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Promoter Effects on Iron-Based, SBA-15 Supported Ultra-High Temperature Fischer-Tropsch Catalysts

by

David P. Weber

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

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# TABLE OF CONTENTS

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

CHAPTER 1: INTRODUCTION ............................................................................................. 1
  1.1 Motivation ...................................................................................................................... 1
  1.2 Objectives ..................................................................................................................... 4
  1.3 Scope of Work .............................................................................................................. 5

CHAPTER 2: BACKGROUND AND LITERATURE SURVEY ............................................. 6
  2.1 Background .................................................................................................................. 6
  2.2 Literature Survey ....................................................................................................... 11

CHAPTER 3: METHODS USED .......................................................................................... 21
  3.1 Synthesis Methods ....................................................................................................... 21
  3.2 Characterization Methods ........................................................................................... 23
  3.3 Testing Methods ......................................................................................................... 25
  3.4 Models Used ................................................................................................................ 26

CHAPTER 4: RESULTS AND DISCUSSION ....................................................................... 28
  4.1 Synthesis Results ....................................................................................................... 28
  4.2 Characterization Results ............................................................................................ 29
  4.3 Test Results ................................................................................................................ 36

CHAPTER 5: CONCLUSION AND SUGGESTIONS FOR FUTURE WORK ......................... 44

REFERENCES ...................................................................................................................... 45

APPENDICES ...................................................................................................................... 46
  Appendix A: Carbon Balances ......................................................................................... 47
  Appendix B: Loading Calculations .................................................................................. 48
LIST OF TABLES

Table 4.1: Physisorption Results for 15Fe/SBA-15................................................................. 35
Table 4.2: Activity and Selectivity of SBA-15 Supported Catalyst at 3h on Stream .............. 38
Table 4.3: Repeatability of Experiments (at 3h on Stream, All Conditions as above in
Table 4.2) ................................................................................................................................. 39
Table 4.4: Composition of Product Gas at 3h on Stream for 1.4Mn15Fe, 430°C,
Ambient Pressure, H₂:CO Ratio 2:1, Space Velocity 1190hr⁻¹ (43.6
sccm/gcat) ................................................................................................................................ 42
Table 4.5: Activity and Selectivity of SBA-15 Supported Catalysts at 12h on Stream........ 42
Table A1: Carbon Balance 15Fe, 3h on Stream................................................................. 47
Table A2: Carbon Balance 15Fe, 12h on Stream............................................................. 47
Table B1: Sample Loading Calculation, 15Fe/SBA-15.................................................. 48
LIST OF FIGURES

Figure 1.1: Typical Gas to Liquids Process................................................................. 2
Figure 1.2: Combined Gas to Liquids Process ............................................................ 3
Figure 2.1: Mass Fraction of Carbon Numbers vs. Alpha........................................... 11
Figure 4.1: XRD Spectroscopic Analysis of 15Fe ......................................................... 30
Figure 4.2: 15FeSBA-15 at 700x Magnification ............................................................ 31
Figure 4.3: 15FeSBA-15 at 700x Magnification ............................................................ 31
Figure 4.4: 15FeSBA-15 at 3000x Magnification .......................................................... 32
Figure 4.5: 15FeSBA-15 at 7000x Magnification .......................................................... 32
Figure 4.6: Temperature Programmed Reduction of 1.4Mn15Fe-SBA-15 (Filtered) ........ 34
Figure 4.7: Temperature Programmed Reduction of 15Fe-SBA-15 (Filtered) ................. 35
Figure 4.8: C5+ Selectivity of Manganese Promoted and Unpromoted Catalyst .......... 40
Figure 4.9: C2-C4 Selectivity of Manganese Promoted and Unpromoted Catalyst ........ 40
Figure 4.10: Methane Selectivity of Manganese Promoted and Unpromoted Catalyst .... 41
ABSTRACT

Promoter effects on SBA-15 supported iron Fischer-Tropsch catalysts were investigated for their potential to improve high temperature catalyst performance. FTS catalysts promoted by manganese (0.15%-1.4%), copper (0.15%-1%), and potassium (0.5%-3%), with all percentages stated on the basis of mass percentage of final catalysts, were prepared and tested at 430°C and ambient pressure in a fixed bed reactor. Manganese showed the ability to promote the FT reaction, increasing both the CO conversion and the average chain length of hydrocarbon products. Compared to the unpromoted catalyst composed only of iron supported on SBA-15, 1.4%Mn (mass) promotion of 15% (mass) iron on SBA-15 improved CO conversion from 29% to 32%, increased alpha from 0.21 to 0.34, decreased carbon dioxide selectivity from 76% to 50%, increased C2-C4 selectivity from 9.6% to 30% and increased C5+ selectivity from 0.21% to 2.2%. Copper promotion gave increased conversion, but did not significantly affect alpha or carbon dioxide selectivity. Potassium promotion in the range of 0.5% to 3% by mass, on the other hand, had a negative effect on CO conversion at all concentrations tested.
CHAPTER 1:
INTRODUCTION

1.1 Motivation

The need for advances in renewable fuel technologies has increased in recent years as worldwide energy consumption continues to increase. This trend is almost certain to continue in the future, with emerging nations accounting for the majority of the increase. According to the 2017 International Energy Outlook, the total energy consumption worldwide will increase from 575 quadrillion BTU in 2015 to 663 quadrillion BTU by 2030 and 736 quadrillion BTU by 2040, representing a 28% increase by 2040 [1]. Oil price trends will impact total energy use and also the proportion of energy utilized as liquid fuels, with the expected liquid consumption increasing from 191 quadrillion BTU in 2015 to 228 quadrillion BTU in 2040, when it will make up 31% of total world energy use [1]. On a volumetric basis, worldwide liquid fuel consumption is projected to increase from 95 million barrels/day (bpd) in 2015 to 113 million bpd in 2040 [1].

A GTL (gas to liquids) process converts gasses such as natural gas or biogas into liquid fuels. If the feedstock gas is biogas, the process is known as BTL (biomass to liquids). A gas to liquids process consists of two main chemical conversion steps. First, the feedstock gas must be converted to syngas (a mixture of carbon monoxide and hydrogen) by steam reforming. The methane steam reforming reaction is shown below, with the corresponding enthalpy of reaction at standard conditions:
This process is endothermic and takes place optimally at high temperature (800°C-900°C). Next, this syngas is converted by the Fischer-Tropsch process to syncrude. The Fischer-Tropsch reaction converts syngas into hydrocarbons via a polymerization mechanism, resulting in a mixture of hydrocarbons of varying carbon chain lengths. The reaction is shown below:

\[ nCO + (2n + 1)H_2 \rightarrow +C_nH_{2n+2} + nH_2O \]

\[ \Delta H_{\text{rxn}}^{\circ} = -166 \text{ KJ/mol} \]

This process is exothermic, as seen by the negative enthalpy change, and takes place optimally at a relatively lower temperature (220°C-350°C). A typical gas-to-liquids process is shown in Figure 1.1 below:

**Figure 1.1.** Typical Gas-to-Liquids Process.
There exists potential to combine these two processes in a single process step. Advantages of this process synthesis would be decreased capital costs by replacing two reactors with one, and decreased operating costs by utilizing the energy from the exothermic Fischer-Tropsch reaction to drive the endothermic steam reforming reaction. This approach would require three main technological developments: a steam reforming catalyst capable of operating at a relatively low temperature, a Fischer-Tropsch catalyst capable of operating at a relatively high temperature, and a method of separating the two catalysts which allows transport of small molecules (methane, water, carbon monoxide, and hydrogen) but hinders transport of large molecules (long-chain hydrocarbons). This last requirement is necessary since steam reforming catalysts also catalyze the decomposition of long-chain hydrocarbons to lower chain hydrocarbons or CO.

