene). The signal of propene from the TPSR was used to quantify the corresponding number of Brønsted acid sites (Kresnawahjuesa et al., 2002; Milina et al., 2013; Milina et al., 2014; Tittensor et al., 1992).
3.3.3 Catalysts testing (MeOH-TPSR experiments)

The effect of microwave radiation on hydrocarbon yields from methanol conversion was tested on the Methanol-Temperature Programmed Surface Reaction (MeOH-TPSR) using Micromeritics AutoChem II 2920 coupled with MKS Cirrus™2 Benchtop Atmospheric Pressure Gas Analysis System. The MeOH-TPSR experiment was carried out as follows. About 0.20 g of sample was pretreated in situ at 500 °C for about an hour maximum under flowing helium gas (He) and then cooled to ambient temperature. Methanol was chemisorbed at ambient temperature by passing He as a carrier gas through a saturator containing methanol. The sample was then purged for about an hour afterwards in flowing helium to remove any physically adsorbed methanol, and then the temperature was increased at a temperature ramp of 10 °C/min up to 550 °C.

For MeOH-TPSR technique in the present study, the temperature of the sample (the microwave-treated and untreated catalysts) was increased linearly with time, and the production of hydrocarbons and consumption of methanol was also monitored. The desorbing species were continuously monitored by their characteristic mass fragments (m/e): 16 (methane), 28 (ethane and ethene), 29 (propane), 41 (propene and butene), 42 (pentene), 43 (butane and pentane), 78 (benzene), and 91 (toluene and xylene). The intensities were then corrected to eliminate interferences from other compounds to account for contributions to our desired hydrocarbon yield from methanol conversion.
References


CHAPTER 4
Results and Discussion

4.1 Introduction

The results that were found from catalysts characterization and MeOH-TPSR experiments in the MTH process are stated and discussed in this chapter to observe the effect of microwave radiation.

4.2 Catalysts characterization

In this section, the results obtained from characterizing prepared catalysts to see the effect of microwave radiation are presented and discussed in detail.

4.2.1 X-ray diffraction analysis

The XRD analysis was conducted to investigate the influence of loading Fe cations and the effect of microwave irradiation on the zeolite structure. Figure 4.1(a-b) shows the powder XRD patterns for the HZSM-5 with varying Si/Al ratio (30 and 80) and for microwave-treated and untreated catalysts after iron impregnation on the HZSM-5 zeolites. The samples were analyzed to check the influence of iron loading and the effect of microwave treatment. The diffractograms of the microwave-treated and untreated (0.5FeX100/0-700 and 0.5FeZ100/0-700) catalysts and for the parent HZSM-5 zeolites were similar, and identical to that of a typical MFI structure (Moreno-Recio et al., 2016), depicting that the MFI framework structure of ZSM-5 zeolite was well maintained even after both iron impregnation and microwave post-treatment of the catalysts. The diffraction signals associated to iron oxide phases were not detected on the XRD profiles of iron-containing samples (0.5FeX100/0-700 and 0.5FeZ100/0-700), indicating that the iron cations were uniformly dispersed onto the zeolite framework (Moreno-Recio et al., 2016; Aziz et al., 2016), and low iron loading on the parent HZSM-5 zeolite was
the cause of undetected diffraction signals associated to any iron oxide phases (Rasouli et al., 2017).

**Figure 4.1:** XRD patterns for the parent zeolites (HZSM-5) and microwave-untreated and treated catalysts: (a) 0.5FeZ\textsubscript{10/700} and (b) 0.5FeX\textsubscript{10/700}.

Slight intensity decreases in the diffraction peaks at 2\(\theta\) angle between 23–25\(^{\circ}\) on the diffractogram of the parent HZSM-5(30) zeolite were also observed after iron impregnation, and these were due to the higher adsorption coefficient of iron oxide for x-ray radiation (Figure 4.1(a)). The intensity decreases of iron-containing catalysts confirmed the existence of iron species. As for microwave-treated catalysts in Figure 4.1(a), there were some changes in the diffractogram intensities compared to that of the parent HZSM-5 (30) zeolite. When the microwave power level was increased from 280 to 595 W, there was an increase in the diffractogram intensities of 0.5FeZ\textsubscript{10/280} to 0.5FeZ\textsubscript{10/595} catalysts and then decreases for 0.5FeZ\textsubscript{10/700} catalyst. The diffractogram intensities of the 0.5FeZ\textsubscript{10/0} and 0.5FeZ\textsubscript{10/119} catalysts were the same but lower than for the above-mentioned catalysts. The increasing diffractogram intensities of the microwave-treated catalysts, with increasing microwave power level maybe associated with crystal growth within the catalysts and pronounced response to microwave irradiation due to the higher number of iron cations per unit cell for the HZSM-5 (30) than for HZSM-5 (80).
The crystal growth may proceed under microwave irradiation provided that there are many nuclei in the sample being irradiated which then undergo crystallite growth (Anuwattana et al., 2008; Somani et al., 2003). Inui et al., (1986) showed that small amount of iron ions plays a role in providing nuclei in the crystal growth in high-silica zeolites. The decrease in diffractogram intensity for 0.5FeZ\textsubscript{10/700} catalyst may suggest the partial disintegration of the zeolite framework. The structure directing agent (tetrapropylammonium bromide), used when preparing the used HZSM-5 zeolites in the present study, is well known to suffer Hoffmann degradation during synthesis time (Arafat et al., 1993), and also fast degradation under microwave irradiation (Li and Yang, 2008; Arafat et al., 1993). Figure 4.1(b) shows slight changes at 2θ angle between 23–25° on the diffractogram intensities of the parent HZSM-5 (80) zeolite and its based microwave-treated catalysts (0.5FeX\textsubscript{10/119-700}). This indicates that microwave-treated catalysts (0.5FeX\textsubscript{10/119-700}) did show some crystallinity changes upon microwave irradiation.

### 4.2.2 Nitrogen adsorption-desorption analysis

The nitrogen adsorption-desorption analysis was conducted to investigate the influence of loading Fe cations and the effect of microwave irradiation on the physicochemical properties of the prepared catalysts. The physicochemical properties of microwave-treated and untreated catalysts are summarized in Table 4.1. The BET surface areas for 0.5FeX\textsubscript{100-700} and 0.5FeZ\textsubscript{100-700} catalysts were found to be 343–366 m\textsuperscript{2}/g and 346–376 m\textsuperscript{2}/g, respectively. This difference is attributed to different parent HZSM-5 zeolites used with varying Si/Al ratios (30 for 0.5FeZ\textsubscript{100-700} based catalysts and 80 for 0.5FeX\textsubscript{100-700} based catalysts). Table 4.1 shows that there was a linear BET surface area decrease (376 m\textsuperscript{2}/g to 346 m\textsuperscript{2}/g) and a linear micropore volume (0.119 cm\textsuperscript{3}/g to 0.108 cm\textsuperscript{3}/g) decrease, with increasing microwave power level from 0 to 595 W for the 0.5FeZ\textsubscript{100-595} catalysts except for the 0.5FeZ\textsubscript{10/700} catalyst, where the BET surface area and micropore volume was 356 m\textsuperscript{2}/g and 0.111 cm\textsuperscript{3}/g, respectively. This effect may be related to the microwave absorption capability of the iron cations within the zeolite framework with lower Si/Al ratio. This also shows that the iron cations may have agglomerated in the HZSM-5 zeolites micropores and decreased the BET surface area and the total pore volume.
Figure 4.2: N$_2$ adsorption-desorption isotherms of microwave-treated and untreated catalysts at -196 °C: (a) 0.5FeZ$_{10/0}$-700 and (b) 0.5FeX$_{10/0}$-700 catalysts.

