ABSTRACT

BHUANA, DONNY SATRIA. Core-Shell Fischer-Tropsch Catalysts for Combined Liquid Fuel Synthesis and Upgrading. (Under the direction of Dr. Fanxing Li).

The combined Fischer-Tropsch Synthesis (FTS) – CO\textsubscript{2} hydrogenation process represents an environmentally friendly method for producing liquid fuel from carbon dioxide and hydrogen. In order for such a process to be feasible, better catalysts that are capable of enhancing the reaction performance are required. In response to these needs, new catalysts are to be investigated and introduced in this work. The incorporation of zeolite into the iron-based FTS catalyst will help refine the produced hydrocarbons and shift the product distribution from the typical FTS product range to the middle iso-paraffins, which is a gasoline range, and eventually increase the yield of the liquid fuel. Coating of zeolite onto the iron-based FTS catalyst to form a core-shell structure is intended to enhance the ease of migration of the reactant and thus increasing the catalytic activity and shifting the product distribution towards the gasoline range. This study aims to develop catalyst for producing liquid fuel, particularly gasoline, from carbon dioxide and hydrogen. The pH of the catalysts is found to have significant effect on the catalytic activity due to its ability to control the amount of promoter to be precipitated in the catalyst, which results in a lower reduction temperature. Physically mixing the iron-based FTS catalyst with zeolite was found to have little effect on the catalytic activity and the product distribution, apart from slightly increasing the selectivity of iso-paraffins, which is the indication of isomerization activity. Zeolite shell has been successfully coated uniformly on the iron-based core using hydrothermal synthesis technique, however, the formation of thick zeolite shell might have blocked the active FTS sites on the iron-based catalyst and is believed to contribute to the low activity of the core shell catalyst. Hydrogenation of CO\textsubscript{2} carried out on iron catalyst did not seem to significantly affect the typical FTS product distribution, indicating that CO\textsubscript{2} can safely be incorporated into the existing Fischer Tropsch Synthesis.
Core-Shell Fischer-Tropsch Catalysts for Combined Liquid Fuel Synthesis and Upgrading

by

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DEDICATION

This thesis is dedicated to my beloved parents, H. Rustam Effendi, MBA and Hj. Rr. Mega Rustiany, for their precious long-life love, patience, supports, thoughts, prayers, and everything throughout the course of my life and particularly throughout the entire course of this thousands-of-miles-away journey...
BIOGRAPHY

Donny Satria Bhuana was born to parents Hajji Rustam Effendi and Hajjah Raden Roro Mega Rustiany in Magelang, Central Java, Indonesia. He spent early years in Magelang before relocating to East Timor with the family, following his father’s service as an Indonesian Army. He later moved back to Java for the sake of a more conducive environment and a better education at the time. His brother and him lived in Kamal, a small town in Madura Island with his grand parents, where he completed his elementary and junior high school. He decided to move to Surabaya to get an even better education, where he graduated from SMA Negeri 5 Surabaya before attending Sepuluh Nopember Institute of Technology. Four years later, he received his Bachelor of Engineering in Chemical Engineering and worked in some multinational companies in Jakarta and Surabaya for some time before embarking upon academia to follow his childhood dream, i.e. to become a Professor. He received a scholarship from Australian government to pursue his master’s study in Australia, where he graduated with Master of Science in Chemical Engineering from The University of Adelaide. The following year, he received a Fulbright-DIKTI scholarship to undertake higher education in the United States.
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Chapter 1

Introduction

Carbon dioxide emitted from anthropogenic activities is considered to be a significant contributor to global climate change. Converting carbon dioxide into renewable liquid fuel is considered to be one of the most promising solutions to resolve the problem. However, relatively little effort have been put into developing the technology. With the increasing concern about carbon dioxide being a major contributor to greenhouse gas emission, more research have been directed towards finding the best approach to mitigate carbon dioxide emission. These efforts include capturing CO$_2$ either from industrial flue gas by amine scrubbing$^1$ or direct removal from the atmosphere through inorganic oxide bond$^2$, before sequestering it in a depleted geological reservoir. On the other hand, instead of considering the carbon dioxide as a “waste”, alternative approaches tend to look at the carbon dioxide as a feedstock that can be converted into valuable liquid fuels or chemicals$^3$. This is supported by the fact that global fuel prices have been fluctuating within the last few years in response to the anticipated shortage of oil supply. In terms of CO$_2$ utilization, a number of
approaches including photochemical, electrochemical, and thermochemical conversions have been investigated. Among these, thermochemical conversion of carbon dioxide in the presence of a heterogeneous catalyst has shown the highest reaction rate and CO$_2$ conversion. As opposed to the catalytic thermochemical CO$_2$ conversion, the electrochemical routes have several drawbacks, such as low conversion and efficiency as well as lack of long chained hydrocarbon production and thus, it is still under early stage of development$^3$. Likewise, the major challenges for implementing the photochemical reduction of carbon dioxide in a wide scale lie on the material cost used for synthesis and efficiency of the catalysts. The photo-assisted electrochemical reduction of CO$_2$ could have a better prospect if the cost of photocatalysts and photoelectrocatalysts are reduced and the efficiency and lifetime are improved$^4$. The problems faced by the two technologies bring up the fact that thermochemical approach for converting carbon dioxide into liquid fuel is the most suitable approach to take at the moment. One challenging problem that typically arises from the thermochemical conversion of CO$_2$ is the need for continuous supply of carbon dioxide and hydrogen in such an efficient way that the thermochemical process can be economically viable. Still related to that, carbon dioxide is reported to be more abundant in the ocean compared to its availability in the air, with the CO$_2$ concentration in the air being 0.7 mg/L as opposed to 100 mg/L of CO$_2$ available
in the ocean. Hence, this could become one promising alternative to the problem faced by thermochemical conversion of carbon dioxide into liquid fuel.

Recent studies revealed that thermochemical conversion of CO\textsubscript{2} into liquid fuel in the presence of heterogeneous catalysts includes two reactions\textsuperscript{6-8}. The first reaction is to convert the carbon dioxide into carbon monoxide by reacting it with hydrogen, whereas the second reaction includes reacting the carbon monoxide with hydrogen to produce liquid fuel. The first reaction is called Reversed Water-gas Shift (RWGS) reaction and the second reaction is called the Fischer-Tropsch (FT) reaction. The combined Fischer-Tropsch – CO\textsubscript{2} hydrogenation process represents an environmentally friendly method for producing liquid fuel from carbon dioxide and hydrogen. In order for such a process to be feasible, better catalysts that are capable of enhancing the reaction performance are required.

In response to these needs, new catalysts are to be investigated and introduced in this work. The basic idea is to incorporate a RWGS and F-T bi-functional catalyst into a shell that is both active for RWGS and isomerization / hydrocracking. By combining the catalysts, promoters, and supports of the Fischer-Tropsch and the water-gas shift reactions, it is expected that the catalysts’ activity will increase and thus, increasing the selectivity of the longer-chained hydrocarbon produced and eventually increase the yield of the liquid fuel accordingly. The incorporation of zeolite into the iron-based FTS catalyst will help refine the produced hydrocarbons and shift the product distribution
from the typical FTS product range to the middle iso-paraffins, which are gasoline range hydrocarbons. Coating of zeolite onto the iron-based FTS catalyst to form a core-shell structure will be more effective in shifting the product distribution to the gasoline range due to the ease of migration of the reactant gases. This study aims to develop catalyst for producing liquid fuel, particularly gasoline, from carbon dioxide and hydrogen. The required steps include catalyst preparation by co-precipitation technique and hydrothermal synthesis, reactor design and construction, and investigation of the catalytic activity, yield, and selectivity of the liquid hydrocarbon produced in both the FT and CO\textsubscript{2} hydrogenation reactions.

Since a key function of the proposed catalyst is to perform F\textsuperscript{-}T synthesis, the F\textsuperscript{-}T reaction, its mechanism, and F\textsuperscript{-}T catalyst composition and performance are reviewed in the following sections. Franz Fischer and Hans Tropsch discovered a process for converting carbon monoxide and hydrogen to hydrocarbons in 1922 using an iron catalyst through the following reaction\textsuperscript{8}:

\[
\text{n CO } + \text{(2n+1) H}_2 \rightarrow \text{C}_n\text{H}_{2n+2} + \text{n H}_2\text{O}
\]

The Fischer-Tropsch process is a heterogeneous catalytic process for the production of clean liquid fuels from synthesis gas, which can be obtained from non-petroleum sources such as coal, biomass, and natural gas through steam reforming, partial or autothermal oxidation, or gasification. Since the discovery,
different supported and unsupported catalysts such as Fe, Co, Ni, Ru and Rh have been used to improve syngas (mixture of CO and H\textsubscript{2}) conversion to liquid fuels. Water is the major byproduct of the process. The product distribution of the Fischer-Tropsch reaction follows the Anderson-Schulz-Flory (ASF) distribution, which typically is not favorable to having high conversion to liquid hydrocarbons over other products, such as waxes and methane\textsuperscript{10}.

A number of different sources of hydrocarbon feedstock, such as coal, natural gas, and biomass can be converted into a mixture of synthesis gas (CO and H\textsubscript{2}), by undergoing either partial oxidation or steam reforming processes\textsuperscript{11}. The Fischer-Tropsch synthesis is a technology of converting carbon monoxide and hydrogen (syngas) into synthetic liquid fuel over metal catalysts that has been continuously improved since the first time it was discovered in 1923 by Franz Fischer and Hans Tropsch at the Kaiser Wilhelm Institute for Coal Research\textsuperscript{12}. In their original study, Fischer and Tropsch reported that CO hydrogenation at 180-250°C and under atmospheric pressure over iron, cobalt, and nickel catalysts resulted in linear hydrocarbon product mixture. The Fischer-Tropsch products consist of linear and branched hydrocarbon as well as oxygenates, with the main products being linear paraffin and \(\alpha\)-olefin.

Fischer-Tropsch reactions convert synthesis gas to predominantly straight-chain hydrocarbons, which can be in the form of paraffins from CH\textsubscript{4} to waxes \(C_nH_{2n+2}\).
with n from 1 to over 100, olefins from ethylene to much longer molecules 
\((C_nH_{2n}, \text{with } n>2)\), and to a lesser extent oxygenated products such as alcohols\(^{13}\). 
Due to highly exothermic reaction, the FT synthesis reaction generates large 
amounts of heat. The process can be represented by a simplified reaction 
equation below:

\[
\text{FTS} : \text{CO} + 2\text{H}_2 \rightarrow \text{CH}_2^+ + \text{H}_2\text{O} \quad -165 \text{ kJmol}^{-1}
\] (1.1)

A more detailed list of reactions that can take place in the Fischer-Tropsch 
reactor are summarized in Table 1.1:

Table 1.1: Major reactions in the F-T synthesis\(^{11}\)

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<tr>
<td>2. Olefins (2n\text{H}<em>2 + n\text{CO} = C_n\text{H}</em>{2n} + n\text{H}_2\text{O})</td>
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<td>3. Water-gas shift (\text{H}_2\text{O} + \text{CO} = \text{CO}_2 + \text{H}_2)</td>
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</tr>
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<td>(M_x\text{O}_y + y\text{CO} = y\text{CO}_2 + xM)</td>
</tr>
<tr>
<td>7. Bulk carbide formation (xM + yC = M_xC_y)</td>
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1.1. Fischer-Tropsch synthesis product distribution

At a molecular level, the FT synthesis is composed of CO hydrogenation and polymerization steps. The hydrogenation reaction is signified by the fact that the C·O bond needs to be broken so that C·H bond can be formed. Furthermore, C·C bonds also need to be formed in order to accommodate hydrocarbon chain-growth. The carbon number distribution of the FT products follows a statistical function called the Anderson-Schulz-Flory (ASF) distribution\textsuperscript{14}. The competing mechanisms between chain-growth and chain termination are characterized by a chain-growth probability factor, called $\alpha$ value. The higher the $\alpha$ value, the longer the hydrocarbon chain and the heavier the hydrocarbon mixture produced. According to Anderson (1956), the product distribution of the FT synthesis can be formulated by defining the Anderson-Schulz-Flory (ASF) distribution. Under an ideal condition, the chain-growth probability ($\alpha$) that is determined by the rates of chain-growth ($R_p$) and chain termination ($R_t$) is expressed as $\alpha = R_p / (R_p + R_t)$ and is independent of carbon chain length. The mass fraction of a hydrocarbon with a chain length (carbon number) of $n$ is given by equation 2\textsuperscript{14}:

$$W_n = n(1 - \alpha)^2 \alpha^{n-1} \quad (1.2)$$
The hydrocarbon product distribution of the FT synthesis can then be constructed by plotting Eq. 1.2, and can be shown in Fig. 1.1 below. The statistical distribution of F-T products is inherently nonselective for a specific range of hydrocarbons.\textsuperscript{15-20} For example, the maximum selectivity to C\textsubscript{5}–C\textsubscript{11} (gasoline range) and C\textsubscript{12}–C\textsubscript{20} (diesel range) hydrocarbons are roughly 45 and 30\%, respectively. In this context, the current F-T technology generally aims at producing long chain alkanes (waxes, C\textsubscript{21+}). Subsequently, the waxes are transformed into liquid fuels by hydrocracking over metal-acid dual functional catalysts. To take full advantage of this two-stage approach, the F-T synthesis should be operated at high $\alpha$ values (>0.9) to minimize the formation of undesired light products, especially methane.\textsuperscript{13, 21-26}
Based on reaction temperature, the Fischer-Tropsch synthesis can be categorized as high-temperature Fischer-Tropsch (HTFT) and low-temperature Fischer-Tropsch (LTFT) processes. The high-temperature Fischer-Tropsch operations are normally carried out at temperature range from 320 to 350°C with the reaction products being essentially in the gas phase. This process is carried out in either fluidized bed or fixed-bed reactors. Alkali-promoted iron catalysts appear to suit this process since cobalt-based catalysts would essentially be able to only
produce methane at this temperature. The low-temperature Fischer-Tropsch synthesis processes are normally operated at temperature between 200 and 250°C. For this particular type of operation, both cobalt and iron-based catalysts would be effective for use in the reaction, even though cobalt would be more suitable over certain portion of the lower temperature range compared to the iron-based catalysts. High quality middle distillates, such as diesel and jet fuels are typically produced from the LTFT synthesis after the hydrocracking of long chain waxes, while the naphtha of the process contains feedstocks for naphtha steam crackers, typically producing ethylene and propylene.\textsuperscript{13}

In the early years of the technology development, only fixed-bed reactors were originally used for the Fischer-Tropsch Synthesis. Due to the need to reduce the pressure drop in the stationary bed, the size of the catalysts was maintained in the range of millimeter. However, this has apparently caused intra-particle diffusion resistance that was reported to have limited the catalyst utilizations and significantly affect the product distribution due to the different rates of diffusion for CO and H\textsubscript{2} that results in a higher H\textsubscript{2}/CO ratio at the center of the catalyst bed.\textsuperscript{13} In addition, the exothermic nature of the FTS reaction also contributes to the non-uniform profile of the reactor temperature both axially and radially. In response to those problems, slurry bubble column reactors were developed to provide solutions to the problems faced in the fixed-bed reactors.
The design of the reactor, in which the syngas is bubbled through in a direct contact with the solid catalyst and the liquid products, allows the use of a small enough particle size that can eliminate the intra-particle diffusion resistance problem. Furthermore, the problem with the non-isothermal reactor temperature can be overcome by the presence of the well-mixed liquid products.\textsuperscript{13}

1.2. Fischer-Tropsch catalysts

The most common catalysts for Fischer-Tropsch are Group VIII metals. Vannice discussed the activity of Group VIII metals for use in the FT process and found that the metal activity can be ranked as\textsuperscript{27}:

\[ \text{Ru} > \text{Fe} > \text{Ni} > \text{Co} > \text{Rh} > \text{Pd} > \text{Pt} \]

Of the possible catalysts from Group VIII metals, the most common are Fe, Co, and Ru, as well as Ni and Rh\textsuperscript{28}. Iron and cobalt are more widely used as catalysts for FT process. Cobalt-based catalysts possess a number of advantages in terms of high activity and long life. They also have higher tendency of producing long chained hydrocarbon as well as lower tendency of producing undesired carbon dioxide due to low activity in the water-gas shift reaction in
comparison with iron-based catalyst. The limitations to cobalt-based F-T catalysts include low tolerance towards syngas with low H₂/CO ratio and contaminants as well as relatively high cost. Iron is one of the most commonly used catalysts for Fischer-Tropsch thanks to a number of advantages, such as low cost compared to other metal catalysts, high water-gas shift activity (thus, effective for use in a CO-rich syngas), high selectivity towards olefins, as well as high stability when a H₂-rich syngas is to be used in the FTS\textsuperscript{29}.

In general, iron catalyst is effective for use in the hydrogen-lean syngas Fischer-Tropsch synthesis due to its high activity towards the Water-gas Shift (WGS) reaction. However, the excessive CO₂ production from WGS reaction often raises concern when the technology is brought to a larger scale\textsuperscript{3}. Furthermore, Riedel and co-workers (2001) reported from their study that water has inhibiting effect on the reaction rates during the hydrogenation. While alternative approaches such as the use of water-permeable membranes has been proposed to mitigate the presence of water during the reaction, they are at early stages of development\textsuperscript{30-32}. Using a Pt-promoted cobalt catalyst, Dorner and co-workers (2010) studied the influence of gas feed composition and pressure on the catalytic conversion of CO₂ to liquid hydrocarbons through a Fischer-Tropsch process. This study was conducted in a CSTR by varying feed gas ratio of CO₂ and H₂ as well as operating pressure\textsuperscript{3}. The results indicate that as the H₂ feed composition
is reduced, the higher-chain hydrocarbon products become more abundant. Furthermore, as the pressure is reduced from 450 to 150 psi, it is reported that the selectivity shifts toward longer-chained hydrocarbons and away from methane in order to support for the C₂-C₄ paraffin. In addition, Adesina mentioned that a cobalt-based catalyst requires a lower operating pressure for use in the FT process than does an iron-based catalyst. Riedel and co-workers investigated the effect of varying CO / CO₂ ratios in the synthesis gas. With increasing CO₂ content, the product composition shifted from hydrocarbon mixtures to a more exclusively methane.