Figure 1.2. Combined Gas-to-Liquids Process.
Figures 1.1 and 1.2 show the general process flow for a standard and combined gas-to-liquids process, but some details are left out for clarity in the figures. Syncrude is a general name for synthetically derived crude oil, and can be termed biocrude if the feedstock gas is from a renewable resource. Also, in gas-to-liquids processes, steam reforming is often replaced with partial methane oxidation to produce syngas from combustion of methane with a less than stoichiometric amount of oxygen.

1.2 Objectives

The objective of the work was to determine a catalyst type with the best possible performance at high temperature (~430°C), then to study the effects of promoters in order to determine if the catalyst performance can be improved by promoter addition. Information on the effects of promoters on the performance of iron-based FT catalysts at high temperature (~430°C) is not prevalent in the literature review shown in chapter 2, but iron-based catalysts dominate in the high temperature regime. This is due to iron catalysts reduced tendency to shift to methanation at high temperatures at the expense of higher molecular weight hydrocarbons. Cobalt catalysts tend to produce exclusively methane at elevated reactor temperatures. Iron catalysts also shift to shorter chain hydrocarbons as temperature increases, but the change is less rapid.

Iron catalysts loaded at 15% on SBA-15 (a mesoporous silica) were found by Cano et al. to perform relatively well as FT catalysts at 430°C, giving a range of hydrocarbon products, and these catalysts will be referred to as 15Fe/SBA-15. For this study, 15Fe/SBA-15 was synthesized as Cano et al. without promoters, and tested for FT activity at 430°C and 1 atmosphere [2]. Then, a series of promoted 15Fe/SBA-15 catalysts were
synthesized and tested at 430°C and 1 atmosphere. Promoters used were manganese, copper, and potassium. Promoted samples were always single-element promoted in order to elucidate specific effects of the promoter added. Combinations were not tested.

The catalysts were tested in a fixed bed reactor with conditions held constant for all tests. Activation conditions were also held constant for all tests. This allowed for determination of specific effects of each promoter.

1.3 Scope of Work

Iron catalysts supported on SBA-15 were synthesized and tested with varying Manganese, Copper, and Potassium promoter loading. The catalysts were tested in a fixed bed reactor with conditions held constant for all tests. Activation conditions were also held constant for all tests. This allowed for determination of specific effects of each promoter.

All reactions were carried out at 430°C and ambient pressure. Activation, reaction, temperature and flow conditions were held constant in each reaction.
CHAPTER 2:
BACKGROUND AND LITERATURE SURVEY

2.1 Background

A future increase in liquid fuel consumption is projected to take place despite the clear effect of rising atmospheric carbon dioxide levels on the global climate, instability in oil-producing countries continues, and the finite nature of world petroleum resources. A shift to electric vehicles equipped with batteries of increasing capacity is underway, but the high energy density of liquid petroleum-based fuels makes other technologies difficult to implement or cost prohibitive currently, so liquid fuels derived from petroleum have dominated the transportation market in the first part of the 21st century.

This high energy density of liquid fuels and the low cost of petroleum-derived fuels in general combine to explain the dominance of petroleum derived gasoline and diesel in the transportation sector. The burning of liquid hydrocarbon fuels delivers stored energy originating from either sunlight captured by prehistoric plants in the case of petroleum fuels, or one of a variety of energy inputs to a biocrude plant in the case of modern GTL (gas to liquids) processes. In either case, the energy density of liquid hydrocarbon fuels is difficult to exceed. On both a volumetric and mass basis, hydrocarbon fuels store an exceptional amount of energy. Compared to gasoline, diesel has a similar energy content per unit mass, but surpasses gasoline on a volumetric basis [3]. Compressed propane is comparable to gasoline and diesel on a mass basis, but requires more volume [3]. Several
currently utilized energy storage media are inferior to these three fuels on both a mass and volumetric basis [3]. These include batteries of several types, methanol, and ethanol [3]. Liquefied natural gas (LNG), compressed natural gas (CNG), cooled liquid hydrogen and compressed hydrogen gas all exceed the storage capacity of gasoline on a mass basis, but are inferior on a volumetric basis [3]. There are no currently utilized technologies in the transportation sector utilizing energy storage surpassing gasoline/diesel in energy density on both a volumetric and mass basis [3].

In addition to the energy density considerations above, compressed gases carry storage challenges, requiring heavy-walled pressure-rated tanks which add to the cost and weight of the vehicle, and also present distribution challenges. Batteries similarly add to the up-front cost of the vehicle but have the advantage of sourcing power from the grid. This removes the dependence of battery-powered vehicles on a specific fuel source, taking primary energy from the sources supplying the grid. Nevertheless, liquid hydrocarbon fuels have clear advantages as transportation fuels that are likely to continue their position in the transportation market for the foreseeable future.

Liquid hydrocarbon fuels can be refined from fossil remains or synthesized from carbon containing materials like coal, natural gas, or biogas. Synthetically produced crude oil is known as syncrude, and if the feedstock is a renewable source, it is known as synthetic biocrude. Currently, there are significant environmental and economic drivers that favor synthetic biocrude. When fossil fuels are burned, they release carbon dioxide to the atmosphere previously locked in subterranean reserves, increasing atmospheric concentrations of this greenhouse gas. This process has been clearly linked to increasing global average temperatures. Syncrude, however, can be produced from either fossil fuels
(coal, natural gas) or from renewable fuels (biogas). In general, syncrude produced from gaseous feedstock is termed gas-to-liquid (GTL), and if raw material used is biomass, the process is termed biomass-to-liquid (BTL). Biocrude produced in a BTL process can have a net-zero emission of carbon dioxide when burned, negating impacts on atmospheric levels.

One of the main challenges facing BTL implementation is the large up-front capital cost of the process equipment. Economies of scale make large GTL plants economically feasible in some locations, especially where stranded gas is utilized. However, BTL process depend generally on smaller feed streams of gas from municipal solid waste (MSW) facilities or anaerobic digesters. Gas from anaerobic decomposition of municipal solid waste is termed landfill gas (LFG) and is typically flared at the stack to convert methane to carbon dioxide, or it is burned in reciprocating engine gen-sets so it has potential to be better utilized by using it in a BTL process. Also, crops grown specifically for biomass production can be used as a feedstock to an anaerobic digestion process, which outputs biogas for use in a BTL process. In both cases, reducing processing equipment costs and operating costs is critical to making the BTL process economically feasible.

A promising technology for replacing fossil fuels with renewable fuels is based on the Fischer-Tropsch reaction for alkane production:

\[
 nCO + (2n + 1)H_2 \rightarrow C_nH_{2n+2} + nH_2O \\
 \Delta H_{rxn}^{o} = -166 KJ/mol
\]

As seen above, the reaction is a polymerization of CH₂ units, and straight chain alkanes are the main product. Diesel fuel is composed of predominantly straight chain
alkanes, so FTS is ideally suited for diesel fuel production. Branched alkanes, terminal alkenes, internal alkenes, and alcohols can also be produced in varying quantities by FTS, depending on the catalyst and process conditions utilized.

This process has been successfully used commercially for decades. The reaction is flexible, in that it requires a source of syngas (a mixture of hydrogen and carbon monoxide), which can be produced from several different carbon containing feedstocks. Traditional feedstocks for a Fischer-Tropsch plant are coal and natural gas, since these have been cheap and plentiful. However, the reaction can also utilize renewable carbon sources, such as biogas from anaerobic digestion of plant waste. This occurs in landfills, for example, and landfill gas is one promising source of non-fossil-fuel inputs to a Fischer-Tropsch process.