Figure 4.2(a) shows the N$_2$ adsorption-desorption isotherms of the microwave-treated and untreated (0.5FeZ$_{10/0}$-700) catalysts with type IV(a) isotherms with H3-shaped hysteresis loops according to IUPAC classification (Thommes et al., 2015), Type IV(a) isotherms are given by mesoporous adsorbents (Thommes et al., 2015). This shows that these catalysts possessed mainly mesopores. The hysteresis loop of 0.5FeZ$_{10/700}$ catalyst in Figure 4.2(a) was smaller than that of the corresponding catalysts (0.5FeZ$_{10/0}$-595), and this could be associated with the agglomeration of iron oxide particles leading to a blocking of the channels and/or the degradation of the HZSM-5 zeolite framework under microwave irradiation.

As for the 0.5FeX$_{10/0}$-700 based catalysts, there was no such linear agreement between the microwave power level and their corresponding BET surface areas (Table 4.1). However, there was still an effect on the BET surface areas and an increase in mesopore volume (0.0919 cm$^3$/g to 0.0995 cm$^3$/g) of the catalysts as the microwave power level was increased. There was a
linear increase in mesopore volume as the microwave power level was increased (119 W to 700 W). The microwave-treated catalysts (0.5FeX_{10/119-700}) have lower BET surface areas (343 m²/g to 357 m²/g) than that of the microwave-untreated catalyst (0.5FeX_{100}) with BET surface area of 366 m²/g. This may be ascribed to the agglomeration of the iron particles on the micropores and resulting in decreasing the BET surface area upon microwave irradiation of the catalysts. The absence of linear agreement between the BET surface area and microwave power level maybe ascribed to the deficiency of microwave absorbing cations within the parent HZSM-5 zeolite, as the weakly bonded iron cations are likely to be expelled by the increasing Si/Al ratio (Inui et al., 1986).

The N₂ adsorption-desorption isotherms of the microwave-treated and untreated (0.5FeX_{10/0-700}) catalysts at different power levels (0–700 W) are illustrated in Figure 4.2(b). All the catalysts exhibited the Type IV isotherms with the H₄-shaped hysteresis loops at p/p₀ > 0.4 according to IUPAC classification (Thommes et al., 2015), due to the formation of textural mesoporosity originating from the crystal intergrowth. The pronounced hysteresis loops for 0.5FeX_{10/336-700} catalysts as the microwave power level was increased from 336 W to 700 W, may be associated with the microwave treatment’s ability to enhance the generation of mesopores between very small iron oxide crystallites dispersed on the surface of the HZSM-5 zeolite.
Table 4.1: Physicochemical properties of microwave-untreated and treated catalysts (0.5FeX<sub>10/0-700</sub> and 0.5FeZ<sub>10/0-700</sub>).

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>BET Surface Area /m²/g&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Total Pore Volume /cm³/g&lt;sup&gt;b&lt;/sup&gt;</th>
<th>Micropore Volume /cm³/g&lt;sup&gt;c&lt;/sup&gt;</th>
<th>Mesopore Volume /cm³/g&lt;sup&gt;d&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5FeX&lt;sub&gt;10/0&lt;/sub&gt;</td>
<td>366</td>
<td>0.194</td>
<td>0.0950</td>
<td>0.0990</td>
</tr>
<tr>
<td>0.5FeX&lt;sub&gt;10/119&lt;/sub&gt;</td>
<td>343</td>
<td>0.182</td>
<td>0.0901</td>
<td>0.0919</td>
</tr>
<tr>
<td>0.5FeX&lt;sub&gt;10/280&lt;/sub&gt;</td>
<td>348</td>
<td>0.183</td>
<td>0.0904</td>
<td>0.0926</td>
</tr>
<tr>
<td>0.5FeX&lt;sub&gt;10/336&lt;/sub&gt;</td>
<td>348</td>
<td>0.187</td>
<td>0.0943</td>
<td>0.0927</td>
</tr>
<tr>
<td>0.5FeX&lt;sub&gt;10/462&lt;/sub&gt;</td>
<td>357</td>
<td>0.192</td>
<td>0.0958</td>
<td>0.0962</td>
</tr>
<tr>
<td>0.5FeX&lt;sub&gt;10/595&lt;/sub&gt;</td>
<td>352</td>
<td>0.192</td>
<td>0.0929</td>
<td>0.0991</td>
</tr>
<tr>
<td>0.5FeX&lt;sub&gt;10/700&lt;/sub&gt;</td>
<td>355</td>
<td>0.193</td>
<td>0.0935</td>
<td>0.0995</td>
</tr>
<tr>
<td>0.5FeZ&lt;sub&gt;10/0&lt;/sub&gt;</td>
<td>376</td>
<td>0.233</td>
<td>0.119</td>
<td>0.114</td>
</tr>
<tr>
<td>0.5FeZ&lt;sub&gt;10/119&lt;/sub&gt;</td>
<td>374</td>
<td>0.233</td>
<td>0.118</td>
<td>0.115</td>
</tr>
<tr>
<td>0.5FeZ&lt;sub&gt;10/280&lt;/sub&gt;</td>
<td>367</td>
<td>0.229</td>
<td>0.117</td>
<td>0.112</td>
</tr>
<tr>
<td>0.5FeZ&lt;sub&gt;10/336&lt;/sub&gt;</td>
<td>364</td>
<td>0.229</td>
<td>0.113</td>
<td>0.116</td>
</tr>
<tr>
<td>0.5FeZ&lt;sub&gt;10/462&lt;/sub&gt;</td>
<td>357</td>
<td>0.225</td>
<td>0.111</td>
<td>0.114</td>
</tr>
<tr>
<td>0.5FeZ&lt;sub&gt;10/595&lt;/sub&gt;</td>
<td>346</td>
<td>0.216</td>
<td>0.108</td>
<td>0.108</td>
</tr>
<tr>
<td>0.5FeZ&lt;sub&gt;10/700&lt;/sub&gt;</td>
<td>356</td>
<td>0.222</td>
<td>0.111</td>
<td>0.111</td>
</tr>
</tbody>
</table>

<sup>a</sup> Brunauer-Emmett-Teller (BET) surface area;

<sup>b</sup> Total pore volume at p/p<sub>0</sub> = 0.99;

<sup>c</sup> Micropore volume determined by t-plot;

<sup>d</sup> Mesopore volume calculated as total pore volume – micropore volume.
4.2.3 Thermogravimetric analysis

The thermogravimetric analysis was conducted to determine the amount of deposited coke on the prepared catalysts. The amounts of coke deposited on the used microwave-treated and untreated catalysts after the MeOH-TPSR tests are given in Table 4.2. The deposited coke amounts were determined by the weight loss upon the thermogravimetric analysis (TGA). Microwave-untreated catalysts, 0.5FeX_{10/0} and 0.5FeZ_{10/0} possessed higher coke amounts, 31.7 mg_{cokeg_{cat}}^{-1} and 46.4 mg_{cokeg_{cat}}^{-1} respectively, than their corresponding microwave-treated catalysts (0.5FeX_{10/119-700} and 0.5FeZ_{10/119-700}). 0.5FeX_{10/119-700} and 0.5FeZ_{10/119-700} catalysts possessed the coke amounts in the range of 2.84-31.0 mg_{cokeg_{cat}}^{-1} and 16.2-44.7 mg_{cokeg_{cat}}^{-1}, respectively. As the microwave power level under which the catalysts were irradiated at was increased from 0–700 W, the coke deposition decreased. The results show that the microwave-untreated catalysts have a comparatively higher carbon capacity, which was later reduced somewhat after microwave irradiation.