1.3. Dopant and Promoters

In order to improve the performance of iron-based catalysts, promoters are usually added to improve their selectivity, activity, and/or lifetime. Common promoters for iron-based catalyst include potassium, manganese, copper, and magnesium. Potassium is known to have favorable effects on the catalytic of iron-based for the CO₂ hydrogenation. In addition to improving catalyst activity and selectivity towards olefins and long-chain hydrocarbons in the products, potassium promoted iron catalysts can also increase CO₂ conversion. On reporting the work of Dry (1969), Dorner and co-workers (2010) mention that potassium that is doped on iron acts as an electronic promoter that can improve
dissociative adsorption of CO while at the same time reduce the adsorption ability of hydrogen. This would result in the olefin hydrogenation being suppressed and leads to the increase in the olefin selectivity. In addition to being used as a structural promoter, the addition of manganese to an iron-based catalyst is effective to reduce the selectivity of methane and to increase the olefin to paraffin ratio in both CO and CO$_2$ hydrogenation Fischer-Tropsch Synthesis. The mechanism of electronic promotion by manganese is reported to include several aspects, such as the promotion of catalyst reduction, the dispersion and carburization of the Fe$_2$O$_3$ precursor, and the increase in surface basicity of the catalyst, which is presumably taking place by incorporation into the lattice structure of the iron. However, having excessive amount of promoter on the iron-based catalyst is typically avoided due to the reversed effect of the promoter that can block the active FTS sites on the iron that could result in the decrease in catalytic activity and shift the product distribution to the formation of unwanted products. Copper has similar effects on iron as manganese and thus, can replace manganese as a promoter for iron-based CO$_2$ hydrogenation Fischer-Tropsch Synthesis. In addition to acting as a reversed water-gas shift catalyst, copper is reportedly capable of enhancing the reduction of hematite during carburization as well as improving the catalytic dispersion.$^3$
1.4. Effect of catalyst support

Catalyst supports have several roles, such as to disperse the active phase and provide a high surface area of the phase, to stabilize the active phase, and to support the catalyst’s mechanical strength\textsuperscript{10}. Oxides such as Al\textsubscript{2}O\textsubscript{3}, SiO\textsubscript{2}, and TiO\textsubscript{2} are the most widely used supports for cobalt catalysts. A number of studies have been carried out to determine the effects of these supports on catalytic properties of supported Co catalysts. Davis and co-workers examined the catalytic performances of cobalt catalysts using various supports, such as Al\textsubscript{2}O\textsubscript{3}, SiO\textsubscript{2}, and TiO\textsubscript{2} over Ru\textsuperscript{-} and Pt\textsuperscript{-}promoted cobalt\textsuperscript{33}. They concluded that supports have significant effects on the reduction of Co oxide species and can be presented in the order Al\textsubscript{2}O\textsubscript{3} > TiO\textsubscript{2} > SiO\textsubscript{2}. In terms of iron, the active phase dispersed on certain type of supports exhibit higher activity and selectivity. In general, supports are beneficial in avoiding sintering or Oswald ripening of the catalytically active particles during the reaction.\textsuperscript{34} Dorner and co-workers (2010) reported that alumina has been considered as the best support for hydrogenation due to the fact that it tends to hinder sintering through strong metal-support interactions. They further mentions that the improved activity of the alumina-supported catalysts may be attributed to the support that forms a catalytically active phase with the catalysts. In the case where alumina and potassium are introduced to the hydrogenation catalysts, according to them, potassium alanate
(KAlH$_4$) is possible to form. This compound is known for its reversible hydrogen sorption at moderate temperatures (250-350°C). The potassium alanate would lead to the reduction of hydrogenation of surface-bound carbonaceous species and acts as a hydrogen reservoir, which would give a higher olefin and lower methane productions$^{35}$.

1.5. Dry-mixed Catalysts

Hydrocarbon produced from the Fischer-Tropsch synthesis follows the Anderson Schulz Flory (ASF) distribution$^{36}$. Consequently, the products contain a wide distribution of hydrocarbons based on carbon number. In addition, these hydrocarbons, even after hydrocracking, contains mainly normal aliphatic hydrocarbon with high cetane number but low octane number. Thus, the FTS-derived fuel is suitable for diesel fuel but not for gasoline$^{37}$. According to the data from the US Department of Energy in 2009, 62% of fuel used for transportation in the United States is in the form of gasoline, while diesel consumption for transportation is in the second place with only 22% of the total fuel consumed. Therefore, there is a growing need to independently convert gasoline from natural gas/coal derived syngas. Converting the Fischer-Tropsch hydrocarbon into synthetic gasoline requires further refining of the FT products, such as isomerization. Shell plant commercially produces branched hydrocarbons from
syngas using two steps, the first step is to convert syngas to linear paraffin through the Fischer-Tropsch, and the second step includes the hydrocracking and isomerization reactions to produce iso-paraffin of gasoline range. These processes are carried out in separate reactors. The processes are considered to be complicated with the F-T step being prone to having catalyst deactivation issue due to the wax deposition on the catalyst surface. Therefore, carrying out the processes in one step would be beneficial to avoid catalyst deactivation problem, and in this case, designing a multifunctional catalyst for direct conversion of iso-paraffin from syngas would be advantageous.

A number of efforts have been put to combine the Fischer-Tropsch hydrogenation catalysts with those for refinery processes. The concept of physically mixing the conventional FT catalysts and zeolite has been previously studied. Yoneyama and co-workers (2005) conducted a study on hybrid catalyst of iron and zeolite by physically mixing varied amount of zeolite and iron catalyst to accommodate direct synthesis of iso-paraffin from syngas. Four different compositions of zeolite-iron dry-mixed catalysts were synthesized and tested in the Fischer-Tropsch reactor. The four catalysts exhibited no significant activity difference in terms of CO conversion, which can be well explained by the fact that the same amount of iron-based FT catalyst was used in the dry-mixed catalysts. In terms of product selectivity, it is reported that the more amount of zeolite added to the
dry-mixed catalysts resulted in the increase of both CH$_4$ and CO$_2$ selectivity to some extent$^{37}$. This is attributed to the formation of α-olefins as an FT product in addition to n-paraffins, which could get re-adsorbed on the zeolite pores and eventually decompose as methane, thus increasing the methane selectivity$^{39}$.

Furthermore, with regards to product distribution, the study suggests that in general with traditional Fischer-Tropsch iron catalyst, the FTS products contain heavy normal paraffin from C1 to C16. However, after the addition of zeolite by physical mixing, the heavy normal paraffins disappeared and the product distribution shifted towards the formation of lighter chained hydrocarbons, i.e. C1-C10 that are rich in iso-paraffins. Increased amount of zeolite in the dry-mixed catalysts resulted in the increased selectivity of lighter hydrocarbons. Other study reported that cobalt-based dry-mixed catalysts exhibit heavier products compared to the iron-based$^{40}$. In addition, iron-based hybrid dry-mixed catalyst gave lower methane selectivity as compared to the cobalt-based catalyst under the same operating conditions$^{37}$. It is also pointed out from the study that the use of carbon monoxide or syngas as a reducing gas gives a higher conversion compared to when hydrogen was used as a reducing gas. This is mainly attributed to the formation of iron carbide as an active species of the catalyst that can effectively activate the FT synthesis as a result of the reduction with CO or syngas$^{41}$. The effect of copper addition and the effect of reaction
temperature were also investigated in the study by Yoneyama and co-workers (2005). Thanks to its ability to promote catalyst reduction, the dispersion and carburization of the precursor Fe$_2$O$_3$-state while also greatly increasing the catalyst’s surface basicity, increasing the copper content as a promoter to the iron-based catalyst is reported to increase CO conversion during the Fischer-Tropsch synthesis. Temperature-wise, Yoneyama and co-workers (2005) mentioned that due to the fact that the temperature above 280°C was reportedly favorable for the catalyst activity in terms of CO conversion during the Fischer-Tropsch synthesis, all their experiments were carried out at 300°C. Furthermore, increasing the reaction temperature was also reported to have the following impacts on the FTS products: increase olefin production, decrease CO$_2$ production and thus, suppress water-gas shift reaction, and yet hardly affect methane selectivity.

1.6. Core-Shell Catalysts

Fischer-Tropsch based fuels have some beneficial properties over its conventional petroleum derived fuel, such as sulphur-free, aromatic-free, and nitrogen-free that makes it ideal for use as transportation fuel. The FT-based fuels, however, are only suitable to be used as synthetic diesel fuel due to the presence of normal paraffin comprising the fuels. Additional processes such as
hydrocracking and isomerization are required to convert the linear paraffins into branched paraffins in order to produce synthetic gasoline\textsuperscript{11, 42-43}. While physically mixing the Fischer-Tropsch catalyst with that of hydrocracking and isomerization can actually suppress the formation of longer-chained hydrocarbon as well as increase the selectivity of branched paraffins to some extent, the performance can still be improved. For the iron-zeolite dry-mixed catalysts, the active sites are distributed in random locations on the catalyst surface, which results in unrestricted reaction sites that allow both FTS reaction and hydrocracking & isomerization reaction to occur randomly and independently. This suggests that there is a chance for the FTS products to leave the catalyst surface directly without further reacting with the active sites of zeolite. In addition to physically mixing the metal-based FT and zeolite catalysts, a number of other research studies have attempted to synthesize the bifunctional metal/zeolite catalysts in a different format, i.e. by utilizing an FT catalyst supported on zeolite for the direct production of isoparaffins\textsuperscript{44-45}. However, this method resulted in a substantially low CO conversion and low degree of reduction due to the extremely strong interaction between the metal and the zeolite as a support. The ease of migration and mobility of the FTS products appears to play important roles in determining the successful formation of middle iso-paraffin hydrocarbons. To foster this concept, a novel multifunctional catalyst with core shell structure has been introduced\textsuperscript{46-47}. The core part consists
of conventional FTS catalysts while the shell comprises a layer of H-type zeolite enwrapping the core. The syngas passes through the shell to reach the core catalyst and eventually undergo FTS reaction to form linear paraffins. Prior to leaving the catalysts, all the linear paraffins must first pass through the zeolite shell and that is where hydrocracking and isomerization reactions take place and the linear paraffins have a better chance of getting converted into iso-paraffins on the acidic sites of zeolite. Owing to its ability to improve the collision possibility between linear paraffins and zeolite acidic sites, the core shell catalyst is expected to give higher selectivity towards iso-paraffins compared to the physically mixed catalyst.

Bao and co-workers (2008) synthesized the bifunctional catalysts using three different catalyst preparations, i.e. cobalt supported on alumina, physical mixture of cobalt supported on alumina and β-zeolite, and core-shell structure of alumina-supported cobalt coated by β-zeolite. From the catalytic performance on the FT reactor, the three catalysts exhibit no significant difference in terms of CO conversion, with the pure core catalyst exhibiting the highest CO conversion followed by the dry-mixed Co/Al₂O₃/β-zeolite and the β-zeolite coated Co/Al₂O₃, respectively, with each of which showing a slight decrease in CO conversion from the pure core catalyst. The relatively low CO conversion of the zeolite coated cobalt-based catalyst can be attributed to the coverage of some of the cobalt
active sites by zeolite membrane that might have restricted the adsorption activity of H₂ and CO to some extent. Furthermore, selectivity towards methane and carbon dioxide decreased as the catalysts were physically mixed and coated with zeolite, respectively, with the zeolite-coated Co/Al₂O₃ exhibiting the lowest CH₄ and CO₂ selectivity compared to both the pure core and the physically mixed catalysts. As in the case of iron-based catalysts, the pure conventional cobalt-based catalyst follows the ASF product distribution in which linear paraffins are the main products. Physically mixing the cobalt-based catalysts with the zeolite increased the selectivity towards isoparaffins and olefins even though heavy paraffins up to C₂₀ were still present. Coating the cobalt-based catalysts with zeolite completely suppressed the formation of C₁₂⁺ hydrocarbons while maintaining the high selectivity of isoparaffins.

Apart from cobalt-based FT catalysts, iron-based catalyst cores have also been studied, although less extensively. Bao and co-workers (2011) studied the synthesis of fused iron-zeolite core shell catalyst and tested the performance of the catalysts. The tested core-shell catalysts exhibit the ability to suppress long chained hydrocarbons C₁₀⁺ and increase the selectivity of the middle isoparaffins. It is reported from the study that there were up to C₁₄ hydrocarbons with no isoparaffins were produced when fused iron catalyst was used. Physical mixing of the iron catalyst with zeolite was effective enough to form isoparaffins.
even though longer chain hydrocarbons were still present. The core-shell structure of the iron/zeolite catalysts completely suppress the C_{10}^+ hydrocarbons and thus, shifting the main product to middle isoparaffins^{48}. Moreover, the study highlights some notable information, such as the dependence of hydrocarbon diffusion rate on the chain length. The longer the hydrocarbon chain the longer it takes to diffuse through the zeolite layer and therefore, the greater chance it can be converted into isoparaffins via hydrocracking and isomerization processes. In terms of catalyst activity, the study suggests that there is no significant difference with regards to CO conversion amongst the three catalysts, i.e. fused iron, dry-mixed iron/zeolite, and the core-shell structured iron/zeolite catalysts, indicating that the presence of zeolite shell on the fused iron core does not significantly affect the ease of migration of all the reactant gases. In contrast, the study suggests that the core-shell structured catalyst exhibit a significantly lower selectivity towards methane and carbon dioxide, respectively. The low CO$_2$ selectivity can be attributed to the low Water-gas Shift (WGS) reaction activity. Consequently, with the low WGS activity more unreacted water and carbon monoxide are expected to get trapped in between the core and the shell region, contributing to the lower ratio of H$_2$/CO inside the catalyst and would eventually lead to less formation of methane^{48}. While the above studies confirm the advantages of coating zeolite onto iron catalyst cores, further studies
on promoted iron catalysts, which are known to be more active and selective than fused iron catalysts, are highly desired.

1.7. CO$_2$ Hydrogenation

Compared to the extensive literature resources on F-T synthesis, thermochemical CO$_2$ hydrogenation is relatively less studied with less than a few dozen published work. Production of hydrocarbons directly from CO$_2$ is essentially a modified process of the Fischer-Tropsch Synthesis, in which carbon dioxide rather than carbon monoxide is used in the reactor. A number of catalysts such as cobalt, iron, copper, and zinc have been used in the CO$_2$ hydrogenation to produce hydrocarbons. Some studies suggest that the CO$_2$ hydrogenation proceeds through one of two different mechanism pathways, i.e. methanol mediated and non-methanol mediated pathways, respectively. The methanol-mediated pathway comprises of the production of methanol followed by subsequent process to convert methanol into hydrocarbons. The non-methanol mediated pathway proceeds through reversed water-gas shift reaction to produce syngas, followed by Fischer-Tropsch synthesis to produce ranges of hydrocarbons.$^{49}$ Dorner and co-workers (2009) conducted a study to investigate the influence of gas feed composition and pressure on the catalytic conversion of CO$_2$ to hydrocarbons using traditional cobalt-based Fischer-Tropsch catalysts.
(Co-Pt/γ-Al₂O₃). Three different feed gas ratios were used, i.e. H₂/CO₂ ratio of 3:1, 2:1, and 1:1. It is reported that with the cobalt-based catalyst, the products of the CO₂ hydrogenation was initially predominantly methane, however, as the hydrogen content in the feed gas was reduced the selectivity shifted towards longer chain hydrocarbons. In addition, reducing the pressure (from 450 to 150 psig) was found to reduce the conversion of CO₂ and H₂, respectively, as well as slightly lower the methane conversion, which is favorable for chain-growth probability in order to produce higher-chain hydrocarbons. Furthermore, they also discussed two possible CO₂ hydrogenation schemes, one is via direct hydrogenation of CO₂ and the other is via reversed water-gas shift reaction followed by subsequent Fischer-Tropsch Synthesis. Another interesting finding from their study suggests that the decrease in methane production as the hydrogenation reaction takes place may be partially attributed to the deactivation of methane-producing active sites of the catalyst in addition to the change in feed gas composition. Consequently, this leads to the production of longer chain hydrocarbons (above methane) being slightly increased with the increasing TOS (time on stream) regardless the H₂/CO₂ ratio. In other related study, Akin and co-workers (2002) investigated low selectivity of desired hydrocarbon products over Co/Al₂O₃ catalyst, in which the methane product of the hydrogenation reaction reached up to 70 mol %. This confirms what has been previously investigated by Riedel and co-workers (1999), stating
that using Co/MnO/SiO$_2$/Pt catalyst the methane selectivity keeps increasing upon replacing CO content in the syngas with CO$_2$, until a point where it reaches up to 95% at zero concentration of CO.$^{1, 50}$ In addition, they also reported the effect of temperature on production rates, in which during the CO hydrogenation, the rate of CO$_2$ production decreased with increasing temperature, suggesting that WGS reaction is favored. On the other hand, during the CO$_2$ hydrogenation the production rate of CO increase with increasing temperature, indicating the existence of Reversed Water-gas Shift (RWGS) reaction. Riedel and co-workers (1999) investigated a study on Fischer-Tropsch Synthesis with H$_2$/CO and H$_2$/CO$_2$ syngas by employing iron-based and cobalt-based catalysts, respectively. The study suggests that iron and cobalt catalysts exhibit different behavior in CO$_2$ hydrogenation. For iron-based catalyst, both H$_2$/CO and H$_2$/CO$_2$ syngas feed gave the same hydrocarbon product composition without any excessive methane formation. However, with the cobalt catalyst the product composition shifted from Fischer-Tropsch hydrocarbon products to almost exclusively methane upon changing the syngas feed from H$_2$/CO to H$_2$/CO$_2$. $^{1, 50}$ The different catalytic behavior of the cobalt-based catalyst on the two types of hydrogenation is attributable to the hypothesis that during the CO$_2$ hydrogenation, a low C/H ratio is obtained owing to the slow CO$_2$ adsorption on the surface, which is more favorable for the hydrogenation of surface-adsorbed intermediates, and thus, resulting in the
increase in methane formation and consequently, a decrease in chain-growth. In short, these studies suggest that the Fischer-Tropsch CO₂ hydrogenation is favored on iron-based catalyst⁵¹.

To summarize, zeolite-coated, promoted iron catalysts have not been studied in either F-T synthesis or CO₂ hydrogenation. Compared with conventional iron catalysts, such a core-shell catalyst configuration can possess a number of potential advantages including high FTS and WGS activity as well as favorable product selectivity for the production of gasoline from direct hydrogenation of CO₂. The current thesis focuses on synthesis and testing of H-ZSM coated iron catalyst for both syngas and CO₂ conversions. This study is divided into four major parts, i.e. reactor design and experimental procedure, catalysts synthesis and characterization, catalytic performance of the catalysts during CO hydrogenation, and catalytic performance of the catalysts during CO₂ hydrogenation. Details about the design of the Fischer Tropsch Synthesis reactor system and its components, including the standard operational procedures are discussed in the first part, while details on catalyst preparation procedure, including catalysts precursors used and several modified procedures used in this study as well as the characterization of the synthesized catalysts are presented in the following chapter. The next two chapters mainly discuss about the catalytic performances of the synthesized catalysts during CO and CO₂
hydrogenations, respectively. Operating conditions affecting the catalytic activity and product selectivity during the hydrogenations are discussed in these two chapters as well.
Chapter 2
Experimental

2.1. Fischer-Tropsch Reaction System

The hydrogenation reaction apparatus comprises of three major components, i.e. fixed-bed reactor, hot trap, and cold trap condensers. All the units are mounted on a 28” (length) x 24” (width) x 35” (height) supporting box. The reactor is a 0.065” thick and 0.5” outside diameter stainless steel tube, whereas the hot trap and cold trap condensers are a 0.065” thick and 1.0” outside diameter stainless steel tube. The reactor and both condensers are equipped with heat tracings to maintain the desired temperature level, with heating tapes being used in the reactor and the hot trap, and a cooling coil with refrigerant for the cold trap. The fixed-bed temperature is axially monitored using a K-type thermocouple. A backpressure regulator is installed and attached to the apparatus to maintain the pressure of the system at the desired level. A pressure relief valve is also installed in the gas line leading to the reactor inlet to ensure appropriate supply of the inlet pressure to the system.
Figure 2.1: Diagram of the Fischer-Tropsch Synthesis System
Fig. 2.1 shows the diagram of the Fischer-Tropsch Synthesis system. Reactant gases, such as CO, H₂, and N₂ enter the reactor from the gas-mixing panel attached on the supporting box. Mass flow controllers are used to control the flow of the gases. In order to determine the performance of different types of catalysts, a catalyst-inert mixture with 1:2 ratio is introduced to the fixed-bed reactor to undergo Fischer-Tropsch Synthesis reaction over a certain period of time. The resulting wax and liquid products are periodically drained from the hot trap and cold trap condensers, respectively. The outlet gases line is connected to a gas chromatography (GC, Agilent CP-490 Micro-GC) instrument that allows direct measurement of the gaseous product composition. The Micro GC instrument is equipped with a Thermal Conductivity Detector (TCD) and four sampling columns, including two Molsieve 10A, Pora Plot U, and CP-Sil 5 CB, with Argon and Helium as carrier gases. The apparatus also has a bypass line connected to it that allows unreacted gases to go to the GC instrument for inspection purpose.
2.2. Design and Principles of Fischer-Tropsch Reactor

2.2.1. Design of supporting box

The Fischer-Tropsch reactor consists of a fixed-bed reactor, a hot trap, a cold trap, a backpressure regulator, mass flow controllers, and temperature controllers. These equipments are installed on a steel-supporting box. Electronic circuits and cable connections for temperature controllers are attached on a portable panel inside the box. The diagram and dimension of the supporting box are presented in Fig. 2.2.