Whether biogas, landfill gas, natural gas or coal is used as a feedstock, the appropriate reaction must first be carried out in order to convert the feedstock into syngas. Typically, this involves methane steam reforming, in which water and methane are reacted over a suitable catalyst at 900°C. This produces a mixture of carbon monoxide and hydrogen (syngas).

\[
CH_4 + H_2O \leftrightarrow CO + 3H_2
\]

\[
\Delta H^\circ_{rxn} = +206 \text{ KJ/mol}
\]

The Fischer-Tropsch reaction can then utilize the syngas produced. Depending on the type of catalyst used in the Fischer-Tropsch reactor, an intermediate water-gas-shift (WGS) step may be required. Cobalt catalysts require this step because cobalt doesn't
catalyze the WGS reaction. Iron catalysts, however, are effective WGS catalysts in addition to having FTS activity, so a separate WGS step is not required when iron FTS catalysts are used.

Only by carefully controlling the catalyst design and operating conditions can longer chain hydrocarbons be produced in quantity by the Fischer-Tropsch reaction at elevated temperature. The product distribution is described by the ASF (Anderson-Schultz-Flory) equation [4]. This mathematical model assumes the rates of the polymerization propagation and termination steps are constant and independent of carbon number, so that the parameter $\alpha$ defines the product distribution for molecules of n-alkanes for all carbon numbers 1 through $\infty$. The equation in terms of mass fraction is:

$$y_{N_c,M} = N_c^{(1-\alpha)^2} \propto (N_c^{-1})$$

with the chain growth probability defined as:

$$\alpha = \frac{r_p}{r_p + r_t}$$

and $r_p$ and $r_t$ are the rates of chain propagation and termination, respectively [5]. This product distribution shifts from predominantly methane as alpha approaches zero to predominantly long-chain heavy waxes as alpha approaches 1. At intermediate values of alpha, a mixture of medium-chain liquid hydrocarbons is produced.
Figure 2.1. Mass Fraction of Carbon Numbers vs. Alpha.

2.2 Literature Survey

The use of iron-based catalysts in Fischer-Tropsch synthesis dates back to the discovery of the reaction by Hans Fischer and Franz Tropsch in Germany in the 1920s. Fischer and Tropsch employed an iron and zinc oxide catalyst at a temperature of 250-300°C in their original system [6]. Since that time, many authors have investigated the use of iron catalysts using various promoters, supports, preparation methods, and operating conditions. A brief review of those studies is given below with a focus on those of interest in the development of a catalyst which can be used at 430°C with the highest possible activity and C5+ selectivity. The second requirement is of particular importance in this
work, because methane is the thermodynamically favored product of the Fischer-Tropsch reaction. Methane is not desired, since the feed to a GTL (gas-to-liquids) process typically contains methane as the carbon source, and liquid fuels (C5+) are the desired products. Producing methane by Fischer-Tropsch would in this case simply regenerate the feedstock.

Fischer-Tropsch synthesis can be used to synthesize fuels or chemical feedstocks such as olefins for polymer manufacture. However, the current work focuses on the use of Fischer-Tropsch synthesis to make fuels, so hydrocarbon chains in the range of C5-C10 (gasoline) or C11-C20 (diesel fuel) are desired. In general, the greater the number of carbons in a straight-chain hydrocarbon molecule, the higher the boiling point of the material. Thus, very short chains are gasses at room temperature, intermediate lengths form liquids at room temperatures, and very long chains form solids (waxes). Liquid hydrocarbon fuels are most readily usable as transportation fuels, so these intermediate chain lengths are desirable products in synthetic fuel production.

Industrial scale LTFT (low temperature Fischer-Tropsch) reactors at SASOL in South Africa are typically operated at approximately 230°C and 2.7 MPa while HTFT (high temperature Fischer-Tropsch) reactors are typically operated at 320°C [4]. As the reaction temperature increases, the thermodynamically favored short chain products become dominant, and at high enough temperatures, methane is produced as the sole hydrocarbon product. Catalysts designed for high polymerization propagation rates and low termination rates can achieve values of alpha high enough to extend the reaction temperature range above the typical HTFT temperature of 320°C and still give hydrocarbon products longer than methane.
The LTFT reactors at SASOL have an estimated alpha value of 0.88-0.95, while the HTFT reactors have an estimated alpha of 0.7 [7]. This decrease in alpha with increasing temperature comes despite catalyst design and reactor optimization for high alpha in the HTFT reactors. The dramatic negative effect of increasing temperature on alpha presents a significant challenge to the production of liquid hydrocarbon fuels by Fischer-Tropsch at temperatures in excess of 400°C [7].

In the LTFT regime, cobalt is the catalyst of choice industrially because of its high activity and low cost relative to ruthenium, which is also a very active FT catalyst. As the reaction temperature increases, iron catalysts become preferred because their inferior activity is less problematic at high temperatures where the rate is driven by the elevated temperature. Iron catalysts have the attractive property of a less rapid change to low alpha values than cobalt with increasing temperature. Thus, cobalt catalysts have methane selectivities which become high when the temperature is raised above the LTFT range, while iron catalysts follow the same pattern, but to a lesser extent. For this reason, the best catalysts for operation above 400°C are expected to be iron-based.

Iron is typically promoted with small amounts of other metals to effect certain desirable catalyst properties. Potassium is added to nearly all iron-based FT catalysts to increase the surface basicity, causing an increase in CO adsorption and subsequent increase in activity and decrease in methane selectivity, with a shift to longer chain products [8]. At 300°C, Yang et al. found an increasing trend in average chain length as K content was increased from 0.2 to 3%(wt) in a precipitated Fe/Mn/K catalyst operating at 2.5MPa and a GHSV of 1000 hr⁻¹. As the average chain length increased with increasing K content, methane selectivity decreased from 30.3 to 10.4 [8].
Similarly, Yang et al. found that potassium added to a precipitated iron-manganese catalyst decreased the methane selectivity in the FTS reaction at temperatures ranging from 523K to 593K at 2.5MPa, a H2:CO ratio of 2.0, and a space velocity of 1000 hr⁻¹. They also found that catalyst activity increased with increasing potassium content up to 0.7wt% K, while further addition of potassium decreased activity, and that average product chain length and olefin selectivity both increased with increasing potassium content [8].

Gaube et al. found that the addition of alkali to an iron catalyst had little effect on the activity of the catalyst, but a strong positive effect on both the 1-alkene selectivity and the average product chain length [9].

Copper is often added as a reduction promoter, as it has been shown to aid in the effectiveness of the activation step which converts the iron oxides in the calcined catalyst into the active iron carbide phase by facilitating reduction [10]. It is generally agreed upon that in quantities used for promotion, copper has a negligible effect on catalyst performance post-reduction, but a significant effect on the rate and effectiveness of reduction.

Manganese addition to iron catalysts has been seen to increase selectivity to higher hydrocarbons and to increase FT activity of iron catalysts even at high (50/50 by mass) manganese to iron ratios [11]. Li et al. found optimal manganese addition at 7% of the total iron mass [12].

After an FTS catalyst is synthesized by impregnation of the support followed by calcination, the calcined catalyst must be activated in order to attain its catalytic properties. This involves exposing the catalyst to a reducing environment at elevated temperatures. Common reducing gases are hydrogen or syngas (a mixture of hydrogen and carbon
monoxide). This step converts the iron oxides into iron carbide and metallic iron. Significant disagreement remains in the literature about the active phases, and whether the iron carbide phase is solely responsible for the FT catalytic effect or if alpha-iron and specific phases of iron oxide (Fe$_2$O$_3$/Fe$_3$O$_4$) also have catalytic effect. It is generally agreed upon, however, that iron carbide is at least the primary active phase. Thus, the main purpose of activation is to convert the iron oxides present in the calcined catalyst into iron carbide or into a form readily converted to iron carbide by syngas.

