June 2019

Effect of Promoter (Mn) on the Performance of SBA-15 Supported Iron Catalysts for High Temperature Fischer-Tropsch Synthesis

Sreya Mariya Seby
University of South Florida, sreyaseby@mail.usf.edu

Follow this and additional works at: https://scholarcommons.usf.edu/etd

Part of the Chemical Engineering Commons

Scholar Commons Citation

This Thesis is brought to you for free and open access by the Graduate School at Scholar Commons. It has been accepted for inclusion in Graduate Theses and Dissertations by an authorized administrator of Scholar Commons. For more information, please contact scholarcommons@usf.edu.
Effect of Promoter (Mn) on the Performance of SBA-15 Supported Iron Catalysts for High Temperature Fischer-Tropsch Synthesis

by

Sreya Mariya Seby

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in Chemical Engineering Department of Chemical and Biomedical Engineering College of Engineering University of South Florida

Co-Major Professor: Babu Joseph, Ph.D.
Co-Major Professor: John Kuhn, Ph.D.
Scott Campbell, Ph.D.

Date of Approval:
June 24, 2019

Keywords: Synthetic Fuel, Biofuel, Heterogeneous Catalysis, Syngas

Copyright © 2019, Sreya Mariya Seby
ACKNOWLEDGMENTS

Working on this thesis on “Effect of Promoter (Mn) on the Performance of SBA-15 supported iron catalysts for High Temperature FTS” provided immense knowledge to me. I would like express my sincere gratitude to my Co-major professors Dr. John Kuhn and Dr. Babu Joseph for giving me an opportunity to work on this thesis and guiding me with valuable support throughout the journey. I would also like to thank Dr. Scott Campbell for being my committee member and giving me good feedback. I would also like to acknowledge all Heterogeneous Catalysis & Materials Chemistry Group members for their continuous support and assistance in my work. Finally, I would like to thank my family for their support.
TABLE OF CONTENTS

LIST OF TABLES ........................................................................................................ iii
LIST OF FIGURES ..................................................................................................... iv
ABSTRACT .................................................................................................................. vi

CHAPTER 1: INTRODUCTION ..................................................................... 1
  1.1 Motivation ........................................................................................................ 1
  1.2 Specific Objectives ...................................................................................... 5
  1.3 Significance .................................................................................................... 5
  1.4 Scope ............................................................................................................... 5
  1.5 Outline of the Thesis ..................................................................................... 6

CHAPTER 2: BACKGROUND AND LITERATURE SURVEY ................. 7
  2.1 FTS Chemistry ............................................................................................ 10
  2.2 FTS Mechanism .......................................................................................... 11
  2.3 Modes and Reactors of FTS ..................................................................... 11
  2.4 FTS Catalysts .............................................................................................. 12
  2.5 Effect of Catalyst Support on FTS ............................................................. 13
  2.6 Effect of Activation Conditions ................................................................. 14
  2.7 Effect of Promoters .................................................................................... 14

CHAPTER 3: EXPERIMENTAL METHODS ........................................... 18
  3.1 Synthesis Methods .................................................................................... 18
  3.2 Characterization Methods ....................................................................... 19
  3.3 Catalytic Testing Methods ....................................................................... 21

CHAPTER 4: RESULTS AND DISCUSSION ........................................ 24
  4.1 Synthesis Results ....................................................................................... 24
  4.2 Characterization Results ........................................................................... 24
    4.2.1 XRD .................................................................................................... 24
    4.2.2 N\textsubscript{2} Physisorption ................................................................. 25
    4.2.3 Temperature Programmed Reduction ............................................... 26
    4.2.4 Scanning Electron Microscopy ............................................................ 28
  4.3 FTS Test Results ........................................................................................ 30
    4.3.1 Effect of Manganese Loading ............................................................. 30
    4.3.2 Effect of Operating Temperature ....................................................... 35

CHAPTER 5: CONCLUSION AND FUTURE WORK ............................. 39
5.1 Conclusion........................................................................................................................................... 39
5.2 Future Work........................................................................................................................................... 40

REFERENCES........................................................................................................................................... 41

APPENDICES ........................................................................................................................................... 48
  Appendix A: Loading Calculations ........................................................................................................... 49
  Appendix B: Carbon Balance Calculations ............................................................................................ 52
  Appendix C: Calibration of Rotameter .................................................................................................... 54
  Appendix D: Reproducibility of Experiments ...................................................................................... 55
LIST OF TABLES

Table 1.1: Methods of conversion of biomass to biofuels ................................................................. 2
Table 1.2: Relative costs of catalysts used for FTS reaction ................................................................. 4
Table 4.1: Physisorption results ........................................................................................................... 26
Table 4.2: CO conversion and yield from promoted and unpromoted iron catalysts tested at 3 hr on stream .................................................................................................................. 31
Table 4.3: CO conversion and yield from 15Fe/SBA-15 catalysts ......................................................... 36
Table 4.4: CO conversion and yield from 2.8Mn/15Fe/SBA-15 catalysts ............................................. 36
Table A1: Methodology to synthesize 15Fe/SBA-15 with 15% of iron loading .............................. 49
Table A2: Methodology to synthesize 1.4Mn/15Fe/SBA-15 with 1.4% of manganese and 15% of iron loading .......................................................................................................................... 50
Table B1: Carbon balance of 15Fe/SBA-15 ....................................................................................... 52
Table B2: Carbon balance of 2.8Mn/15Fe/SBA-15 ........................................................................... 53
Table B3: Yield calculation of 2.8Mn/15Fe/SBA-15 ......................................................................... 53
Table D1: CO conversion of 2.8Mn/15Fe/SBA-15 ............................................................................ 55
Table D2: Yield calculation from experiment 1 .................................................................................. 55
Table D3: Yield calculation from experiment 2 .................................................................................. 55
Table D4: Yield calculation from experiment 3 .................................................................................. 56
LIST OF FIGURES

Figure 1.1: BTL process based on biomass gasification ................................................................. 3

Figure 2.2: Proposed Intensified Process for direct conversion of biogas to syncrude ................................................................. 4

Figure 2.1: Conversion of biomass to renewable fuels ........................................................................ 7

Figure 2.2: Overview of a bio-refinery utilizing biomass as a feedstock to produce transportation fuels via FTS process ............................................... 9

Figure 2.3: Mass fraction of hydrocarbons products as a function of the chain growth parameter (Alpha) ........................................................................ 17

Figure 3.1: Catalyst preparation, activation and FTS testing.............................................................. 19

Figure 3.2: FTS reactor setup ............................................................................................................. 22

Figure 4.1: XRD analysis of 2.8 Mn/15Fe/SBA-15 ........................................................................... 25

Figure 4.2: Temperature Programmed Reduction of 15Fe/SBA-15 ................................................. 27

Figure 4.3: Temperature Programmed Reduction of 2.8Mn/15Fe/SBA-15................................. 27

Figure 4.4: SEM image of 15Fe/SBA-15 at 700x magnification ....................................................... 28

Figure 4.5: SEM image of 15Fe/SBA-15 at 3000x magnification ..................................................... 29

Figure 4.6: SEM image of 2.8Mn/15Fe/SBA-15 at 3000x magnification ......................................... 29

Figure 4.7: SEM image of 2.8Mn/15Fe/SBA-15 at 6000x magnification .......................................... 30

Figure 4.8: C_{2}-C_{4} yield of the catalysts tested at 430°C and 1 bar for 3 hr with H_{2}/CO=2:1 .......................................................................................... 32

Figure 4.9: CH_{4} yield of the catalysts tested at 430°C and 1 bar for 3 hr with H_{2}/CO=2:1 .......................................................................................... 33

Figure 4.10: C_{5+} yield of the catalysts tested at 430°C and 1 bar for 3 hr with H_{2}/CO=2:1 .......................................................................................... 33
Figure 4.11: CO conversion of 2.8Mn/15Fe/SBA-15 catalyst tested at 430°C and 1 bar for 10 hr with H₂/CO=2:1 .................................................. 34

Figure 4.12: C₂- C₄ and CO₂ yield of 2.8Mn/15Fe/SBA-15 catalyst tested at 430 °C and 1 bar for 10 hr with H₂/CO= 2:1 .......................................................... 35

Figure 4.13: Effect of temperature on CO conversion ................................................................. 37

Figure C1: Rotameter calibration with CO .................................................................................. 54
ABSTRACT

Development of an effective High Temperature Fischer-Tropsch Synthesis (HTFTS) catalyst is of interest in process intensification that combines methane reforming with long chain hydrocarbon production. Literature indicates iron catalysts supported on mesoporous silica performed relatively well in high temperature applications. In this work, we investigated the effect of manganese promoter on iron catalysts for FTS at 430 °C as it was known from previous studies that manganese promotion could enhance the CO conversion with higher hydrocarbon yields. Also, the effect of temperature on FTS activity was evaluated by testing the base and promoted Fe/SBA-15 catalysts for temperature ranging from 370 to 430 °C.