Figure 2.2: Diagram of supporting box
2.2.2. Design of fixed-bed reactor

The fixed-bed FTS reactor is consisted of a 304 stainless steel tube with 0.5 inch outside diameter, 12-inch height, and 0.065-inch wall-thickness. An OMEGA®STH series heating tape is wrapped around the reactor and used as a heating medium throughout the reaction. The reactor temperature is continuously monitored by a K-type thermocouple and controlled by an OMEGA®CN414-R1-R2 series temperature controller. The fixed-bed reactor is mounted on the supporting box by using saddle-type clamp holders to keep the reactor securely in place. The reactor is equipped with two safety O-rings surrounding the thermocouple in order to avoid any catalyst particle getting entrained out during the reaction. The O-rings are made of porous metal that are engineered in such a way to give maximum protection for the catalyst particles, however, still permeable enough for the gases to pass through. Two safety O-rings are used in the reactor and located at the upper part and lower part of the reactor, respectively, as shown on Fig. 2.3. The bottom part of the lower O-ring has some gas sparger holes on it in order to allow adequate supply of reactant gases.
Reactor parts

1: Thermocouple
2: Reactor tube
3: High temperature heating tape
4: Upper safety porous metal ring
5: Ceramic fiber insulation
6: Upper packing material: Glass wool
7: Catalyst bed
8: Aluminum tape
9: Lower packing material: Quartz wool
10: Lower safety porous metal ring

Figure 2.3: Schematic diagram of FTS fixed-bed reactor
2.2.3. Design of hot trap and cold trap

Both hot trap and cold trap tubes were built with stainless tubes and have the same dimension, i.e. 0.065 inch, with 1.0 inch outside diameter and 16.0 - inch tube height. The hot trap is equipped with a wide heavily insulated heating tape, OMEGA®SWH series, to provide continuous heating during the FTS catalytic test. The temperature of the hot trap is continuously monitored by a 0.25 inch K-type thermocouple mounted inside the tube and controlled by an OMEGA®CN414-R1-R2 series temperature controller. The cold trap is equipped with a copper cooling coil wrapped around it and the cold trap temperature is maintained at about 1°C at all times by continuously supplying cold water that is circulated inside the cooling coil by a Fisher® water chiller. Two types of Swagelok valves, i.e. ball valve and needle valve, are installed at the bottom of each trap for sampling purposes, as shown on Fig 2.4. Two saddle-type clamp
holders are attached onto the supporting box to securely hold the traps in place. The hot trap is typically operated at 120 °C.

2.2.4. Pressure control system

The pressure of the reactor is set constant at a certain value during the reaction by utilizing an Equilibar® Backpressure regulator (Fig. 2.5), installed at the outlet line of the cold trap and before the line enters into GC for gas analysis. The pressure of the regulator is controlled by an independent pressurized N₂ source provided from a separate gas tank with a two-stage regulator.

![Figure 2.5: Backpressure Regulator (courtesy of Equilibar®)](image)

2.2.5. Design of gas mixing panel

The gas mixing panel consists of three OMEGA®FMA5500 series MFC controlling the flow of reactant and inert gases, such as H₂, CO, CO₂, and N₂. The controllers are capable of controlling the flow of the gases within the range
of zero to 500 mL/min. Typical gas flow rates used in this study ranges from 100 to 150 mL/min, depending on the space velocity, with 10% of the flow being the inert gas, while that of other gases depending on the syngas composition used in the reaction. The flow rate of CO and CO$_2$ is controlled interchangeably by one mass flow controller depending upon the hydrogenation type. The arrangement of the gas-mixing panel is presented in Fig. 2.6.

![Figure 2.6: Arrangement of gas mixing panel](image-url)
2.2.6. Temperature controllers & electronic circuit arrangement

Temperatures of the reactor, hot trap, and the lines in between those apparatus are controlled by OMEGA®CN414-R1-R2 series temperature controllers. OMEGA®STH series heating tapes are wrapped around the fixed-bed reactor and the hot trap and used as heating elements whose temperatures are monitored by K-type thermocouples. Detailed electronic arrangement of the heating system is presented on Fig. 2.7.
There are several steps that need to be sequentially followed as part of the initial FTS reactor start-up procedure. These include GC calibration, catalyst loading, reactor leak test, catalyst activation, and FTS reaction.
2.3.1. GC Calibration

Prior to using the GC for measuring gas composition, it is important to periodically check the sensitivity and accuracy of the reading. One way of keeping the GC reading accurate is by regularly calibrating the instrument. The calibration is also required to provide the baseline for every new standard gas. The calibration procedure consists of several basic steps, such as determining the composition for each calibration level in all the four channels, performing the calibration, and evaluating the calibration results.

2.3.2. Catalyst loading

In order to avoid problems such as catalyst entrainment, gas leak from the reactor due to loosened Swagelok connections caused by catalyst particles that get trapped in between thread and nut, and other technical problems due to improper handling during the loading of the catalyst into the reactor, it is important to follow procedures to safely load the catalyst into the FTS reactor prior to running the FTS reaction. The first thing to do before the solid catalyst is loaded into the reactor is to protect the metal parts of the reactor that are in contact with the catalyst during the loading by covering them with “Parafilm”. This is done to avoid any powder particle spill that can potentially get trapped in between the thread and nut of the Swagelok connection. Two grams of solid
catalyst is physically mixed with inert material of the same size, such as aluminum oxide grit, with the mass ratio of catalyst to inert is equal to 1:2. A catalyst particle size range of 150 to 250 µm has been used since the synthesis of the first-generation core catalyst. Several different particle size of the catalysts from previous study is presented in Table 2-1.

Adequate amount of quartz wool/glass wool or ceramic fiber is put on both ends of the FTS reactor as a packing material and also to keep the catalyst bed in place. Ceramic fiber is chosen as a packing material due to its superior heat resistance and thus, making it best suited for use under high temperature condition. During this loading procedure, it is important to make sure that the catalyst is loaded into the reactor in such a way that the thermocouple tip touches the catalyst bed. Failing to do so could result in the reactor being overheated and the catalysts deactivating quickly. In addition, as previously mentioned, the reactor is also equipped with a safety porous metal o-ring surrounding the thermocouple to avoid particle entrainment during the reaction. Four OMEGA® heating tapes and heating cords are wrapped around as heating elements from the reactor all the way through the line just before the cold trap and controlled by OMEGA®CN414-R1-R2 series temperature controllers. Some layers of ceramic fiber and aluminum tape are wrapped around the heating tape
surrounding the reactor in order to provide adequate insulation during the highly exothermic FTS reaction.

Table 2.1: List of catalyst particle size from previous study

<table>
<thead>
<tr>
<th>No</th>
<th>Particle size (µm)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>850 - 1700</td>
<td>Bao Yoneyama Tsubaki (2011)</td>
</tr>
<tr>
<td>5</td>
<td>355 - 710</td>
<td>Liu Li Asami Fujimoto (2006)</td>
</tr>
<tr>
<td>6</td>
<td>37 - 74</td>
<td>Huang X et al (2011)</td>
</tr>
<tr>
<td>7</td>
<td>100 - 180</td>
<td>Jacobs et al (2007)</td>
</tr>
<tr>
<td>8</td>
<td>850 - 1700</td>
<td>Jingjiang Yoneyama Tsubaki (2005)</td>
</tr>
<tr>
<td></td>
<td>380 - 500</td>
<td>Yang Yoneyama Tsubaki (2007)</td>
</tr>
<tr>
<td></td>
<td>180 - 250</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>74 - 246</td>
<td>Li Wang Wu Lu Tsubaki (2008)</td>
</tr>
<tr>
<td>10</td>
<td>401 - 840</td>
<td>Li Asami Luo Fujimoto (2004)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Yoneyama Tsubaki (2005)</td>
</tr>
</tbody>
</table>
2.3.3. Reactor leak test

Since the Fischer-Tropsch Synthesis includes some harmful reactant gases, such as carbon monoxide (extremely hazardous) and hydrogen (flammable) and due to the fact that the reactor operates under high pressure, it is mandatory to have a “zero leak” before the FTS reaction can proceed. Once the catalyst has been loaded into the reactor, the leak test is performed over certain period of time using inert gases such as nitrogen. Some inspections and necessary adjustments on the Swagelok connections are made in case leaks still exist in the reactor and reactor lines.

2.3.4. Catalyst activation

Catalyst activation is carried out to reduce the oxides phase of the precipitated iron catalyst into metal iron ($\alpha$-Fe) and subsequently into iron carbide ($\chi$-$\text{Fe}_5\text{C}_2$), which is considered as the active phase of iron catalyst for Fischer-Tropsch synthesis. During the early stage of the research, a catalytic activation with CO was carried out at 400°C for 10 hours. However, due to some coking that was observed during the activation using this condition, a lower reduction temperature at 280°C was used since then.
2.3.5. Fischer-Tropsch Synthesis reaction

a. CO Hydrogenation

Upon completion of the catalyst activation, the reactor temperature is reduced to 180°C while nitrogen is flowed to the reactor system and let it flow for about 12 hours before the FTS reaction starts. Reactant gases, consisting of CO, \( \text{H}_2 \), and \( \text{N}_2 \) (as an inert) are sent to the reactor with certain flow rates depending upon the space velocity used and the syngas composition with which the FTS catalytic test is to be performed. The flow rates of the reactant gases are controlled by OMEGA®FMA5500 series mass flow controllers. The reactant gases sent to the reactor are previously calibrated with “Definer flow meter” before being sent to the reactor in order to give accurate information on the reading of the gas flow rates throughout the reaction. Reactor temperature is set to and maintained at 270°C for most variables of the research, while hot trap temperature is set to and maintained at 120°C using OMEGA®CN414-R1-R2 series temperature controllers. Cold trap temperature is maintained at 1°C by means of a cooling coil connected to a Fisher® water chiller. The reactor line is pressurized to 120 psi or in some cases up to 150 psi and maintained at that level during the reaction period by activating the Equilibar® back pressure regulator. Complete operating conditions for the FTS catalytic test of CO hydrogenation are summarized in Table 2.2. Sampling of gaseous products is
carried out periodically with the Micro GC to give information about product composition at certain point of time.

Table 2.2: Summary of FTS CO hydrogenation operating conditions

<table>
<thead>
<tr>
<th>No</th>
<th>Catalyst name</th>
<th>Type</th>
<th>Time on stream (hr)</th>
<th>T (°C)</th>
<th>P (psi)</th>
<th>H₂/CO ratio</th>
<th>GHSV (nL.hr⁻¹.gr cat⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>FeCuAl-K-ZSM5</td>
<td>Core-Shell</td>
<td>2.5</td>
<td>280</td>
<td>150</td>
<td>2:1</td>
<td>6.0</td>
</tr>
<tr>
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<td></td>
<td></td>
<td>5.5</td>
<td>300</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Commercial A</td>
<td>Core</td>
<td>33</td>
<td>220</td>
<td></td>
<td>2:1</td>
<td>6.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>18</td>
<td>240</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>9</td>
<td>250</td>
<td>120</td>
<td>2:1</td>
<td>6.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>18</td>
<td>270</td>
<td></td>
<td></td>
<td></td>
</tr>
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<td></td>
<td>6</td>
<td>290</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Commercial B</td>
<td>Core</td>
<td>5</td>
<td>240</td>
<td></td>
<td>2:1</td>
<td>6.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>5</td>
<td>270</td>
<td>120</td>
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<td>300</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Commercial C</td>
<td>Core</td>
<td>5</td>
<td>240</td>
<td></td>
<td>2:1</td>
<td>6.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>5</td>
<td>270</td>
<td>120</td>
<td>2:1</td>
<td>6.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>5</td>
<td>300</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>FeCuSi-ZSM5</td>
<td>Core-Shell</td>
<td>24</td>
<td>270</td>
<td>120</td>
<td>2:1</td>
<td>6.0</td>
</tr>
<tr>
<td>6</td>
<td>FeCuAl-K-01</td>
<td>Core</td>
<td>24</td>
<td>270</td>
<td>120</td>
<td>2:1</td>
<td>6.0</td>
</tr>
<tr>
<td>7</td>
<td>FeCuAl-K-02</td>
<td>Core</td>
<td>24</td>
<td>270</td>
<td>120</td>
<td>2:1</td>
<td>6.0</td>
</tr>
<tr>
<td>8</td>
<td>FeCuAl-K-04</td>
<td>Core</td>
<td>100</td>
<td>270</td>
<td>120</td>
<td>2:1</td>
<td>6.0</td>
</tr>
</tbody>
</table>
b. CO$_2$ Hydrogenation

All the catalysts used in the CO$_2$ hydrogenation are pre-treated in a similar way as they are during the CO hydrogenation, including catalyst activation. Reactant gases consisting of CO$_2$, H$_2$, and N$_2$ (as an inert) are first sent to the reactor at certain flow rates. A gas hourly space velocity (GHSV) of 6 nL per gram of catalyst was used during the first couple of runs of the experiment before the value was reduced to 3nL per gram of catalyst for the rest of the study. The CO$_2$ flow was controlled by the same mass flow controller as...
that used for controlling CO flow during the CO hydrogenation. All other operating conditions, such as pressure, temperatures of reactor and traps are maintained at the same values as those during the CO hydrogenation. Two different syngas compositions are used during the CO₂ hydrogenation in this study, i.e. H₂/CO₂ = 3:1 and H₂/CO₂ = 5:1, respectively. Complete operating conditions during the FTS CO₂ hydrogenations are summarized on Table 2.3. Product sampling is carried out using the same procedure as the previous one applied during the CO hydrogenation and is discussed in a more detailed in the following sections.

Table 2.3: Summary of FTS CO₂ hydrogenation operating conditions

<table>
<thead>
<tr>
<th>No</th>
<th>Catalyst name</th>
<th>Type</th>
<th>Time on stream (hour)</th>
<th>T (°C)</th>
<th>P (psi)</th>
<th>H₂/CO₂ ratio</th>
<th>GHSV (nL.hr⁻¹.gr cat⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>FeAl-CuK-01</td>
<td>Core</td>
<td>62 48</td>
<td>270</td>
<td>120</td>
<td>3:1 5:1</td>
<td>3.0</td>
</tr>
<tr>
<td>2</td>
<td>FeAl-CuK-01-ZSM5</td>
<td>Dry Mix</td>
<td>48 48</td>
<td>270</td>
<td>120</td>
<td>3:1 5:1</td>
<td>3.0</td>
</tr>
<tr>
<td>3</td>
<td>FeAl-CuK-02</td>
<td>Core</td>
<td>48</td>
<td>270</td>
<td>120</td>
<td>5:1</td>
<td>3.0</td>
</tr>
<tr>
<td>4</td>
<td>FeAl-CuK-02-ZSM5</td>
<td>Dry Mix</td>
<td>48</td>
<td>270</td>
<td>120</td>
<td>5:1</td>
<td>3.0</td>
</tr>
</tbody>
</table>
2.4. Product Sampling and Analysis Procedure

The products of the FTS reaction are typically present in the form of gaseous, liquid, and wax. The gaseous products are periodically analyzed on a GC to monitor the flue gas composition.

2.4.1. Sampling of gaseous products: Peak identification, Peak quantification

Sampling of the gaseous products is carried out on an Agilent 490 series Micro GC equipped with a TCD detector and four capillary columns, i.e. two Molsieve 5A columns (with Argon and Helium as a carrier gas, respectively), Pora Plot U (PPU), and CP-Sil 5 CB columns. The Molsieve columns are mainly effective to identify gases, such as H₂, O₂, N₂, CH₄, and CO, whereas the PPU and the CP-Sil columns are effective to identify CO₂ and some lower chained hydrocarbons. The analyzed gases are identified as peaks by the GC and the identified peaks are interpreted and quantified in terms of area percentage that can be converted into volume and mole percentage, respectively, which can be used to give information about the conversion of the reactants and the selectivity of the products.
2.4.2. Sampling of liquid and solid products

Sampling of liquid and solid (wax) products is carried out at the end of each FTS reaction. Two types of Swagelok valves, i.e. ball valve and needle valve, are installed at the bottom of each trap for sampling purposes. The ball and the needle valves are installed in such an arrangement that product sampling can be safely carried out at any time during the reaction without interrupting the operating conditions inside the reactor system. It can also prevent any gases inside the traps from leaking during the sampling. As mentioned previously, the flue gas form the reactor contains some toxic and flammable gases such as CO and H₂ and therefore, it is important to keep all these gases securely placed during the sampling. A double-necked sampling flask that is connected to the vent is used for sampling the liquid product. A vial is placed inside the flask and is used to collect the liquid samples. Prior to collecting the liquid samples, it is important to always make sure that the hose is tightly connected from the flask to the vent and the rubber probe is securely tightened to the flask. Once everything is ready, the ball valve is carefully opened and kept in an open position for about a minute or two. Close the ball valve afterwards and then carefully open the needle valve so that the liquid sample will start dripping.
2.5. Data Analysis Procedure

The instantaneous and average conversions of hydrogen and carbon monoxide were calculated from the following equations:

\[ X_{\text{H}_2} = \frac{F_{\text{H}_2,\text{in}} - F_{\text{H}_2,\text{out}}}{F_{\text{H}_2,\text{in}}} \quad (2.1) \]

\[ X_{\text{CO}} = \frac{F_{\text{CO},\text{in}} - F_{\text{CO},\text{out}}}{F_{\text{CO},\text{in}}} \quad (2.2) \]

\[ \overline{X}_{\text{H}_2} = \frac{\sum_{i}^{N} [(X_{\text{H}_2,i} + X_{\text{H}_2,i+1})(t_{i+1} - t_{i})]}{2tr} \quad (2.3) \]

\[ \overline{X}_{\text{CO}} = \frac{\sum_{i}^{N} [(X_{\text{CO},i} + X_{\text{CO},i+1})(t_{i+1} - t_{i})]}{2tr} \quad (2.4) \]

Where \( X \) is the instantaneous conversion at time \( t \), and \( \overline{X} \) is the average conversion of the whole run. \( F_{\text{in}} \) is the molar flowrate at the inlet of reactor (mol/min), \( F_{\text{out}} \) is the molar flowrate at the outlet of col trap (mol/min). \( N \) is the sampling number. \( \Delta t \) the sampling interval (min) and \( tr \) is the period of whole reaction (min).

The instantaneous and average selectivity of carbon dioxide and hydrocarbons were calculated from Eq. 2.5 to Eq. 2.8:

\[ S_{\text{CO}_2} = \frac{F_{\text{CO}_2,\text{out}}}{F_{\text{CO},\text{in}} - F_{\text{CO},\text{out}}} \quad (2.5) \]

\[ S_{\text{HC}} = \frac{n F_{\text{HC, out}}}{F_{\text{CO, in}} - F_{\text{CO, out}}} \quad (2.6) \]
\[
\overline{S_{CO2}} = \frac{\sum_{i}(S_{CO2,i}+x_{CO2,i+1})(t_{i+1}-t_{i})}{2\Delta t} = \frac{\sum_{i}(S_{CO2,i}+S_{CO2,i+1})\Delta t}{2\Delta t} \tag{2.7}
\]

\[
\overline{S_{HC}} = \frac{\sum_{i}(S_{HC,i}+S_{HC,i+1})(t_{i+1}-t_{i})}{2\Delta t} = \frac{\sum_{i}(S_{HC,i}+S_{HC,i+1})\Delta t}{2\Delta t} \tag{2.8}
\]

Where \( S \) and \( \overline{S} \) corresponds to instantaneous and average selectivity. \( n \) is the carbon number of hydrocarbons.