When hydrogen is used as the reducing gas without addition of carbon monoxide, the iron carbide phase forms only after syngas flow begins. Thus, the initial flow of syngas may react to some degree, but the catalyst active sites are not fully formed until syngas flow as continued long enough to compete the conversion to iron carbide. When syngas is used as the reducing gas, however, iron carbide is formed during the reduction step and the catalyst is activated fully before the reaction step begins. In a stable iron FT catalyst, surface conversion to the carbide phase occurs, while a stable oxide core remains [13].

In supported iron catalysts, the nature of the support has several effects. The local interactions between the support and the iron and promoters can alter the surface properties of the catalyst, which can either inhibit or promote CO and H$_2$ adsorption. On a more macroscopic level, porous supports can act as size selective structures, as is the case with supports such as carbon nanotubes and silica supports with highly ordered pore structures such as SBA-15. These supports can alter the way the reactants, intermediates and products diffuse through the support, which can have dramatic effects on the activity and selectivity of the catalyst. They can also control to some extent the physical size and shape characteristics of the active sites, which affects the reaction rate and selectivity in
structure sensitive reactions such as Fischer-Tropsch. Structure sensitive reactions are affected not only by the chemical and electronic environment on the active site, but also its geometry. Thus, active metal clusters of identical composition may influence the FT reaction in dramatically different ways depending on the size and shape of the cluster.

According to Cano et al., the highly uniform pore structure of SBA-15 enables the formation of iron oxide crystals in a narrow range of widths, enhancing the catalytic properties due to the structure sensitive nature of FTS catalysis. This means that not only the chemical nature of the active site, but also the physical size and structure of the active site influences the catalytic behavior. SBA-15 has very uniform pores, with diameters in a narrow range, but the diameter can be varied in the range of 5-30nm by changing the synthesis conditions [2]. This led the group to synthesize SBA-15 with a pore diameter of 8.1 nm (actual, by BET) and subsequently deposit iron from ethanolic solution of Fe(NO$_3$)$_3$. BET is a characterization technique developed by Stephen Brunauer, Paul Hugh Emmett, and Edward Teller which allows for determination of surface properties of a material by analyzing the adsorption behavior with an inert gas, typically nitrogen. The methane selectivity of catalyst prepared in this way decreased with increasing reaction temperature, which makes this catalyst possibly very useful for high temperature FTS. Most catalysts show increasing methane selectivity with increasing temperature.

Iron catalysts for Fischer-Tropsch synthesis are typically either fused iron (for high temperature use) or precipitated iron (for low temperature use). The higher activity of precipitated iron catalysts makes them more useful in low temperature operation where the reaction rate is lower and high catalyst activities are critical. At higher temperatures, the reaction rate increases so the activity of the catalyst is not as important, and selectivity
becomes a bigger concern. This is especially true due to the general tendency of Fischer Tropsch catalysts to have higher methane selectivity at higher temperature. Fused iron has the attractive property that the selectivity to longer chains is generally better at elevated temperatures than similarly composed precipitated iron catalysts. In other words, fused iron catalysts generally have higher alpha values than precipitated iron catalysts at higher temperatures.

Sasol uses fused iron catalysts in its HTFT reactors, either in slurry phase reactor configuration or fluidized bed configuration. In these reactors, the limited surface areas of the fused iron catalysts is not as problematic because mass transfer is increased substantially by the turbulent two-phase or three-phase flow around the catalyst particles. In a fixed bed configuration, two problems arise from the use of fused iron catalysts. First, the lower surface area of these catalysts is hard to overcome as it is with fluidized bed and slurry phase reactors. Second, to get reasonable reaction rates, small catalyst particles must be used in order to get as much specific surface area as possible, and these small particles tend to cause excessive backpressure in fixed bed reactors. The backpressure increases with time-on-stream as the Boudouard reaction:

\[
2CO \rightleftharpoons CO_2 + C
\]

\[
\Delta H_{rxn} = +172 \text{ KJ/mol}
\]

deposits coke on the catalyst surface, blocking the interstitial space between catalyst particles. After sufficient coke deposition, flow can be sufficiently blocked to cause backpressure in excess of system limitations.
Precipitated iron catalysts can be either supported or unsupported. The most common support is porous silica, but alumina is also commonly used. Zeolites and carbon nanotubes have also found applications as supports for precipitated iron catalysts in Fischer-Tropsch synthesis. The support serves several purposes. At its most fundamental, the support provides a porous substrate upon which to deposit active catalyst to achieve maximum surface area for the Fischer-Tropsch reaction to take place for a given amount of active catalyst. As a second effect, the nature of the support material can influence the active site’s size and ability to adsorb reactants onto their surface. Thirdly, the geometry of the pores in the support can exert influence over the reaction due to influence on the size and geometry of the active sites. Lastly, the pores can also exhibit mass transfer effects. Pores that are in the size range of the reactants or products can direct the reaction by influencing diffusion rates of reactants and products across active sites.

Given the many ways the support can influence catalyst properties, it is not surprising that the use of certain supports can dramatically affect catalyst performance. A mesoporous silica known as SBA-15 was used by Cano et al. and found to give good high temperature performance [2]. This support was found in the current work to give superior results compared to fumed silica, so SBA-15 was used as the support in this study.

SBA-15 is a mesoporous silica with a highly ordered pore network of uniform pore sizes. The structure is similar to that of carbon nanotubes, but the structure is composed of SiO2 units. It is synthesized by condensing tetraethylorthosilicate (TEOS) in acidic solution with a structure directing agent such as copolymer P-123. Careful control of the synthesis temperature and aging temperature allow for synthesis of stable, repeatable structures.
with uniform pores. The structure directing agent can then be removed from the pores by washing and calcination, leaving the silica framework behind.

There are a number of reactions which compete with the Fischer-Tropsch reaction on iron catalysts. Previously mentioned was the Boudouard reaction which deposits coke on the catalyst surface, blocking the interstitial space between catalyst particles.

\[
2CO \rightleftharpoons CO_2 + C
\]

\[
\Delta H_{rxn}^{\circ} = +172 \text{ KJ/mol}
\]

This reaction is favored at high temperature, and by Le Chatlier’s principle, high pressure also favors the reaction due to conversion of two gas molecules into one as the reaction proceeds. A second competing reaction is the Water Gas Shift (WGS) reaction, in which steam and carbon monoxide react to form hydrogen and carbon dioxide:

\[
CO + H_2O \rightleftharpoons CO_2 + H_2
\]

\[
\Delta H_{rxn}^{\circ} = -41.2 \text{ KJ/mol}
\]

This reaction is catalyzed by iron catalysts, so it is a significant side reaction. However, it can be exploited to adjust the \( H_2/CO \) ratio in hydrogen rich syngas typical of steam reforming product streams by allowing the equilibrium reaction to proceed in the reverse direction. This is also knows as the Reverse Water Gas Shift (RWGS) reaction. The ratio can be adjusted in situ closer to the ideal 2:1 ratio needed for Fischer-Tropsch from the 3:1 ratio which comes from a stoichiometric methane steam reforming product stream.
Based on the survey of the available literature as outlined in this chapter, it's clear that the complex nature of FTS on iron catalysts makes the design of a catalyst for use outside the optimized temperature and pressure range is non-trivial. Temperatures above the ideal FTS regime tend to favor methane production, and low pressures tend to favor reduced reaction rates and shorter average chain length. However, the work of Cano et al. gave the best evidence of a catalyst giving longer hydrocarbon chains at elevated temperature (430°C) and ambient pressure [2].
CHAPTER 3:
METHODS USED

3.1 Synthesis Methods

Synthesis of the catalysts began with synthesis of the silica support. The support for the catalysts is a mesoporous silica known as SBA-15. Its structure is highly ordered, and the uniform pores are in the mesoporous range, making it highly suitable as a catalyst substrate. It was synthesized hydrothermally using tetraethylorthosilicate (TEOS) as a silica source and copolymer P-123 as a structure directing agent.