Moreover, some researchers used changes in methane formation as the indication for measuring catalyst deactivation by coking (Wen et al., 2016; Schulz, 2010; Villacampa et al., 2003). Microwave-treated catalysts produced less methane gas than the microwave-untreated catalysts (Figure 4.8(a-b)). From methane profiles in Figure 4.8(a-b), microwave-treated catalysts (0.5FeX_{10/119-700} and 0.5FeZ_{10/119-700}) produced less methane. As the microwave power level was increased, the peak intensities of methane profiles for 0.5FeZ_{10/119-700} catalysts were effectively decreased relative to those of 0.5FeX_{10/119-700} catalysts (Figure 4.8(a-b)), and this seems to be related to the high ability of 0.5FeZ_{10/119-700} based catalysts to respond to microwave radiation due to the lower Si/Al of 30. 0.5FeZ_{10/0-700} based catalysts have higher coke amounts and methane formation than 0.5FeX_{10/0-700} based catalysts (Table 4.2 and Figure 4.8(a-b)). There is a proportional relationship between coke deposition, methane formation and Si/Al ratio. Similar observations were previously reported by Gao et al. (2016); As the Si/Al ratio was increased from 30 to 80, Gao et al, 2016 showed that the coke amount was decreased.
from 126.0 mg\textsubscript{coke g\textsuperscript{-1} cat.} to 78.8 mg\textsubscript{coke g\textsuperscript{-1} cat.} and methane formation decreased from 8.1% to 5.1%, respectively.

Table 4.2: Coke quantity for Methanol-To-hydrocarbons conversion over microwave-treated and untreated catalysts (0.5FeX\textsubscript{10/0-700} and 0.5FeZ\textsubscript{10/0-700}).

<table>
<thead>
<tr>
<th>Used Catalyst</th>
<th>Coke deposited (mg\textsubscript{coke g\textsuperscript{-1} cat.})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5FeX\textsubscript{10/0}</td>
<td>31.7</td>
</tr>
<tr>
<td>0.5FeX\textsubscript{10/119}</td>
<td>21.7</td>
</tr>
<tr>
<td>0.5FeX\textsubscript{10/280}</td>
<td>31.0</td>
</tr>
<tr>
<td>0.5FeX\textsubscript{10/336}</td>
<td>27.4</td>
</tr>
<tr>
<td>0.5FeX\textsubscript{10/462}</td>
<td>23.8</td>
</tr>
<tr>
<td>0.5FeX\textsubscript{10/595}</td>
<td>14.0</td>
</tr>
<tr>
<td>0.5FeX\textsubscript{10/700}</td>
<td>2.84</td>
</tr>
<tr>
<td>0.5FeZ\textsubscript{10/0}</td>
<td>46.4</td>
</tr>
<tr>
<td>0.5FeZ\textsubscript{10/119}</td>
<td>24.3</td>
</tr>
<tr>
<td>0.5FeZ\textsubscript{10/280}</td>
<td>44.7</td>
</tr>
<tr>
<td>0.5FeZ\textsubscript{10/336}</td>
<td>38.1</td>
</tr>
<tr>
<td>0.5FeZ\textsubscript{10/462}</td>
<td>33.8</td>
</tr>
<tr>
<td>0.5FeZ\textsubscript{10/595}</td>
<td>25.0</td>
</tr>
<tr>
<td>0.5FeZ\textsubscript{10/700}</td>
<td>16.2</td>
</tr>
</tbody>
</table>

4.2.4 Scanning electron microscopy (SEM) analysis

Figure 4.3 and Figure A1 show SEM images of microwave-untreated (0.5FeX\textsubscript{10/0} and 0.5FeZ\textsubscript{10/0}) and microwave-treated catalysts (0.5FeX\textsubscript{10/119-700} and 0.5FeZ\textsubscript{10/119-700}) with non-
uniform size. SEM images of 0.5FeZ\textsubscript{10/0-700} catalysts depicted that the small crystallites agglomerate together and formed larger spherical stacks. This may be attributed to their high surface Gibbs energy. No differences in surface morphologies were clearly observed between the SEM images of 0.5FeZ\textsubscript{10/119-700} catalysts and microwave-untreated (0.5FeZ\textsubscript{10/0}) catalyst. Unlike 0.5FeZ\textsubscript{10/119-700} catalysts SEM images, microwave-treated (0.5FeX\textsubscript{10/119-700}) catalysts SEM images clearly showed that upon increased microwave power level, the nanosized aggregates clustered together into micro- and mesosized stacks with visually seen spaces between the stacks. SEM images of 0.5FeX\textsubscript{10/0-700} catalysts depicted that the crystallites exhibit coffin-like shapes.
Figure 4.3: SEM micrographs of microwave-treated and untreated catalysts.
4.2.5 Fourier Transform Infrared (FT-IR) Spectroscopy

The FT-IR spectra of the parent zeolites and the microwave-untreated and treated catalysts (0.5FeZ\textsubscript{1000-700} and 0.5FeX\textsubscript{1000-700}) in the range 400–1500 cm\textsuperscript{-1} are shown in Figure 4.4(a-b). The ratios of the band intensities of the FT-IR spectra and the relative crystallinity estimated from FT-IR spectra are given in Table 4.3. As it can be observed in Figure 4.4(a-b), in all the samples basically similar bands appeared, even though upon Fe-loading and subsequent microwave treatment, their intensities were found to be drastically changed. The band intensities of HZSM-5(80) based samples were found to be increasing with increasing microwave power level from 0-700 W and even after Fe-loading as shown in Figure 4.4(b). However, the band intensities for HZSM-5(30) based samples were found to fluctuate with increasing microwave power level and even after Fe-loading as shown in Figure 4.4(a).

![Figure 4.4](image-url)

**Figure 4.4:** FT-IR spectra for the parent zeolites (HZSM-5) and microwave-untreated and treated catalysts: (a) 0.5FeZ\textsubscript{1000-700} and (b) 0.5FeX\textsubscript{1000-700} catalysts.

All the FT-IR spectra depicted all the bands which typically characterize the MFI zeolite structure, with absorption bands at 1221-1225, 1072-1105, 795-800, 544-550, and 432-451 cm\textsuperscript{-1} as shown in Figure 4.4(a) and at 1223-1225, 1072-1095, 785-797, 544-546, and 434-446 cm\textsuperscript{-1}.
as shown in Figure 4.4(b). The band around 1225 cm\(^{-1}\), 1080 cm\(^{-1}\), 796 cm\(^{-1}\), 546 cm\(^{-1}\) and 441 cm\(^{-1}\) were associated with external asymmetric stretching of Si-O which clearly characterized the zeolites containing one or four chains of five-membered rings (Jacobs et al., 1981; Jansen et al., 1984), internal asymmetric stretching of Si-O-T (Ismail et al., 2006), symmetrical stretching of Si-O-Si (Jiang et al., 2015), double five-membered rings of the ZSM-5 zeolites (Rasouli et al., 2017), and T-O bending vibration of the SiO\(_4\) and AlO\(_4\) internal tetrahedral (Coudurier et al., 1982), respectively.

The ratio of the band intensities near A and B, as shown in Table 4.3, can be used to estimate the zeolite crystallinity even though quantitative FT-IR data are not very accurate (Ismail et al., 2006; Coudurier et al., 1982). There are slight differences between crystallinity values estimated using FT-IR and XRD data (Coudurier et al., 1982). As it can be observed from Table 4.3 after 0.5 wt.% Fe was loaded on HZSM-5(30) and HZSM-5 (80), the relative crystallinity value decreased from 46.6-46.3% and increased to 43.0-55.8%, respectively. Upon increased microwave power level to 119–700 W, the relative crystallinity values fluctuated in the range 48.5–58.2% for 0.5FeZ\(_{10/119-700}\) catalysts and the relative crystallinity values for 0.5FeX\(_{10/119-700}\) catalysts increased to ≥ 61.3%. This showed that microwave radiation enhanced crystallinity. The results were almost similar to the XRD results reported in Figure 4.1(a-b). As shown in Table 4.3, the 0.5FeX\(_{10/462-700}\) catalysts were said to be highly crystalline than other microwave treated catalysts since their A/B ratios were greater than 0.7 and any material having A/B ratio less than 0.7 can be regarded as amorphous (Coudurier et al., 1982).
### Table 4.3: Effect of Fe loading, and microwave post-modification on the ratio of the band intensities of the FT-IR spectra and relative crystallinity estimated from FT-IR spectra.