The yield of liquid and solid product was calculated from the following equations:

\[
Y_W = \frac{m_W}{14\times t \times F_{CO, in}} \tag{2.9}
\]

\[
Y_L = \frac{m_L}{14\times t \times F_{CO, in}} \tag{2.10}
\]

Where \( Y_L \) and \( Y_W \) are the yield of liquid hydrocarbons and wax, respectively. \( m_L \) and \( m_W \) are the mass of liquid hydrocarbons and wax (g), respectively. We assumed the molecular weight of hydrocarbons was 14\( n \) g/mol.
Chapter 3

Catalysts Synthesis and Characterization

This chapter discusses catalyst synthesis procedure and characterizations. As will be discussed in the following sections, both core and core shell catalysts are synthesized. Their composition, structure, morphology, and reducibility are characterized using a number of methods.

3.1. Core catalysts

The core catalysts are synthesized according to a co-precipitation method between a number of precursors, such as iron and copper nitrates as a source of metal and promoter, respectively. Aluminum nitrate is added as a source of support, while sodium carbonate is added as a source of basic precursor for ammonium hydroxide and reacts with the metal nitrates to form metal hydroxides suspension after the precipitation. Apart from the addition of potassium as a promoter, sodium carbonate can also be used to adjust the
basicity during the synthesis procedure. As previously reported, the addition of alkali metals or metal hydroxides during precipitation can improve the activity and selectivity of the catalyst.\textsuperscript{52} A number of core catalysts have been synthesized using some different preparation techniques, such as impregnation, co-precipitation, as well as some modified co-precipitation procedures. Particularly for the catalysts synthesized using co-precipitation technique, three different procedures have been carried out to date. The difference between the three procedures lies in several aspects, such as the types of precursors used, the order of which the precursors are added and mixed, and the mixing techniques. The very first-generation of the core catalysts, i.e. the catalysts synthesized using impregnation technique, were not catalytically tested in the Fischer-Tropsch reactor due to some issues, such as immature preparation technique, poor characterization results of the catalysts, and some other factors affecting the quality of the catalysts.

3.1.1. The first-generation of co-precipitated core catalysts

This early generation of preparing the core catalysts by co-precipitation technique was similar to the work of Bukur and co-workers.\textsuperscript{53-55} The core catalysts synthesized using this method include Fe/Cu/Si/K and Fe/Cu/Al/K,
respectively. In this method, iron nitrate and copper nitrate were used as the precursors for iron catalyst and Cu promoter, respectively. Potassium carbonate and potassium silicate were used as a source of K promoter and SiO$_2$ support, respectively. In the case where Al$_2$O$_3$ was used as a support, aluminum nitrate was introduced as a precursor. Furthermore, ammonium hydroxide solution was used as an alkali reactant and reacted with the nitrates precursors to form metal hydroxides precipitates. The mixing between the metal precursors and the alkali solution was carried out by pouring certain amount of the alkali solution into the heated and stirred solution of metal precursors until pH around 7.0 was achieved. After aging step, the formation of deep blue solution was visually observed in all cases during the core catalyst synthesis using this particular method. The deep blue solution came from the “cupramine” complex ion, $[Cu(NH_3)_4]^{2+}$, a byproduct from the reaction between copper hydroxide that further reacts with the ammonium hydroxide according to the following reaction:

$$Cu(NO_3)_2 + NH_4OH \rightarrow Cu(OH)_2 + NH_4NO_3 \quad (3.1)$$

$$Cu(OH)_2 + NH_4OH \rightarrow [Cu(NH_3)_4]^{2+} \quad (3.2)$$

By looking at the deep blue appearance of the cupramine complex ion solution that was formed following the precipitation step, it was easily observable that a large amount of copper has been dissolved in the solution rather than
precipitating along with iron. In order to check to what extent the decrease of the copper content due to the formation of the complex ion solution would affect the reducibility of the Cu-promoted catalyst, a number of temperature-programmed reduction (TPR) analyses using hydrogen were carried out. The TPR analysis for the FeCuK-SiO$_2$ catalyst was taken a couple of times using different samples from the same catalyst in order to keep the homogeneity of the result. From Fig. 3.1, it appears that the results are quite repeatable and consistent in terms of the reduction peak locations. The first peak appears to be typically located between 340°C and 350°C whereas the second peak appears to

![Figure 3.1: TPR Profile of FeCuK-SiO$_2$ catalyst](image)

Figure 3.1: TPR Profile of FeCuK-SiO$_2$ catalyst
be constantly located between 560°C and 580°C. The copper content in the catalyst can usually be identified by the presence of a peak that appears on the shoulder, right before the first reduction peak. Thus, in general, the copper promoter would be able to reduce the reduction temperature. However, as shown from Fig. 3.1, such peaks are insignificant, indicating copper loss. Therefore, due to the copper loss during the co-precipitation preparation of the core catalyst, some modification on the preparation procedure was performed accordingly.

3.1.2. The second-generation of co-precipitated core catalysts

The second-generation of the core catalysts prepared by co-precipitation is basically a modification from the previous generation. Some modified aspects include the type of alkali solution used, and the use of syringe pump to keep the reactants at a constant flow rate during the mixing. In the new generation, solution of sodium carbonate in water was introduced as an alkali reactant, replacing the use of ammonium hydroxide that was previously found to have prevented the copper promoter from precipitating in the catalyst. The catalysts synthesized using this modified procedure and catalytically tested in the FTS
reactor include: FeCuAl-K-01, FeCuAl-K-02, FeCuAl-K-04, and FeCuAl-K-08. The co-precipitation procedure was carried out based on the mixing between two solutions. The first solution consists of metal nitrates in water, while the second solution is the alkali solution consisting of sodium carbonate in water. Unlike the previous procedure, the formation of complex ion solution was no longer observed during the co-precipitation using this modified procedure.

Figure 3.2: XRD patterns of Fe/Al/Cu/K core materials
In order to study the effect of co-precipitation conditions, an XRD analysis was performed on core catalysts having different precipitation pH, i.e. FeAlCu·K·01 (pH = 4.75) and FeAlCu·K·04 (pH = 7.85), as shown on Fig. 3.2. As can be seen from the XRD pattern, the crystalline state of core materials is weakly affected by the co-precipitation conditions. Furthermore, a TPR analysis was also performed for each catalyst synthesized using this newly modified method in order to gain fundamental insights into the activation process and how the modification on the procedure has affected the reducibility of the catalyst. In general, precipitated iron precursors are converted to magnetite first during activation, irrespective of the gas used. For hydrogen, $\alpha$-Fe is the final iron phase. However, for CO, Hägg-carbide ($\chi$-Fe$_5$C$_2$) is the final iron species. Under the working conditions, several iron species like $\alpha$-Fe and Fe$_3$O$_4$ coexist with $\chi$-Fe$_5$C$_2$, which is believed to the active phase toward F-T synthesis. Oxidic iron species are responsible for WGS reaction. Previous studies suggest that activation under CO gives the best performance in terms of syngas conversion and methane selectivity compared to those from the H$_2$-activated or syngas-activated catalysts. In addition, CO-activated catalyst is likely to exhibit a relatively high WGS activity, which is very useful for a coal-derived syngas that has a naturally low H$_2$/CO ratio. From the TPR analysis results shown on Fig. 3.3 and Fig. 3.4 (for FeCuAl·K08 relative to the third-generation core catalysts),
as the temperature ramps up from 100 to 1000°C, iron oxides are reduced to magnetite (Fe₃O₄) and α-Fe, corresponding to two main peaks on the TPR curves, one located between 300 and 500°C and the other centered around 590°C on Fig. 3.3. Our findings suggest that the pH at which the precipitate was aged significantly affects the reduction behavior. Particularly, as the pH increases from 4.75 to 6.98, the lower reduction peak’s temperature appears shifting from 407 to 342°C. As previously mentioned, the pH has little effect on the crystalline state of iron oxides. Thus, the favorable reduction condition is not determined by the nature of certain iron species that are present in the catalyst but rather, it has more to do with the concentration of the promoters. As the pH increases, more copper will precipitate from the solution, resulting in a higher Cu content of the catalyst. It is well known that Cu can promote the reduction of iron compounds during the pretreatment, most likely because of hydrogen spillover from the Cu surface to the iron oxide surface.

Furthermore, it can be seen that no significant change was observed in terms of the location of the reduction peaks of the three catalysts shown on Fig. 3.3 compared to the results from the previous catalysts, except the location of the first peak of FeCuAl-K-01 that exhibits a slightly higher reduction temperature compared to the other catalysts, indicating that the catalyst could potentially result in a lower catalytic performance during the FTS testing compared to that
of other catalysts. As for the FeCuAl-K-08 catalyst, the reduction peaks have significantly shifted towards higher temperature, mainly attributed to the relatively low pH of the catalyst during the synthesis, i.e. below 4.

![Figure 3.3: Reduction in H₂ for catalysts prepared with modified procedure](image)

Figure 3.3: Reduction in H₂ for catalysts prepared with modified procedure

In addition to the location of the reduction peaks, one important thing to notice is the presence of smaller peak appearing on the shoulder of the first reduction peak of almost all the modified catalysts, suggesting that copper has been successfully incorporated into these catalysts. These “shoulder peaks”, however,
were only observed in some of the newly modified catalysts, such as FeCuAl-K-02 and FeCuAl-K-04, respectively. The one spotted on the FeCuAl-K-01’s first peak’s shoulder was actually located after the taller peak showed up, thus, requiring further investigation since we were not sure whether it corresponds to copper or other element.

Figure 3.4: TPR profile of 2\textsuperscript{nd} generation vs 3\textsuperscript{rd} generation catalysts
3.1.3. The third-generation of core catalysts: FeAl-CuK-01 & FeAl-CuK-02

The modified co-precipitation procedure carried out to prepare the second-generation core catalysts has indicated some promising results in terms of successfully incorporating copper promoter into the core catalysts. Even though from the TPR analysis results copper peaks were observable only in some of the core catalysts prepared by the second-generation procedure, at least no more formation of complex ion solution, and thus, no sign of copper loss, was observed. In order to increase the consistency level of keeping the copper in the core catalysts as well as to improve the reduction temperature, some further modifications have been made to the second-generation co-precipitation procedure. These modifications include the use of ammonium hydroxide, replacing sodium carbonate as a source of base solution. The difference here is that in this newest generation, the copper promoter was added to the catalyst mixture at a later stage of the synthesis compared to the previous preparation procedure. Instead of being added to the metal nitrates solution before the contact with the alkali solution, in this latest generation the copper nitrate was added to the dried metal hydroxide precipitates. The reason to modify the order of precursor addition is to minimize the risk of losing the precipitated copper
during filtration and washing steps since copper would play an important role in reducing the reduction temperature and thus, maximizing the formation of iron carbide species, which has been considered to provide active sites for catalyzing the Fischer-Tropsch Synthesis. A solution containing copper nitrate and potassium nitrate, as a K-promoter precursor, was prepared before certain amount of dried metal hydroxide precipitates was added into it. This is done to avoid direct contact between copper nitrate and ammonium hydroxide that could result in the formation of copper-intensive complex ion solution, just as the case with the previous generation catalysts. Furthermore, no modification was made in terms of mixing procedure. The nitrates solution and the alkali solution were still continuously contacted each other at a continuous constant flow by means of syringe pump to form the precipitates, the exact same procedure used in the previous generation.

The catalysts synthesized with this latest generation procedure were also used to make the structured modified catalysts, such as dry-mixed and core–shell, and therefore, their catalytic performances can be directly compared. Two core catalysts with different pH, i.e. FeAl·CuK·01 and FeAl·CuK·02, respectively, were synthesized using this latest co-precipitation procedure. The former has a pH of 9.4 while the latter is a little less alkaline, with a pH of 8.4. Characterization of the two catalysts using the temperature-programmed
reduction (TPR) conducted in H₂ as shown in Fig. 3.3, suggests that the more alkaline catalyst (FeAl·CuK-01) exhibits a slightly lower reduction temperature compared to its more acidic counterpart. This may indicate that the alkaline catalyst has potential to be more catalytically favorable than the acidic catalyst. The catalytic testing in the FTS reactor has been carried out to determine the catalytic performance of the two catalysts synthesized with the third-generation procedures and the complete results are presented in the next chapter.

3.2. Dry-mixed Catalysts

Incorporating zeolite into iron-based Fischer-Tropsch catalysts has been considered to be one effective way of designing a multifunctional catalyst for direct conversion of iso-paraffin from coal-based syngas. A number of method to accommodate the addition of zeolite into the iron-based FTS catalysts have been previously studied. Physically mixing the zeolite with the iron-based catalysts appears to be one of the most practical and convenient way to do the job. A number of efforts to physically mix the zeolite and the iron-based catalysts have been carried out, and the resulted dry mix catalysts have been catalytically tested in the FTS reactor.
3.2.1. The first-generation of physical mixing catalyst: binder-facilitated dry-mixed

The first attempt to physically mix the zeolite with the iron-based catalysts was carried out by incorporating the use of aluminum hydroxide as a "chemical binder" during the mixing process. A weight portion of 4 : 2 : 1 between iron-based catalyst : zeolite : binder was used during this mixing process. A minimum amount of water was added to the dry-mixed powder to help facilitate the mixing. The slurry-like mixture was then heated under 120°C for 12 hours and calcined accordingly at 300°C for 5 hours. The final dry mix catalyst was tested in the temperature-programmed reduction (TPR) to determine its reducibility profile in hydrogen, shown in Fig. 3.5 is the TPR analysis result.
The TPR profile of both the core and the dry mix catalysts suggests that the mixing process does not significantly affect the reducibility of the catalyst, with the dry-mixed catalyst’s reduction peaks only slightly shifting to the left and causing the reduction to shift to lower temperatures. The reduction peaks shift to lower temperatures might be attributed to the strong bond between the iron-based catalyst, the zeolite, and the aluminum hydroxide binder that could potentially affect the pH of the mixture and thus, eventually bringing down the reduction temperature.

Figure 3.5: Reducibility profile in H$_2$ of FeAl-CuK-01 core vs. FeAl-CuK-01-ZSM5 dry mix
3.2.2. The second-generation of physical mixing catalyst: binder-less dry-mixed

With the binder-based dry-mixed catalyst exhibiting a low catalytic performance, the following generation of the physically mixed catalyst was prepared in the absence of any chemical binder. The iron-based catalyst and the zeolite were physically mixed directly without any additional precursors or treatments. The iron-based catalyst used was FeAl-CuK-02 and the dry-mixed catalyst was FeAl-CuK-02-ZSM5-DM. The final mixture of the catalyst was

![TPR Profile]

Figure 3.6: Profile of reducibility in H\textsubscript{2} for FeAl-CuK-02-core vs FeAl-CuK-02-ZSM5-dry mix
characterized for its reducibility in hydrogen using the temperature-programmed reduction (TPR) and the profile is shown in Fig. 3.6. From the TPR profile, it can be seen that no significant change in terms of the reduction peak temperature was observed for the dry-mixed catalyst compared to the core catalyst. This suggests that the direct physical mixing between the iron-based catalyst and the zeolite has no significant effect on the catalyst reducibility.

3.3. Core-Shell Catalysts

While physically mixing the Fischer-Tropsch catalyst with that of hydrocracking and isomerization can actually suppress the formation of longer-chained hydrocarbon as well as increase the selectivity of branched paraffins to some extent, the performance can still be improved. For the iron-zeolite dry-mixed catalysts, the active sites are scattered around and randomly distributed on the surface of the catalysts, which leads to unrestricted reaction sites that allow both FTS reaction and hydrocracking & isomerization reaction to occur randomly and independently. This suggests that there is a chance for the FTS products to leave the catalyst surface directly without further reacting with the active sites of zeolite. In addition to physically mixing the metal-based FT and zeolite catalysts, a number of other research studies have attempted to
synthesize the bifunctional metal/zeolite catalysts in a different format, i.e. by utilizing an FT catalyst supported on zeolite for the direct production of isoparaffins. However, this method resulted in a substantially low CO conversion and low degree of reduction due to the extremely strong interaction between the metal and the zeolite as a support. The ease of migration and mobility of the FTS products appears to play important roles in determining the successful formation of middle iso-paraffin hydrocarbons. To foster this concept, a novel multifunctional catalyst with core shell structure has been introduced. The core part consists of conventional FTS catalysts while the shell comprises a layer of H-type zeolite enwrapping the core. The syngas passes through the shell to reach the core catalyst and eventually undergo FTS reaction to form linear paraffins. Prior to leaving the catalysts, all the linear paraffins must first pass through the zeolite shell and that is where hydrocracking and isomerization reactions take place and the linear paraffins have a better chance of getting converted into iso-paraffins on the acidic sites of zeolite. Owing to its ability to improve the collision possibility between linear paraffins and zeolite acidic sites, the core shell catalyst is expected to give higher selectivity towards iso-paraffins compared to the physically mixed catalyst.
3.3.1. First-generation core-shell catalysts

Our works to coat the zeolite onto the iron-based catalysts in a core-shell structure were mostly based on the work of the Japanese group (Tsubaki and co-workers). A number of modifications to improve the quality of the core-shell catalysts and their catalytic performances have been made in terms of the synthesis procedure and types of precursors used. The first-generation of the core-shell catalysts were synthesized via a hydrothermal synthesis method adapted from the work of Tsubaki and co-workers. Some general precursors such as de-ionized water, ethanol, tetra propyl ammonium hydroxide (TPAOH), tetra ethyl ortho silicate (TEOS), and aluminum nitrate were commonly used in synthesis of ZSM-5. Water and ethanol are used as a solvent, while TPAOH, TEOS, and aluminum nitrate are introduced as a structure template, source of silica, and source of alumina, respectively. A gel solution was obtained after adding all the precursors and keeping the solution stirred over certain period of time.

The iron-based catalyst was added as a “core” to the gel solution right before a hydrothermal synthesis was carried out inside a metal hydrothermal reactor that was typically heated for 48 hours at 180°C. The hydrothermal reactor was periodically rotated every 2 hours with a rotational speed of 2 rpm. Washing,
filtration, drying, and calcination steps are following at the end of the hydrothermal synthesis. More details on the synthesis procedure and characterization of this core-shell catalyst are presented elsewhere in the previous chapter. Two core-shell catalysts have been synthesized using this early generation preparation procedure, namely FeCuSi-K@ZSM5 and FeCuAl-K@ZSM5, with the former incorporating silica and the latter using alumina as a support. The core parts for these core-shell catalysts, i.e. FeCuSi-K and FeCuAl-K, respectively, were synthesized using the first-generation of the core catalyst preparation procedure. Some characterization tests have been done to determine the status of the catalysts. Some SEM images have been taken for both core-shell catalysts and shown in Fig. 3.7 and Fig. 3.8, respectively. SEM images for both catalysts suggest that zeolites have been successfully grown on the surface of the iron-based catalysts using this procedure. However, it is also noticeable from the SEM images of both core-shell catalysts that some particles are only partially coated by the zeolites. As far as reducibility of the catalyst, as shown from Fig. 3.9 for the alumina-supported catalyst, having the zeolites coated on the iron-based catalyst has reduced the reduction temperature of the core catalyst for some reasons. The incorporation of zeolites into the core catalyst using hydrothermal synthesis method was found to give an additional peak during the TPR analysis.
Figure 3.7: SEM images for FeCuSi-K@ZSM5 core-shell catalyst
Figure 3.8: SEM images for FeCuAl-K@ZSM5 core-shell catalyst
3.3.2. Modified first-generation core-shell catalyst:

FeCuSi@ZSM5

At this stage, attentions are focused on how to find the most optimum method to uniformly coat the iron-based core with the zeolites shell that can lead to an improved catalytic performance of the core-shell catalyst. Following the
previous success in growing the zeolites on the surface of iron-based catalysts, another core-shell catalyst has been attempted to synthesize using the same preparation procedure as before. The only difference was the order of which the precursors were added to make the gel solution. In this modified procedure, the iron-based core was added at an earlier step to the mixture.

