

**PREPARATION AND CHARACTERIZATION OF COBALT BASED  
AND ZINC PROMOTED CATALYST FOR FISHER TROPSCH  
SYNTHESIS**

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## ABSTRACT

The purpose of this research is to compare the characterization of SBA-15 and TiO<sub>2</sub> supported cobalt catalyst for Fischer-Tropsch synthesis based on effect of cobalt loading. In order to complete this research, the catalyst must be prepared by incipient wetness impregnation method. The catalysts were prepared with different cobalt loading, which are 5%, 10% and 15% and using zinc as a promoter. To characterize these catalysts, different methods were used. First of all, characterization of SBA-15 and TiO<sub>2</sub> were compared by using Fourier Transform Infrared Spectroscopy (FTIR). Then the catalysts were tested using Scanning Electron Microscope (SEM). Through this characterization, the surface of catalysts was compared. The surface structure of Co/SBA-15 is more ordered when compared to Co/TiO<sub>2</sub> catalyst. This is compared by the SEM image taken. Therefore, Co/TiO<sub>2</sub> is also a good catalyst with advantages when compared to Co/SBA-15 catalyst. The conclusion of this research when comparing the characterization of Co/SBA-15 and TiO<sub>2</sub> catalysts, is Co/SBA-15 catalyst is a good catalyst when compared to Co/TiO<sub>2</sub> catalyst.

## ABSTRAK

Tujuan kajian ini ialah membandingkan ciri-ciri SBA-15 dan  $\text{TiO}_2$  disokong mangkin kobalt untuk sintesis Fischer-Tropsch berdasarkan pengaruh pembebanan kobalt. Dalam rangka untuk menyelesaikan kajian ini, mangkin harus disediakan dengan kaedah impregnasi basah/lembap. Mangkin disusun dengan memuatkan kobalt yang berbeza, iaitu 5%, 10% dan 15% dan zink bertindak sebagai promotor. Bagi menganalisa ciri-ciri mangkin, kaedah yang berbeza digunakan. Pertamanya, ciri-ciri SBA-15 dan  $\text{TiO}_2$  dibandingkan dengan menggunakan Fourier Transform Infrared Spectroscopy (FTIR). Kemudian, mangkin diuji menggunakan Scanning Electron Microscope (SEM). Melalui perbandingan ciri-ciri yang telah dilakukan dengan kaedah tersebut, permukaan mangkin dibandingkan. Permukaan Co/SBA-15 didapati lebih padat dan tersusun berbanding permukaan mangkin Co/ $\text{TiO}_2$ . Perbezaan ini dibandingkan dengan melihat gambar SEM yang telah diambil. Oleh kerana itu, Co/SBA-15 adalah mangkin yang lebih bagus berbanding Co/ $\text{TiO}_2$ . Kesimpulan yang dapat dibuat dari kajian ini ketika membandingkan ciri-ciri kedua-dua mangkin iaitu Co/SBA-15 dan Co/ $\text{TiO}_2$ , ialah mangkin Co/SBA-15 adalah lebih bagus berbanding mangkin Co/ $\text{TiO}_2$ .

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## LIST OF ABBREVIATIONS

<b>Al<sub>2</sub>O<sub>3</sub></b>	Alumina
<b>CFB</b>	Circulated Fluidized Bed
<b>Co</b>	Cobalt
<b>CoO</b>	Cobalt Oxide
<b>Fe</b>	Iron
<b>FT</b>	Fisher Tropsch
<b>FTIR</b>	Fourier Transform infrared Spectra
<b>GTL</b>	Gas to liquid
<b>IWI</b>	Incipient Wetness Impregnation
<b>MSI</b>	Metal Surface Interaction
<b>N<sub>2</sub></b>	Nitrogen
<b>Ni</b>	Nickel
<b>Pb</b>	Plumbum
<b>Pt</b>	Platinum
<b>Re</b>	Rethium
<b>Ru</b>	Ruthenium
<b>SCR</b>	Selective Catalytic Reduction
<b>SEM</b>	Scanning Electron Microscopy
<b>TEM</b>	Transmission Electron Microscopy
<b>TEOS</b>	Tetraethylorthosilicate
<b>TGA</b>	Thermogravimetric Analysis