SBA-15 is a mesoporous silica with a highly ordered and uniform pore network. The mesoporous nature of this material makes it desirable as a support for its ability to control the size distribution of the active metal clusters with a narrow range \[2\]. It was synthesized hydrothermally by a method similar to Cano et al. \[2\]. However, Cano et al. used a 90°C hold temperature during the hydrothermal aging step, while in this study aging at 110°C was found to be beneficial.

In a typical preparation of SBA-15 for this work, 12.0g of copolymer-123 (Aldrich, lot# MKBG8245V) was dissolved in a solution of 60ml of 37% HCl in 360ml DI water. The dissolution was carried out for 3h with stirring at 40°C on a hot plate. Following dissolution, 12.5 ml of tetraethylorthosilicate (Aldrich, Batch MKBC8227) was added dropwise over the course of approximately 10 minutes while heating and stirring.
continued. The reaction was then allowed to proceed for 24h with stirring at 40°C. The suspension was then transferred to a sealed screw-top polyethylene bottle and placed in an oven for aging at 110°C overnight. Following this, the suspension was triple washed with DI water and the purified SBA-15 left to dry at room temperature. The dry SBA-15 was calcined at 500°C for 6h with a ramp rate of 1°C/min.

The calcined catalyst was impregnated by incipient wetness from ethanolic solution. Saturation volume of the prepared SBA-15 was measured at 3.41cm³/gm so this volume was used in the synthesis of each catalyst during the incipient wetness impregnation step.

The appropriate amount of iron(III)nitrate nonahydrate (Aldrich, Lot MKBW6908V), along with promoter sources copper(II)nitrate trihydrate (Aesar, Lot B02Q01), manganese (III) acetate or nitrate (Aldrich, Lot 288740-250), or potassium nitrate/acetate were added to achieve the target final loading for each catalyst. The metal salts were dissolved in the appropriate amount of ethanol (3.41cm³/g SBA-15) and the solution added dropwise to the SBA-15 prepared earlier. After addition, the impregnated SBA-15 was left to dry overnight at room temperature. It was then calcined at 450°C for 4h with a ramp rate of 1°C/min.

Prior to the current study, which focused solely on SB15 supported FTS catalysts, several catalysts were synthesized similarly using a fumed silica support. The catalysts were synthesized by dissolving the nitrate salts of Fe(III), Cu(II) and K in the minimum volume of water, depositing them on Cab-O-Sil (a commercial fumed silica used as support) at a rate which resulted in 20% loading of iron, then allowing evaporation of the water to leave metal nitrate crystals on the silica support, and finally calcining the catalyst to decompose the nitrates, leaving metal oxide clusters on the silica support. These catalysts
were then activated in hydrogen and tested for FT activity/selectivity under methanation conditions (10:1 H₂/CO). Data on activity at each temperature (400°C/450°C/500°C) was gathered, but selectivity was not analyzed during these experiments since the GC had not been calibrated at that time for hydrocarbons other than methane.

Cab-O-Sil is a fumed silica, manufactured by aggregating small non-porous silica particles. It forms branched, chain-like aggregates a few tenths of a micron long. This differs from many catalyst supports which contain pores with tunnel-like structure. Thus, when Cab-O-Sil is used as a catalyst support, it is likely that most of the active catalyst is deposited on the surface of the support particles. The small particle size (.2-.6 micron) result in high exterior surface area despite the more limited porous surface area.

The Cab-O-Sil supported catalysts were examined extensively but in all cases showed alpha values approaching zero (methane was the sole hydrocarbon). For this reason, the focus of the study shifted to SBA-15 supported catalysts, which had been shown by Cano et al. to give a mixture of hydrocarbon chain lengths at the conditions required.

### 3.2 Characterization Methods

Temperature Programmed Reduction is a technique used to elucidate information about the reduction characteristics of a catalyst. A reducing gas (in this case hydrogen diluted with helium) was flowed over the catalyst in a U-Tube reactor inside a Thermoscientific Thermolyne tube furnace. A Cirrus MKS mass spectrometer (MS) connected in-line with the u-tube reactor, and the input gas flowrates were controlled with Alicat Scientific mass flow controllers. Before the experiment was begun, a 30 minute hold at 110°C was carried out to drive off moisture present in the sample. In this way, water
concentration measured in the outgas as the temperature ramps will correspond to the reduction temperature, and the area under the curve will correspond to the extent of reduction. Following cool down of the reactor back to ambient temperature, the Eurotherm 3110 PID controller was used to set the furnace to ramp from room temperature to 900°C at a rate of 10°C/min while 2.5 sccm of hydrogen and 47.5 sccm of helium flowed through the reactor.

SEM is short for Scanning Electron Microscopy, and the technique allows for investigation of the surface morphology of the catalyst. The principle of operation is based on the interaction of the surface of the sample with excited electrons, causing secondary electrons to become dislodged, then detected. A Hitachi model S-800 instrument was used for all images.

X-Ray Diffraction, or XRD, is a technique used to gather information about the crystalline phases present in a bulk sample. Each of the planes in a crystal structure diffracts x-rays at different angles, and these angles (2θ), known as Bragg angles, can be plotted against intensity of the diffraction signal, and the resulting plot interpreted for analysis of crystalline phases present. XRD analysis was performed with a Bruker AXS diffractometer.

A Quantachrome Autosorb-IQ instrument was used to determine the Brunauer Emmett and Teller (BET) surface area as well as pore diameters and pore volumes. Approximately 50-55 mg of catalyst was used in the analysis.
3.3 Testing Methods

FTS reactions were carried out in a quartz U-tube fixed-bed reactor fed by mass flow controllers supplying carbon monoxide and hydrogen. After loading catalyst samples into the fixed bed (84.6mg catalyst), the bed was purged with helium for 15 minutes at ambient temperature, then syngas flow at a 2:1 hydrogen:CO ratio (total flow 15sccm) was started while the temperature ramped from ambient to 430°C over 80 minutes. This equated to a ramp rate of 5.1°C/min. This initial activation served to reduce the catalysts and form the active catalyst species. An additional 60 minutes at 430°C and 15sccm total flow was carried out for additional activation of the catalyst sample. Afterward, the temperature was maintained, and the flow was reduced to 2.5 sccm hydrogen and 1.3 sccm CO, beginning the reaction phase. The 2:1 H₂:CO ratio was maintained through reduction and reaction phases. Reactions were carried out for 3h from the end of the reduction step, with the outlet gas composition analyzed by Perkin Elmer GC/TCD.

All testing was run at ambient pressure (1 atm absolute), a reaction temperature of 430°C and constant space velocity of 43.6 sccm/gcat. Activation in all cases was with syngas in a 2:1 ratio of Hydrogen:CO. The total flow of syngas during the activation step was four times the flow during reaction, but the ratio was held constant. The reactor was purged with helium for 15 minutes, followed by syngas flow and a temperature ramp from room temperature to 430°C over 80 minutes, then an additional 60 minutes of activation syngas flow before the reaction phase was begun.