Instead of being added to the final solution when the gel has been formed, the core was added to the first solution containing water, ethanol, and TPAOH, followed by subsequent stirring over certain period of time. After one hour, TEOS was added to the first solution under constant stirring condition and let stirred for another three hours before aluminum nitrate was added to the second solution. This modification was done to allow longer contact period between the core and the structure template (TPAOH) that was expected to be able to result in a more uniform zeolite coating on the core catalyst. A mass ratio of 3:4 of core versus shell was introduced during the synthesis. Some characterization tests, such as XRD, TPR, and SEM were carried out before a catalytic test on FTS reactor was performed.
Results from SEM images shown on Fig. 3.10 suggest that zeolites are successfully grown on the core catalyst and appear more evenly distributed compared to the previous generation of the core-shell catalysts. From Figure 3.11 (a), the hydrothermal synthesis method used to prepare the core-shell catalyst seems to have affected the reduction temperature of the catalyst, causing it to shift to a slightly higher temperature. However, the increase in the reduction temperature does not appear to be a significant one, thus, should not substantially affect the catalytic performance of the catalyst. In order to prove this, a catalytic test on the FeCuSi@ZSM5 has been carried out at 270°C and 120 psi.
3.3.3. Second-generation core-shell catalyst: Dry gel

In order to keep improving the quality of the core-shell catalyst, especially in terms of the ability to uniformly coat the zeolites on the surface of the iron-based catalyst, some modifications in the preparation method have been done, such as the introduction of dry gel method during the mixing step prior to the hydrothermal synthesis. While keeping the previous procedure remain the same as before in terms of the order of precursor’s addition to the mixture, the modification done on the mixing procedure includes an additional drying step.
after the gel solution is formed in order to form a “dry gel”. This is essentially carried out by placing the Teflon container, in which all the precursors were mixed, inside a heated beaker containing the mixture of water and ethylene glycol while keeping the solution stirred until all the water content was vaporized and a paste-like gel was formed. The heater temperature was set at 65°C under 600 rpm rotational speed, and typically kept for 5 to 8 hours before the dry gel started to form. The dried gel was then put inside the hydrothermal reactor to go through a hydrothermal synthesis at 180°C, typically over 48-hour period. Once the hydrothermal synthesis was completed, the final coated catalyst was washed and filtered, dried, and calcined, before being activated in-situ in CO and catalytically tested in the FTS reactor. Some characterizations, including SEM, XRD, and TPR have also been done accordingly.
Figure 3.12: SEM images for FeAl-CuK-01@ZSM5 core-shell catalyst

Figure 3.13: XRD Spectra for FeAl-CuK-01-based catalysts
As shown from Fig. 3.12, some of the SEM images collected for the core-shell FeAl-CuK-01@ZSM5 exhibit the formation of a thick and fluffy zeolites shell was observed in almost all parts throughout the sample, thus, making it hard to be visually able to spot the core part of the catalyst. This indicates that a massive zeolites formation have been uniformly covering the iron-based core catalyst, suggesting that the latest dry gel-based procedure to coat the zeolites on the iron-based core catalyst seems promising. The formation of zeolites on the core catalyst has also been confirmed from the XRD spectrum results of the FeAl-CuK-01-based catalysts, as shown in Fig. 3.13. Furthermore, the reducibility of

Figure 3.14: Reducibility Profile in H₂ for FeAl-CuK-01-based catalysts
the zeolite-coated catalysts does not seem to be much affected by the presence of zeolite shell, in which only a slight increase in reduction temperature was observed in both core-shell catalysts synthesized based on the dry gel method, as shown from Fig. 3.14 and Fig. 3.15, respectively.

Figure 3.15: Reducibility Profile in H₂ for FeAl·CuK·02-base catalysts
3.3.4. Zeolite shell coated on commercial catalysts

Following the promising results demonstrated from the first-generation core-shell catalysts in terms of growing the zeolites shell on the surface of iron-based core, some attempts have been made to coat the shell on the surface of commercial catalysts as well. Commercial catalyst A was used as a core catalyst and a hydrothermal synthesis method based on the first-generation preparation procedure was used to grow zeolites and coat it onto the core catalyst.

![Figure 3.16: (a) Reducibility in H₂ (b) XRD spectra for Comm-A@ZSM5 core-shell](image)

Figure 3.16: (a) Reducibility in H₂ (b) XRD spectra for Comm-A@ZSM5 core-shell
Results from the catalytic characterization shown on Fig. 3.16 suggest that zeolite has been successfully grown in this trial. However, SEM images collected on the core-shell sample, shown on Fig. 3.17, suggest a separate phase between the core and the zeolite was clearly observed, indicating that there is no or very limited interaction between the commercial A core and the zeolites formed. The commercial A – zeolites mixture looks more like the dry-mixed catalyst in terms of physical appearance rather than a core-shell catalyst. This problem seems to be attributed to the physical structure of the Commercial A core catalyst that for some reasons has prevented the zeolites shell from coating onto it. Due to the unsuccessful effort to coat the Commercial A catalyst with zeolites, no catalytic test was carried out on the catalyst.

Figure 3.17: SEM images on Comm-A@ZSM5 core-shell
Chapter 4
Catalytic Performance:
Part I – CO Hydrogenation

4.1. Fischer-Tropsch Catalytic Performance

The performance of the catalysts with respect to Fischer Tropsch Synthesis (FTS) and other related reactions, such as water-gas shift (WGS), reversed water-gas shift (RWGS), hydrocracking and isomerizations are presented in terms of catalytic activity and selectivity towards certain products, respectively. Catalytic activity is presented in terms of several parameters, such as conversion with respect to carbon monoxide and hydrogen reactants for CO hydrogenation, and to carbon dioxide and hydrogen for the direct hydrogenation of CO₂. Product distributions resulted from the FTS and other refining reactions using each catalyst is presented and their patterns are analyzed based on the theoretical Anderson-Schulz-Flory (ASF) Distribution. The resulting product distribution from the CO hydrogenation is also used to analyze the effectiveness of combining the conventional FTS catalyst (iron-based) with that for refinery
purposes (zeolites). Two different methods of incorporating the zeolites into the FTS’ iron-based catalyst, i.e. physical mixing and core-shell structured, respectively, are comparatively evaluated based on the performance of the catalysts and the resulting product distributions. Some results from the catalysts’ characterization, especially from the reducibility analysis using TPR and morphology observation using SEM, which are related to their catalytic performances are included in the discussion section throughout this chapter, even though information about synthesis procedure of the catalysts and their characterizations are presented in more details in the previous chapter. Even though the reducibility analysis was only performed with hydrogen throughout this research, we believe the same trend would apply to the case where the catalyst is activated in CO. Precipitated iron precursors are typically converted into magnetite first during activation, irrespective of the gas used. α-Fe is the final iron phase if hydrogen is used to activate the iron precursors. However, in the case where CO is introduced during the activation process, Hägg-carbide (χ-Fe5C2) would be the final iron species.13 Under the working conditions, several iron species, such as α-Fe and Fe3O4 coexist with χ-Fe5C2, which is believed to be the active phase for the FTS synthesis. Iron oxides species are responsible for WGS reaction.26 Previous studies suggest that activation under CO yields the best performance in terms of syngas conversion and methane selectivity compared to activating the catalyst with hydrogen or syngas. 13 In addition, the
final catalyst exhibits a relative high WGS activity. This is very useful for a coal-derived syngas, which has a low H₂/CO ratio. For example, Illinois coal was used as the starting carbon source, in which the syngas produced in the entrained flow gasifier has a H₂/CO ratio of 0.45 to 0.7. This ratio is by far lower than the stoichiometric ratio of ~ 2 for typical F-T reactions. Therefore, Fe-based catalysts were activated in CO atmosphere throughout this research.

4.1.1. Core catalysts

A number of catalysts that are used as a base catalyst in this study have been synthesized by employing several different preparation procedures and have also been catalytically tested accordingly in the FTS reactor. As mentioned in the previous chapter, preparation procedure such as incipient wetness impregnation was used in the early generation of the core catalyst preparation. However, due to the unsuccessful results, no further steps were carried out on the catalysts. Similar case was observed with the core catalysts prepared with the first-generation co-precipitation procedure. While iron-based catalysts have been successfully synthesized using the procedure, it is the copper loss problem that has apparently become a major drawback.
4.1.1.1. Second-generation core catalysts

Catalytic tests using the FTS reactor have been carried out to determine the catalytic performance of the newly synthesized catalysts and the results are summarized on Table 4·1.

### Table 4.1: Summary of reducibility and catalytic performance of core catalysts

<table>
<thead>
<tr>
<th>Core Catalyst</th>
<th>pH</th>
<th>1st peak of reduction (C)</th>
<th>Conversion (%)</th>
<th>Selectivity (%)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>CO</td>
<td>H₂</td>
<td>CO₂</td>
</tr>
<tr>
<td>FeCuAlK-01</td>
<td>4.75</td>
<td>407</td>
<td>24.32</td>
<td>10.72</td>
<td>28.44</td>
</tr>
<tr>
<td>FeCuAlK-02</td>
<td>5.85</td>
<td>342</td>
<td>40.63</td>
<td>18.95</td>
<td>30.05</td>
</tr>
<tr>
<td>FeCuAlK-04</td>
<td>6.98</td>
<td>295</td>
<td>17.23</td>
<td>10.39</td>
<td>30.30</td>
</tr>
<tr>
<td>FeCuAlK-08</td>
<td>3.8</td>
<td>447</td>
<td>12.52</td>
<td>10.76</td>
<td>31.49</td>
</tr>
</tbody>
</table>

Operating conditions: T = 270°C, P = 120 psi, H₂/CO = 2:1, space velocity = 6.0 L. hr⁻¹. (gr cat.)¹

Table 4.1 summarizes the catalytic performance of several core catalysts synthesized based on the second-generation co-precipitation procedure. The third column of Table 4.1 refers to the first peak that shows up during the reduction in hydrogen using temperature-programmed reduction (TPR). The conversions
presented on the Table 4.1 are based upon the average values for certain period of reaction time. Thus, at some points during the reaction course, higher values of syngas conversions were observed. The yield of oil and wax are based on the organic oil and wax products, respectively, that are collected at the end of every reaction batch. Particularly for the wax product, the collected sample at the end of the reaction does not necessarily correspond to the actual wax for that particular batch. In some cases, some residual wax is left over from the previous reaction batch and thus, contributing to the added amount of wax collected from the following batch. Draining the wax product from the hot trap at the end of the reaction can be somewhat tricky at the earlier stage of the experiment since the wax tends to stick strongly to the hot trap tube wall, especially when some very long chained hydrocarbon waxes are formed. As shown from Table 4-1, results
from all the tested catalysts suggest that more favorable catalytic performances towards some products were observed if catalysts with higher pH are used. Except for the FeCuAl-K-04 catalyst, the higher the pH of the catalysts the higher CO conversions were obtained. This confirms a direct correlation between catalytic activity and the level of acidity of the catalyst. However, the hydrogen conversion did not seem to necessarily follow the trend, as it is also strongly affected by the presence of hydrogen product from water-gas shift reaction. The selectivity of CO$_2$ and CH$_4$ also do not seem to follow the trend. The carbon
dioxide resulted during the reaction mainly corresponds to the activity of the water-gas shift reaction. Since the catalytic tests on these catalysts, except FeCuAl-K-04, were only carried out for not longer than 24 hours, it is hard to tell whether the steady reaction has been really achieved. As shown from Fig. 4.1, the syngas conversion for FeCuAl-K-01 appears progressively heading towards steady-state condition over the FTS reaction period with no significant fluctuation in terms of conversion was observed. The conversion of FeCuAl-K-02 seems to progressively keep increasing over time, however, the rate seems to slow down towards 24 hour period, thus, it can be assumed to be nearing the steady-state condition. FeCuAl-K-08 exhibits the lowest catalytic activity among the second-generation core catalysts due mainly to the low pH of the catalyst, as discussed above.

Particularly for FeCuAlK-04 catalyst, some unexpected technical problems occurred during the FTS reaction that might have had a significant effect on the overall catalytic performance of the catalyst. These include fluctuation in the hydrogen flow going to the FT reactor about four hours after the start-up of the reactor, which most likely is caused by the flow instability of the mass flow controller under the pressurized reactor system. Resetting the hydrogen mass flow controller’s set point back to the desired value might have affected the overall equilibrium of the ongoing reaction. As can be seen from Fig. 4.2, the
Syngas conversion appears to be on an increasing trend over the first four hours of the reaction before a sharp decrease of the conversion was observed and from that point on the conversion remained relatively steady at a lower level over the rest of the reaction course. Thus, based on the overall trend and the finding about the malfunctioned mass flow controller, it is worthwhile considering that the FeCuAlK-04 catalyst could have catalytically performed better than its actual performance if the technical problem did not take place during the reaction.

![Syngas Conversion for FeCuAlK-04](image)

Figure 4.2: Syngas conversion over time of FeCuAlK-04 catalyst
4.1.1.2. The third-generation of core catalysts: FeAl-CuK-01 & FeAl-CuK-02

The catalytic testing in the FTS reactor has been carried out to determine the catalytic performance of the two catalysts synthesized with the third-generation procedure.

![Figure 4.3: Syngas conversion profile over time for FeAl-CuK-01 and FeAl-CuK-02](image-url)
The FeAl·CuK-01 and FeAl·CuK-02 catalysts have been tested for about 50 hours in the FTS reactor and the syngas conversion profile over time for each catalyst is presented in Fig. 4.3, providing information about the effect of different catalyst pH on the catalytic activity. Results of the FTS catalytic testing on the two catalysts under some different operating conditions is summarized in table 4.2. Two different syngas compositions, i.e. H\textsubscript{2}/CO = 1:1 and H\textsubscript{2}/CO = 2:1, respectively, were introduced during the FT synthesis catalytic performance test for both catalysts over certain period of time.

The conversion presented on Fig. 4.3 was based on the syngas ratio of H\textsubscript{2}/CO = 2:1. As indicated from the figure, the FeAl·CuK-02 catalyst exhibits a higher syngas conversion compared to that of the FeAl·CuK-01. Despite having a less alkaline pH, i.e. 8.4 versus 9.4 (for FeAl·CuK-01), the FeAl·CuK-02 catalyst was found to be more catalytically favorable in terms of activity. This appears contradictory from the trend discussed in the previous section. Further discussion regarding this condition is presented in the later section.

The profiles of the syngas conversion over time for different catalysts under different syngas compositions are presented in Fig. 4.4 and Fig. 4.5. The reduced hydrogen to carbon monoxide ratio introduced to the reactor during the FT synthesis catalytic performance test (H\textsubscript{2}/CO = 1:1) was intended to give useful
information about the actual condition of CO-rich coal based syngas, in which the iron-based catalysts are expected to give a better catalytic performance over other FTS catalysts, such as cobalt. For the FeAl·CuK-02 catalyst, stoichiometric syngas composition exhibit a higher conversion with respect to syngas compared to the case where 1:1 syngas ratio was used during the catalytic FTS testing.

Table 4.2: Summary of FTS catalytic testing on FeAl·CuK-01 and FeAl·CuK-02

<table>
<thead>
<tr>
<th>Core Catalyst</th>
<th>H₂/CO ratio</th>
<th>Conversion (%)</th>
<th>Selectivity (%)</th>
<th>Yield (%)</th>
<th>α-value</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>CO</td>
<td>H₂</td>
<td>CO₂</td>
<td>CH₄</td>
</tr>
<tr>
<td>FeAl·CuK-01</td>
<td>1:1</td>
<td>24.52</td>
<td>19.69</td>
<td>37.10</td>
<td>3.72</td>
</tr>
<tr>
<td>FeAl·CuK-01</td>
<td>2:1</td>
<td>40.26</td>
<td>12.91</td>
<td>46.52</td>
<td>9.57</td>
</tr>
<tr>
<td>FeAl·CuK-02</td>
<td>1:1</td>
<td>28.57</td>
<td>19.51</td>
<td>38.65</td>
<td>3.11</td>
</tr>
<tr>
<td>FeAl·CuK-02</td>
<td>2:1</td>
<td>69.01</td>
<td>30.90</td>
<td>35.08</td>
<td>6.55</td>
</tr>
</tbody>
</table>

Operating conditions: T = 270°C, P = 120 psi, space velocity = 3.0 L. hr⁻¹. (gr cat.)⁻¹

With regards to selectivity towards carbon dioxide and methane, there seems to be no exact pattern on how different pH of the catalyst and different syngas composition would affect the selectivity of CO₂ and CH₄, respectively. High CO₂ selectivity of all the catalysts presented on Table 4.2 is an indicator that high activity of water-gas shift reaction has occurred. However, there is no exact clue
on how the CO₂ selectivity would behave under different pH and different syngas composition as the trend from the catalytic testing results appear to be scattered. With regards to different syngas ratio, the use of non-stoichiometric syngas ratio, i.e. H₂/CO = 1:1, would trigger the production of additional hydrogen from WGS reaction to make up for the hydrogen deficit before stoichiometric Fischer-Tropsch Synthesis can proceed. In this case, the use of iron-based catalyst would be best as the catalyst has a high activity towards the WGS reaction. Therefore, the use of 1:1 syngas ratio would be theoretically more likely to result in a high CO₂ selectivity due to the more intense WGS reaction as

![Figure 4.4: Syngas conversion over time of FeAl-CuK-01 at different syngas composition](image-url)
opposed to where stoichiometric syngas ratio was employed. The use of non-stoichiometric syngas ratio could also theoretically affect the formation of methane. The abundance of hydrogen in the reactant would favor the production of lower chain hydrocarbons, particularly methane. Thus, having a restricted amount of hydrogen in the reactant could result in a lower methane production. With regards to pH, the effect of different pH of the catalysts will be discussed in the later section of this chapter.