Incipient wetness impregnation method was used to prepare the catalysts. The catalysts used in this work were un-promoted iron (15 wt%) and Mn promoted (1.4, 2.8, 4.2, 5.6, 11.2 wt%) iron (15 wt%) catalysts supported on SBA-15. The catalysts were characterized using XRD, TPR, N₂ Physisorption, and SEM. These catalysts were first activated in synthesis gas (H₂: CO = 2:1) at 430 °C and then tested for their catalytic performance at the same temperature and atmospheric pressure. Prior work with SBA-15 supported iron catalysts showed that manganese promotion could improve the CO conversion when compared to copper and potassium.

The main goal of this work was to study the effect of varying the manganese content on SBA-15 supported iron catalysts to determine the optimum loading of Mn along with the effect of temperature. It was found that CO conversion increases from 27% to
74% with increasing the amount of manganese. The yield of CO$_2$ increased substantially with higher Mn loadings. When different Mn promoted iron catalysts were compared, the catalysts with 2.8 wt% Mn loading showed the best performance in terms of the CO conversion and yield of C$_{2+}$ hydrocarbons. Catalyst with 2.8 wt% of manganese loading yielded a CO conversion of 54%, with a methane yield of 17%, 32% (carbon) yield of C$_2$-C$_4$ and 9%(carbon) yields of C$_5+$ hydrocarbon products, respectively.

The effect of operating temperature on the catalytic performance of both the base catalyst 15Fe/SBA-15 and the promoted 2.8Mn/15Fe/SBA-15 catalyst was also examined. The unpromoted iron catalyst showed an improved catalytic activity at 400 °C with the total CO conversion of 38% and a higher yields of C$_5+$ hydrocarbons. A significant decrease was also observed in the yields of CH$_4$ and CO$_2$. The methane and carbon dioxide yield increased from 11% and 8% to 25% and 40%, respectively, as the temperature increased from 400 to 450 °C. The catalyst with 2.8 wt% of manganese promotion gave better CO conversion and hydrocarbon product yields at 430 °C. Lower temperature showed negative effect on hydrocarbon product yield for manganese promoted catalysts.
CHAPTER 1
INTRODUCTION

1.1 Motivation

Currently, the energy needs in the world relies heavily on fossil fuels, including coal, natural gas, and petroleum. The price of fossil fuels have been increasing over the years. This combined with the concern about CO$_2$ emission and global warming has led to increased investment in renewable energy sources. Biomass has been proposed as a potential renewable energy source to replace petroleum. Fischer-Tropsch Synthesis (FTS) of long chain hydrocarbon fuels from renewable sources such as biomass has garnered considerable interest in recent years.

The main means for producing biofuels from biomass are$^1$:

i. Anaerobic Digestion

ii. Gasification

iii. Pyrolysis/Liquefaction

iv. Hydrothermal carbonization/Torrefaction

v. Fermentation

Anaerobic digestion and Fermentation are bio-chemical way of converting biomass to produce biofuels. Gasification, pyrolysis and hydrothermal carbonization are some thermo-chemical means of producing biofuels.
Table 1.1: Methods of conversion of biomass to biofuels

<table>
<thead>
<tr>
<th>Method</th>
<th>Conversion Method</th>
<th>Biomass source</th>
<th>Fuel output</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anaerobic Digestion</td>
<td>Bio-chemical</td>
<td>Municipal Solid Waste (MSW), sewage sludge</td>
<td>CH₄/CO₂(Biogas)-medium Btu gas</td>
</tr>
<tr>
<td>Gasification</td>
<td>Thermo-chemical</td>
<td>Agricultural and forest residues, MSW</td>
<td>Biogas, Syngas</td>
</tr>
<tr>
<td>Pyrolysis/Liquefaction</td>
<td>Thermo-chemical</td>
<td>Agricultural residues, MSW</td>
<td>Gas, liquid and solid fuels</td>
</tr>
<tr>
<td>Hydrothermal carbonization/</td>
<td>Thermo-chemical</td>
<td>MSW, Agricultural residue, sewage sludge</td>
<td>Bio-coal, Hydrochar</td>
</tr>
<tr>
<td>Torrefaction</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fermentation</td>
<td>Bio-chemical</td>
<td>Crops such as corn, sugarcane, crop residues</td>
<td>Ethanol</td>
</tr>
</tbody>
</table>

*Adapted from Elsayed

A biomass to liquid (BTL) process can be used for the conversion of biomass to liquid fuels in three steps:

i. Conversion of biomass to biogas
   
ii. Dry reforming of biogas to produce syngas
   
iii. The conversion of syngas to syncrude via Fischer-Tropsch Synthesis

Biogas can be produced by anaerobic digestion or by steam gasification of the biomass. Biogas consists of methane, hydrogen, carbon monoxide, carbon dioxide. The second step is the steam reforming of methane and CO₂ to produce syngas.

Steam reforming:  
\[ \text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2 \]  
\( \Delta H (298K) = 206 \text{ kJ/mole} \)  

Dry reforming:  
\[ \text{CH}_4 + \text{CO}_2 \rightarrow 2\text{CO} + 2 \text{ H}_2 \]  
\( \Delta H (298K) = 247 \text{ kJ/mole} \)

The third step converts the syngas to heavier hydrocarbons:
Fischer-Tropsch Synthesis: \((2n + 1)H_2 + nCO \rightarrow C_nH_{2n+2} + nH_2O\) \(\Delta H (298K) = -206 \text{ kJ/mole, when } n = 1, \text{but } n \text{ can vary from 1-30}\)

Fischer-Tropsch Synthesis (FTS) is a process which involves the conversion of carbon monoxide (CO) and hydrogen (H\(_2\)) into water and hydrocarbons. The main products of FTS reaction are alkanes (or paraffins) with some side products of alkenes (or olefins) and oxygenated items (alcohols). Specifically, methane (C\(_1\)), oil gas (C\(_2\)-C\(_4\)), gas (C\(_5\)-C\(_{11}\)), diesel (C\(_{12}\)-C\(_{20}\)) and wax (C\(_{21+}\)) are formed from FTS reaction. Additional gasoline and diesel fuel can be produced by hydrocracking of heavier waxes.

Methane reforming usually occurs at a high temperature around 800 – 900 °C while FTS occurs relatively at low temperature that is 250 – 350 °C.

**Figure 1.1: BTL process based on biomass gasification**

Reforming is an energy intensive process that requires large amounts of heat at high temperature. FTS is an exothermic process at milder temperatures and produces large amounts of energy at a low temperature. Thus, there is an interest in developing “intensified” process that combine these two steps. Currently, research is underway to develop catalysts that are capable of carrying out low temperature reforming. This,
combined with high temperature FTS catalysts, will allow the development of an intensified single step process to convert biogas to liquid fuels in a single step making it more economical, especially in small scale applications.

![Diagram](image.png)

**Figure 1.2: Proposed Intensified Process for direct conversion of biogas to syncrude.**

The above Figures 1.1 and 1.2 show the process flow of general and combined gas to liquid process.

The main objective of this thesis is to explore options for a high temperature FTS catalyst. The catalysts used in FTS include Ni, Ru, Co, Fe in order of activity. Traditionally, Co has been used as a low temperature FTS catalyst while Fe has been suggested for high temperature FTS processes. Each of these catalysts have their own abilities to favor the reactions. Ni catalysts are highly selective to methane formation while the other three catalysts promote olefin and paraffins.

**Table 1.2: Relative costs of catalysts used for FTS reaction**

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Fe</th>
<th>Co</th>
<th>Ni</th>
<th>Ru</th>
</tr>
</thead>
<tbody>
<tr>
<td>Relative cost*</td>
<td>1</td>
<td>85</td>
<td>35</td>
<td>25,0000</td>
</tr>
</tbody>
</table>

*Based on prices in June 2019
1.2 Specific Objectives

The specific objective of this work is study the effect of Mn promoter on Fe catalysts for Fischer-Tropsch Synthesis (FTS) and evaluate its performance at high temperature (430 °C). The second objective is to evaluate the effect of temperature on unpromoted and Mn promoted Fe catalysts supported on silica. We want to establish the optimum loading of manganese for improved activity and decreased carbon dioxide formation.

Cano, L.A., et al3 showed that the catalysts supported on SBA-15 with 15 wt% iron loading (Fe/SBA-15) showed good FTS catalytic performance at higher temperatures (~430 °C). Here we study the performance of promoted and unpromoted Fe/SBA-15 catalysts (manganese is used as a promoter) at 430 °C and 1 atmosphere in a fixed bed reactor. After establishing the optimum loading of manganese, the FTS reactions is carried out at different temperatures ranging from 370 °C to 450 °C to evaluate the effect of temperature on the catalytic activity.

1.3 Significance

The development of a high temperature FTS catalyst will take us one step closer to developing an intensified process of combining reforming and FTS steps. The intensified process should lower the overall cost of converting biogas to liquid fuels and this enable the building of small scale BTL process.