The GC/TCD was calibrated to detect the reactant species as well as carbon dioxide and hydrocarbons up to 6 carbons in chain length. A cold trap was installed at the outlet of the reactor in order to condense longer chain hydrocarbons (C5+) and keep them from
accumulating in the process tubing or the instrument. By using data from the GC/TCD, conversion of CO was calculated for each reaction, and also the relative concentrations of hydrocarbons in the reactor outlet allowed for calculation of alpha, and ultimately a model based prediction of the full hydrocarbon product distribution (see Models Used section).

3.4 Models Used

The size of the fixed bed reactor (4mm ID) constrained the mass of catalyst in the bed, and therefore the rate of product formation. Liquid hydrocarbons in larger reactors could expediently be collected in a cold trap and sampled for analysis, directly measuring the hydrocarbon product distribution of each catalyst. A method was developed instead in this work, in which the C1-C3 hydrocarbons were measured by GC/TCD, and the product distribution determined by fitting the C1-C3 data to the ASF (Anderson-Schultz-Flory) equation [5]. This mathematical model assumes the rates of the polymerization propagation and termination steps are constant and independent of carbon number, so that the parameter $\alpha$ defines the product distribution for molecules of n-alkanes for all carbon numbers 1 through $\infty$. The equation in terms of mass fraction is:

$$y_{N_c,M} = N_c^{(1-\alpha)^2} \alpha^{(N_c-1)}$$
with the chain growth probability defined as:

\[ \alpha = \frac{r_p}{r_p + r_t} \]

and \( r_p \) and \( r_t \) are the rates of chain propagation and termination, respectively [5]. This product distribution shifts from predominantly methane as alpha approaches zero to predominantly long-chain heavy waxes as alpha approaches 1. At intermediate values of alpha, a mixture of medium-chain liquid hydrocarbons is produced.

Using this theoretical framework, a Matlab model was created to correlate the C1-C3 hydrocarbon production rates to a full hydrocarbon product distribution. The model calculates the hydrocarbon distribution (C1 to C10) for alpha values in increments of 0.001 between 0 and 1. It then minimizes the sum of squared error to find the best fit of alpha to the experimental data, generating the full hydrocarbon product distribution.
CHAPTER 4:
RESULTS AND DISCUSSION

4.1 Synthesis Results

A series of iron Fischer-Tropsch catalysts supported on SBA-15 was prepared and tested for high temperature activity and selectivity to determine promoter effect on these catalysts at elevated reaction temperatures. Reactions were carried out at 430°C, while the ideal FT temperature range is 220-270°C. The aim of this study was to investigate the potential of these catalysts to produce value-added products at elevated temperature for use in a modified synthesis process involving combined steam reforming and FT reactions. Since the FT reaction increasingly favors methane and short-chain hydrocarbons as temperature increases above the ideal range, the goal of this study was to evaluate promoters with potential to maximize alpha and FT activity at high temperatures, as well as to evaluate promoter effect on the potential for production of value-added non-fuel products.

The catalysts were prepared by incipient wetness impregnation of SBA-15, as by Cano et al. [2]. An unpromoted catalyst composed of 15% (mass gm Fe/gm catalyst) loaded on SBA-15 was synthesized and tested, referred to as 15Fe. Then, catalysts of a similar type with added promoters were prepared by modifying the impregnation step to include salts of the promoter metal ions in varying concentrations. These are referred to similarly, with the mass loading and atomic symbol of promoter indicated in the name.
These promoted catalysts were then tested and compared to the unpromoted catalyst. Addition was of a single promoter in each synthesized catalyst, in order to elucidate the specific effects of each promoter. Characterization of the base catalyst by XRD pre-reaction and post-reaction was performed for analysis of the catalyst’s crystalline structural changes during activation and reaction.

4.2 Characterization Results

The 15Fe catalyst was analyzed by XRD and the results shown in Figure 4.1 below. It was analyzed again post-reaction to determine what changes to the crystalline structure occurred.

Peaks at 2 theta values of 24, 34, 50, 55, 63, and 64 are indicative of gamma-Fe$_2$O$_3$. The disappearance of peaks at 24, 34, 50 and 55 indicate reduction to metallic iron and/or iron carbide occurred in-situ during the activation and reaction steps.

The peak at 2 theta value equal to 45 in the post-reaction XRD data is representative of alpha-iron, and analysis by the Scherer equation gives an average particle size of 4.8 nm. This peak wasn’t present in the fresh catalyst because reduction had to occur in order to form the alpha-iron phase. The Scherrer equation is:

$$D_p = \frac{0.94 \lambda}{\beta \frac{1}{2} \cos \theta}$$
The peak at 2 theta value of 31 in the post-reaction plot is representative of alpha-$\text{Fe}_2\text{O}_3$. Analysis by the Scherer equation gives an average particle size of 1.7 nm.

![XRD Spectroscopic Analysis of 15Fe](image)

**Figure 4.1.** XRD Spectroscopic Analysis of 15Fe.

SEM images of the base case 15Fe-SBA-15 catalyst at magnifications between 700x and 7000x magnification are shown below.

In Figure 4.2, the rod-like structure of SBA-15 can be seen, with a rod diameter approaching 20 $\mu$m. Similar structures can be seen in Figures 4.3, 4.4 and 4.5.
Figure 4.3 shows the Fe/SBA-15 catalyst at 700x magnification also, and in this view, several of the rod-like SBA-15 structures are visible.

Figure 4.2. 15FeSBA-15 at 700x Magnification.

Figure 4.3. 15FeSBA-15 at 700x Magnification.

In Figure 4.4, a similar rod-like SBA-15 particle can be seen at 3000x magnification in the upper left corner of the image. The channels which make up the macrostructure are beginning to become visible.
In Figure 4.5, the magnification to 7000x makes the channels more evident. The macro structure of the SBA-15 takes the form of rods, but within each rod, many channels exist, each containing a multitude of pore channels. It is within these pores that the bulk of the active catalyst is deposited.

Figure 4.4. 15FeSBA-15 at 3000x Magnification.

Figure 4.5. 15FeSBA-15 at 7000x Magnification.

Temperature-programmed reduction was performed on the base catalyst and the best performing catalyst – the 1.4Mn15Fe-SBA-15 sample. Results of the TPR analyses are shown below in Figures 4.6 and 4.7.
As seen in Figures 4.6 and 4.7, peaks at 370°C and 640°C can be clearly seen in both samples. These peaks correspond to the two reduction steps in iron (III) oxide. In the first step, Fe₂O₃ is reduced to Fe₃O₄, and in the second step, Fe₃O₄ is reduced to metallic iron Fe.

The data shown in these figures has been filtered by symmetrical 12-point rolling average, due to noise in the instrument. However, clear peaks can be seen and indicate that similar iron oxide deposition occurred in both samples. The slightly increased amplitude and width of the first reduction curve (370°C) in the manganese promoted sample indicates that manganese had some effect on the reduction of the bulk oxide, enhancing the first reduction step. The absence of a separate peak in the manganese promoted sample indicates that reduction to metallic manganese occurs concurrently with iron reduction.
Figure 4.6. Temperature Programmed Reduction of 1.4Mn15Fe-SBA-15 (Filtered).
Determination of surface area, pore volume, and average pore diameter were analyzed and are presented in Table 4.1 below:

**Table 4.1.** Physisorption Results for 15Fe/SBA-15.

<table>
<thead>
<tr>
<th>BET Surface Area (m²g⁻¹)</th>
<th>BJH Pore Volume (cm²/g)</th>
<th>BJH average pore diameter (nm)</th>
<th>DFT surface area (m²g⁻¹)</th>
<th>DFT Pore Volume (cm²/g)</th>
<th>DFT average pore diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>368</td>
<td>0.79</td>
<td>11.2</td>
<td>338</td>
<td>0.81</td>
<td>9.4</td>
</tr>
</tbody>
</table>
4.3 Test Results

After calcination, 84.6mg of catalyst was loaded into a quartz U-tube fixed bed reactor and reduction was carried out by flowing 10sccm hydrogen and 5sccm carbon monoxide for 90 minutes while the temperature of the reactor ramped from room temperature to 430°C. This equated to a ramp rate of 5.1°C/min. After this initial reduction, an additional 60 minutes of reduction at 430°C was carried out with the same flowrates. At the end of this 60 minute period, the flowrates were adjusted to 1.25 sccm carbon monoxide and 2.5 sccm hydrogen, beginning the reaction phase. The 2:1 Hydrogen:CO ratio was maintained through reduction and reaction phases. Reactions were carried out for 3h from the end of the reduction step, with the outlet gas composition analyzed by Perkin Elmer GC/TCD.