<table>
<thead>
<tr>
<th>Sample</th>
<th>A/B ratio*</th>
<th>Relativity crystallinity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HZSM-5(80)</td>
<td>0.430</td>
<td>43.0</td>
</tr>
<tr>
<td>0.5FeX_{100}</td>
<td>0.558</td>
<td>55.8</td>
</tr>
<tr>
<td>0.5FeX_{10/119}</td>
<td>0.677</td>
<td>67.7</td>
</tr>
<tr>
<td>0.5FeX_{10/280}</td>
<td>0.613</td>
<td>61.3</td>
</tr>
<tr>
<td>0.5FeX_{10/336}</td>
<td>0.651</td>
<td>65.1</td>
</tr>
<tr>
<td>0.5FeX_{10/462}</td>
<td>0.724</td>
<td>72.4</td>
</tr>
<tr>
<td>0.5FeX_{10/595}</td>
<td>0.714</td>
<td>71.4</td>
</tr>
<tr>
<td>0.5FeX_{10/700}</td>
<td>0.712</td>
<td>71.2</td>
</tr>
<tr>
<td>HZSM-5(30)</td>
<td>0.466</td>
<td>46.6</td>
</tr>
<tr>
<td>0.5FeZ_{100}</td>
<td>0.463</td>
<td>46.3</td>
</tr>
<tr>
<td>0.5FeZ_{10/119}</td>
<td>0.485</td>
<td>48.5</td>
</tr>
<tr>
<td>0.5FeZ_{10/280}</td>
<td>0.582</td>
<td>58.2</td>
</tr>
<tr>
<td>0.5FeZ_{10/336}</td>
<td>0.473</td>
<td>47.3</td>
</tr>
<tr>
<td>0.5FeZ_{10/462}</td>
<td>0.511</td>
<td>51.1</td>
</tr>
<tr>
<td>0.5FeZ_{10/595}</td>
<td>0.574</td>
<td>57.4</td>
</tr>
<tr>
<td>0.5FeZ_{10/700}</td>
<td>0.486</td>
<td>48.6</td>
</tr>
</tbody>
</table>

*A/B ratios for HZSM-5(30) based samples were calculated using the band intensities in these ranges; A (544–550 cm\(^{-1}\)) and B (432–451 cm\(^{-1}\)) bands and A/B ratios for HZSM-5(80) based samples were calculated using the band intensities in these ranges; A (544–546 cm\(^{-1}\)) and (434–446 B cm\(^{-1}\)) bands.
4.2.6 \( C_3H_9N \)-TPSR for acidic sites determination

The effect of microwave radiation on the concentration of Brønsted acidic sites \( (c_B) \) was studied using \( n \)-propylamine-temperature programmed surface reaction (\( C_3H_9N \)-TPSR), and the results are presented in Figure 4.5(a-b), Table 4.4, and Figure 4.6(a-b). As an alternative to ammonia, Gorte and co-workers have reported successive works regarding the use of TPSR of reactive amines to characterize solid acids (Farneth and Gorte, 1995; Gorte, 1999; Kresnawahjuesa et al., 2000; Parrillo et al., 1995). Reactive amine which are primarily used includes but not limited to primary amines which can be stoichiometrically adsorbed on the Brønsted acidic sites, and then undergo Hofmann elimination upon heating to alkenes and ammonia (Kresnawahjuesa et al., 2000; Kresnawahjuesa et al., 2002; Milina et al., 2013; Milina et al., 2014). Figure 4.5(a-b) depict the \( C_3H_9N \)-TPSR profiles for the desorption of \( n \)-propylamine, propylene and ammonia between 120 °C and 500 °C. All 0.5FeX100-700 and 0.5FeZ100-700 catalysts follow a similar trajectory to one presented in Figure 4.5(b), and Figure 4.5(a), respectively. However, the only differences are brought about the differences in peak intensities and desorption temperatures due to increasing microwave power level (0-700 Watts). The first peak around 205 °C and 198 °C in Figure 4.5(a) and Figure 4.5(b), respectively may be attributed to the desorption of physisorbed \( n \)-propylamine which may be associated with hydroxyl defects, Lewis acid sites or hydrogen bonded to other protonated amines at Brønsted acidic sites (Gorte, 1999).

![C3H9N-TPSR profiles](image)

**Figure 4.5:** \( C_3H_9N \)-TPSR data profiles for \( n \)-propylamine decompostion to propylene and ammonia.
At elevated temperatures above 270 °C, propylene and ammonia were evolved at different temperatures for every sample studied. As shown in Figure 4.6(a), 0.5FeZ\textsubscript{100-700} catalysts have two well-resolved peaks – the first ones centered at 337-345 °C temperature range (Table 4.4) and the second small ones around 400 °C which seem to be fading away upon increasing microwave power level (0-700 W). 0.5FeX\textsubscript{100-700} catalysts have only one and first well-resolved peak centered at 339-347 °C temperature range as shown in Table 4.4 and Figure 4.6(b). Those first peaks centered at aforementioned temperature ranges are indicative characteristics of surface reactions of adsorbed n-propylamine on the Brønsted acidic sites. Consequently, the amount of desorbed propylene can be used alternatively as way to quantify the concentration of Brønsted acidic sites \((c_B)\), and the data is presented in Table 4.4. Upon increasing microwave power level (0-700), the concentration of Brønsted acidic sites decreased from 88.8 \(\mu\)mol\textsubscript{C\textsubscript{3}H\textsubscript{6}} g\textsuperscript{-1} to the lowest value of 69.6 \(\mu\)mol\textsubscript{C\textsubscript{3}H\textsubscript{6}} g\textsuperscript{-1} for 0.5FeZ\textsubscript{100-700} catalysts, and from 57.4 \(\mu\)mol\textsubscript{C\textsubscript{3}H\textsubscript{6}} g\textsuperscript{-1} to the lowest value of 37.5 \(\mu\)mol\textsubscript{C\textsubscript{3}H\textsubscript{6}} g\textsuperscript{-1} for 0.5FeX\textsubscript{100-700} catalysts. It can be observed that microwave untreated catalysts, 0.5FeX\textsubscript{100} and 0.5FeZ\textsubscript{100} exhibited highest concentration of Brønsted acidic sites of 57.4 \(\mu\)mol\textsubscript{C\textsubscript{3}H\textsubscript{6}} g\textsuperscript{-1} and 88.8 \(\mu\)mol\textsubscript{C\textsubscript{3}H\textsubscript{6}} g\textsuperscript{-1}, respectively than microwave treated catalysts (Table 4.4). Similar remarks can also be made in Figure 4.6(a-b), that microwave untreated catalysts (0.5FeX\textsubscript{100} and 0.5FeZ\textsubscript{100}) have higher peak intensities than microwave treated catalysts (0.5FeX\textsubscript{10/119-700} and 0.5FeZ\textsubscript{10/119-700}). This indicated that microwave radiation reduced the concentration of Brønsted acidic sites.