<b>TiO<sub>2</sub></b>	Titanium (II) Oxide
<b>WGS</b>	Water Gas Shift
<b>XRD</b>	X-Ray Diffraction
<b>Zn</b>	Zinc

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## CHAPTER 1

### INTRODUCTION

#### 1.1 Background of the Study

##### 1.1.1 Fischer-Tropsch Synthesis

Fischer-Tropsch (FT) synthesis is part of gas-to-liquid (GTL) technology and used to convert carbon monoxide and hydrogen into liquid transportation hydrocarbon fuel (O. González *et al.*, 2009). This catalytic chemical reaction is named after the original German inventors, Franz Fischer and Hans Tropsch in the 1920s. During World War II, FT synthesis provided the needed synthetic hydrocarbon fuels for the German war effort. Later, South Africa turned to FT synthesis from coal gasification to supply significant quantities of its hydrocarbon fuel demand, and since then many refinements and adjustments to the technology have been made, including catalyst development and reactor design. Depending on the source of the syngas, the technology often referred as coal-to-liquid (CTL) and/or GTL (H. Schulz, 1999). The fuel produced by this catalytic reaction is known as synthetic fuel that consists primarily of linear paraffins and further characterized by low aromatic, zero sulfur content, has high molecular weight and are straight chain hydrocarbons (Dae Jung Kim *et al.*, 2005 & Shan Yuanyuan *et al.*, 2009).

Franz Fischer and Hans Tropsch are two German scientists who went on to win the Nobel Prize by developing GTL technology in 1922 (Wisam Al-shalchi,2006). They used the FT process in Germany during the Second (2<sup>nd</sup>) World War to produce approximately 600,000 bbl per year of liquid transportation fuels from coal. Carthage Hydrocol conducted further development in Brownsville, Texas, from 1948 to 1953 to convert natural gas rather than coal. The plant they constructed had a production of 365,000 bbl per year but was shut down and dismantled when there was a dramatic rise in natural gas prices. South Africa began using the FT process in 1955 using coal as feedstock.



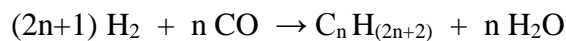
**Figure 1.1:** Franz Fischer and Hans Tropsch (Wisam, 2006)

In 1986, Mobil built a GTL plant that processed natural gas from a giant gas field off New Zealand into methanol, then into gasoline. However, when oil prices collapsed the plant was no longer profitable and was sold to Fletcher Challenge Ltd. in 1993. Since then, there have been several new entrants into the market. The number of announced projects and demonstration projects has increased dramatically in the past five (5) years.

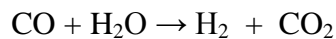
FT converts synthesis gas ( $\text{CO}$  and  $\text{H}_2$ ) which can be made from coal, natural gas, petroleum residues, biomass, and any carbonaceous materials to long chain hydrocarbons. If liquid petroleum-like fuel, lubricant, or wax is required, then the

Fischer-Tropsch process is the right process that can be applied. This is an alternative route to obtain fuels and chemicals rather than the current dominant petroleum resources. Fischer-Tropsch synthesis now is becoming competitive to petroleum due to its improved catalysts and processes (Wisam, 2006).

The FT process is a catalytic chemical reaction in which CO and H<sub>2</sub> in the syngas are converted into hydrocarbons of various molecular weights according to the following equation:



Where n is an integer. Thus, for n=1, the reaction represents the formation of methane, which in most CTL or GTL applications is considered an undesirable byproduct. The FT process conditions are usually chosen to maximize the formation of higher molecular weight hydrocarbon liquid fuels which are higher value products. There are other side reactions taking place in the process, among which the water-gas-shift reaction



is predominant. Depending on the catalyst, temperature, and type of process employed, hydrocarbons ranging from methane to higher molecular paraffins and olefins can be obtained. The FT synthesis reaction, in theory, is a condensation polymerization reaction of CO. Its products obey a well-defined molecular weight distribution according to a relationship known as Shultz-Flory distribution ([www.netl.doe.gov](http://www.netl.doe.gov)).