1.4 Scope

The work reported here is limited to Mn promoted Fe catalysts supported on SBA-15 with 15 wt% Fe loading. All experiments were carried out at atmospheric pressure with temperatures ranging from 370 to 450 °C. A 2:1 ratio of H2/CO was used in all studies. All reactions were carried out in a fixed-bed micro-reactor.
1.5 Outline of the Thesis

Chapter 2 provides brief background study and literature survey on high temperature FTS. This includes a brief history of FTS, FTS Chemistry, modes of FTS, FTS reaction mechanism, types of catalysts used for FTS, effect of activation conditions, effect of different supports and promoters used.

Chapter 3 focuses on experimental methods used to carry out the study which includes synthesis, characterization and testing of the catalysts.

In Chapter 4, relevant results from different experiments conducted are discussed.

The 5th chapter gives the general conclusions on the effect of manganese on SBA-15 supported iron catalysts for HTFTS. Also, the effect of temperature on the same is described.
CHAPTER 2
BACKGROUND AND LITERATURE SURVEY

Renewable fuels can be used as a replacement for fossil fuels which can be produced from biomass. Figure 2.1 shows multiple pathways by which renewable fuels can be produced from biomass.

Figure 2.1: Conversion of biomass to renewable fuels

Among these processes, gasification along with FTS reaction is considered as a promising technology for the production of chemicals and liquid fuels.

FTS was initially developed to convert coal to liquids during the First World War. This process, which involved the reaction of syngas to produce a mixture of hydrocarbons...
and oxygenated compounds was first discovered by Franz Fischer and Hans Tropsch in 1923\(^4\). This has been used commercially for decades for converting coal to synthetic petroleum in South Africa starting in the late 1950s. Sasol and Shell are considered to be the two major companies utilizing FTS commercially\(^5\). The overall FTS based process for converting biogas includes 3 main steps:

i. Syngas production and purification.

ii. Fischer-Tropsch Synthesis

iii. Upgrading and separation of the products

Syngas is produced from biogas by reforming processes. The syngas is purified to get rid of impurities like CO\(_2\) and tars and its composition adjusted to achieve roughly 2:1 mole ratio of CO to H\(_2\) needed for FTS using a water gas shift reactor. FTS produces a range of hydrocarbons (paraffins, olefins and alcohols). The products from FTS are then recovered and upgraded by refinery processes such as catalytic reforming, isomerization, and hydrocracking. These products include various types of fuel like LPG, Diesel, gasoline as well as chemical intermediates\(^6\). Fuels derived from FTS processes have better properties than those derived from crude oil.
Figure 2.2: Overview of a bio-refinery utilizing biomass as a feedstock to produce transportation fuels via FTS process.

Adapted from Pratibha

At present, FTS is carried out commercial on very large scales and is used today to convert natural gas (or coal) to liquids for easy transportation. However, when biomass is considered as a feedstock, the scale must be reduced significantly due to the distributed...
nature of biomass availability. However, small scale FTS plants are not currently economical and therefore this technology has not been used for conversion of biomass to liquids on a commercial scale.

2.1 FTS Chemistry

The FTS is basically a polymerization reaction which results in the production of a range of hydrocarbons. Alkanes and alkenes are the main products that are formed from FTS reactions. Some oxygenates like alcohols and carboxylic acids can also be formed. The product formation from FTS are shown in the equations below:

- Methanation: \( H_2 + CO \rightarrow CH_4 + H_2O \)
- Alkanes: \((2n + 1)H_2 + nCO \rightarrow C_nH_{2n+2} + nH_2O\)
- Alkene: \((2n)H_2 + nCO \rightarrow C_nH_{2n} + nH_2O\)
- Alcohol: \((2n)H_2 + nCO \rightarrow C_nH_{2n+1}O + nH_2O\)
- Carboxylic acids: \((2n−1)H_2 + nCO \rightarrow C_nH_{2n}O_2 + (n−2)H_2O\)

Water gas shift (WGS) reaction will also take place during a FTS reaction which is shown in the equation below:

- WGS: \( H_2O + CO \rightleftharpoons CO_2 + H_2 \)

Water gas shift reaction is considered as beneficial when the syngas feed (H₂/CO) ratio is less than 2 as it leads to the formation of hydrogen which can be used in reactions. FTS is an exothermic process and the heat of formation of the hydrocarbon products are always negative. At higher temperatures, the formation of methane is favored over the other higher hydrocarbons. The choice of a catalyst and its morphology can significantly affect the product yield and composition. Temperature, pressure and feed composition also have a significant role in the performance of the FTS process.
2.2 FTS Mechanism

The formation of products from FTS reaction has been studied in many papers\textsuperscript{9}. FTS reaction is basically a polymerization reaction which includes\textsuperscript{10,11}:

i. Adsorption of the reactant (CO)

ii. Chain initiation by CO dissociation directly or assisted by hydrogen atoms

iii. Chain propagation and chain growth by reaction monomer

iv. Chain termination to yield paraffins and olefins

v. Product desorption from surfaces

vi. Re-adsorption and further reactions

When the primary products interact with another catalytic site, it leads to a series of secondary reactions which includes\textsuperscript{11}:

i. Hydrogenation to paraffins

ii. Isomerization

iii. Cracking and hydrogenolysis

iv. Insertion into growing chains

v. Re-adsorption and initiation of hydrocarbon chains

2.3 Modes and Reactors of FTS

Traditionally, FTS reaction is done in two modes: It can either be done at a high (HTFTS, $T \approx 300 – 350 ^\circ C$) or at a low temperature (LTFTS $\approx 220 – 270 ^\circ C$) depending on the desired products\textsuperscript{12-14}. HTFTS favors the formation of olefins and gasoline while LTFTS is used when the desired products are diesel and hard wax. The three main types of reactors used for FTS are fluidized bed reactors which are used for HTFTS, fixed bed and slurry bubble column reactors which are used for LTFTS. Reactions in fluidized bed
usually leads to the production of gasoline while fixed and slurry bed reactors can be used for the production of heavier products\textsuperscript{15}. Fixed bed reactors can be scaled up easily and safely while slurry bed reactor requires less amount of catalysts and can be operated at a higher temperature. Another reason for which fixed bed reactors are chosen is because of the less catalyst loss and higher conversion.

2.4 FTS Catalysts

A variety of catalysts can be used for FTS reaction. Precious metals are the most common since they can adsorb hydrogen and carbon monoxide dissociatively. Iron, nickel, cobalt and ruthenium are the main metals with required FTS activity for the commercial application. It was reported by Sabatier and Senderens\textsuperscript{16} that using nickel or cobalt catalyst at atmospheric pressure, hydrocarbon (methane) can be produced from syngas\textsuperscript{16} while ruthenium was reported to have less selectivity to methane and more selectivity to higher hydrocarbons\textsuperscript{17}. Since Ru is very expensive, Fe and Co have been used in the past for large FTS applications. Co catalysts are usually used for LTFTS reactions as they are considered to be more active than Fe catalysts with lower activity towards carbon dioxide production\textsuperscript{1,18,19} whereas Fe catalysts can be used for both HTFTS and LTFTS. Iron catalyst are always preferred over cobalt catalysts since iron is considered as an active water gas shift catalyst and also because it is inexpensive when compared to cobalt\textsuperscript{1,19}. Another reason for which iron is considered as a better catalyst when compared to cobalt is that the selectivity towards methane is high when cobalt catalysts are used at higher temperatures.
2.5 Effect of Catalyst Support on FTS

The catalyst support also plays an important role in FTS reaction rate and product selectivity. Some supports can cause dramatic effects on catalytic performance due to their chemical and structural properties. Thus support selection and synthesis is critical during the catalyst preparation.

Different supports that can be used for FTS catalysts include SiO$_2$, Al$_2$O$_3$, TiO$_2$, ZrO$_2$, CeO$_2$ etc. S. Storsæte and Borg have reported that the catalyst support have a significant effect on product selectivity and the selectivity of C$_5$+ hydrocarbons increased in the order of Al$_2$O$_3$< SiO$_2$< TiO$_2$ for Co catalysts $^{20-22}$. The textural properties of Al$_2$O$_3$ helps in loading more metals and thus provide more active sites. Graphite, carbon nanotubes (CNTs), carbon nano-horns (CNHs), carbon nanofibers (CNFs) are some reported carbon materials that can be used as support for FTS catalysts because of better mesoporosity with thermal stability and strength $^{23}$. It was stated by Shan et al $^{24}$ that the iron catalysts supported with SiO$_2$ has greater FTS activity when compared to Al$_2$O$_3$ supported catalysts. It was also mentioned that addition of SiO$_2$ could also lead to a decrease in methane selectivity and could enhance the C$_5$+ selectivity $^{24}$. There are some recent studies on SBA-15 and MCM–41 (Mobil Catalytic Material number 41), which are ordered mesoporous silica that can be used as FTS catalyst support because of high surface areas and large pore diameter. SBA-15 has a structure similar to carbon nanotubes which is also used as a FTS catalyst support $^{25}$. According to Cano et al $^{3}$, the highly uniform pore structure of SBA-15, enhances the catalytic properties of FTS catalysis $^{3}$ by enabling the formation of iron oxide crystals. The narrow pore size
distribution along with good hydrothermal stability are the two main characteristics that makes SBA-15 a good catalyst support\textsuperscript{20, 26, 27}.