![Figure 4.6](image_url): Propylene profiles obtained from the C\textsubscript{3}H\textsubscript{9}N-TPSR experiments over varying Si/Al ratio; 30 (a) and 80 (b) for determining the concentrations of Brønsted acidic sites \((c_B)\).
The concentration and strength of acidic sites play a vital role in the MTH process. Thus, altering the acidic sites, especially the Brønsted acidic sites, affects the product distribution and also the catalyst lifetime. Modifying ZSM-5 zeolite with the metal does not only increases the selectivity towards desired hydrocarbons, but also increase the catalyst lifetime as metal loading effectively decreases the concentration of Brønsted acidic sites (Chen et al., 2015; Dyballa et al., 2013; Li et al., 2016; Li et al., 2016). Several approaches have been developed to overcome coke by preparing mesoporous or hierarchical ZSM-5 from microporous ZSM-5 zeolite. Chemical leaching as one of the developed approaches for example, decreases the concentration of Brønsted acidic sites, and by so doing increases the catalyst lifetime, decreases coke formation and increases selectivity towards desired hydrocarbons (Wei et al., 2015; Zhou et al., 2017).

As it can be observed in Table 4.4, there is no such linear relationship between increasing microwave power level (0-700) and decreasing concentration of Brønsted acidic sites. This may be attributed to low iron loading (0.5 wt.% Fe) and the fact that ZSM-5 zeolite, on its own, is microwave transparent. Whittington and Milestone, (1992) reported that either hydrated or dehydrated Na/ZSM-5 or Na/USY do not undergo any large temperature increase under microwave irradiation and stated that this may be due to the low sodium content, but may be also correlated to cavity size of ZSM-5, and the fact that these zeolites are hydrophobic. Microwave absorption in metal-based ZSM-5 catalysts can be further increased by taking advantage of increasing the metal loading which already has some benefits. Therefore, further decreasing the concentration of Brønsted acidic sites, and increasing the selectivity and catalyst lifetime without using expensive templates and performing many steps to create mesoporous or hierarchical catalysts can be easily and cheaply achieved within a short period of time using microwave radiation.
Chapter 4: Results and Discussion

Table 4.4: Determination of Brønsted acidic sites from C₃H₉N-TPSR.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>(c_B) (/(\text{µmol C}_3\text{H}_6 \text{ g}^{-1}))</th>
<th>Temperature(^+) (/(°\text{C}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5FeX(_{10/0})</td>
<td>57.4</td>
<td>342</td>
</tr>
<tr>
<td>0.5FeX(_{10/119})</td>
<td>41.6</td>
<td>347</td>
</tr>
<tr>
<td>0.5FeX(_{10/280})</td>
<td>41.2</td>
<td>347</td>
</tr>
<tr>
<td>0.5FeX(_{10/336})</td>
<td>42.8</td>
<td>342</td>
</tr>
<tr>
<td>0.5FeX(_{10/462})</td>
<td>39.8</td>
<td>341</td>
</tr>
<tr>
<td>0.5FeX(_{10/595})</td>
<td>37.5</td>
<td>339</td>
</tr>
<tr>
<td>0.5FeX(_{10/700})</td>
<td>39.8</td>
<td>339</td>
</tr>
<tr>
<td>0.5FeZ(_{100})</td>
<td>88.8</td>
<td>339</td>
</tr>
<tr>
<td>0.5FeZ(_{10/119})</td>
<td>83.1</td>
<td>341</td>
</tr>
<tr>
<td>0.5FeZ(_{10/280})</td>
<td>83.8</td>
<td>337</td>
</tr>
<tr>
<td>0.5FeZ(_{10/336})</td>
<td>84.6</td>
<td>341</td>
</tr>
<tr>
<td>0.5FeZ(_{10/462})</td>
<td>69.6</td>
<td>345</td>
</tr>
<tr>
<td>0.5FeZ(_{10/595})</td>
<td>73.9</td>
<td>343</td>
</tr>
<tr>
<td>0.5FeZ(_{10/700})</td>
<td>73.7</td>
<td>339</td>
</tr>
</tbody>
</table>

* Concentrations of Brønsted acidic sites \((c_B)\).

\(^+\) Temperature at which first maximum peak appears.

4.3 Catalysts Testing (MeOH-TPSR experiments)
In this section, the results obtained from MeOH-TPSR experiments in the MTH process to see the effect of microwave radiation are presented and discussed in detail.

4.3.1 MeOH-TPSR
MeOH-TPSR experiments on the iron (III)-exchanged MFI zeolite (0.5wt.%Fe/ZSM-5, with Si/Al ratio = 30 and 80) samples were performed to study the effect of microwave radiation on the catalyst characteristics regarding the MTH process product distribution, maximum desorption peak temperatures \((T_{\text{max}}\) values) and peak intensities. MeOH-TPSR profiles for the
as-prepared catalysts (0.5FeX_{100-700} and 0.5FeZ_{100-700}) were divided into three temperature regions for clarity: 172-277 °C and 202-254 °C (region I), 252-290 °C and 246-265 °C (region II), and 324-376 °C and 327-363 °C (region III) for 0.5FeX_{100-700} and 0.5FeZ_{100-700} catalysts, respectively. In every temperature region, the detailed information (T_{max} values and peak intensities) of mainly the desired reactant (methanol) and products (H_2O, DME, aliphatic and aromatic hydrocarbons) are listed and shown in Table A1 and Figure 4.7 for clarity.

![Figure 4.7](image)

**Figure 4.7:** MeOH-TPSR data profiles for methanol conversion to C_1–C_5 aliphatic and C_6–C_8 aromatic hydrocarbons.

It is well-known that methanol is converted to hydrocarbons via three main reaction steps namely: methanol is firstly dehydrated to produce dimethyl ether (DME), and the equilibrium mixture is then formed, comprised of methanol, DME, and water. Produced DME undergoes dehydration also to produce light olefins. Subsequently, the conversion of light olefins to paraffins, higher olefins, aromatics, and naphthenes occurs (Lee *et al.*, 2014). As it can be observed in Figure 4.7, the desorption peaks of methanol, DME and the first peak of water appeared in the region I. It could be understood that methanol dissociatively adsorbs on the surfaces of the as-prepared catalysts (0.5FeX_{100-700} and 0.5FeZ_{100-700}) to generate DME and
water. The dissociative adsorption may be proposed to take place via two ways: (i) by adsorption on surface hydroxyl groups with the formation of methoxy groups and water, or (ii) methoxy groups react on the surface of the catalyst to produce DME via condensation of two neighboring methoxy groups (Bianchi et al., 1995).

As for region II, the second peak of water which is more intense than the first broad asymmetric one which appeared in region I and C$_1$-C$_5$ aliphatic hydrocarbons peaks were observed. The second peak of water is attributed to DME dehydration to produce the C$_1$-C$_5$ aliphatic hydrocarbons. Lastly, as for region III in Figure 4.7, C$_6$-C$_8$ aromatics (benzene, toluene and xylene) peaks were observed, showing the occurrence of an aromatization reaction as the reaction temperature was increased to 550 °C. Previously, it has been accepted that propylene and ethylene are primary intermediates for producing BTX aromatics by a series of processes such as dehydrogenation, cyclization and aromatization at elevated temperature.