The light hydrocarbon (C1-C3) composition of the outlet gas was fit to a standard one-parameter ASF model to calculate the corresponding alpha value of each catalyst, according to the equation:

\[ y_{N_{C,M}} = N_{C}^{(1-\alpha)^2} \propto (N_{C}-1) \]

An aim of this study was to synthesize a catalyst with maximal alpha value at 430°C in order to maximize the potential usefulness of products as liquid fuels or chemical feedstocks. Since Fischer-Tropsch catalysts show a marked decrease in alpha as temperature increases above the standard reaction temperature of 220C-270C, alpha values approaching those of the best commercial FT catalysts under ideal conditions were not expected. For example, SASOL operates two types of state of the art reactors at their
plants in South Africa. The low temperature reactor operates at 220°C with an alpha value of 0.88-0.95. The high temperature reactor operates at 325°C with an alpha value of 0.7 [4].

For the promoters selected, several catalysts were prepared and tested with the promoter loading varied, and the catalyst showing highest activity in each series was selected for further analysis. Those showing low conversion, leading to missing or very small peaks for C1-C3 hydrocarbons were not further analyzed, since potentially large error in analysis could result due to small peak areas the GC/TCD data approaching the detection limits of the instrument.

Table 4.2 below shows CO conversion, alpha, and CO2 composition of the outlet gas for each catalyst selected. Carbon balance calculations for 15Fe/SBA 15 at 3h on stream and at steady state are shown in Appendix A.

Conversion of the base case catalyst (15Fe/SBA-15) was higher than that found by Cano et al. in who's study it was found that 15Fe/SBA-15 gave 8.6% conversion at 7h on stream, reaching a maximum of 12.1% at 24h on stream, then decreasing to 10.0% at 144h on stream when activated in syngas [2]. As a percentage of all hydrocarbon products, they found approximately 6% methane selectivity, 9% C2-C4 selectivity, 26% C5-C12 selectivity, 53% C13-C18 selectivity, and 6% C19+ selectivity.

Both the 0.45Cu15Fe catalyst and the 1Cu15Fe catalyst showed increased CO conversion and similar alpha value compared to 15Fe; however, the high CO2 production indicates there was little benefit to the FT activity compared to water gas shift activity, so the performance improvement of the catalyst by copper promotion in this range is limited to increased conversion.
Table 4.2. Activity and Selectivity of SBA-15 Supported Catalysts at 3h on Stream.

Reaction conditions were 430°C and ambient pressure, H₂:CO ratio 2:1, space velocity 1190hr⁻¹ (43.6 sccm/gcat). C5+ selectivity was calculated from the alpha value fit to the experimental data. Any value indicated by ‘*’ indicates that one or more of the C1-C3 hydrocarbon peaks in the GC/TCD data required for analysis by the Matlab model was below the detection limit of the instrument.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>% CO conversion</th>
<th>α</th>
<th>Methane Selectivity</th>
<th>CO₂ Selectivity</th>
<th>C2-C4 Selectivity</th>
<th>C5+ Selectivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>15Fe-SBA-15</td>
<td>29%</td>
<td>0.21</td>
<td>14%</td>
<td>76%</td>
<td>9.6%</td>
<td>0.21%</td>
</tr>
<tr>
<td>0.15Cu15Fe-SBA-15</td>
<td>11%</td>
<td>*</td>
<td>*</td>
<td>*</td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td>0.45Cu15Fe-SBA-15</td>
<td>39%</td>
<td>0.22</td>
<td>15%</td>
<td>74%</td>
<td>10%</td>
<td>0.23%</td>
</tr>
<tr>
<td>Cu15Fe-SBA-15</td>
<td>35%</td>
<td>0.20</td>
<td>10%</td>
<td>82%</td>
<td>7.2%</td>
<td>0.18%</td>
</tr>
<tr>
<td>0.15Mn15Fe-SBA-15</td>
<td>18%</td>
<td>*</td>
<td>*</td>
<td>*</td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td>0.45Mn15Fe-SBA-15</td>
<td>16%</td>
<td>0.23</td>
<td>14%</td>
<td>69%</td>
<td>16%</td>
<td>1.5%</td>
</tr>
<tr>
<td>1.4Mn15Fe-SBA-15</td>
<td>32%</td>
<td>0.34</td>
<td>18%</td>
<td>50%</td>
<td>30%</td>
<td>2.2%</td>
</tr>
<tr>
<td>0.5K15Fe-SBA-15</td>
<td>9.1%</td>
<td>*</td>
<td>*</td>
<td>*</td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td>1K15Fe-SBA-15</td>
<td>8.3%</td>
<td>*</td>
<td>*</td>
<td>*</td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td>3K15Fe-SBA-15</td>
<td>8.6%</td>
<td>*</td>
<td>*</td>
<td>*</td>
<td>*</td>
<td>*</td>
</tr>
</tbody>
</table>

The 1.4Mn15Fe catalyst showed both increased CO conversion and dramatically decreased CO₂ production, along with a significant increase in the alpha value. This indicates that the FT activity of the catalyst was significantly promoted by the addition of manganese. The 0.45Mn15Fe catalyst also showed increased alpha and decreased CO₂ selectivity, albeit with lower overall CO conversion. From these two samples, the ability of manganese promotion to increase chain length and promote the FT reaction is clear.
Figure 4.8 shows the impact of manganese promotion on C5+ hydrocarbon selectivity. This is a combined result of decreased carbon dioxide production and increased average chain length, as seen in the increasing alpha values with increasing manganese content.

Figure 4.9 shows the increasing trend in C2-C4 selectivity with increasing manganese content. The shift away from methanation and toward longer hydrocarbon chains is seen as with C5+ selectivity with increasing manganese content.

**Table 4.3** Repeatability of Experiments (at 3h on Stream, All Conditions as above in Table 4.2).

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Trial</th>
<th>%CO Conversion</th>
<th>Mean Conversion</th>
<th>Standard Deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>15Fe/SBA-15</td>
<td>1</td>
<td>15%</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>15Fe/SBA-15</td>
<td>2</td>
<td>17%</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>15Fe/SBA-15</td>
<td>3</td>
<td>29%</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>15Fe/SBA-15</td>
<td>4</td>
<td>19%</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td><strong>15Fe/SBA-15</strong></td>
<td></td>
<td></td>
<td><strong>20%</strong></td>
<td><strong>6.2</strong></td>
</tr>
<tr>
<td>1.4Mn15Fe/SBA-15</td>
<td>1</td>
<td>32%</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>1.4Mn15Fe/SBA-15</td>
<td>2</td>
<td>29%</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td><strong>1.4Mn15Fe/SBA-15</strong></td>
<td></td>
<td><strong>31%</strong></td>
<td><strong>2.1</strong></td>
<td></td>
</tr>
</tbody>
</table>
Figure 4.8. C5+ Selectivity of Manganese Promoted and Unpromoted Catalyst.