2.6 Effect of Activation Conditions

After the synthesis of an FTS catalyst which is in the form of a metal oxide, the next main step is to activate the catalyst for FTS reaction. Activation of the catalysts includes keeping the catalyst at an elevated temperature and flowing reducing gas which is done to convert the iron oxide in the catalyst to iron carbide. The reduction can be done in syngas, or in carbon monoxide at temperatures between 200 °C to 500 °C. It was also found by Shrof that the transformation to carbide phase from oxide phase takes place more rapidly with CO activation\textsuperscript{28}. Bukur et.al has reported that the catalysts got a better FTS activity with low selectivity towards methane and high \( C_5^+ \) selectivity when activated with CO and \( \text{H}_2/\text{CO} \) compared to \( \text{H}_2 \) flow\textsuperscript{29}. Studies have also shown that rate of reaction increases with reduction temperature\textsuperscript{30, 31}.

2.7 Effect of Promoters

Many studies have\textsuperscript{32-35} been done to study the effect of different promoters on catalytic activity during the FTS reactions. Promoters are components that helps in altering the catalyst properties without taking part in the reaction. They act as structural or textural modifier.

Promoters such as Ni, Cu, Mo, Zr, Mn and noble metals like Pt, Ru, Pd, Au are added to the Fe catalysts to enhance their catalytic activity by altering the chain growth probability\textsuperscript{36}. It was reported by Ngantsoue-Hoc that there will a large variation in CO conversion with the use of promoters\textsuperscript{37}.
Potassium used as a promoter helps in increasing the selectivity towards hydrocarbons especially olefins \(^{38}\) and also the FTS and water gas shift activity. It was found by Yang and Xu \(^{39}\) that loading potassium in a higher amount can lead to deactivation of the catalyst. Copper helps in the activation of the catalysts by helping in the reduction of Fe\(_2\)O\(_3\) to Fe or FeC. Wang has reported that it requires very low temperature for the reduction of Fe\(_2\)O\(_3\) to Fe when Cu is used as a promoter. It was mentioned by Li that an increase in methane selectivity can be observed in Cu promoted catalysts \(^{32, 40}\). According to Bukur \(^{29}\), promoting FTS catalysts with Cu would help in improving the FTS activity and product selectivity. Zinc is another promoter that can be used in FTS. Previous studies on Zn promotion for FTS have mentioned that optimum Zn/Fe ratios would help in getting better FTS rates and product selectivity \(^{32}\).

Addition of manganese to FTS catalysts is reported to suppress the CH\(_4\) formation and enhance the higher hydrocarbon selectivity \(^{35}\). This happens because addition of Mn decreases the hydrogenation rate. Structural and electronic effects of Mn on Fe catalysts have also been studied by Barrault \(^{41}\) reported that it helps in the transformation of syngas to olefins because of strong metal support interaction. Loading of Mn in smaller amounts also helps in metal dispersion. It has also been reported by Noritatsu that use of Mn as a promoter could help in the production of olefins \(^{42}\). It was also mentioned that by the introduction of Mn into Fe based FTS catalysts produced a negative effect on the catalytic stability. This can be avoided by optimizing the pre-activation conditions \(^{43}\). Another advantage of adding manganese as a promoter is that it helps in improving the water gas shift reaction and also decreases the chance of oxidation of iron carbides during the reaction \(^{44}\). Manganese promotion is also reported to increase the yield of higher molecular
weight hydrocarbons\textsuperscript{45}. It is reported by Li\textsuperscript{46} that the addition of appropriate amount of Mn promotes the catalyst reduction and carburization in syngas\textsuperscript{46}. The amount of Mn promoter also has a great influence in the hydrocarbon product distributions. Manganese promotion is also reported to show higher WGS selectivity when tested at 270 °C and 12 atm\textsuperscript{47}.

Anderson, Schulz and Flory\textsuperscript{48} proposed a model called the ASF model to obtain the product distribution from FTS reaction. They defined a parameter called alpha, the chain growth probability in their model:

\[
\frac{W_n}{n} = (1 - \alpha)^2 \alpha^{n-1}
\]

where, \( W_n \) is the mass fraction of hydrocarbons formed with \( n \) number of carbon atoms and \( \alpha \) is the chain growth probability. The above equation is usually linearized into the following equation:

\[
\log(W_n/n) = n \log(\alpha) + \log\left(\frac{1 - \alpha}{\alpha}\right)^2
\]
α value can be found using the above equation from the experimental data. As α approaches 1 from 0, the product distribution changes to long chain hydrocarbons from methane. Since gasoline and diesel are the main desired products, a high α value is desirable. From figure 2.3, we can see that an α value of 0.8 will yield a large fraction of C_{11+} products. However it also might yield substantial amount of wax, which will require further hydro-treating.
CHAPTER 3
EXPERIMENTAL METHODS

3.1 Synthesis Methods

The synthesis of the silica support (specifically, mesoporous silica called SBA-15) is the first step during catalyst preparation. SBA-15 has a highly ordered structure with uniform pores and large surface area which makes it a very good catalyst support. SBA-15 can be synthesized using Pluronic triblock co-polymer (P123) which acts as structure directing agent and tetra-ethyl-ortho-silicate (TEOS) (98% pure) as silica source. All chemicals used were purchased from Aldrich unless otherwise mentioned.

A process described by Cano et al. was followed. A mass of 6 g of P123 copolymer was dissolved in a solution of 180 ml of deionized distilled water and 30 ml of 37% HCl. This solution was heated to 40 °C in a hot plate while stirring. Stirring was continued for 3 hr after which 13.5 ml of tetra-ethyl-ortho-silicate (TEOS) was added dropwise. Stirring was continued for another 24 hr at 40°C. The suspension was kept for aging in a sealed polyethylene bottle at 110 °C for 8 hr followed by washing and centrifuging. Calcination of the SBA-15 was done at 500 °C for 6 hr with the ramp rate of 1 °C/min.

The wet impregnation of calcined catalyst was done by incipient wetness using ethanolic solution. Wet impregnation of the SBA-15 was done using Iron (III) nitrate nano hydrate as well as a mixture of and Iron (III) nitrate nano hydrate and manganese (III) acetate. Appropriate amount of Iron (III) nitrate nano hydrate (<98 % pure; Lot
MKBW6908V), with manganese (III) acetate or nitrate (97 % pure; Lot 288740-250), was added by first dissolving in ethyl alcohol solution to get a final loading of 15 wt% of iron and 0, 1.4, 2.8, 4.2, 5.6, and 11.2 wt% of manganese for each catalyst. The loading calculations of the base and promoted catalysts are shown in Appendix A. SBA-15 was impregnated with the above solution by dropwise addition at room temperature. It was then kept for overnight drying at room temperature and then calcined for 4 hr at 450 °C at a ramp rate of 1 °C/min. The obtained Fe/SBA-15 and Fe/Mn/ SBA 15 catalysts were then activated in H₂/CO (10:5) flow at 430 °C with a ramp rate of 4 °C/min for 3 hr.

![Diagram of catalyst preparation, activation and FTS testing](image)

**Figure 3.1: Catalyst preparation, activation and FTS testing**

### 3.2 Characterization Methods

Characterization of the catalysts were done by X-ray diffraction (XRD), Temperature Programmed Reduction (TPR), Scanning Electron Microscopy (SEM) and N₂ Physisorption.
X-ray diffraction (XRD) was used to determine the information on the crystalline structure of the catalysts. This was performed using the Bruker AXS X-ray diffractometer which had a Cu Kα radiation source with $\lambda = 0.154$ nm at 40 kV and 40 mA.

Temperature Programmed Reduction (TPR) was used to get the information on the reduction behavior of the catalysts. Hydrogen (99.99% pure; Airgas, UN1049) was used (as the reducing gas) through the catalyst in a U-tube reactor kept inside a Thermoscientific Thermolyne tube furnace connected to a Cirrus MKS mass spectrometer (MS). Alicat Scientific mass flow controllers were used to control the gas flow rates. The temperature of the furnace was controlled using a Eurotherm 3110 PID controller. Heating tape was used to wrap the gas feed and the outlet to prevent condensation before entering the MS. In order to remove the moisture content, the sample was heated up to 110 °C by flowing helium at the rate of 50 sccm for 30 min before starting the experiment. The sample was then cooled to ambient temperature followed by heating up to 900 °C at a rate of 10 °C/min while flowing 2.5 sccm of hydrogen and 47.5 sccm of helium through the reactor. The reduction temperature can be found from water concentration measured and the area under the curve can be used to measure the extent of reduction.