Table A1 shows the typical TPSR data obtained for methanol on the microwave-untreated catalysts (0.5FeX$_{100}$ and 0.5FeZ$_{100}$) and for other microwave treated catalysts. Methanol profiles have two peaks – a broad asymmetric profile with a $T_{\text{max}}$ at 183 °C and a more intense narrow profile with a $T_{\text{max}}$ at 237 °C for 0.5FeX$_{100}$ catalyst, and one broad asymmetric profile with $T_{\text{max}}$ at 246 °C for 0.5FeZ$_{100}$ catalyst (Table A1). Upon increasing microwave radiation power level from 0-700 W, the $T_{\text{max}}$ values for desorbed methanol and evolved products (H$_2$O, DME, aliphatic and aromatic hydrocarbons) from methanol conversion shifted to either lower or higher $T_{\text{max}}$ values than for those of 0.5FeX$_{100}$ and 0.5FeZ$_{100}$ catalysts as shown in Table A1. Moreover, the profile shapes for methanol desorption and for products formation were found to be almost similar upon increasing microwave level (0-700 W) for each Si/Al ratio. However, only the peak intensities were found to be significantly changing. Very different peak
intensities of the profiles and the $T_{\text{max}}$ values observed for different catalysts obtained using different Si/Al ratios (30 and 80) and varying microwave power levels (0-700 W) indicated the presence of different active surface sites having very different chemical activity and selectivity properties.

**Figure 4.8:** $C_1$ Alkane (Methane) profiles obtained from the MeOH-TPSR experiments over varying Si/Al ratio: 30 (a) and 80 (b).

During the MeOH-TPSR experiments over $0.5\text{FeX}_{10/0}-700$ and $0.5\text{FeZ}_{10/0}-700$ catalysts, water and DME formation profiles were included, but for simplicity, more focus was paid on the aliphatic and aromatic hydrocarbon profiles to see the effect of microwave radiation. As for methane profiles, upon increasing microwave power level from 0-700 W (Figure 4.8(a)), the peak intensities decreased. Microwave-untreated catalyst ($0.5\text{FeZ}_{10/0}$) showed pronounced peak intensity on methane profile than microwave-treated catalysts ($0.5\text{FeZ}_{10/119-700}$). This shows that less methane was formed upon increasing microwave power level. Under increased microwave power level (0-700 W), the $T_{\text{max}}$ values for methane profiles were found to be fluctuating in the range of 246–260 °C (Table A1 and Figure 4.14(a)).
Microwave-untreated catalyst (0.5FeX\textsubscript{10/100}) showed pronounced peak intensities for methane formation compared to microwave-treated catalyst (0.5FeX\textsubscript{10/119-700}) as shown in Figure 4.8(b). Upon increasing microwave power level, there was no such tremendous decrease in methane peak intensities when using 0.5FeX\textsubscript{10/119}, 0.5FeX\textsubscript{10/336} and 0.5FeX\textsubscript{10/700} catalysts unlike when using 0.5FeX\textsubscript{10/280}, 0.5FeX\textsubscript{10/462} and 0.5FeX\textsubscript{10/595} catalysts. The fluctuating peak intensity response for methane profiles over microwave-treated catalysts (0.5FeX\textsubscript{10/119-700}) may be attributed to increased Si/Al ratio (80) which expels the weakly bonded cations to the zeolite framework. Therefore, the number of active iron cations per unit cell were decreased, resulting in uneffective response of these catalysts (0.5FeX\textsubscript{10/119-700}) to microwave radiation compared to other microwave-treated 0.5FeZ\textsubscript{10/119-700} catalysts prepared using ZSM-5 zeolite with Si/Al = 30.

Under 119–700 W microwave irradiation (Table A1 and Figure 4.14(b)), the $T_{\text{max}}$ values for methane profiles shifted from 252 °C to $T_{\text{max}}$ values $\geq$ 255 °C. It can be deduced that microwave irradiation of the catalysts enhanced the rate of reorientation of the intermediates (C\textsubscript{7}H\textsubscript{9}$^+$-C\textsubscript{12}H\textsubscript{19}$^+$) in the MTH process and facilitated the proton back-donation process to the zeolite framework. This process facilitated the recovery of the acidic site of the catalysts and the release of the corresponding arene to overcome coke formation, as the rate of methane formation was slow. Wen et al. (2016) showed that the rate of reorientation of the intermediates and the rate of methane formation via demethylation are two competing reactions.
Figure 4.9: C$_2$ Aliphatic hydrocarbons (Ethane and Ethylene) profiles obtained from the MeOH-TPSR experiments over varying Si/Al ratio; 30 (a) and 80 (b).

Figure 4.9(a) shows similar profiles in shape for C$_2$ aliphatic hydrocarbons (Ethylene and Ethane) like the ones for methane formation when using 0.5FeZ$_{100/-700}$ catalysts. Upon increasing microwave power level, there was a decrease on the C$_2$ aliphatic hydrocarbons peak intensities except for microwave-untreated catalyst (0.5FeZ$_{100}$). 0.5FeZ$_{100}$ catalyst shows pronounced C$_2$ aliphatic hydrocarbons peak intensities than microwave-treated catalysts (0.5FeZ$_{10/119/-700}$). Figure 4.9(b) shows that microwave-treated (0.5FeX$_{10/119}$ and 0.5FeX$_{10/700}$) catalysts exhibit pronounced peak intensities on the C$_2$ aliphatic hydrocarbon profiles than other microwave-treated catalysts (0.5FeX$_{10/280/-595}$) and microwave-untreated catalyst (0.5FeX$_{100}$). The shapes of the C$_2$ aliphatic hydrocarbon profiles remained similar, and only the peak intensities were affected during increased microwave power level (0–700 W) as shown in Figure 4.9(b).
Figure 4.10: $C_3$ Alkane (Propane) profiles obtained from the MeOH-TPSR experiments over varying Si/Al ratio; 30 (a) and 80 (b).

Figure 4.10(a-b) show that upon increased microwave power level (0–700 W), the peak intensities on the propane profiles were suppressed. As a result, microwave-untreated catalysts ($0.5FeX_{100}$ and $0.5FeZ_{100}$) showed the highest peak intensities on the propane profiles. Microwave irradiation resulted in decreased propane formation. The microwave-untreated catalyst ($0.5FeZ_{100}$) shows pronounced peak intensities on the $C_3$-$C_5$ aliphatic hydrocarbon profiles namely, propylene, butene, pentene, butane and pentane compared to the microwave-treated catalysts ($0.5FeZ_{100/119-700}$) as shown in Figure 4.11(a) and Figure A2-A3(a). Figure 4.11(b) and Figure A2-A3(b) show that microwave-treated catalyst ($0.5FeX_{104/62}$) showed the highest peak intensity on $C_3$-$C_5$ aliphatic hydrocarbon profiles than microwave-untreated catalyst ($0.5FeX_{100}$) and corresponding microwave-treated catalysts.
Figure 4.11: C₃-C₄ Alkenes (Propylene and Butene) profiles obtained from the MeOH-TPSR experiments over varying Si/Al ratio; 30 (a) and 80 (b).

As for Figure 4.11(a) and Figure A2-A3(a), and Figure 4.11(b) and Figure A2-A3(b), similar C₃-C₅ aliphatic hydrocarbon profiles in shape, distribution and adsorption but with different peak intensities were observed over 0.5FeZ₁₀₀-70₀ and 0.5FeX₁₀₀-70₀ catalysts, respectively. Moreover, C₃-C₅ aliphatic hydrocarbons appeared to have similar $T_{\text{max}}$ values like for C₁-C₂ aliphatic hydrocarbons (Table A1 and Figure 4.14(a-b)). From the $T_{\text{max}}$ values for C₁-C₅ aliphatic hydrocarbons, upon increased Si/Al ratio to 80, and increased microwave power level, the $T_{\text{max}}$ values shifted to higher temperatures from 252 °C. This shows that increased Si/Al ratio and microwave power level resulted in increased desorption temperatures for the C₁-C₅ aliphatic hydrocarbons (Table A1). Upon decreased Si/Al ratio to 30, and increased microwave power level (Table A1), $T_{\text{max}}$ values were below 260 °C for C₁-C₅ aliphatic hydrocarbons. This shows that the C₁-C₅ aliphatic hydrocarbons were easily formed at lower temperatures than for Si/Al ratio of 80.
Figure 4.12: C₆ Aromatic hydrocarbon (benzene) profiles obtained from the MeOH-TPSR experiments over varying Si/Al ratio; 30 (a) and 80 (b).