In general, there are three (3) types of reactor design used in FT synthesis, which are fixed bed reactor, fluidized bed reactor and slurry bed reactor. All these type are in used commercially. The multitubular fixed bed reactors were used by Sasol to produced heavy FT liquid and hydrocarbons and waxes in Sasolburg and it now called as their Low-Temperature FT Synthesis Process, aiming for liquid fuels production. However, most of this type of reactor are be replaced by slurry bed reactors, which is considered the state-of-the-art technology for low temperature FT synthesis. This is because slurry

bed reactor offers temperature control and higher conversion. As for the fluidized bed reactor, it is developed for high temperature FT synthesis to produce low molecular gaseous hydrocarbons and gasoline. It was originally developed in a circulating mode and now be replaced by a fixed fluidized bed type of design called Advanced Synthol reactors. These types of reactors have high throughputs (H. Schulz, 1999).

### **1.1.2 Catalyst for Fischer-Tropsch**

Commercially, cobalt (Co) and iron (Fe) were used as a catalyst for FT synthesis to produce, hydrocarbons, oxygenates and chemicals including unrefined gasoline, diesel and wax ranges (Ahmad Nafees *et al.*, 2007). Cobalt based catalyst have been used as a catalyst for FT synthesis because of their high conversion, high selectivity for heavy hydrocarbons, low water gas-shift activity, and comparatively low price (Shan Yuanyuan *et al.*, 2009). The cobalt catalyst was first discovered in early 1920s and it is considered as the best suitable catalyst for FT synthesis. However, from 1950s until late 1980s, iron based catalyst dominated both industrial and R&D area. But, in early 1990s, development of cobalt based technologies takes place again. As a result of improvement in catalyst design technology, the performance and selectivity of the cobalt based catalyst for FT synthesis has been improved (Ahmad Nafees *et al.*, 2007). A brief comparison of Co and Fe catalyst is given in Table 1.1.



**Table 1.1:** Comparison of Cobalt and Iron FT Catalyst (Khodakov *et al.*, 2007)

<b>Parameter</b>	<b>Cobalt catalysts</b>	<b>Iron catalyst</b>
Cost	More expensive	Less expensive
Lifetime	Resistance to deactivation	Less resistance to deactivation
Activity at low conversion	Comparable	Comparable
Productivity at high conversion	Higher, less significant effect of water on the rate of carbon monoxide conversion	Lower, strong negative effect of water on the rate of carbon
Maximal chain growth probability	0.94	0.95
water gas shift reaction $\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$	Not very significant, more noticeable at high conversion	Significant
Maximal sulphur content	<0.1 ppm	<0.2 ppm
Flexibility (temperature and pressure)	Less flexible, significant influence of temperature and pressure on hydrocarbon selectivity	Flexible, methane selectivity is relatively low even at 613K

## 1.2 Problem Statement

The different type of support used in preparing cobalt based catalyst for FT synthesis will affect the performance of the catalyst. The best suitable support may enhance the activity of the cobalt based catalyst. The activity of cobalt based catalyst depends on the overall amount exposed metal atom. Thus, a highly active catalyst requires a high dispersion of cobalt metal (Dae Jung Kim *et al.*, 2005).

Cobalt dispersion and reducibility are two parameters that determined by the cobalt-support interaction strength (O. González et al., 2009). The mesoporous silica such as TiO<sub>2</sub> and SBA-15 are used to be the support for the cobalt based catalyst in FT synthesis. Cobalt based catalyst was selected as the best suitable catalyst for FT synthesis because of it high conversion, high selectivity for heavy hydrocarbons, low water-gas-shift activity, and comparatively low price.