Scanning Electron Microscopy (SEM) was done using a Hitachi model S-800 instrument to get the details on the surface morphology of the catalysts.

$N_2$ Physisorption experiments were done using Quantachrome Autosorb-IQ at 77 K to determine Brunaur Emmett and Teller (BET) surface area as well as pore diameters and pore volumes which were estimated by the Barret–Joyner–Halenda (BJH) method. The experiments were done using approximately 50 – 60 mg of the catalyst in a small
bulb 6 mm quartz cell. Before physisorption was done, the sample was kept for out
gassing at 200 °C to remove water or other adsorbed gases.

3.3 Catalytic Testing Methods

The FTS reactions of Fe/SBA 15 and Fe/Mn/SBA 15 were done in a quartz u tube micro reactor using around 90 mg of the catalysts. The catalysts (90 mg) were placed between the layers of high temperature quartz wool. The activation of the catalyst was done before the reaction for 3 hr at a temperature of 430 °C with a ramp rate of 4 °C/min by flowing syngas (H₂ (99.99% pure; Airgas, UN1049) and CO (99.5% pure; Airgas, UN1016)) at a ratio of 2:1 with a total flow rate of 15 sccm. This step of activation of the catalysts was done to reduce the catalysts and to form the active species. The FTS reaction was done at temperatures ranging from 370 to 450 °C for which the flow rate was reduced to a total of 3.75 sccm with 2.5 sccm of hydrogen and 1.25 sccm of carbon monoxide. The typical time on stream (TOS) was 3 hr for reactions at each temperature.

Mass flow controllers were used to measure and control the gas flow rates. The total outlet flowrates were measured using a rotameter. Reactions were carried out for 3 hr after the reduction step. The reactor outlet was connected to a Perkin Elmer Gas Chromatography (GC) to analyze the effluent gas from reactor thermal conductivity detector (TCD).

All reactions were done at atmospheric pressure. The hydrogen to carbon monoxide ratio (2:1) was held constant during the reduction and reaction.
Figure 3.2: FTS reactor setup

The reaction products (carbon dioxide, hydrocarbons, carbon monoxide and water) were detected using the GC/TCD. The data from the GC was used to calculate the CO conversion by finding the change in CO moles before and after FTS reaction. The CO conversion and the yield of the products were calculated using the following equations:

\[
\text{CO conversion (\%)} = (1 - \frac{\text{moles of CO out}}{\text{moles of CO in}}) \times 100 \%
\]

\[
\text{Yield (\%)} = \left(\frac{\text{moles of carbon in the product}}{\text{moles of CO converted}}\right) \times 100 \%
\]

where moles of CO converted is based on the difference between CO in the feed and CO in the product.

The product distribution was determined by using the C\textsubscript{1} – C\textsubscript{3} hydrocarbon data measured using GC/TCD by fitting it to the ASF (Anderson-Schultz-Flory) equation in which the model assumes that the rate of polymerization propagation and termination steps are constant and independent of carbon number.

The product distribution was determined using the parameter \(\alpha\) in the equation below:
\[
\frac{W_n}{n} = (1 - \alpha)^2 \alpha^{n-1}
\]

here, \(W_n\) is the mass fraction of the species with carbon number \(n\). Due to the difficulty in measuring small concentrations of C5+ hydrocarbons, their yields were estimated by fitting the data for C1-C4 using the ASF distribution.
CHAPTER 4
RESULTS AND DISCUSSION

FTS reactions were carried at 430 °C to determine the optimum Mn loading and once the optimum Mn amount was found, the reactions were carried out at different temperatures ranging from 370 to 450 °C to determine the effect of temperature. This study was mainly done to determine the effect of Mn on conversion and yield at higher temperatures. This was followed by tests for temperature varying from 370 to 450 °C.

4.1 Synthesis Results

The synthesis of catalysts was done by incipient wetness impregnation by following the method described by Cano et al. Thus, a catalyst which is not promoted with Mn was first synthesized, which is composed of 15% (weight) of iron impregnated on SBA-15 and was referred as 15Fe/SBA-15. Catalysts were then tested for FTS activity at 430 °C. Manganese was added as a promoter in different amounts (1.4, 2.8, 4.2, 5.6, and 11.2 wt%) with 15 wt% of iron to synthesize these catalysts. These catalysts with different amounts of Mn was then tested and compared to un-promoted iron catalysts for FTS activity.

4.2 Characterization Results

4.2.1 XRD

The structural properties of Mn promoted iron catalysts (before reduction) were characterized using XRD. The analysis was done again after the FTS reaction to study the changes occurred to the crystalline structure.
Figure 4.1: XRD analysis of 2.8 Mn/15Fe/SBA-15

The diffraction lines at 25, 32, 35, 50, 63 and 65 ° for the 2 theta values shows the presence of Y-Fe₂O₃.

After the reaction, it was also observed that diffraction lines at 25, 35 and 50 ° appeared, which showed the presence of Y-Fe₂O₃ has disappeared indicating the reduction of iron oxide to iron carbide/ metallic iron.

The appearance of peak at 43 ° after the reaction confirmed the presence of α-Fe which was not present in the XRD of the fresh catalyst. The formation of α-Fe phase occurs only after the reduction step.

4.2.2 N₂ Physisorption

Analysis of textural properties of the catalysts was done by N₂ physisorption. Outgassing of the samples were done before running physisorption to remove water or
any gas adsorbed on it. The surface area, pore volume and pore diameter of the support and the catalysts were determined by N\textsubscript{2} physisorption and presented in the table below:

**Table 4.1: Physisorption results**

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Specific surface area (m\textsuperscript{2}/g)</th>
<th>Pore volume (cc/g)</th>
<th>Pore diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SBA-15</td>
<td>770</td>
<td>1.00</td>
<td>7.8</td>
</tr>
<tr>
<td>15Fe/SBA-15</td>
<td>661</td>
<td>0.58</td>
<td>7.7</td>
</tr>
<tr>
<td>1.4Mn/15Fe/SBA-15</td>
<td>602</td>
<td>0.55</td>
<td>7.5</td>
</tr>
<tr>
<td>2.8Mn/15Fe/SBA-15</td>
<td>556</td>
<td>0.48</td>
<td>7.4</td>
</tr>
<tr>
<td>4.2Mn/15Fe/SBA-15</td>
<td>458</td>
<td>0.40</td>
<td>7.3</td>
</tr>
</tbody>
</table>

The data from the above table indicates that some pores of SBA-15 are blocked by the iron oxides as the surface area of the catalysts is much lower when compared to the surface area of SBA-15. The addition of the promoter seems to also significantly lower the surface area and pore volume.

**4.2.3 Temperature Programmed Reduction**

Temperature programmed reduction is usually performed to determine the reduction temperature of the catalyst. TPR was done on the base 15Fe/SBA-15 catalyst and the 2.8Mn/15Fe/SBA-15 catalyst.

The TPR results of the catalysts are given below:
Figure 4.2: Temperature Programmed Reduction of 15Fe/SBA-15

Figure 4.3: Temperature Programmed Reduction of 2.8Mn/15Fe/SBA-15
From the above figures, it is clear that both the sample reduced at 360 and 600 °C. From literature it was known that there will be two main reduction peaks which corresponds to the reduction of Fe₂O₃ to Fe₃O₄ and Fe₃O₄ to Fe which was verified in this work. The first peak around 350 to 360 °C represents the reduction of Fe₂O₃ to Fe₃O₄ and the second peak at 600 to 650 °C represents the reduction of Fe₃O₄ to Fe. The small peak around 750 °C shows the presence of FeO.

4.2.4 Scanning Electron Microscopy

The catalysts are also characterized by SEM to get the information on surface morphology. SEM analysis of the catalysts 15Fe/SBA-15 and 2.8Mn/15Fe/SBA-15 were done and the SEM images are given below:

![SEM image of 15 Fe/SBA-15 at 700x magnification](image)

**Figure 4.4**: SEM image of 15 Fe/SBA-15 at 700x magnification
Figure 4.5: SEM image of 15 Fe/SBA-15 at 3000x magnification

Figure 4.6: SEM image of 2.8 Mn/15 Fe/SBA-15 at 3000x magnification
Figure 4.7: SEM image of 2.8 Mn/15 Fe/SBA-15 at 6000x magnification

Figure 4.5 shows a tangled rope like structure for the Fe catalysts similar to that seen in SBA-15. The addition of Mn leads to spheroidal shaped particles and a disruption of the rope like structure as seen from figure 4.7. This is supported by the Physisorption studies which showed a significant decrease in pore volume and surface area.