As for 0.5FeX₁₀/₀-700 and 0.5FeZ₁₀/₀-700 catalysts in region III, in each figure (Figure 4.12(a-b) and Figure 4.13(a-b)), the shape, distribution and adsorption of the peaks for the profiles were found to be similar, but the peak intensities and the Tₘₐₓ values of the products (benzene (Figure 4.12(a-b)), toluene and xylene (Figure 4.13(a-b))), were tremendously different. The microwave-treated catalyst (0.5FeZ₁₀/700) showed the highest peak intensity in benzene profiles than microwave-untreated catalyst (0.5FeZ₁₀/0) and other corresponding microwave-treated catalysts (0.5FeZ₁₀/119-595) as shown in Figure 4.12(a). This implies that more benzene was generated on the 0.5FeZ₁₀/700 catalysts. However, upon increased Si/Al ratio to 80 from 30 and under the same microwave power levels for irradiation and Fe loading, microwave-untreated catalyst (0.5FeX₁₀/0) showed the highest peak intensity on benzene profiles than microwave-treated catalysts (0.5FeX₁₀/119-700) as shown in Figure 4.12(b).
Figure 4.13: C<sub>7</sub>-C<sub>8</sub> Aromatics (Xylene and Toluene) profiles obtained from the MeOH-TPSR experiments over varying Si/Al ratio; 30 (a) and 80 (b).

The microwave-untreated catalyst (0.5FeZ<sub>100</sub>) showed the highest peak intensity in toluene and xylene profiles followed by 0.5FeZ<sub>10/700</sub> catalyst as shown in Figure 4.13(a). When the Si/Al ratio was increased from 30 to 80, 0.5FeX<sub>10/700</sub> catalyst showed the highest peak intensity in toluene and xylene profiles followed by 0.5FeX<sub>10/0</sub> and 0.5FeX<sub>10/595</sub> catalysts as shown in Figure 4.13(b). It is plausible that under optimized reaction conditions, feed composition and suitable metal loading on the zeolite, upon increased microwave power level for catalyst post-treatment, the rate of aromatization in the MTH process intermediates can be enhanced to form BTX. Compared with the peak intensities for C<sub>2</sub>-C<sub>5</sub> aliphatic hydrocarbons, only trace amounts of BTX can be observed over 0.5FeZ<sub>100/700</sub> and 0.5FeX<sub>10/0/700</sub> in region III (as shown in Figure 4.12(a-b), and Figure 4.13(a-b)) as the peak intensities of the BTX profiles were lower. This shows that most of the primary intermediates (ethylene and propylene) obtained over 0.5FeX<sub>10/0/700</sub> and 0.5FeZ<sub>10/0/700</sub> catalysts were not converted to BTX products. The enhanced peak intensities in region II (as shown in Figure 4.9-4.11(a-b) and Figure A2-A3(a-b)) for C<sub>2</sub>-C<sub>5</sub> aliphatic hydrocarbons compared with the peak intensities for BTX in region III (as shown in Figure 4.12(a-b) and Figure 4.13(a-b)), indicated that incorporation of iron promotes the formation of the intermediates in MTH process over the aromatization steps to form BTX, even under microwave post-treatment of the catalysts.
As observed in Table A1 and Figure 4.14(a-b), the $T_{\text{max}}$ values for benzene over the $0.5\text{FeX}_{100-700}$ and $0.5\text{FeZ}_{100-700}$ catalysts fluctuates at lower temperature ranges, 324–361 °C and 327–348 °C, respectively as compared to $T_{\text{max}}$ values for xylene and toluene. This suggests that the benzene was more easily generated at lower temperatures, followed by a benzene methylation process occurring at higher temperatures to produce xylene and toluene. Based on the shift on $T_{\text{max}}$ values for toluene and xylene to higher temperatures, $\geq 331$ °C and $\geq 339$ °C over $0.5\text{FeX}_{100-700}$ and $0.5\text{FeZ}_{100-700}$ catalysts, respectively (Table A1), it is thought that increased microwave power level under which the catalysts were post-treated can lead to an increased toluene and xylene formation temperatures. As shown in Figure 4.14(a-b), the microwave power level has an effect on the $T_{\text{max}}$ values in the MTH process.

**Figure 4.14:** Increasing power level against maximum peak temperature for MTH process over $0.5\text{FeZ}_{100-700}$ catalysts (a) and $0.5\text{FeX}_{100-700}$ catalysts (b).
References


CHAPTER 5
Conclusions and Recommendations

5.1 Conclusions

The iron-containing precursors containing 0.5 wt.% iron (0.5Fe/ZSM-5), were prepared using the incipient wetness impregnation method and subsequently post-modified under microwave irradiation. The resulting 0.5FeX_{100-700} and 0.5FeZ_{100-700} catalysts were characterized and tested in the MeOH-TPSR experiment to understand the effect of microwave radiation on these catalysts and their activity for methanol conversion to hydrocarbons. Upon increased microwave power level from 0 to 700 W, it was found that:

(i) The MFI zeolite structure for all the catalysts was maintained even after iron loading as confirmed by XRD and FT-IR analysis. However, their peak intensities and crystallinities were found to be drastically changing. The relative crystallinity values increased from 46.3% to values ≥ 47.3% for 0.5FeZ_{100-700} catalysts and the relative crystallinity values for 0.5FeX_{100-700} catalysts increased from 55.8% to values ≥ 61.3%. The 0.5FeX_{100-700} catalysts were more crystalline than 0.5FeZ_{100-700} catalysts.

(ii) BET surface area and micropore volume decreased from 376 m$^2$/g to 346 m$^2$/g and 0.119 cm$^3$/g to 0.108 cm$^3$/g, respectively for 0.5FeZ_{100-595} catalysts except for the 0.5FeZ_{100-700} catalyst. The BET surface area decreased from 366 m$^2$/g to values ≤ 357 cm$^2$/g and the mesopore volume increased to 0.0995 cm$^3$/g for 0.5FeX_{100-700} catalysts.

(iii) Coke amounts decreased from 46.4 mg$_{\text{coke}}$/g$_{\text{cat}}$ to 16.2 mg$_{\text{coke}}$/g$_{\text{cat}}$ and from 31.7 to 2.84 mg$_{\text{coke}}$/g$_{\text{cat}}$ for 0.5FeZ_{100-700} and 0.5FeX_{100-700} catalysts, respectively. As a
result, the $0.5\text{FeX}_{10/0-700}$ catalysts shown more resistance to coke deposition than the $0.5\text{FeZ}_{10/0-700}$ catalysts.

(iv) SEM images for $0.5\text{FeX}_{10/0-700}$ catalysts clearly showed that nanosized aggregates clustered together into micro- and mesosized stacks with visually seen spaces between the stacks as compared to SEM images for $0.5\text{FeZ}_{10/0-700}$ catalysts.

(v) From the $\text{C}_3\text{H}_6\text{N-TPSR}$ results, the concentration of Brønsted acidic sites decreased from 88.8 $\mu\text{mol}_{\text{C}_3\text{H}_6}\text{g}^{-1}$ to the lowest value of 69.6 $\mu\text{mol}_{\text{C}_3\text{H}_6}\text{g}^{-1}$ for $0.5\text{FeZ}_{10/0-700}$ catalysts, and from 57.4 $\mu\text{mol}_{\text{C}_3\text{H}_6}\text{g}^{-1}$ to the lowest value of 37.5 $\mu\text{mol}_{\text{C}_3\text{H}_6}\text{g}^{-1}$ for $0.5\text{FeX}_{10/0-700}$ catalysts, respectively.