Figure 4.5: Syngas conversion over time of FeAl-CuK-02 under different syngas composition
4.1.1.3. Commercial catalysts

In order to figure out the performance our own iron-based core catalysts compared to the commercial catalysts used in industry, several commercial catalysts have been catalytically tested in the FTS reactor under some different operating conditions. Three different commercial catalysts, namely Commercial A, B, and C have been tested in the FTS reactor at various temperatures ranging from 220°C to 300°C for certain period of time and the results are presented in Table 4.3.
Table 4.3: Summary of FTS catalytic testing on commercial catalysts

<table>
<thead>
<tr>
<th>Core Catalyst</th>
<th>T (°C)</th>
<th>Conversion (%)</th>
<th>Selectivity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>CO</td>
<td>H₂</td>
</tr>
<tr>
<td>Commercial A</td>
<td>220</td>
<td>1.75</td>
<td>0.89</td>
</tr>
<tr>
<td>Commercial A</td>
<td>240</td>
<td>7.12</td>
<td>3.92</td>
</tr>
<tr>
<td>Commercial A</td>
<td>250</td>
<td>24.74</td>
<td>13.35</td>
</tr>
<tr>
<td>Commercial A</td>
<td>270</td>
<td>26.94</td>
<td>6.29</td>
</tr>
<tr>
<td>Commercial A</td>
<td>290</td>
<td>75.07</td>
<td>27.12</td>
</tr>
<tr>
<td>Commercial B</td>
<td>240</td>
<td>16.36</td>
<td>10.00</td>
</tr>
<tr>
<td>Commercial B</td>
<td>270</td>
<td>23.58</td>
<td>16.57</td>
</tr>
<tr>
<td>Commercial B</td>
<td>300</td>
<td>71.17</td>
<td>31.01</td>
</tr>
<tr>
<td>Commercial C</td>
<td>240</td>
<td>22.17</td>
<td>14.72</td>
</tr>
<tr>
<td>Commercial C</td>
<td>270</td>
<td>36.41</td>
<td>24.00</td>
</tr>
<tr>
<td>Commercial C</td>
<td>300</td>
<td>66.56</td>
<td>34.56</td>
</tr>
</tbody>
</table>

Operating conditions: P = 120 psi, H₂/CO = 2:1, space velocity = 6.0 L. hr⁻¹. (gr cat.)⁻¹

The average CO conversion during FTS catalytic testing for all the core catalysts is presented in Fig. 4.6. In general, the catalysts synthesized using the latest generation preparation procedure exhibit superior activity in terms of CO conversion compared to other catalysts synthesized with previous generation...
procedure, except for the FeCuAl-K-02, that has quite a comparable activity with its later generation counterparts. The latest-generation catalysts also appear more catalytically active than all the commercial catalysts tested, suggesting a promising method has been applied in terms of preparation procedure for core catalyst.

Figure 4.6: Average CO conversion of different core catalysts
(Operating conditions: T = 270°C, P = 120 psi, H₂/CO = 2:1)
4.1.2. Dry-mixed Catalysts

Incorporating zeolite into iron-based Fischer-Tropsch catalysts has been considered to be one effective way of designing a multifunctional catalyst for direct conversion of iso-paraffin from coal-based syngas. A number of methods to accommodate the addition of zeolite into the iron-based FTS catalysts have been previously studied. Physically mixing the zeolite with the iron-based catalysts appears to be one of the most practical and convenient ways to do the job. A number of efforts to physically mix the zeolite and the iron-based catalysts have been carried out, and the resulted dry mix catalysts have been catalytically tested in the FTS reactor.

4.1.2.1. First-generation physical mixing catalyst: Binder-facilitated dry-mixed

In order to figure out the catalytic performance of this binder-facilitated dry-mixed catalyst, a catalytic test has been carried out in the FTS reactor. Two different syngas compositions were used during the catalytic FTS test, i.e. H₂/CO = 1:1 and H₂/CO = 2:1, respectively. On both cases, as shown from Fig. 4.7 and Fig. 4.8, the syngas conversion of the core catalyst was about
two times higher than that of the dry-mixed catalyst with 2:1 syngas composition, and about three times higher when H₂/CO ratio of 1:1 was used. Other information from the FTS catalytic testing is summarized in table 4.4.

Figure 4.7: Syngas conversion of FeAl·CuK-01 core vs. FeAl·CuK-01·ZSM5·dry mix at H₂/CO = 1:1
Table 4.4: Summary of FTS catalytic testing on FeAl-CuK-01 core & FeAl-CuK-01-ZSM5 DM

<table>
<thead>
<tr>
<th>Core Catalyst</th>
<th>Type</th>
<th>H₂/CO ratio</th>
<th>Conversion (%)</th>
<th>Selectivity (%)</th>
<th>Yield (%)</th>
<th>α-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeAl-CuK-01</td>
<td>Core</td>
<td>1:1</td>
<td>24.52</td>
<td>19.69</td>
<td>37.10</td>
<td>3.72</td>
</tr>
<tr>
<td></td>
<td>Dry-Mix</td>
<td>1:1</td>
<td>7.76</td>
<td>7.98</td>
<td>22.67</td>
<td>4.14</td>
</tr>
<tr>
<td>FeAl-CuK-01-ZSM5</td>
<td>Core</td>
<td>2:1</td>
<td>40.26</td>
<td>12.91</td>
<td>46.52</td>
<td>9.57</td>
</tr>
<tr>
<td></td>
<td>Dry-Mix</td>
<td>2:1</td>
<td>17.33</td>
<td>11.93</td>
<td>20.27</td>
<td>6.69</td>
</tr>
</tbody>
</table>

Operating conditions: T = 270°C, P = 120 psi, space velocity = 3.0 L hr⁻¹, (gr cat.)⁻¹
A dramatic decrease in the catalytic activity of the dry-mixed catalyst was observed during the catalytic test using both syngas compositions, and this could be attributed to the fact that the aluminum hydroxide binds so strongly with the iron-based catalyst and the zeolite that it potentially blocks a large amount of the active sites on the surface of the iron-based catalyst. Further investigation was required to identify the potential cause of these activity-declining phenomena. An adsorption test with carbon monoxide was carried out to determine the total number of active sites of the catalyst, before and after physical mixing.

Figure 4.8: Syngas conversion of FeAl-CuK-01 core vs. FeAl-CuK-01-ZSM5-dry mix at H₂/CO = 2:1
4.1.2.2. Second-generation physical mixing catalyst: Binder-less dry-mixed

A catalytic test on FTS reactor was carried out to figure out the performance of the newer generation of the dry-mixed catalyst. The catalyst was catalytically tested using two different syngas composition, i.e. \( \text{H}_2/\text{CO} = 1:1 \) and \( \text{H}_2/\text{CO} = 2:1 \), respectively. The syngas conversion profiles over time for both conditions are presented in Fig. 4.9 and Fig. 4.10. The syngas conversion appears to take longer to get to steady condition for \( \text{H}_2/\text{CO} = 1:1 \) compared to when the syngas composition of \( \text{H}_2/\text{CO} = 2:1 \) was used. This might be attributed
to the fact that an additional reaction path, i.e. water–gas shift reaction, would be required to make up for the hydrogen deficit if a syngas with a non-stoichiometric ratio was employed. Other than that, the catalytic activity of both the core and the dry-mixed catalysts appear comparable to each other over the entire FTS reaction period, as opposed to the previous dry-mixed catalyst prepared by incorporating the binder material. Other catalytic results of the FTS test on this dry-mixed catalyst under two different syngas compositions is summarized in table 4.5.

Figure 4.10: Syngas conversion over time for FeAl-CuK-02 vs FeAl-CuK-02-ZSM5-Dry Mix at H₂/CO=2:1
Table 4.5: Summary of FTS catalytic testing on FeAl-CuK-02 core & FeAl-CuK-02-ZSM5 DM

<table>
<thead>
<tr>
<th>Core Catalyst</th>
<th>Type</th>
<th>H₂/CO ratio</th>
<th>Conversion (%)</th>
<th>Selectivity (%)</th>
<th>Yield (%)</th>
<th>α⁻ value</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>CO</td>
<td>H₂</td>
<td>CO₂</td>
<td>CH₄</td>
</tr>
<tr>
<td>FeAl-CuK-02</td>
<td>Core</td>
<td>1:1</td>
<td>28.57</td>
<td>19.51</td>
<td>38.65</td>
<td>3.11</td>
</tr>
<tr>
<td>FeAl·CuK-02·ZSM5</td>
<td>Dry-Mix</td>
<td>1:1</td>
<td>37.91</td>
<td>22.28</td>
<td>45.40</td>
<td>3.53</td>
</tr>
<tr>
<td>FeAl-CuK-02</td>
<td>Core</td>
<td>2:1</td>
<td>69.01</td>
<td>30.90</td>
<td>35.08</td>
<td>6.55</td>
</tr>
<tr>
<td>FeAl·CuK-02·ZSM5</td>
<td>Dry-Mix</td>
<td>2:1</td>
<td>62.18</td>
<td>21.94</td>
<td>37.63</td>
<td>7.25</td>
</tr>
</tbody>
</table>

Operating conditions: T = 270°C, P = 120 psi, space velocity = 3.0 L·hr⁻¹ (gr cat.)⁻¹

The effect of physical mixing on the catalytic performance of the catalyst is illustrated in Fig. 4.9 and Fig. 4.10, respectively. In general, higher CO conversion was achieved in both core and dry-mixed catalysts, respectively, if a stoichiometric syngas ratio of H₂/CO = 2:1 was used in the reaction compared to the case where 1:1 H₂/CO ratio was employed. The conversion of CO into hydrocarbons via FTS reaction appears dominant over WGS in the presence of adequate amount of hydrogen in the reactant, i.e. H₂/CO = 2:1, resulting in more CO converted as opposed to when 1:1 H₂/CO ratio was used. In the case of 1:1 H₂/CO ratio, WGS reaction plays an important role in producing hydrogen in order to make up for the hydrogen deficit in the reactant before a stoichiometric
FTS reaction can take place. Consequently, more carbon dioxide was produced as a result from high WGS activity during this synthesis using 1:1 H₂/CO ratio compared to 2:1 H₂/CO ratio, as indicated in Table 4.5. Furthermore, lack of hydrogen in the reactant during the 1:1 H₂/CO ratio based FTS favors the formation of longer-chained hydrocarbon, suppressing the production of methane and thus, resulting in a lower methane selectivity compared to the case of 2:1 H₂/CO ratio. What is interesting to note, during the 1:1 H₂/CO ratio FTS reaction, the dry mix catalyst exhibits a higher syngas conversion compared to the core catalyst, whereas the opposite case occurred when the catalyst was tested under 2:1 H₂/CO ratio. This might be explained as follows: the dry-mixed catalyst consists of two parts, i.e. the iron-based catalyst that is active towards the FTS and the WGS reactions, and the zeolite that is effective in catalyzing WGS, isomerization, and hydrocracking reactions. During the 1:1 H₂/CO ratio based FTS, which is a hydrogen lean process, more CO would be converted into both hydrocarbons (via an iron-based catalyzed FTS) and CO₂ & H₂ (via iron-based & zeolite catalyzed WGS) if a dry-mixed catalyst was used in the reaction as opposed to iron-based catalyst alone. This is attributed to the fact that zeolite itself is active towards the WGS, thus having zeolite mixed with iron-based catalyst would improve the overall activity. Therefore, under a hydrogen-lean syngas condition, the dry-mixed catalyst is more catalytically active towards FTS than the conventional iron-based catalyst. In addition, FTS catalytic test
performed on 1:1 syngas ratio exhibits a higher α value as opposed to the test performed using the 2:1 syngas ratio, suggesting that more waxes (heavier hydrocarbon products) have been produced under the hydrogen-restricted syngas.

4.1.3. Core-Shell Catalysts

While physically mixing the Fischer-Tropsch catalyst with that of hydrocracking and isomerization can actually suppress the formation of longer-chained hydrocarbon as well as increase the selectivity of branched paraffins to some extent, the performance can still be improved. For the iron-zeolite dry-mixed catalysts, the active sites are scattered around and randomly distributed on the surface of the catalysts, which leads to unrestricted reaction sites that allow both FTS reaction and hydrocracking & isomerization reaction to occur randomly and independently. This suggests that there is a chance for the FTS products to leave the catalyst surface directly without further reacting with the active sites of zeolite. In addition to physically mixing the metal-based FT and zeolite catalysts, a number of other research studies have attempted to synthesize the bifunctional metal/zeolite catalysts in a different format, i.e. by utilizing an FT catalyst supported on zeolite for the direct production of
isoparaffins. However, this method resulted in a substantially low CO conversion and low degree of reduction due to the extremely strong interaction between the metal and the zeolite as a support. The ease of migration and mobility of the FTS products appears to play important roles in determining the successful formation of middle iso-paraffin hydrocarbons. To foster this concept, a novel multifunctional catalyst with core shell structure has been introduced. The core part consists of conventional FTS catalysts while the shell comprises a layer of H-type zeolite enwrapping the core. The syngas passes through the shell to reach the core catalyst and eventually undergo FTS reaction to form linear paraffins. Prior to leaving the catalysts, all the linear paraffins must first pass through the zeolite shell and that is where hydrocracking and isomerization reactions take place and the linear paraffins have a better chance of getting converted into iso-paraffins on the acidic sites of zeolite. Owing to its ability to improve the collision possibility between linear paraffins and zeolite acidic sites, the core shell catalyst is expected to give higher selectivity towards iso-paraffins compared to the physically mixed catalyst.
4.1.3.1. First-generation core-shell catalysts

Both core-shell catalysts were catalytically tested on the FTS reactor over certain period of time. However, some coking was observed during the activation of the FeCuSi-K@ZSM5 catalyst with CO at 400°C, resulting in a severe blockage inside the FTS reactor. From this point on, all the catalyst activation in CO has been carried out at a lower temperature, i.e. 280°C, throughout the entire course of the research. The other catalyst, FeCuAl-K@ZSM, was successfully tested on the FTS reactor and the results are summarized in Table 4.6, even though the core catalyst, FeCuAl-K (synthesized using the first-generation procedure), was never catalytically tested in the FTS reactor due to the catalyst running out.

Table 4.6: Summary of catalytic performance of FeCuAl-K@ZSM catalyst

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>T (°C)</th>
<th>Conversion (%)</th>
<th>Selectivity (%)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>CO</td>
<td>H₂</td>
</tr>
<tr>
<td>FeCuAl-K@ZSM5</td>
<td>280</td>
<td>28.60</td>
<td>20.13</td>
<td>22.99</td>
</tr>
<tr>
<td>(Core-Shell)</td>
<td>300</td>
<td>91.34</td>
<td>33.26</td>
<td>59.45</td>
</tr>
</tbody>
</table>

Operating conditions: P = 150 psi, H₂/CO = 2:1, space velocity = 6.0 L. hr⁻¹. (gr cat.)⁻¹
4.1.3.2. Modified first-generation core-shell catalyst:

FeCuSi@ZSM5

As shown in Fig. 4.11, the conversion of CO and H₂ appears increasing continuously over a reaction period of 24 hours. This is due to the reconstruction or transformation among iron species under the reaction conditions. With the same amount of catalysts and reaction conditions, the conversion of CO and H₂ are lower on core-shell catalysts than on core itself. One reaction is that ZSM-5 has little activity toward F-T synthesis, and another factor is that some K may

![Figure 4.11: Syngas conversion over time for FeCuSi@ZSM5 core-shell catalyst](image-url)
lose during coating ZSM-5. The average selectivities of CO$_2$, methane, and oil in 24 h are 7.55, 2.31, and 5.49 %, respectively. Compared with core materials, the low CO$_2$ selectivity is possibly due to the loss of K, which can promote the WGS activity. However, we cannot rule out low fraction of iron oxidic iron species under F-T synthesis conditions, which are responsible for WGS reaction. A very interesting observation is that no wax was collected from the hot trap in 24 h, clearly demonstrating that coating the Fe-based core catalyst with zeolite can suppress the formation of heavier hydrocarbons.
4.1.3.3. Second-generation core-shell catalyst: Dry gel

In order to determine the catalytic performances of these promising catalysts, some catalytic tests using FTS reactor have been carried out. From the profile of syngas conversion over time shown on Fig. 4.12 for all FeAl-CuK-01-based catalysts with three different preparations, i.e. core, dry-mixed, and core shell catalysts, respectively, despite having some steady conversions of syngas over time, it appears that the core-shell FeAl-CuK-01@ZSM5 has a very low catalytic activity, only about 2.25% of CO conversion and 5.75% of H₂ conversion.

Figure 4.13: Syngas conversion profile over time of FeAl·CuK-02-based catalysts at H₂/CO = 1:1
over 48 hours reaction period, the lowest among the three catalysts. The same
trend was observed for FeAl-CuK-02 based catalysts, as shown on Fig. 4.13, in
which the core shell catalyst, FeAl-CuK-02@ZSM5, exhibits by far the lowest
syngas conversion among the three catalysts, with only about 2.28% of CO
conversion and 13.13% of H₂ conversion over 20 hours of reaction. This inactivity
of the catalyst might be attributed to the massive formation of the zeolites shell
that forms a fluffy structure surrounding the entire surface of the iron-based
core and heavily blocks the active sites of the core.

4.2. Effect of operating conditions on FTS catalytic
activity and selectivity

A number of interesting findings have been observed during the Fischer-
Tropsch Synthesis catalytic test of the synthesized catalysts that lead to the
discussion about some important factors that could affect the catalytic activity of
the Fischer-Tropsch Synthesis. Previous studies suggest that operating
conditions such as reaction temperature, syngas composition, space velocity, and
basicity of the iron catalyst are reportedly affecting the catalyst activity and
selectivity. ¹¹
4.2.1. Effect of reaction temperature on catalytic activity and selectivity

Some tests to study the effect of reaction temperature on catalytic activity were carried out on the FTS reactor using commercial catalysts A, B, and C, respectively, and the results are shown on Fig. 4.14. As indicated from the chart, reaction temperature exhibits positive trend on the catalytic activity, in which higher CO conversions were obtained upon increasing the FTS reaction temperature for all the three catalysts. While the analysis of the FTS products to determine the effect of temperature on the selectivity was not particularly
carried out in this study, a number of previous studies have attempted to address this issue. Higher FTS reaction temperatures have been reportedly effective in increasing the production of lower chained hydrocarbons, particularly methane, using iron, cobalt and ruthenium based catalysts.\textsuperscript{11,64-66} Furthermore, it is reported that the ratio of olefin to paraffin (O/P ratio) increases with the increasing reaction temperature performed on potassium-promoted precipitated iron catalysts, while a decrease in olefin selectivity with increasing temperature was observed for un-alkalized iron oxide powders. \textsuperscript{11,14,65}

4.2.2. Effect of syngas composition on catalytic activity and selectivity

Two different syngas compositions were incorporated to test the catalytic performance of some core and dry-mixed catalyst. Syngas with H\textsubscript{2}/CO ratio of 1.0 and 2.0, respectively, were sent to the FTS reactor during the FTS catalytic tests of the following catalysts: FeAl-CuK-01 (core), FeAl-CuK-02 (core), FeAl-CuK-01-ZSM (dry mix), and FeAl-CuK-02-ZSM (dry mix). As shown on Fig. 4.15, the results from all the four catalysts suggest that an increase in CO conversion was observed upon shifting the H\textsubscript{2}/CO ratio from 1.0 to 2.0. With regards to the effect of syngas composition on the selectivity of the catalysts, some α values of the products have been calculated based on the gaseous hydrocarbon products
captured by the GC. While the calculated α values might not be sufficiently representative for the whole product distribution for each variable, the overall α-values could be higher than these values, these are more reliable for lower chained hydrocarbons, ranging from C1 to C5. Thus, the α-values presented in Fig. 4.16 are based on these assumptions and thus, are presumably acceptable to give a general idea about the selectivity of the hydrocarbons produced. As shown on Fig. 4.16, the results from all the four catalysts exhibit the same trend, indicating that a decrease in α-values were observed with the increasing concentration of hydrogen in the reactant. This suggests that the more hydrogen present in the reactant would cause the product distribution to shift towards the
formation of lower chained hydrocarbons. Van der Laan (1999) through the work of Dictor and Bell and Donnelly and Satterfield pointed out that lighter hydrocarbons and lower olefins were produced upon increasing the $\text{H}_2/\text{CO}$ ratio during the FTS reaction. It is also indicated from their work that a decrease in the olefin to paraffin ratio from 6 to 1 was observed upon increasing the $\text{H}_2/\text{CO}$ ratio from 0.3 to 4.$^{11,65,66}$ In addition, Dry (1981) mentioned that in general, increasing total pressure would shift the product distribution towards the formation of oxygenates and longer-chained hydrocarbons.$^{64}$

Figure 4.16: The effect of syngas composition on product selectivity
4.2.3. Effect of catalyst pretreatment on the catalytic activity and selectivity

Catalyst treatment carried out prior to the Fischer-Tropsch Synthesis reportedly has significant effects on the catalytic activity and selectivity. Our findings suggest that the pH at which the precipitate was aged significantly affects the reduction behavior. As indicated from Fig. 4.17, the basicity of the catalyst solution of several different catalysts synthesized with co-precipitation procedure exhibits a strong correlation with the reduction temperature, in which

Figure 4.17: Effect of catalyst precipitation pH on reduction temperature
a decrease in reduction temperature was observed with the increasing pH value in all the tested core catalysts. As mentioned in the previous chapter, the pH has little effect on the crystalline state of iron oxides. As the pH increases, more copper will precipitate from the solution, resulting in a higher Cu content of the catalyst. It is well known that Cu can promote the reduction of iron compounds during the pretreatment, most likely because of hydrogen spillover from the Cu surface to the iron oxide surface. In contrast to cobalt-based catalysts, Dry (2004) reported the importance of promotion with optimum amount of alkali on the iron-based catalysts, suggesting that the catalytic activity and product selectivity of the FTS hydrogenation is heavily dependent upon the correct amount of alkali added to the iron. Furthermore, a correlation between reduction temperature and the catalytic activity is also investigated in this study. As indicated from Fig. 4.18, apart from an outlier caused by technical problem during the FTS test for FeCuAlK-04 catalyst, CO conversion during the FTS exhibits a negative correlation with the reduction temperature for all other catalysts, except for the FeAl·CuK-01. This suggests that the favorable reduction condition is not determined by the nature of certain iron species that are present in the catalyst but rather, it has more to do with the concentration of the promoters. Particularly for the FeAl·CuK-01, despite the fact that it has the highest pH and the lowest reduction temperature compared to all other core catalysts, the catalyst exhibits a surprisingly low catalytic activity. This
Figure 4.18: The effect of reduction temperature on catalytic activity

phenomenon was also reported in the previous study by Anderson (1956), basically suggesting that the catalytic activity increases to a certain level with the increasing pH and then starts decreasing at higher pH levels\textsuperscript{14}. In addition, Dry (1981) also investigated similar pattern with the catalytic activity of the precipitated iron catalyst in the form of unsupported iron upon the addition of
potassium promoter, confirming the results from the previous study about the influence of alkali content on the FTS catalytic performance during the CO hydrogenation\textsuperscript{64, 67}. With regards to how selectivity is affected by the catalytic pretreatment, Bukur and co-workers have studied the effect of catalytic pretreatment on the activity and product selectivity using promoted iron catalysts. The results from their studies suggest a strong correlation between selectivity of hydrocarbons and the catalytic pretreatment conditions and are summarized in Fig. 4.19.