4.3 FTS Test Results

4.3.1 Effect of Manganese Loading

The total CO conversion, alpha value and the yield of different products formed for the FTS reaction carried out at 430 °C with typical time on stream (TOS) of 3 hr are given in the table below:
Table 4.2: CO conversion and yield from promoted and unpromoted iron catalysts tested at 3 hr on stream. T=430 °C, P = 1 atm, Space velocity = 730/hr

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>CO conversion (%)</th>
<th>ASF α value</th>
<th>CH₄ yield*** (%)</th>
<th>Carbon in C₂-C₄ yield**** (%)</th>
<th>Carbon in C₅+ Yield* (%)</th>
<th>CO₂ yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>15Fe/SBA-15</td>
<td>42</td>
<td>0.36</td>
<td>21</td>
<td>37</td>
<td>4</td>
<td>37</td>
</tr>
<tr>
<td>1.4Mn/15Fe/SBA-15</td>
<td>47</td>
<td>0.43</td>
<td>18</td>
<td>30</td>
<td>3</td>
<td>50</td>
</tr>
<tr>
<td>2.8Mn/15Fe/SBA-15</td>
<td>54</td>
<td>0.54</td>
<td>16</td>
<td>31</td>
<td>6</td>
<td>49</td>
</tr>
<tr>
<td>4.2Mn/15Fe/SBA-15</td>
<td>66</td>
<td>0.34</td>
<td>14</td>
<td>21</td>
<td>2</td>
<td>60</td>
</tr>
<tr>
<td>5.6Mn/15Fe/SBA-15</td>
<td>74</td>
<td>0.27</td>
<td>19</td>
<td>18</td>
<td>2</td>
<td>62</td>
</tr>
<tr>
<td>11.2Mn/15Fe/SBA-15**</td>
<td>75</td>
<td>0.25</td>
<td>23</td>
<td>20</td>
<td>1</td>
<td>73</td>
</tr>
<tr>
<td>15Fe/SBA-15 (Cano³)</td>
<td>12</td>
<td>-</td>
<td>8</td>
<td>10</td>
<td>75</td>
<td>5</td>
</tr>
<tr>
<td>15Fe/SBA-15 (Weber²⁵)</td>
<td>29</td>
<td>0.21</td>
<td>14</td>
<td>10</td>
<td>0.2</td>
<td>76</td>
</tr>
<tr>
<td>1.4Mn/15Fe/SBA-15 (Weber²⁵)</td>
<td>32</td>
<td>0.34</td>
<td>18</td>
<td>30</td>
<td>2.2</td>
<td>50</td>
</tr>
</tbody>
</table>

* Estimated from ASF distribution; **Carbon balance was not closing. So, the data is not reliable; ***Based on CO converted; **** Based on moles of carbon in product/moles of CO reacted.

When compared to the total CO conversion reported by Cano et al.³ given in Appendix C, the base 15Fe/SBA-15 catalyst showed a higher conversion since we used a smaller space velocity. However, we were not able to get the higher yield of heavier hydrocarbons reported by Cano et al. My results are closer to those reported by Weber, though here also there were differences in both conversion and yield. The sample calculations for CO conversion and carbon balance are given in Appendix B.

From the Table 4.2, it was found that the catalyst with 2.8 wt% of manganese loading has better catalytic activity when compared to other catalysts. The CO conversion has increased from 42% to 75% with increase in manganese content. However, the C₅⁺ hydrocarbon product yield has also increased with manganese content from 0 to 2.8%,
and further increase in manganese content led to a decrease in the hydrocarbon product yield due to site blocking effect. As the Mn content is increased, it blocks the reactive sites on Fe and thus, the reactants could not reach the reactive sites which resulted in reduced yield of heavier hydrocarbons. The alpha value was also found to increase from 0.36 to 0.54 with increasing manganese loading up to 2.8 wt%. A decrease in the alpha value was found with further increase in the manganese loading.

**Figure 4.8**: C₂-C₄ yield of the catalysts tested at 430 °C and 1 bar for 3 hr with H₂/CO= 2:1

The effect of manganese loading on C₂-C₄ yield is showed in the Figure 4.8. It was found that the catalyst with 2.8 wt% of manganese loading has a better C₂-C₄ yield of 31%. A relative decrease was found in the yield for further increase in the manganese loading.
Figure 4.9: CH₄ yield of the catalysts tested at 430 °C and 1 bar for 3 hr with H₂/CO=2:1

Figure 4.10: C₅⁺ yield of the catalysts tested at 430 °C and 1 bar for 3 hr with H₂/CO=2:1. C₅⁺ yield was estimated by ASF model
The trends in CH$_4$ and C$_{5+}$ yields with the manganese loading are shown in the Figures 4.9 and 4.10. The promoted catalysts with 2.8 wt% of manganese was found to have higher yields of C$_{5+}$ with 9% and a significant low yield for methane with 16%. Thus, it was verified that the addition of optimum amount of manganese could suppress the CH$_4$ formation and lead to higher yields of heavy hydrocarbons.

Results show that the amount of manganese loading has a strong influence on the product formation. It was stated in the literature that addition of excessive amount of manganese could suppress the catalyst carburization which was verified in this work. It was showing a higher CO conversion as the manganese amount was increased. However, the higher CO conversion indicated more production of carbon dioxide which got less benefit to FTS activity.

![Figure 4.11: CO conversion of 2.8Mn/15Fe/SBA-15 catalyst tested at 430 ºC and 1 bar for 10 hr with H$_2$/CO= 2:1](image-url)
The FTS testing of the promoted 2.8Mn/15Fe/SBA-15 catalysts was also done for 10 hr on stream to determine the steady state data. The reaction was carried out at same conditions at 430 °C. Figure 4.11 shows that the CO conversion increased with time and reached the point of steady state by 10 hr with total CO conversion of 56%. This is due to the pore filling and shows that the pores get saturated after 10 hr. Also, the results show that the C\textsubscript{2}- C\textsubscript{4} yield has increased up to 33% and then showed a relative decrease with time. There was also a significant increase in the CO\textsubscript{2} yield with time.

**4.3.2 Effect of Operating Temperature**

The base catalyst 15 Fe/SBA-15 and the 2.8Mn/15 Fe/SBA-15 catalyst which showed the best performance with manganese promotion were used to study the temperature effects at a range of temperature between 370 to 450 °C. The activation of the catalyst was first done at 430 °C by ramping at a rate of 4 °C/min before each reaction.
by flowing total 15 sccm of syngas (H$_2$:10 sccm and CO: 5 sccm) for 3 hr. The typical time on stream for each reaction was 3 hr.

The total CO conversion, alpha value and the yield of different products formed for the FTS reaction carried out at different temperatures are given in the table below:

**Table 4.3: CO conversion and yield from 15Fe/SBA-15 catalysts. Tested at different temperatures after 3 hr on stream**

<table>
<thead>
<tr>
<th>Temperature</th>
<th>CO conversion (%)</th>
<th>ASF $\alpha$- value</th>
<th>CH$_4$ yield** (%)</th>
<th>Carbon in C$_2$-C$_4$ yield*** (%)</th>
<th>Carbon in C$_5$+* yield (%)</th>
<th>CO$_2$ yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>370</td>
<td>36</td>
<td>0.33</td>
<td>19</td>
<td>47</td>
<td>3</td>
<td>30</td>
</tr>
<tr>
<td>400</td>
<td>38</td>
<td>0.38</td>
<td>22</td>
<td>45</td>
<td>5</td>
<td>29</td>
</tr>
<tr>
<td>430</td>
<td>42</td>
<td>0.36</td>
<td>20</td>
<td>39</td>
<td>4</td>
<td>37</td>
</tr>
<tr>
<td>450</td>
<td>58</td>
<td>0.29</td>
<td>25</td>
<td>29</td>
<td>2</td>
<td>41</td>
</tr>
</tbody>
</table>

** Estimated from ASF distribution; **Based on CO converted; *** Based on moles of carbon in product/moles of CO reacted.