(vi) From the $\text{MeOH-TPSR}$ results, the $T_{\text{max}}$ values for desorbed methanol and evolved products ($\text{H}_2\text{O}$, DME, aliphatic and aromatic hydrocarbons) shifted in either lower or higher $T_{\text{max}}$ values than for those of $0.5\text{FeX}_{10/0}$ and $0.5\text{FeZ}_{10/0}$ catalysts. The peak intensities for methane profiles decreased over $0.5\text{FeX}_{10/119-700}$ and $0.5\text{FeZ}_{10/119-700}$ catalysts. This shows that microwave radiation inhibits methane production. Microwave radiation enhanced the rate of reorientation of the intermediates ($\text{C}_7\text{H}_9^+\text{-C}_{12}\text{H}_{19}^+$) in the MTH process as methane production was decreased. Ethane and ethene peak intensities decreased and fluctuated, propane peak intensities decreased, propene, butene, pentene, butane, pentane peak intensities decreased and fluctuated, over the $0.5\text{FeZ}_{10/0-700}$ and $0.5\text{FeX}_{10/0-700}$ catalysts, respectively. The $0.5\text{FeZ}_{10/700}$ catalyst showed pronounced peak intensity on benzene profiles while peak intensities for benzene profiles decreased over $0.5\text{FeX}_{10/0-700}$ catalysts. This shows that $0.5\text{FeZ}_{10/700}$ give rise to more benzene formation than all the catalysts studied. The peak intensities for xylene and toluene decreased over $0.5\text{FeZ}_{10/0-700}$ catalysts while $0.5\text{FeX}_{10/700}$ catalysts showed pronounced peak intensity on xylene and toluene profiles.
Chapter 5: Conclusions and Recommendations

It was observed that, generally the microwave radiation has an effect on the catalytic properties of 0.5Fe/ZSM-5 catalysts prepared which then results in either positive or negative enhancement of the peak intensities in the MeOH-TPSR experiments. This work successfully met the set aim which was to use microwave radiation to create mesoporous or hierarchical catalysts to overcome coke formation which is associated with high methane production.

5.2 Recommendations

This work may be considered successful; however, there are some recommendations that could be further carried over for future work, and some recommendations are stated below.

- Owing to successful application of microwave radiation as a post-synthesis modification step, apart from the already reported methods in the literature like chemical leaching and templating approaches to create mesoporous or hierarchical catalysts from microporous catalysts, to reduce mass transfer limitations encountered in microporous catalysts in the process like MTH, microwave radiation should be employed especially in heterogeneous catalysis.

- To increase the ability of metal-based ZSM-5 catalysts to absorb microwave radiation effectively, the effect of metal loading should be carried out.

- Examining of the zeolite samples using micro-XRD to see if there are any structural changes induced by microwave radiation should be carried out.

- The effect of microwave radiation should be further tested over a number of elements across the periodic table using ZSM-5 zeolite as a support in the MTH process.

- Further work using microwave radiation should be carried out to be able to quantify how much is being produced of the desired hydrocarbons (olefins/aromatics) from methanol conversion.
Figure A1: SEM micrographs of microwave-treated catalysts.
Table A1: Maximum desorption peak temperatures ($T_{\text{max}}$ values) from MeOH-TPSR data for adsorbed methanol over microwave untreated (0.5FeX$_{10/0}$ & 0.5FeZ$_{10/0}$) and treat (0.5FeX$_{10/119-700}$ & 0.5FeZ$_{10/119-700}$) catalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Methane</th>
<th>Water</th>
<th>Ethane &amp; Ethene</th>
<th>Propane</th>
<th>Methanol &amp; Propene</th>
<th>Butane &amp; Pentane</th>
<th>Dimethyl Ether</th>
<th>Benzene</th>
<th>Toluene &amp; Xylene</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5FeZ$_{10/0}$</td>
<td>254</td>
<td>207</td>
<td>257</td>
<td>253</td>
<td>253</td>
<td>253</td>
<td>253</td>
<td>248</td>
<td>339</td>
</tr>
<tr>
<td>0.5FeZ$_{10/119}$</td>
<td>256</td>
<td>203</td>
<td>258</td>
<td>256</td>
<td>256</td>
<td>256</td>
<td>256</td>
<td>247</td>
<td>327</td>
</tr>
<tr>
<td>0.5FeZ$_{10/280}$</td>
<td>260</td>
<td>207</td>
<td>265</td>
<td>260</td>
<td>247</td>
<td>260</td>
<td>260</td>
<td>254</td>
<td>347</td>
</tr>
<tr>
<td>0.5FeZ$_{10/336}$</td>
<td>249</td>
<td>205</td>
<td>252</td>
<td>249</td>
<td>245</td>
<td>248</td>
<td>248</td>
<td>243</td>
<td>334</td>
</tr>
<tr>
<td>0.5FeZ$_{10/462}$</td>
<td>246</td>
<td>202</td>
<td>252</td>
<td>246</td>
<td>241</td>
<td>246</td>
<td>246</td>
<td>246</td>
<td>333</td>
</tr>
<tr>
<td>0.5FeZ$_{10/995}$</td>
<td>249</td>
<td>205</td>
<td>255</td>
<td>249</td>
<td>237</td>
<td>249</td>
<td>249</td>
<td>243</td>
<td>345</td>
</tr>
<tr>
<td>0.5FeZ$_{10/700}$</td>
<td>250</td>
<td>205</td>
<td>256</td>
<td>250</td>
<td>246</td>
<td>250</td>
<td>250</td>
<td>248</td>
<td>337</td>
</tr>
<tr>
<td>0.5FeX$_{10/0}$</td>
<td>252</td>
<td>195</td>
<td>254</td>
<td>252</td>
<td>183</td>
<td>252</td>
<td>252</td>
<td>241</td>
<td>324</td>
</tr>
<tr>
<td>0.5FeX$_{10/119}$</td>
<td>255</td>
<td>196</td>
<td>256</td>
<td>255</td>
<td>172</td>
<td>255</td>
<td>255</td>
<td>237</td>
<td>325</td>
</tr>
<tr>
<td>0.5FeX$_{10/280}$</td>
<td>289</td>
<td>218</td>
<td>290</td>
<td>289</td>
<td>197</td>
<td>289</td>
<td>289</td>
<td>277</td>
<td>361</td>
</tr>
<tr>
<td>0.5FeX$_{10/336}$</td>
<td>275</td>
<td>204</td>
<td>276</td>
<td>275</td>
<td>189</td>
<td>275</td>
<td>275</td>
<td>275</td>
<td>353</td>
</tr>
<tr>
<td>0.5FeX$_{10/462}$</td>
<td>282</td>
<td>212</td>
<td>283</td>
<td>282</td>
<td>195</td>
<td>282</td>
<td>282</td>
<td>266</td>
<td>356</td>
</tr>
<tr>
<td>0.5FeX$_{10/995}$</td>
<td>278</td>
<td>209</td>
<td>279</td>
<td>278</td>
<td>188</td>
<td>278</td>
<td>278</td>
<td>278</td>
<td>354</td>
</tr>
<tr>
<td>0.5FeX$_{10/700}$</td>
<td>273</td>
<td>210</td>
<td>275</td>
<td>273</td>
<td>187</td>
<td>273</td>
<td>273</td>
<td>274</td>
<td>354</td>
</tr>
</tbody>
</table>

Figure A2: C$_5$ Alkene (Pentene) profiles obtained from the MeOH-TPSR experiments over varying Si/Al ratio; 30 (a) and 80 (b).
**Figure A3**: C₄-C₅ Alkanes (butane and Pentane) profiles obtained from the MeOH-TPSR experiments over varying Si/Al ratio; 30 (a) and 80 (b).