Among the conventional supports such as Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, SiO<sub>2</sub> and ZrO<sub>2</sub> that usually used for FT synthesis reaction, SBA-15 that has been studied recently was chosen as the best suitable support for cobalt based catalyst because of it highly ordered mesoporous molecular sieve with a narrow pore size distribution and large surface area (Shan Yuanyuan et al., 2009).

Numerous studies show that introduction of noble metals (Ru, Rh, and Pt) has strong impact on the structure and dispersion of cobalt species and FT reaction rates (Khodakov, 2009). But recently this noble's metal are higher in cost (Zhang *et al.*, 2003). As example Shell's plant in Malaysia employs cobalt catalysts. Ruthenium catalysts have excellent FT reactivity; however, no commercial ruthenium catalyst has ever been used, mainly due to its high cost. Ruthenium and zinc has been used to improve the reduction and reactivity of cobalt catalysts (Zhang *et al.*, 2003). Because Zn has a low price than other, it was selected as favorable noble metal for this research.

### **1.3 Objective of the Study**

The objective of this study is to prepare and characterize the cobalt based catalyst of different support for FT synthesis with zinc as the promoter. The catalyst was prepared by incipient wetness impregnation method and characterized by using Fourier Transform Infrared spectroscopy (FTIR) and Scanning Electron Microscopy (SEM).

### **1.4 Scope of Research**

The scopes of this research were to produce cobalt based catalyst with different supports and zinc as a promoter for FT synthesis. The catalysts were prepared by using incipient wetness impregnation method and using different cobalt loading which are 5%, 10% and 15% of cobalt loading. The catalysts that were prepared y using this method are Co/Zn/TiO<sub>2</sub> and Co/Zn/SBA-15 catalysts.

The other scope of this research is to characterize the catalysts. The method used to characterize are FTIR and SEM. From the FTIR and SEM tests, the structure and activity of catalyst with different cobalt loading are discussed.

## 1.5 Rationale & Significance

The rationale and significance of this research is the FT synthesis that has been used in CTL and GTL processes. The FT synthesis reaction is a method used to produce synthetic fuels that have cetane numbers ( $>70$ ), low sulfur content and aromatics (A.Y. Khodakov et al., 2003). Due to the increasing demand for clean fuels, the FT synthesis process has aroused new interest in both industrial and academic field (O. González et al., 2009).

In order to produce hydrocarbons with a broad range of chain length and functionality, transition metal such as Co, Fe and ruthenium (Ru) were used in the FT synthesis process. However, among them Co is considered as the most suitable metal for synthesis long chain hydrocarbon from synthesis gas. Co was chosen as the most suitable metal due to its high activity per weight of metal compared to Fe, high selectivity to linear paraffins, high stability toward deactivation by water, low water-gas shift activity and low price compared to other noble metal such as Ru, rhenium (Re), or platinum (Pt). Therefore, Co is more convenient for production of higher hydrocarbons (O. González et al., 2009).

Various supports have been used for cobalt based catalyst such as silica, alumina, kieselguhr, zeolite, titania, carbon and magnesia (A.Y. Khodakov *et al.*, 2003). In this research, SBA-15 and  $\text{TiO}_2$  were used a support for cobalt based catalyst. As a highly ordered mesoporous structure, SBA-15 is more favorable as support for cobalt based catalyst in FT synthesis.

## **CHAPTER 2**

### **LITERATURE REVIEW**

#### **2.1 Fischer-Tropsch (FT) Synthesis**

At the beginning of 20<sup>th</sup> century, due to lack of domestic petroleum supply in Germany, the government at that time devotes a large amount of diligence and money towards research on alternative fuel resources. Their researchers' main focus is on conversion of coal into synthetic liquid fuels. In early 1923, Franz Fischer (1877-1947) and Hans Tropsch (1889-1935) at the Kaiser Wilhem Institute for Coal Research (KWI) in Mülhem, Ruhr, invented a process that convert syngas into higher gaseous, liquids and solid hydrocarbons. This process was carried out in a catalytic reactor under atmospheric pressure in the presence of cobalt and iron as catalyst. This process was later named as FT synthesis. The invention of FT synthesis was then upgraded to industrial plant in 1935 by Ruhrechemie A.G., and within a short period of time, eight (8) industrial plants were operating in Germany and all of them were using FT technology for fuel production. Since then, many plants that using FT technology were built all over the world such as in Europe (France and Great Britain), Asia (Japan) and United States in North America (Elbashir, 2004).