**Table 4.4: CO conversion and yield from 2.8Mn/15 Fe/SBA-15 catalysts. Tested at different temperatures after 3 hr on stream**

<table>
<thead>
<tr>
<th>Temperature</th>
<th>CO conversion (%)</th>
<th>ASF $\alpha$- value</th>
<th>CH$_4$ yield*** (%)</th>
<th>Carbon in C$_2$-C$_4$ yield**** (%)</th>
<th>Carbon in C$_5$+* yield (%)</th>
<th>CO$_2$ yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>370**</td>
<td>20</td>
<td>0.06</td>
<td>15</td>
<td>4</td>
<td>-</td>
<td>20</td>
</tr>
<tr>
<td>400</td>
<td>25</td>
<td>0.16</td>
<td>19</td>
<td>25</td>
<td>1</td>
<td>53</td>
</tr>
<tr>
<td>430</td>
<td>54</td>
<td>0.54</td>
<td>16</td>
<td>31</td>
<td>6</td>
<td>50</td>
</tr>
<tr>
<td>450</td>
<td>65</td>
<td>0.28</td>
<td>22</td>
<td>22</td>
<td>1</td>
<td>56</td>
</tr>
</tbody>
</table>

* Estimated from ASF distribution; ** Experiment is not accurate because of low conversion; *** Based on CO converted; **** Based on moles of carbon in product/moles of CO reacted.
Tables 4.2 and 4.3 show the effect of temperature on the FTS activity of the promoted and un-promoted iron catalysts. As expected, the CO conversion increased with increasing temperature. The 15Fe/SBA-15 catalysts showed an enhanced FTS activity at 400 °C with a total CO conversion of 38% and relatively lower yields towards CH₄ and CO₂ while the best FTS activity of promoted catalysts with 2.8 wt% of manganese was at 430 °C with 54% of total CO conversion. However, as mentioned in previous studies manganese loading also did not seem to have much effect on hydrocarbon product yield when tested at lower temperatures.³³, ⁵²

Figure 4.13: Effect of temperature on CO conversion. Reaction conditions: T=370 °C – 450 °C, P=1 bar for 3 hr with H₂/CO= 2:1

Figure 4.13 shows the CO conversion of the promoted and un-promoted iron catalysts with temperature ranging from 370 to 450 °C. It was found that the reaction temperature has a significant influence on the catalytic performance. A significant change
in the yield of products was seen with increase in the reaction temperature. At higher temperatures addition of manganese improves the CO conversion significantly compared to the unpromoted catalysts. This can be because the addition of promoter might improve the activation energy $E_a$ of the reaction.
CHAPTER 5
CONCLUSION AND FUTURE WORK

5.1 Conclusion

High temperature FTS was studied over the SBA-15 supported iron catalysts with varying Mn amount to find the optimum Mn loading for the syngas ratio (H₂/CO) of 2:1. The effect of temperature was also studied by carrying out the FTS reactions at different temperatures.

The amount of Mn loading was varied to study its effect on FTS catalytic activity and selectivity. The initial FTS reactions at 430 °C with the base 15Fe/SBA-15 catalysts showed a CO conversion of 42 mole% with methane and carbon dioxide yield of 22 mole% and 37 mole% respectively. It was found that when manganese was added as a promoter, the CO conversion also increased. The manganese loading has a great influence on product distribution. The catalyst with 2.8 wt% Mn loading enhanced CO conversion to 54%. It also showed a higher yields for heavier hydrocarbons with a decrease in CH₄ yield. When the catalysts with 0 wt% and 2.8 wt% Mn were tested at a range of temperatures from 370 °C to 450 °C, the conversion increased from 36 and 20% to 58 and 65% respectively. The base 15Fe/SBA-15 catalysts were found to have the highest catalytic activity at 400 °C. Manganese loading did not seem to have much effect on hydrocarbon product yield when tested at lower temperatures. The results show that the reaction temperature should not be too low when testing manganese promoted iron
catalysts as it leads to low catalytic activity. Increasing the reaction temperature will also increase the formation of unwanted products like methane and carbon dioxide.

5.2 Future Work

The trends in the results show that, manganese (2.8 %wt) promoted iron catalysts has good catalytic performance at 430 °C with high yields of C₅⁺ hydrocarbons when compared to the other catalysts with different loadings. Thus FTS activity of the manganese promoted catalysts with intermediate loading between 1.4 wt% and 2.8 wt% should be done. Also the thus verified HTFTS can be used to convert methane to longer chain hydrocarbons by combining FTS and reforming steps in a single intensified process.
REFERENCES


10. Adesina, A. A., Hydrocarbon synthesis via Fischer-Tropsch reaction: Travails and

at Fischer-Tropsch Synthesis Using Flushing Experiments. *Ind Eng Chem Res* 2011, 50,
(8), 4359-4365.

for High-Temperature Fischer-Tropsch Process: Determination Place of Intensifier
Reactor Perspective. *International Journal of Chemical Reactor Engineering* 2014, 12,
(1).

in a novel hydrogen-permselective membrane reactor in Fischer-Tropsch synthesis of


16. Sabatier, P.; Senderens, J. B., New methane synthesis. *Cr Hebd Acad Sci* 1902,
134, 514-516.

over the group VIII metals: II. The kinetics of the methanation reaction over supported


APPENDICES
Appendix A: Loading Calculations

Table A1: Methodology to synthesize 15Fe/SBA-15 with 15% of iron loading

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Molar mass of Fe(NO₃)₃.9H₂O</td>
<td>403.9 g/mole</td>
</tr>
<tr>
<td>Fe molar mass</td>
<td>55.85 g/mole</td>
</tr>
<tr>
<td>Wt % loading of Fe(per gram final catalyst)</td>
<td>15</td>
</tr>
<tr>
<td>Mass of SBA-15</td>
<td>1g</td>
</tr>
<tr>
<td>Mass of Fe required</td>
<td>0.176g</td>
</tr>
<tr>
<td>Mole of Fe required</td>
<td>0.00316 mole</td>
</tr>
<tr>
<td>Mass of Fe(NO₃)₃.9H₂O required</td>
<td>1.277g</td>
</tr>
</tbody>
</table>

\[
\frac{(\text{Molecular wt of Fe})}{\text{Molecular wt of Fe(NO₃)₃.9H₂O}} = \frac{55.845}{404} = 0.138
\]

15% Fe on 1 g of SBA-15 = \( \frac{x}{x+1} = 0.15 \)

\( x = 0.176 \)

\( \frac{0.176}{0.138} = 1.278 \text{ g} \)

Thus, 1.227 g of Fe(NO₃)₃.9H₂O is required to synthesize SBA-15 supported iron catalyst with 15 wt% iron loading
Table A2: Methodology to synthesize 1.4 Mn/15Fe/SBA-15 with 1.4% of manganese and 15% of iron loading

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Molar mass of Fe(NO₃)₃.9H₂O</td>
<td>403.9 g/mole</td>
<td></td>
</tr>
<tr>
<td>Fe molar mass</td>
<td>55.85 g/mole</td>
<td></td>
</tr>
<tr>
<td>Wt % loading of Fe (per gram final catalyst)</td>
<td>15%</td>
<td></td>
</tr>
<tr>
<td>Molar mass of C₆H₉MnO₆•2H₂O</td>
<td>268.13 g/mole</td>
<td></td>
</tr>
<tr>
<td>Mn molar mass</td>
<td>54.94 g/mole</td>
<td></td>
</tr>
<tr>
<td>Wt % loading of Mn (per gram final catalyst)</td>
<td>1.4%</td>
<td></td>
</tr>
<tr>
<td>Mass of SBA-15</td>
<td>1 g</td>
<td></td>
</tr>
<tr>
<td>Mass of Fe required</td>
<td>0.176 g</td>
<td></td>
</tr>
<tr>
<td>Mole of Fe required</td>
<td>0.00316 mole</td>
<td></td>
</tr>
<tr>
<td>Mass of Fe(NO₃)₃.9H₂O required</td>
<td>1.277 g</td>
<td></td>
</tr>
<tr>
<td>Mass of Mn required</td>
<td>0.01674 g</td>
<td></td>
</tr>
<tr>
<td>Mole of Mn required</td>
<td>0.002 mole</td>
<td></td>
</tr>
<tr>
<td>Mass of C₆H₉MnO₆•2H₂O required</td>
<td>0.0835 g</td>
<td></td>
</tr>
</tbody>
</table>

\[
\frac{\text{Molecular wt of Fe}}{\text{Molecular wt of Fe(NO₃)₃.9H₂O}} = \frac{55.85}{404} = 0.138
\]

\[
\frac{\text{Molecular wt of Mn}}{\text{Molecular wt of C₆H₉MnO₆•2H₂O}} = \frac{54.93}{268.1} = 0.20
\]

15% Fe on 1 g of SBA = 15 = \( \frac{x}{x + y + 1} \) = 0.15

1.4% Mn on 1 g of SBA = 15 = \( \frac{y}{x + y + 1} \) = 0.014
\[ x = 0.176 \]

\[ y = 0.01674 \]

\[ \frac{0.176}{0.138} = 1.227 \text{ g} \]

\[ \frac{0.016}{0.20} = 0.0835 \text{ g} \]

Thus, 1.227 g of \( \text{Fe(NO}_3\text{)}_3\cdot9\text{H}_2\text{O} \) and 0.0835 g of \( \text{C}_6\text{H}_9\text{MnO}_6 \cdot 2\text{H}_2\text{O} \) are required to synthesize manganese promoted iron catalyst with 15 wt% iron and 1.4 wt% manganese loading.
## Appendix B: Carbon Balance Calculations