![Figure 4.19: Effect of pretreatment conditions on hydrocarbon selectivity\textsuperscript{68}](image-url)
Based on the product distribution profile shown on Fig. 4.19, high selectivity of long chained hydrocarbons ($C_{12+}$), low methane selectivity, with about 20% selectivity of $C_2$-$C_4$ and $C_5$-$C_{11}$ (gasoline range) hydrocarbons, respectively, were observed for reduction conditions using CO or syngas with various compositions. Whereas reductions with hydrogen at $280^\circ$C are reported to result in higher selectivity of gasoline range hydrocarbons than those performed with CO or syngas.$^{53,54,68}$ Furthermore, olefin selectivity is reported to decrease with reductions in hydrogen as opposed to the treatment in CO or syngas. Typical product distribution of iron-based catalysts that we have synthesized is shown on Fig. 4.20.

![Product Distribution of FeCuAlK-02](image)

Figure 4.20: Product distribution of FeCuAlK-02 catalyst
4.2.4. Effect of physical mixing on catalytic activity and selectivity

While discussion on the catalytic activity over the period of time on stream and the effect of syngas composition on the activity of the dry-mixed catalysts are presented in more details in the previous section, this section mainly talks about to what extent physical mixing has affected the catalytic performance. As shown from Fig. 4.21, the dry-mixed form of FeAl-CuK-01 catalyst exhibits a significantly lower activity compared to its core catalyst during the FTS test.

![Figure 4.21: Effect of physical mixing on catalytic activity](image-url)
with both syngas compositions. This could be attributed to the presence of aluminum hydroxide as a binder during the preparation that might have created such a strong bond between the iron-based catalyst and the zeolite that could result in the blockage of the FTS active sites on the catalyst. The dry-mixed form of the second catalyst (FeAl-CuK-02), however, exhibits a more comparable activity in terms of CO conversion with its core form. The effect of physical mixing on the product selectivity is based on the analysis of product distribution.

Figure 4.22: Product distribution of FeAl-CuK-01 (core) catalyst
The profiles of product distribution for both the core and dry mix forms of FeAl-CuK-01 catalysts are presented on Fig. 4.22 and Fig. 4.23. As can be seen from the product distribution profiles, in general the core and the dry mix catalysts exhibit similar distribution of products with respect to straight chained paraffins, with the core catalyst showing a slightly lower concentration of n-paraffin at C9-C10 but slightly higher at longer carbon numbers compared to its later condition after physical mixing with ZSM5, suggesting that no significant cracking activity was observed upon physically mixing the core catalyst with
ZSM5 zeolite. The selectivity of olefins appears increasing post-physical-mixture step between iron-based core catalyst and ZSM5 for hydrocarbons ranging from C8 to C12, but looks slightly decreasing at some higher carbon numbers. One interesting phenomena was observed in the product distribution with respect to the selectivity of iso-paraffins on the core catalyst post-physical mixing with the ZSM5, which is indicated to have decreased from its initial value for most of the hydrocarbons, particularly C8+ carbon numbers, prior to the physical mixing. This could be attributed to the presence of aluminum hydroxide as a chemical

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**Figure 4.24:** Product distribution of FeAl-CuK-02 (Core) catalyst
binder, which in the previous discussion was considered to have inhibited the catalytic activity by blocking the active sites of the catalyst. However, a more detailed mechanism on how the binder could suppress the selectivity of the iso-paraffins is still unknown. The effects of physical mixing on the hydrocarbon selectivity are evaluated based on the product distribution profile of the dry-mixed catalyst and its iron-based core synthesized with the second-generation physical mixing procedure that are presented in Fig. 4.24 and Fig. 4.25, respectively. The initial iron-based core catalyst exhibits a relatively evenly
distributed composition among straight paraffin, branched paraffin, and olefin, with hydrocarbons up to C19 were observed from the organic oil product. A decrease in lower olefins' selectivity was observed upon the physical mixing, particularly from C5 up to C9, however, the olefins selectivity appears increasing from its pre physical mixing condition for higher hydrocarbons C10+. The selectivity of iso-paraffins significantly increases upon physically mixing the core catalyst with ZSM5 zeolite, suggesting that isomerization might have successfully taken place to some extent during the FTS reaction. Furthermore, despite the fact that some upper middle hydrocarbons, from C12 and above, were observed in a larger percentage upon the physical mixing as opposed to its initial condition, there is no significant difference in terms of the hydrocarbon product distribution in general, suggesting that no significant cracking activity was observed during the FTS reaction. In one of the previous studies, Bao and co-workers (2008) evaluated the product distribution of their cobalt-based FTS catalyst upon physical mixing with β-zeolite and observed a slight increase in olefins selectivity and a significant increase in the selectivity of iso-paraffins with no significant change in terms of the distribution of hydrocarbon products.\(^{46}\)
4.2.5. Effect of core-shell structure on the catalytic activity and selectivity

Profiles of the syngas conversion over time for the FTS catalytic test on the core-shell catalysts are presented in the previous section, with both catalysts exhibiting very low activity over the entire reaction period. Fig. 4.26 clearly indicates a poor activity of both core-shell catalysts compared to the original iron-based core and the dry-mixed catalysts. As previously mentioned this inactivity could be strongly attributed to the massive formation of the zeolites shell that forms a fluffy structure surrounding the entire surface of the iron-based core and heavily blocks the active sites of the core. While growing the zeolites shell that can evenly coat the core has been an important step in designing an effective multifunctional catalyst, it appears that having abundance of zeolite shell can be quite problematic as well due to the mass transfer limitation problem. Results from previous study by Bao and co-workers (2008) indicates that physically mixing the alumina-supported cobalt-based core with β-zeolite has decreased CO conversion of the core catalyst by 5% whereas coating the β-zeolite on the alumina-supported cobalt-based catalyst’s surface was responsible for about 12% decrease in CO conversion, suggesting that the catalytic activity of the modified catalysts do not seem to be significantly inhibited by the direct addition of zeolite or the hydrothermal synthesis.
procedure in order to grow zeolite shell on the core catalyst. With regards to the effect of core-shell structure on the product selectivity, a comparison between the product distribution profiles for three different catalyst types is presented in Fig. 4.27. As seen from the figure, a decrease in the olefins selectivity and a slight increase in the selectivity of iso-paraffins are observed upon coating the ZSM5 shell onto the iron-based core, indicating a mild activity of isomerization might have occurred during the FTS reaction. Despite the fact that the product distribution appears shifting to the increasing production of middle
hydrocarbons from C10 to C16 upon coating the iron-based core with ZSM5 shell, the formation of heavy paraffins are still observed, suggesting that no significant cracking activity has taken place upon the coating. Another important observation includes the high production rate of compounds with relatively low carbon number that is likely to be attributed to the low conversion, in which too much dry gas might have carried low molecular-weight compounds away. Furthermore, no wax formation was observed during the CO hydrogenation on this core shell catalyst. Previous study by Bao and co-workers (2008) indicated that in addition to significantly increasing the selectivity of iso-paraffins, coating of β-zeolite shell onto the cobalt-based core has completely suppressed the formation of heavy paraffins, shifting the product distribution completely to the middle paraffin (gasoline) range, as shown on Fig. 4.28.46
Figure 4.27: Product distribution comparison for: a) FeAl-CuK-02 (core), FeAl-CuK-02-ZSM5 (dry mix), and FeAl-CuK-02@ZSM5 (core-shell)
Figure 4.28: Product distribution for: a) conventional Co/Al₂O₃; b) Dry mix Co/Al₂O₃/β-zeolite; and c) Core-shell Co/Al₂O₃/β-zeolite (Adapted from Bao et al (2008))
Chapter 5
Catalytic Performances:
Part II – CO₂ Hydrogenation

5.1. Overview

Incorporating carbon dioxide in a number of reactions that can produce value added products has been done to mitigate the impact of greenhouse gas emissions. Hydrogenation of carbon dioxide into various chemicals and fuels is one of the most promising approaches to utilize carbon dioxide and thus, eventually can help reduce its concentration in the atmosphere. Several carbon dioxide hydrogenation technologies have been known to exist, including synthesis of hydrocarbons via a modified Fischer-Tropsch Synthesis. A number of studies in the area have been previously done with two of the most commonly used catalysts for FTS, i.e. cobalt and iron, respectively. The mechanism of CO₂ hydrogenation has been considered to proceed via two different steps, i.e. reversed water-gas shift (RWGS) reaction to convert the CO₂ into CO, followed by the conventional Fischer-Tropsch Synthesis. Several aspects of the hydrogenation reaction have been separately studied as well. Riedel and co-
workers (1999) conducted a comparative study of Fischer-Tropsch Synthesis using H₂/CO and H₂/CO₂–based syngas on both iron and cobalt-based catalysts, respectively. In this study, several compositions of H₂/CO/CO₂ syngas was introduced periodically during the FTS reaction. The effect of periodically switching the syngas from the H₂/CO to the H₂/CO₂ was monitored with respect to catalytic activity and product selectivity. Replacing CO with CO₂ with time during the FTS reaction over cobalt catalyst was found to merely reduce the concentration of CO in the syngas, resulting in the large production of short chain hydrocarbons, which eventually shift the product distribution towards the methane formation. However, different phenomena were observed during the FTS reaction using an iron-based catalyst, in which the presence of CO₂ was found to affect nothing in terms of the product selectivity. No excess methane was observed during the reaction, even in the presence of zero CO in the syngas, thus, resulting in the product distribution remaining relatively unchanged from the typical FTS product distribution, suggesting a feasible pathway of FTS-based CO₂ hydrogenation with iron-based catalysts as opposed to cobalt. 1,69-70
5.2. Catalytic Performance of CO₂ Hydrogenation

In this study, CO₂ hydrogenation test was conducted by introducing a H₂/CO₂ syngas with N₂ as an inert gas. Unlike the previous study by Riedel and co-workers (1999), no CO was added into the H₂/CO₂ syngas during the reaction, thus the comparison would be based on the use of either CO₂-free syngas (for CO hydrogenation) or CO-free syngas (for CO₂ hydrogenation). The same iron-based catalysts that are previously tested in CO hydrogenation FTS were used in the CO₂ hydrogenation FTS. Two different H₂/CO₂ syngas compositions were introduced during the FTS test, namely H₂/CO₂ ratio of 3:1 and 5:1, respectively, with other operating conditions remaining constant. During the FTS CO₂ hydrogenation test, extremely small amount of organic oil was collected along with oxygenates emulsion from the cold trap and the liquid wax that was occasionally observed from the hot trap samples.

5.2.1. Effect of basicity of precipitated catalysts on the catalytic activity and product selectivity

The profile of catalytic activity over time for two different iron-based catalysts is presented in Fig. 5.1. The FTS·CO₂ hydrogenation catalytic test was
carried out for 48 hours and as shown from Fig. 5.1, no apparent deactivation was observed during the reaction. Two different core catalysts having different pH were used to study the effect of catalyst basicity on the catalytic activity and selectivity, i.e. FeAl-CuK-01 (pH = 8.4) and FeAl-CuK-02 (pH = 9.4), respectively. In general, the FeAl-CuK-02 exhibits a slightly higher catalytic activity with respect to both CO$_2$ and H$_2$ conversion over the entire reaction path, suggesting a favorable effect of the more alkalized catalysts compared to the less alkalized ones. As discussed in the previous chapter, one important

![Conversion over time (co)](image)

**Figure 5.1: Catalytic activity over time for FeAl-CuK-01 and FeAl-CuK-02 catalysts**

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factor that determines the catalytic activity is the pretreatment condition prior to the FTS reaction. Having a higher concentration of promoter in the catalyst, which is signified by the pH level, was found to have significantly contributed to the decrease in the reduction temperature, which eventually lead to an increase in catalytic activity. Catalytic performances for these catalysts during the FTS-CO hydrogenation are presented on Table 5.1.

Table 5.1: FTS-CO₂ Hydrogenation catalytic performances of iron-based core catalysts

<table>
<thead>
<tr>
<th>Core Catalyst</th>
<th>pH</th>
<th>H₂/CO₂ ratio</th>
<th>Conversion (%)</th>
<th>Selectivity (%)</th>
<th>Yield (%)</th>
<th>α value</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>CO₂</td>
<td>H₂</td>
<td>CO</td>
<td>CH₄</td>
</tr>
<tr>
<td>FeAl·CuK-01</td>
<td>9.4</td>
<td>3.0</td>
<td>19.57</td>
<td>19.60</td>
<td>16.94</td>
<td>9.23</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5.0</td>
<td>21.75</td>
<td>11.43</td>
<td>26.57</td>
<td>26.77</td>
</tr>
<tr>
<td>FeAl·CuK-02</td>
<td>8.4</td>
<td>5.0</td>
<td>29.67</td>
<td>14.76</td>
<td>14.66</td>
<td>20.79</td>
</tr>
</tbody>
</table>

Operating conditions: T = 270°C, P = 120 psi, space velocity = 3.0 L. hr⁻¹. (gr cat.)⁻¹

No specific analysis of product distribution was done on the FeAl·CuK-01 catalyzed FTS CO₂ hydrogenation samples, making it unable to comprehensively study the effect of different catalyst pH on the product selectivity. Some α values calculated based on the gaseous products, however, could be used to estimate the formation of lower chain hydrocarbons.
5.2.2. Effect of syngas composition on the catalytic activity and selectivity

The effect of different syngas composition on the FTS CO₂ hydrogenation catalytic activity and product selectivity was studied on the FeAl·CuK-01 (core) and FeAl·CuK-01 (dry mix) catalysts, respectively. Syngas compositions of H₂/CO₂ ratio of 3:1 and 5:1 were used in the test. All the reactions were left on stream for 48 hours except for the 3:1 H₂/CO₂ FeAl·CuK-01 that ran up to 60 hours.

![Conversion over time (%)](image)

Figure 5.2: Catalytic activity of FeAl·CuK-01 (CORE) for both syngas compositions
hours due to power outage in the middle of the reaction. The profiles of the FTS catalytic activity over time are presented on Fig. 5.2 and Fig. 5.3, respectively.

As shown from the figures, both catalysts exhibit no signs of deactivation during the FTS CO$_2$ hydrogenation reaction. In general, the results from both catalysts suggest that a better catalytic activity in terms of higher CO$_2$ conversion was achieved over the FTS reaction period when the syngas with a H$_2$/CO$_2$ ratio of 5:1 was used as opposed to the 3:1 ratio of H$_2$/CO$_2$. Complete catalytic performances for all the tested catalysts are presented on table 5.2.

![Conversion over time (%)](image)

Figure 5.3: Catalytic activity of FeAl-CuK-01-ZSM5 (DRY MIX) for both syngas compositions
Table 5.2: FTS-CO₂ Hydrogenation performance of various syngas composition

<table>
<thead>
<tr>
<th>Core Catalyst</th>
<th>H₂/CO₂ ratio</th>
<th>Conversion (%)</th>
<th>Selectivity (%)</th>
<th>Yield (%)</th>
<th>α value*</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CO₂</td>
<td>H₂</td>
<td>CO</td>
<td>CH₄</td>
<td>Oil</td>
</tr>
<tr>
<td>FeAl-CuK-01 (Core)</td>
<td>3.0</td>
<td>19.57</td>
<td>19.60</td>
<td>16.94</td>
<td>9.23</td>
</tr>
<tr>
<td></td>
<td>5.0</td>
<td>21.75</td>
<td>11.43</td>
<td>26.57</td>
<td>26.77</td>
</tr>
<tr>
<td>FeAl-CuK-01 (Dry Mix)</td>
<td>3.0</td>
<td>12.94</td>
<td>7.41</td>
<td>32.09</td>
<td>11.01</td>
</tr>
<tr>
<td></td>
<td>5.0</td>
<td>20.07</td>
<td>6.33</td>
<td>30.28</td>
<td>16.37</td>
</tr>
</tbody>
</table>

* Estimated value from gaseous products
Operating conditions: T = 270°C, P = 120 psi, space velocity = 3.0 L hr⁻¹ (gr cat.)⁻¹

Figure 5.4: Effect of syngas composition on activity and selectivity of FeAl-CuK-01
Fig. 5.4 represents a graphical comparison of the average values of CO$_2$ conversion along with the selectivity values of CH$_4$ and CO over two different syngas compositions during the FTS CO$_2$ hydrogenation test on both FeAl-CuK-01 (core) and FeAl-CuK-01-ZSM5 (dry mix) catalysts, respectively. Apart from the slight decrease observed for CO selectivity of the dry mix catalyst, all other values for CO$_2$ conversions and selectivity of CH$_4$ and CO appear increasing with the increase in hydrogen concentration in the syngas for both catalysts.

![Figure 5.5: Effect of syngas composition on CH$_4$ selectivity: CO hydrogenation vs CO$_2$ hydrogenation](image)

Figure 5.5: Effect of syngas composition on CH$_4$ selectivity: CO hydrogenation vs CO$_2$ hydrogenation
Selectivity of methane during the FTS CO$_2$ hydrogenation is affected by the syngas composition in different ways from it is during the CO hydrogenation step. The profile on how methane selectivity has been affected by different syngas compositions during both hydrogenation tests is illustrated on Fig. 5.5.