Figure 4.9. C2-C4 Selectivity of Manganese Promoted and Unpromoted Catalyst.
In Figure 4.10, methane selectivity is seen to be relatively constant among the promoted and unpromoted samples, and this is due to balancing of the opposing effects of decreasing carbon dioxide selectivity and increasing alpha as manganese content increases. Of the hydrocarbon products produced, methane makes up a decreasing fraction of the total as manganese content increases, but hydrocarbons as a fraction of all carbon containing products increase as manganese content increases. This balancing effect is responsible for the minor effect of manganese content on methane selectivity.

Shown in Table 4.4 below is the measured product gas composition of carbon-containing compounds for 3h on stream for the 1.4Mn15Fe catalyst.
Table 4.4. Composition of Product Gas at 3h on Stream for 1.4Mn15Fe, 430°C, Ambient Pressure, H₂:CO Ratio 2:1, Space Velocity 1190hr⁻¹ (43.6 sccm/gcat).

<table>
<thead>
<tr>
<th>Compound</th>
<th>Product Gas Molar Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₄</td>
<td>1.3%</td>
</tr>
<tr>
<td>C₂H₄</td>
<td>0.24%</td>
</tr>
<tr>
<td>C₂H₆</td>
<td>0.59%</td>
</tr>
<tr>
<td>C₃H₈</td>
<td>0.10%</td>
</tr>
<tr>
<td>C₃H₆</td>
<td>N/A</td>
</tr>
<tr>
<td>CO₂</td>
<td>3.6%</td>
</tr>
<tr>
<td>CO</td>
<td>21%</td>
</tr>
</tbody>
</table>

In addition to the testing of all catalysts at 3h on stream, steady-state data was collected for 15Fe and the outlet flowrate measured, allowing the material balance for carbon-containing species to be completed. Data is shown in Table 4.5 below. This reaction was carried out for 12h on stream, with the GC data for 10-12h on stream showing steady-state conditions.

Table 4.5. Activity and Selectivity of SBA-15 Supported Catalysts at 12h on Stream. Reaction conditions were 430°C and ambient pressure, H₂:CO ratio 2:1, space velocity 1190hr⁻¹ (43.6 sccm/gcat). Steady state was indicated by constant conversion of 3 successive samples preceding the 12h point.

<table>
<thead>
<tr>
<th></th>
<th>15Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₀ conversion</td>
<td>46%</td>
</tr>
<tr>
<td>α</td>
<td>0.25</td>
</tr>
<tr>
<td>CO₂ molar concentration in reactor outlet stream</td>
<td>28%</td>
</tr>
</tbody>
</table>
Conversion increased significantly at steady-state conditions and a slight increase in alpha occurred, however a large increase in CO₂ production occurred as well.
CHAPTER 5:
CONCLUSIONS AND SUGGESTIONS FOR FUTURE WORK

In conclusion, SBA-15 supported iron FTS catalysts were prepared and the effect of added promoters analyzed. The catalysts were tested at 430°C and ambient pressure for enhancement of catalyst activity and selectivity to useful products brought about by promoter addition. Promotion with 1.4%(mass) manganese was found to cause increased CO conversion, increased alpha, and decreased CO2 production. A similar trend was seen with manganese promotion at 0.45%(mass), however, CO conversion decreased from the base case in this sample. Copper promotion at 0.45% and 1% increased CO conversion, but increased CO2 production as well, and the effect on alpha was minimal. Promotion by potassium was found to decrease catalyst activity as indicated by decreased CO conversion.

The trends seen in the data indicate that increasing manganese content beyond 1.4% (mass) has potential to improve catalyst performance beyond that seen in this study. The trend with increasing manganese content was toward greater CO conversion, longer chain length, and lower carbon dioxide selectivity. Manganese content of SBA-15 supported iron catalysts should be further explored at higher and intermediate values, as the potential of manganese to promote this class of catalysts in high temperature operation has been seen by markedly improved catalyst performance with increasing manganese content.
REFERENCES

Appendix A: Carbon Balances

Table A1. Carbon Balance 15Fe, 3h on Stream.

<table>
<thead>
<tr>
<th>Outlet mol fraction</th>
<th>Compound</th>
<th>Outlet Molar Flowrate (mol/s)</th>
<th>Carbon atoms/molecule</th>
<th>Outlet Carbon Molar Flowrate (mol/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0229</td>
<td>methane</td>
<td>5.91E-08</td>
<td>1</td>
<td>5.91E-08</td>
</tr>
<tr>
<td>0.00456</td>
<td>ethane</td>
<td>1.18E-08</td>
<td>2</td>
<td>2.35E-08</td>
</tr>
<tr>
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<td>propane</td>
<td>4.62E-09</td>
<td>3</td>
<td>1.38E-08</td>
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<tr>
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<td>3.17E-07</td>
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<td>3.17E-07</td>
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<td>6.03E-07</td>
<td>1</td>
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<table>
<thead>
<tr>
<th>% difference</th>
<th>C Out</th>
<th>C In</th>
</tr>
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<tbody>
<tr>
<td>1.02E-06</td>
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<td></td>
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<tr>
<td>9.30E-07</td>
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<td></td>
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<tr>
<td>9.37E+00</td>
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Table A2. Carbon Balance 15Fe, 12h on Stream.

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<tr>
<th>Outlet mol fraction</th>
<th>Compound</th>
<th>Outlet Molar Flowrate (mol/s)</th>
<th>Carbon atoms/molecule</th>
<th>Outlet Carbon Molar Flowrate (mol/s)</th>
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<tbody>
<tr>
<td>0.0525</td>
<td>methane</td>
<td>9.96E-08</td>
<td>1</td>
<td>9.96E-08</td>
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<tr>
<td>0.00256</td>
<td>ethane</td>
<td>4.86E-09</td>
<td>2</td>
<td>9.71E-09</td>
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<tr>
<td>0.0082</td>
<td>ethylene</td>
<td>1.56E-08</td>
<td>2</td>
<td>3.11E-08</td>
</tr>
<tr>
<td>0.00585</td>
<td>propane</td>
<td>1.11E-08</td>
<td>3</td>
<td>3.33E-08</td>
</tr>
<tr>
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<table>
<thead>
<tr>
<th>% difference</th>
<th>C Out</th>
<th>C In</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.05E-06</td>
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<tr>
<td>-1.25E+01</td>
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</tbody>
</table>

2.5 rotameter reading
2.6 Total Outlet Flow SCCM
1.90E-06 Total Outlet Flow mol/s
7.44E-07 mol/s per sccm at STP
**Appendix B: Loading Calculations**

**Table B1.** Sample Loading Calculation, 15Fe/SBA-15.

<table>
<thead>
<tr>
<th></th>
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<th>g/mol</th>
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<tbody>
<tr>
<td>Fe(NO3)3.9H20 molar mass</td>
<td>403.999</td>
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<tr>
<td>Fe molar mass</td>
<td>55.845</td>
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<tr>
<td>loading (per gram final</td>
<td>0.15</td>
<td>g Fe/g</td>
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<tr>
<td>catalyst)</td>
<td></td>
<td>catalyst</td>
</tr>
<tr>
<td>loading (per gram SBA-15)</td>
<td>0.176</td>
<td>g Fe/g</td>
</tr>
<tr>
<td></td>
<td></td>
<td>SBA-15</td>
</tr>
<tr>
<td>g SBA-15</td>
<td>1</td>
<td>g</td>
</tr>
<tr>
<td>g Fe required</td>
<td>0.176</td>
<td>g</td>
</tr>
<tr>
<td>mol Fe required</td>
<td>0.00316</td>
<td>mol</td>
</tr>
<tr>
<td>g Fe(NO3)3.9H20 required</td>
<td>1.277</td>
<td>g</td>
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