Fischer and Tropsch played an important role in the development of FT technology; however, many scientists have tried to develop the synthesis of liquid fuels. In the years of 1910-25, Friedrich Bergius (1884-1945) in Rheninaw-Mannheim began his work on the Germany drive for energy independence with his invention and early development of high pressure coal hydrogenation of liquefaction. But, after a decade of Bergius' work began, Fischer and Tropsch invented the second (2<sup>nd</sup>) important process for synthesis of liquid fuel FT synthesis technology (Elbashir, 2004).

In 1943, the Bureau of Mines in the United State established a program to develop coal based supply of transportation fuels that involve both direct and indirect processes. This work is done under the direction of H.H. Storch. In 1925, the petroleum produces by United State is almost 70% of the world's petroleum. However, in 1940s, the world and United State faced a serious fear that they would run out of petroleum. Before involving in the design and operation of coal liquefaction plants, the Bureau of Mines was involved in receiving and translating ng the teams that running the German plants and interviewed those who worked in the plants. By 1944, most of the basic idea for the design of FT reactors had been formulated and tested on at least one pilot plant scale. Bureau's work more concentrated on synthesis with the catalyst in the liquid phase, and most of the emphasis was on the oil recirculation process. The catalyst used in catalytic system are cobalt, iron, and nickel in a combination of gas and circulation from the bottom to top of the reactor in order to maintain the catalyst in suspension inside the reactor.

Research interest in FT technology began around 1920s at the Institute of Organic Chemistry of the USSR Academy and Sciences conducted by Prof. Ya. T. Eidus and Prof. A. L. Lapidus. The main emphases were on the design of new catalyst for FT synthesis and the modification on the existing catalyst such as cobalt, iron, copper and manganese. They also study the effect of various promoters on the reaction rate and mechanism. However, much attention and focused were gave to the study about the effect of support, catalyst preparation and regeneration procedures (Elbashir, 2004).

FT synthesis that is also known as a catalytic process converts synthesis gas (CO and H<sub>2</sub>) into long chain hydrocarbons and oxygenates. In other way, FT synthesis provides a practical way for the chemical liquefaction of solid (coal) or gaseous (natural gas) carbon resources. This liquefaction process, which is via FT synthesis, also provides alternatives routes for the production of transportation fuels and petrochemical feedstock instead of classic refining of crude oil.

There are two main companies that are known using this FT synthesis as commercial to produce synthetic fuels which are Sasol in South Africa and Shell in Malaysia. The capacity of the product of Sasol plant is 125, 000 barrel per day while Shell plant in Malaysia produces 12, 500 barrel per day. The interest in FT synthesis technology has been increasing until today. The reasons for the increasing of interest in FT technology are illustrated by four (4) criteria:

- The world reserves of carbon-containing resources;
- The geographic location of these reserves;
- The demand for cleaner feedstock;
- The reduction of CO<sub>2</sub> emissions.

According to Henricus (2001), the worlds proven reserves for natural gas and especially coal are much larger than the proven reserves for crude oil. At the end of 1999, the crude oil reserves are  $140 \times 10^9$  tons while for natural gas, the reserves are  $146 \times 10^{12} \text{ m}^3$ . In the near future, instead of crude oil, the utilization of natural gas will become increasingly important in energy sector and FT synthesis is believed to be one of the key processes to meet this future energy demand (Henricus, 2001).