In general, it is indicated that methane selectivity increased upon switching the syngas composition from H$_2$/CO to H$_2$/CO$_2$. Previous study by Riedel and co-workers (1999) indicates that changing the syngas composition from H$_2$/CO to H$_2$/CO$_2$ over iron-based catalyst does not cause the formation of excessive methane and, thus, will not change the overall product distribution$^1$. Therefore, the increase in the methane selectivity observed in this study is more because of

![Figure 5.6: Effect of syngas composition on α values: CO hydrogenation vs CO$_2$ hydrogenation](image)

Figure 5.6: Effect of syngas composition on α values: CO hydrogenation vs CO$_2$ hydrogenation
the higher concentration of hydrogen in the syngas used during the FTS CO\textsubscript{2} hydrogenation that might have resulted in the higher formation rate of lower chain hydrocarbons, particularly methane, compared to the one introduced in the CO hydrogenation, rather than due to the diluting effect of CO\textsubscript{2}, just like what was previously observed with the cobalt catalyst. In order to confirm the phenomena observed on the methane selectivity due to the different syngas compositions, analysis on $\alpha$ values has been made for the two different hydrogenation conditions, as illustrated on Fig. 5.6. The $\alpha$ values presented on Fig. 5.6 are calculated based on the distribution of gaseous products and, thus, only valid for lower chain hydrocarbons. However, due to the absence of product distribution analysis for some catalysts, it would be acceptable to use these $\alpha$ values just for comparison purpose in this study. As shown from figure 5.6, in general lower $\alpha$ values were obtained from the FTS CO\textsubscript{2} hydrogenation compared to the CO hydrogenation, indicating that lower chain hydrocarbons were more abundant in the product distribution of CO\textsubscript{2} hydrogenation compared to what could be found in that of CO hydrogenation and also confirming previous finding about the higher methane selectivity obtained during CO\textsubscript{2} hydrogenation as opposed to the CO hydrogenation. Nevertheless, just like in the discussion of methane selectivity, the lower $\alpha$ values observed during the CO\textsubscript{2} hydrogenation is more likely to be attributed to the higher concentration of hydrogen present in the syngas, resulting in the higher production rate of lower chain hydrocarbons,
rather than the diluting effect of CO$_2$. In other words, switching the syngas composition from H$_2$/CO = 2.0 to H$_2$/CO$_2$ = 2.0 over iron catalyst might not have as significant effect to the product distribution compared to switching from H$_2$/CO = 2.0 to H$_2$/CO$_2$ = 5.0 due to the same concentration of hydrogen in the syngas. As reported from the previous study, replacing CO with CO$_2$ in the

![Figure 5.7: Product distribution of FeAl·CuK·02 (Core) – H$_2$/CO = 2](image)

**Figure 5.7:** Product distribution of FeAl·CuK·02 (Core) – H$_2$/CO = 2
syngas would not change the overall product distribution over iron-based catalysts as opposed to cobalt-based catalysts\textsuperscript{1,31,69-70}. Analysis of product distribution from liquid samples for both CO and CO\textsubscript{2} hydrogenation conditions is presented in Fig. 5.7 and Fig. 5.8, respectively. The product distribution analysis on the CO\textsubscript{2} hydrogenation were carried out for the liquid samples collected from both the hot and cold trap due to the presence of liquid wax from the hot trap and a large amount of oxygenates from the cold trap. A large amount of alcohols was observed on the samples from both traps during CO\textsubscript{2} hydrogenation as opposed to the CO hydrogenation. Apart from the alcohols formation identified on the CO\textsubscript{2} hydrogenation, in general, similar product distributions were observed for both hydrogenation conditions, confirming the results suggested from the previous study regarding the constant product distribution upon switching CO to CO\textsubscript{2} in the syngas\textsuperscript{1,31}. Furthermore, a substantially higher selectivity of middle range hydrocarbons, from C6 through C11, was particularly observed on the CO hydrogenation samples, contributing to the significantly lower $\alpha$ value for CO hydrogenation compared to those obtained from both samples of CO\textsubscript{2} hydrogenation, i.e. 0.62 vs 0.83. This trend does not confirm the previous results, suggesting that CO hydrogenation samples gave a higher-chain-growth probability based on the $\alpha$ values calculated from the gaseous products. The discrepancy may be partially attributed to some longer chain hydrocarbons from the CO hydrogenation sample not properly
showing up or identified during the analysis with the GC, resulting in a substantially low concentration of heavier hydrocarbons in the sample. Moreover, a slightly wider product distribution was also observed for the samples from CO\textsubscript{2} hydrogenation compared to that of CO hydrogenation. The selectivity of methane was not shown on these figures since methane and other gaseous products leaving the cold trap were separately captured and analyzed using the GC. In addition, as indicated from Fig. 5.8, higher selectivity of linear paraffins and lower selectivity of branched paraffins was observed on the CO\textsubscript{2} hydrogenation sample collected from the hot trap compared to that collected from the cold trap. This could be attributed to the fact that straight chain paraffins have higher boiling points compared to the branched chain paraffins, resulting in a large amount of straight chain paraffins vapor condensing into liquid in the hot trap.
Figure 5.8: Product distribution of FeAl-CuK-02 (Core) – H₂/CO₂ = 5 (Cold)
5.2.3. Effect of physical mixing on the catalytic activity and selectivity

The effect of physical mixing on the catalytic activity and selectivity was studied on FeAl-CuK-01 and FeAl-CuK-02 catalysts, respectively. The profiles of the catalytic activity over time of both dry-mixed catalysts along with their iron-based core are presented in Fig. 5.9 and Fig. 5.10, respectively. From these figures, no sign of deactivation was observed on both cases during the FTS CO$_2$ hydrogenation reaction period. In both cases, the conversions of CO$_2$ and H$_2$ over time for both the core and the dry-mixed catalysts appear to be comparable with each other, with the dry-mixed exhibiting a slightly higher activity than the iron-based core in the case of FeAl-CuK-02 catalyst. In contrast with the iron-based catalyst during CO hydrogenation where the catalytic activity substantially dropped upon physical mixing with zeolite and with the incorporation of aluminum hydroxide as a binder, no significant decrease in catalytic activity was observed on the same catalyst during the CO$_2$ hydrogenation, as shown on Fig. 5.9. Other catalytic performance parameters are summarized in more details on Table 5.3. For the syngas composition of H$_2$/CO$_2$=5, A decrease in methane selectivity was observed upon physically mixing the FeAl-CuK-01 core with zeolite and the binder, whereas in contrast, a
A slight increase was recorded upon physically mixing the FeAl-CuK-02 core with zeolite. The addition of binder to the dry-mixed catalyst might have affected the methane selectivity, however, the mechanism on how the selectivity was affected remains unknown. The selectivity of CO also exhibits mixed results between the FeAl-CuK-01 and the FeAl-CuK-02 catalyst, in which physical mixing has caused an increase in the CO selectivity on the former and a slight decrease on the latter.

![Figure 5.9: Profile of catalytic activity of FeAl-CuK-01 over time](image)

**Figure 5.9: Profile of catalytic activity of FeAl-CuK-01 over time**
Figure 5.10: Profile of catalytic activity of FeAl-CuK-02 over time
Table 5.3: FTS-CO₂ Hydrogenation catalytic performances of dry-mixed vs core catalysts

<table>
<thead>
<tr>
<th>Core Catalyst</th>
<th>H₂/CO₂ ratio</th>
<th>Conversion (%)</th>
<th>Selectivity (%)</th>
<th>Yield (%)</th>
<th>α₁ value</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>CO₂</td>
<td>H₂</td>
<td>CO</td>
<td>CH₄</td>
</tr>
<tr>
<td>FeAl-CuK-01 (Core)</td>
<td>3.0</td>
<td>19.57</td>
<td>19.60</td>
<td>16.94</td>
<td>9.23</td>
</tr>
<tr>
<td></td>
<td>5.0</td>
<td>21.75</td>
<td>11.43</td>
<td>26.57</td>
<td>26.77</td>
</tr>
<tr>
<td>FeAl-CuK-01 (Dry Mix)</td>
<td>3.0</td>
<td>12.94</td>
<td>7.41</td>
<td>32.09</td>
<td>11.01</td>
</tr>
<tr>
<td></td>
<td>5.0</td>
<td>20.07</td>
<td>6.33</td>
<td>30.28</td>
<td>16.37</td>
</tr>
<tr>
<td>FeAl-CuK-02 (Core)</td>
<td>5.0</td>
<td>29.67</td>
<td>14.76</td>
<td>14.66</td>
<td>20.79</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>FeAl-CuK-02 (Dry Mix)</td>
<td>5.0</td>
<td>32.64</td>
<td>18.75</td>
<td>12.97</td>
<td>23.59</td>
</tr>
<tr>
<td></td>
<td></td>
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</tbody>
</table>

* Estimated value from gaseous products; ** Calculated value from liquid products

Operating conditions: T = 270°C, P = 120 psi, space velocity = 3.0 L hr⁻¹. (gr cat.)⁻¹

The effect of physical mixing on the hydrocarbon product selectivity during CO₂ hydrogenation can be investigated from the product distribution analysis done on the samples both before and after the physical mixing. The product distribution profiles of core and dry-mixed catalysts are presented on Fig. 5.11. Analysis on the product distribution was carried out on the samples collected from both hot and cold traps. In general, all samples collected from both traps exhibit substantial amount of alcohols during the CO₂ hydrogenation. A significantly higher selectivity of hydrocarbon was observed on the samples with
respect to all hydrocarbon forms, such as linear paraffin, branched paraffin, and olefin upon physically mixing the iron-based core with the ZSM5 zeolite. Other than that, similar products distributions were observed in terms of the width and the pattern on the samples before and after physically mixing the iron-based core with the zeolite, indicating no significant activity of hydrocracking was observed upon the physical mixing. In addition to analyzing the product distribution, the effect of physical mixing on the hydrocarbon selectivity is also investigated by evaluating the chain-growth probability ($\alpha$) of the catalysts before and after the physical mixing. Some values of the chain-growth probability ($\alpha$) as a function of carbon number during the CO$_2$ hydrogenation for the iron-based core versus the dry-mixed catalysts are presented on Fig. 5.12. In general, nearly similar $\alpha$ values were observed on the samples collected from both traps before and after physical mixing, except a slightly lower value of the dry-mixed sample collected from the hot trap. This indicates no significant difference in terms of the growing hydrocarbon chains was observed, suggesting that physically mixing the iron-based catalyst with zeolites does not actually have effects on the total selectivity of the hydrocarbons during the CO$_2$ hydrogenation in our study, but rather, converting the straight chain into the branched chain paraffins. Furthermore, the physical mixing could have affected the chain-growth probability if heavy range hydrocarbons has been completely suppressed during the hydrogenation, or in other words, a shift in product
distribution towards the formation of middle range hydrocarbons had been observed due to significant activity of hydrocracking. A comparison between the chain-growth probability values observed during the CO hydrogenation versus those during the CO$_2$ hydrogenation for conditions before and after the physical mixing is presented on Fig. 5.13. In general, relatively similar probability of chain-growth has been observed for all conditions, suggesting that switching the syngas composition from CO to CO$_2$ or physically mixing the iron-based catalyst with zeolites does not seem to significantly affect the overall product distribution in terms of the total selectivity of hydrocarbons.$^{1,31,69-70}$

Figure 5.11: Product distribution of FeAl-CuK-02: iron core
Figure 5.12: Product distribution of FeAl-CuK-02 : dry-mixed
Figure 5.13: $\alpha$ values based on liquid products: iron core vs dry-mixed

Figure 5.14: $\alpha$ values: CO hydrogenation vs CO$_2$ hydrogenation
Chapter 6

Summary & Concluding Remarks

Catalyst Synthesis and Characterization

Several attempts have been made to synthesize copper and potassium promoted iron-based FTS catalysts using co-precipitation techniques. Washed away copper that resulted in a low catalytic activity has been a major issue during earlier attempts of the synthesis. The addition of copper to the iron-based catalyst can help improve the reduction temperature due to the formation of copper peak that has a lower temperature than that of iron during the reduction. Related to copper addition, basicity in which the catalyst was precipitated has also been found to have significant effect on the catalytic activity due to the fact that more copper can be precipitated at higher pH. Modifying the synthesis procedure and the catalyst precursors in order to retain the copper content in the promoted catalyst while precipitating catalysts with high pH has been effective to enhance the catalytic performance of the iron-based catalysts. One way to improve the product distribution towards the formation of middle iso-paraffins is to mix the
iron-based FTS catalyst physically with the ZSM-5 zeolite. Physically mixing the iron-based catalyst with zeolite in this study has been carried out in two attempts, with alumina hydroxide being added as a binder during the first attempt and a direct binder-less mixing being incorporated during the second. While the characterization results exhibit no significant change in terms of reduction temperature, the addition of binder to accommodate the physical mixing has been found to substantially reduce the catalytic activity of the dry-mixed catalyst. In contrast, the direct binder-less mixing exhibits a comparable catalytic activity with the iron-based FTS catalyst. In terms of synthesizing the core shell structured catalyst, a zeolite layer has been successfully grown on the conventional iron-based FT catalyst using a hydrothermal synthesis technique. To be able to uniformly coat the iron-based core with the zeolite shell has been one of the biggest challenges. The latest generation of the synthesized core shell catalysts exhibit the most uniform zeolite coating compared to some previous attempts, with a fluffy and thick zeolite layer being observed and completely appears covering the entire area of the iron-based core catalyst. However, this thick zeolite layer might have blocked the FTS active sites of the iron-based catalyst and contributed to the low activity of the catalysts during the CO hydrogenation Fischer-Tropsch Synthesis. In addition, the loss of potassium promoter during the synthesis of core-shell catalysts, diffusion resistance, and a strong interaction between zeolite and the active sites could become other
potential causes as well. Further investigation will need to be done to verify these potential issues.

CO Hydrogenation

CO hydrogenation test has been carried out on the synthesized catalysts with two different syngas compositions, i.e. $\text{H}_2/\text{CO} = 1.0$ and $\text{H}_2/\text{CO} = 2.0$. The effect of reaction temperature has been studied on commercial catalysts, in which higher CO conversions were observed upon increasing the FTS reaction temperatures. The effect of syngas composition on the catalytic performance has also been studied, in which all the tested catalysts exhibit higher CO conversion and higher CH$_4$ selectivity when syngas with higher hydrogen concentration was used as opposed to the lower hydrogen concentration syngas. In terms of the product distribution, higher hydrogen concentration in the syngas favors the formation of lower chain hydrocarbons. Catalytic pre-treatment carried out prior to the FTS CO hydrogenation has been reportedly crucial to determine the performance of the catalysts. The results from this study suggest that the pH at which the precipitate was aged has significantly affected the reduction behavior, in which a decrease in the reduction temperature was observed with the increasing pH of the catalysts. Furthermore, a strong correlation between CO conversion and the reduction temperature has also been investigated in this
study, suggesting that a favorable reduction condition is more strongly determined by the amount of promoters present in the catalyst rather than the formation of certain iron phases. The effect of physical mixing on the catalytic performance has been studied during CO hydrogenation as well. The first-generation of the dry-mixed catalyst synthesized with the aid of aluminum hydroxide as a binder exhibits a lower activity compared to its iron-based core. A strong interaction between the binder and the catalysts that might have blocked the active FTS sites on the iron-based core could be the possible reason to these phenomena. Furthermore, the second-generation dry-mixed catalyst that contains no binder exhibits a comparable activity compared to its iron-based core, confirming the previous concern about the binder being a possible cause to the low activity of the first-generation dry-mixed catalyst. Furthermore, a relatively comparable product distribution was observed upon physically mixing the iron-based core with the zeolite compared to that of the initial condition, indicating no significant hydrocracking activity has occurred. In addition to that, a higher selectivity of iso-paraffins was observed, suggesting that isomerization might have taken place to some extent during the hydrogenation. Last but not least, the effect coating the zeolite on the iron-based core catalysts has also been studied. Despite the successful attempt to uniformly grow the zeolite shell on the iron-based catalyst, a substantially lower catalytic activity with respect to CO conversion was observed during the hydrogenation on the core shell structured
catalyst. The formation of thick and fluffy zeolite layer that covers the entire area of the core might have blocked the active FTS sites on the iron-based core, and thus contributing to the low catalytic activity. As previously mentioned, other potential causes include the loss of potassium promoter during the preparation of core-shell catalysts, diffusion resistance over the zeolite shell, and a strong interaction between zeolite and the active sites.

**CO$_2$ Hydrogenation**

Incorporating carbon dioxide into the existing Fischer-Tropsch Synthesis has been carried out to mitigate the effect of greenhouse gas emissions. Converting carbon dioxide into hydrocarbon fuels using iron catalysts seems promising due to the fact that hydrogenation of CO$_2$ on iron-based catalysts does not significantly shift the typical FTS product distribution. Two different syngas compositions have been incorporated in this study, i.e. H$_2$/CO$_2$ = 3.0 and H$_2$/CO$_2$ = 5.0, respectively. In general, it is reported from the study that iron-based catalyst with higher pH is more catalytically active than those with lower pH. Furthermore, a higher concentration of hydrogen in the syngas has been found to be more favorable with respect to CO$_2$ conversion, as well as CH$_4$ and CO selectivity, respectively, compared to the lower hydrogen content in the syngas. In terms of the product distribution, switching CO to CO$_2$ in the syngas during
the hydrogenation has been found to have little effect on the product distribution. The effect of physical mixing on the catalytic activity and selectivity has also been studied, in which comparable catalytic activity has been observed in terms of CO$_2$ conversion for both the iron-based FTS core and the dry-mixed catalysts. Comparable selectivity with respect to CO and CH$_4$ were investigated between the binder-less dry-mixed and its core iron-based catalysts, even though inconsistent results were obtained upon adding aluminum hydroxide binder during the physical mixing between iron-based catalysts and the zeolite. In terms of the product distribution, apart from the higher hydrocarbon selectivity observed for all types of hydrocarbons upon the physical mixing, relatively comparable products distributions were observed in terms of the width and the pattern on the samples before and after physically mixing the iron-based core with the zeolite, indicating no significant activity of hydrocracking was observed upon the physical mixing.

Concluding Remarks

A number of important findings have been identified and highlighted during this study, such as:
✓ The significant effect of pH on the catalytic activity due to its ability to control the amount of promoter to be precipitated in the catalyst, which results in a lower reduction temperature and a higher catalytic activity

✓ Physically mixing the iron-based FTS catalyst with zeolite does not significantly change the catalytic activity and the product distribution in general, however, it increases the selectivity of iso-paraffins, which is an indication of some isomerization activity

✓ Zeolite shell has been successfully coated uniformly on the iron-based core using hydrothermal synthesis technique, even though the formation of thick zeolite shell might have blocked the active FTS sites on the iron-based catalyst and thus, causing diffusion resistance, and other factors such as strong interaction between zeolite and the active sites and potential loss of potassium promoter during the core-shell preparation are believed to contribute to the low activity of the core shell catalyst

✓ Hydrogenation of CO₂ carried out on iron catalyst does not significantly affect the typical FTS product distribution, indicating that CO₂ can safely be incorporated into the existing Fischer Tropsch Synthesis, given that H₂-rich syngas or renewable hydrogen feedstock is available
References


APPENDICES
Appendix A: Catalysts preparation apparatus

Figure A1: Iron-based core catalysts synthesis apparatus
Figure A2: Modified oven for core-shell’s hydrothermal synthesis