### Table B1: Carbon balance of 15Fe/SBA-15

<table>
<thead>
<tr>
<th>Compound</th>
<th>outlet molar fraction*</th>
<th>outlet molar flowrate (mole/sec)</th>
<th>carbon atom</th>
<th>outlet carbon flow rate (mole/sec)</th>
<th>Total outlet flow rate (mole/sec)</th>
<th>Rotameter reading</th>
<th>Total outlet flow in sccm**</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₄</td>
<td>0.05296</td>
<td>8.87E-08</td>
<td>1</td>
<td>8.87E-08</td>
<td>1.67E-06</td>
<td>4.5</td>
<td>2.25</td>
</tr>
<tr>
<td>C₂H₄</td>
<td>4.53E-03</td>
<td>7.58E-09</td>
<td>2</td>
<td>1.52E-08</td>
<td>1.67E-06</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C₃H₈</td>
<td>5.94E-03</td>
<td>9.94E-09</td>
<td>3</td>
<td>2.98E-08</td>
<td>1.67E-06</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO</td>
<td>0.28669</td>
<td>4.80E-07</td>
<td>1</td>
<td>4.80E-07</td>
<td>1.67E-06</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO₂</td>
<td>0.0942</td>
<td>1.58E-07</td>
<td>1</td>
<td>1.58E-07</td>
<td>1.67E-06</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C₂H₆</td>
<td>0.03183</td>
<td>5.33E-08</td>
<td>2</td>
<td>1.07E-07</td>
<td>1.67E-06</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C₃H₆</td>
<td>7.10E-04</td>
<td>1.19E-09</td>
<td>3</td>
<td>3.57E-09</td>
<td>1.67E-06</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

|               | 3.64E-02               | C out                            | 8.81E-07    | 9.10E-07                         | 7.3                             | 3.65              |

* Obtained from GC  
** From rotameter calibration

| Rotameter reading | 7.3                     | Inlet flow in sccm | 3.65 | Inlet flow in mole/sec | 9.10E-07 | Mole/sec per sccm at STP | 7.48E-07 |

The % difference in carbon balance =3.2 %.
Table B2: Carbon balance of 2.8Mn/15Fe/SBA-15

<table>
<thead>
<tr>
<th>Compound</th>
<th>Outlet molar fraction*</th>
<th>Outlet molar flowrate (mole/sec)</th>
<th>Carbon atom</th>
<th>Outlet carbon flow rate (mole/sec)</th>
<th>Total outlet flow rate (mole/sec)</th>
<th>Rotameter reading</th>
<th>Total outlet flow in sccm**</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₄</td>
<td>0.04854</td>
<td>8.13E-08</td>
<td>1</td>
<td>8.13E-08</td>
<td>1.67E-06</td>
<td>4.5</td>
<td>2.25</td>
</tr>
<tr>
<td>C₂H₄</td>
<td>5.38E-03</td>
<td>9.00E-09</td>
<td>2</td>
<td>1.80E-08</td>
<td>1.67E-06</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C₃H₈</td>
<td>4.13E-03</td>
<td>6.91E-09</td>
<td>3</td>
<td>2.07E-08</td>
<td>1.67E-06</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>CO</strong></td>
<td>0.2492</td>
<td><strong>4.17E-07</strong></td>
<td><strong>1</strong></td>
<td><strong>4.17E-07</strong></td>
<td><strong>1.67E-06</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO₂</td>
<td>0.15</td>
<td>2.51E-07</td>
<td>1</td>
<td>2.51E-07</td>
<td>1.67E-06</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C₂H₆</td>
<td>0.03029</td>
<td>5.07E-08</td>
<td>2</td>
<td>1.01E-07</td>
<td>1.67E-06</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C₃H₆</td>
<td>2.50E-04</td>
<td>4.18E-10</td>
<td>3</td>
<td>1.25E-09</td>
<td>1.67E-06</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C out</td>
<td></td>
<td></td>
<td></td>
<td>C out</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>4.38E-03</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C in</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>9.10E-07</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Obtained from GC  
** From rotamer calibration

Rotameter reading | 7.3
Inlet flow in sccm | 3.65
Inlet flow in mole/ sec | 9.10E-07
Mole/sec per sccm at STP | 7.48E-07

The % difference in carbon balance = 2.2%.

Yield = (outlet molar flow rate of the compound/ (moles of CO converted))×100

Table B3: Yield calculation of 2.8Mn/15Fe/SBA-15

<table>
<thead>
<tr>
<th>Compound</th>
<th>Carbon yield</th>
<th>Yield %</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₄</td>
<td>1.65E-01</td>
<td>1.65E+01</td>
</tr>
<tr>
<td>C₂H₄</td>
<td>3.65E-02</td>
<td>3.65E+00</td>
</tr>
<tr>
<td>C₂H₆</td>
<td>2.05E-01</td>
<td>2.05E+01</td>
</tr>
<tr>
<td>C₃H₈</td>
<td>4.20E-02</td>
<td>4.20E+00</td>
</tr>
<tr>
<td>C₃H₆</td>
<td>2.54E-03</td>
<td>2.54E-01</td>
</tr>
<tr>
<td>CO₂</td>
<td>5.09E-01</td>
<td>5.09E+01</td>
</tr>
<tr>
<td>C₅+</td>
<td>6.91E-02</td>
<td>6.91E+00</td>
</tr>
<tr>
<td>C₄</td>
<td>3.21E-02</td>
<td>3.21E+00</td>
</tr>
</tbody>
</table>
Appendix C: Calibration of Rotameter

The calibration of rotameter was done with different gases and was plotted in graphs as shown below. The average of the slopes were found and used for the conversion of rotameter reading to sccm.

Figure C1: Rotameter calibration with CO
Appendix D: Reproducibility of Experiments

Table D1: CO conversion of 2.8Mn/15Fe/SBA-15

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Trial</th>
<th>CO conversion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.8Mn/15Fe/SBA-15</td>
<td>1</td>
<td>53</td>
</tr>
<tr>
<td>2.8Mn/15Fe/SBA-15</td>
<td>2</td>
<td>54</td>
</tr>
<tr>
<td>2.8Mn/15Fe/SBA-15</td>
<td>3</td>
<td>54</td>
</tr>
</tbody>
</table>

Table D2: Yield calculation from experiment 1

<table>
<thead>
<tr>
<th>Compound</th>
<th>Carbon yield</th>
<th>Yield %</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH4</td>
<td>1.65E-01</td>
<td>1.65E+01</td>
</tr>
<tr>
<td>C2H4</td>
<td>3.65E-02</td>
<td>3.65E+00</td>
</tr>
<tr>
<td>C2H6</td>
<td>2.05E-01</td>
<td>2.05E+01</td>
</tr>
<tr>
<td>C3H8</td>
<td>4.20E-02</td>
<td>4.20E+00</td>
</tr>
<tr>
<td>C3H6</td>
<td>2.54E-03</td>
<td>2.54E-01</td>
</tr>
<tr>
<td>CO2</td>
<td>5.09E-01</td>
<td>5.09E+01</td>
</tr>
<tr>
<td>C5+</td>
<td>2.85E-02</td>
<td>2.85E+00</td>
</tr>
<tr>
<td>C4</td>
<td>1.37E-02</td>
<td>1.37E+00</td>
</tr>
</tbody>
</table>

Table D3: Yield calculation from experiment 2

<table>
<thead>
<tr>
<th>Compound</th>
<th>Carbon yield</th>
<th>Yield %</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH4</td>
<td>1.53E-01</td>
<td>1.53E+01</td>
</tr>
<tr>
<td>C2H4</td>
<td>2.69E-02</td>
<td>2.69E+00</td>
</tr>
<tr>
<td>C2H6</td>
<td>1.54E-02</td>
<td>1.54E+00</td>
</tr>
<tr>
<td>C3H8</td>
<td>2.90E-01</td>
<td>2.90E+01</td>
</tr>
<tr>
<td>C3H6</td>
<td>3.27E-02</td>
<td>3.27E+00</td>
</tr>
<tr>
<td>CO2</td>
<td>4.74E-01</td>
<td>4.74E+01</td>
</tr>
<tr>
<td>C5+</td>
<td>2.59E-02</td>
<td>2.59E+00</td>
</tr>
<tr>
<td>C4</td>
<td>1.34E-02</td>
<td>1.34E+00</td>
</tr>
</tbody>
</table>
Table D4: Yield calculation from experiment 3

<table>
<thead>
<tr>
<th>Compound</th>
<th>Carbon yield</th>
<th>Yield %</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH4</td>
<td>1.65E-01</td>
<td>1.65E+01</td>
</tr>
<tr>
<td>C2H4</td>
<td>3.65E-02</td>
<td>3.65E+00</td>
</tr>
<tr>
<td>C2H6</td>
<td>2.05E-01</td>
<td>2.05E+01</td>
</tr>
<tr>
<td>C3H8</td>
<td>4.20E-02</td>
<td>4.20E+00</td>
</tr>
<tr>
<td>C3H6</td>
<td>2.54E-03</td>
<td>2.54E+01</td>
</tr>
<tr>
<td>CO2</td>
<td>5.09E-01</td>
<td>5.09E+01</td>
</tr>
<tr>
<td>C5+</td>
<td>6.91E-02</td>
<td>6.91E+00</td>
</tr>
<tr>
<td>C4</td>
<td>3.21E-02</td>
<td>3.21E+00</td>
</tr>
</tbody>
</table>