Sasol Company, which is South Africa's largest oil company played important role in recent developments in FT synthesis technologies especially in reactor design and new catalytic system. The construction of Sasol One was led by the worldwide climate in 1940s and the high consumption levels of crude oil reserves, followed by significant increases in the price of crude oil in 1950s. Sasol One is the first project and FT plant

owned by Sasol. In the 1970s, the price of crude oil keeps rising and this led the Sasol to expand its operation by developing two new plants, Sasol Two in 1980 and Sasol Three in 1982. The main technical contribution of Sasol is its scaling-up of Kellogg's pilot plant unit at Sasolburg, South Africa with a capacity of 4-5 barrel per day to 2200 barrel per day by using the first two commercial Circulated Fluidized Bed (CFB) units. Later, Sasol also invented Sasol Advanced Synthol (SAS) technology that uses a less expensive reactor without the CFB complexity of the reactor-hopper-standpipe system suspended in a complex structure.

An overview of the current technologies used in FT synthesis technology is given in Table 2.1. By using Sasol's CFBR and FBR as exceptions, all processes are aimed at high wax selectivity.

**Table 2.1:** The current technologies used in FT synthesis technology (Henricus, 2001)

Licencor	Status	Syngas production	FT reactor	Catalyst	Reference
Sasol	commercial	PO SR	CFBR FBR TFBR SBCR	Fe Fe Fe Fe, Co	Dry (1999), Espinoza <i>et al.</i> (1999), Steyberg <i>et al.</i> (1999)
Shell	commercial	PO	TFBR	Co	Eilers <i>et al.</i> (1990), Geerlings <i>et al.</i> (1999)
Exxon	Pilot plant	CPO	SBCR	Co	Eisenberg <i>et al.</i> (1998)
Syntroleum	Laboratory	ATR	TFBR	?	Reference in Van der Laan and Beenackers (1999)
Energy international	?	PO	SBCR	Co	Wilson and Carr (1999)
Rentech	Pilot plant	PO, SR, ATR	SBCR	Fe	Benham and Bohn (1999)

Syngas manufacturing

PO = partial oxidation

CPO = catalytic partial oxidation

ATR = autothermal reforming

FT reactor

CFBR = circulating fluidized bed reactor

FBR = fluidized bed reactor

TFBR = tubular fluidized bed reactor

SBCR = slurry bubble column reactor



## 2.2 Fischer-Tropsch (FT) Reactor Process Development

Performance of FT synthesis depends on reaction temperature. Increase the temperature will favor selective methane formation, favors deposition of carbon and thereby deactivation of the catalyst which is particularly with iron, and reduces the average chain length of the product molecules. Increasing the reaction temperature also will increase the FT reaction rate (Schulz, 1999).

Currently there are two FT operating modes. One is high temperature (300 – 350 °C) modes with iron based as catalyst and used for the production of gasoline and linear low molecular mass olefins. Another mode is low temperature (200 – 240 °C) modes with either iron or cobalt used as catalyst. This mode is used to produce high molecular mass linear waxes.

FT reactions are highly exothermic. Therefore, it is important to rapidly remove the heat of reaction from the catalyst particles in order to avoid overheating of the catalyst which would otherwise results in increased rate of deactivation to sintering and fouling, and also in the undesirable high production of methane. By forcing the syngas at high linear velocities through long narrow tubes packed with catalyst particle to achieve turbulent flow will result in high rates of heat exchange. However, by operating in fluidized catalyst bed reactor, the result will be better (Dry, 2002).

In general, there are three different types of reactor design that might be used for FT synthesis. They are known as fixed bed reactor, fluidized bed reactor and slurry bed reactor. All these three types of reactors are used commercially. The multitubular fixed bed reactors, also known as Arge reactors, were developed by Lurgi and Ruhrchemie and commissioned in 1955. This type of reactor was used by Sasol in order to produce heavy FT liquid hydrocarbons and waxes in Sasolburg. The process is now called Low Temperature FT Synthesis Process by Sasol, that aiming for liquid fuels production. However, now almost all of Arge reactors were replaced by slurry bed reactors. The