

EFFECT OF COBALT AND ZINC PRECURSOR LOADING
ON THE CATALYST ACTIVITY OF FISCHER
TROPSCH SYNTHESIS

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BORANG PENGESAHAN STATUS TESIS♦

JUDUL: EFFECT OF COBALT AND ZINC PRECURSOR LOADING ON THE CATALYST ACTIVITY OF FISCHER TROPSCH SYNTHESIS

SESI PENGAJIAN: 2011/2012

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Special dedicated to my beloved parents

ACKNOWLEDGEMENT

In the name of Allah the Most Gracious and Most Merciful. First and foremost, thank you to Allah the Al-Mighty for His blessing and grants me a strength to complete this research as scheduled. My deepest and sincere gratitude goes to my beloved parents, brother, sister and other family members for their endless love, support and blessing. Thank you for always standing by me.

Afterwards, I would like to express my greatest appreciation to my supervisor, Madam Nurul Sa'aadah bt Sulaiman for her patient and excellent guidance as well as infinite suggestion throughout my research work.

Special thank also goes to Mr Masri A. Razak who spends his time to help and advise me during experiment in the laboratory. I would like to show my gratitude towards Dr. Cheng Chin Kui for his encouragement, assistance and willingness to share experiences in order to accomplish my research.

Last but not least, I would like to thank all lecturers, administrative staff and teaching engineers at the laboratory for their valuable help. Thank you for being so helpful. Not forgotten to my friends; Nursyilla, Wafa', Intan Diana, Norhidaya, Nor Adila, Nurul Fatin Shazwani, Amirul Mukmin, Diana Linggang, 4BKG classmates, and others. Thank you very much for your sincere help, concern, moral support and kindness. May Allah bless us.

ABSTRACT

Five samples of Co-Zn/SBA-15 catalysts were prepared using wet impregnation method with different composition of cobalt loading (5, 10 and 15 wt % Co) and zinc loading (5, 10 and 15 wt % Zn) and were investigated with respect to physical and chemical properties as well influence on activity and selectivity for conversion of H₂/CO₂ synthesis gas. The catalysts were tested by using Fourier Transform Infrared Spectroscopy (FTIR), X-Ray Diffraction (XRD), Scanning Electron Microscope (SEM), N₂ Adsorption Analysis (BET) and Thermogravimetric Analyzer (TGA). The feed gas of CO₂ instead of CO also had been considered that contributed to product selectivity since cobalt catalyst do not exhibit significantly in Water Gas Shift (WGS) activity and CO₂ neither formed nor produced during Fischer Tropsch (FT) synthesis with cobalt catalyst and H₂/CO. An investigation of catalytic CO₂ hydrogenation into high quality fuels and valuable hydrocarbons was carried out in a glass borosilicate reactor. The operating condition for catalytic testing is at 220 °C and 1 bar using H₂/CO₂ feed ratios of 3:1. Selectivity of products was depending upon the amount of metal loading constituent as well as the syngas mixture that used. It was found that higher metal loading with optimized promoter loading was the best catalyst for Fischer Tropsch synthesis. It is experimentally found that from the result of gas chromatograph, the conversion of CO₂ and product selectivities were calculated. The most efficient catalyst for Fischer Tropsch synthesis is 15% Co/10% Zn-SBA-15. This result was proven by the characteristic of catalyst which is the existence functional groups of cobalt oxides, Si-O-Si, Si-CH₃, zinc oxide, OH band, Si-C, and others, higher intensity that indicates higher cobalt dispersion, possess large surface area as well as pore size, small weight losses that indicate thermal stability and having large number of catalyst particles attaching closely with one another that make it more effective during FT process.

ABSTRAK

Lima sampel Co-Zn/SBA-15 pemangkin disediakan dengan menggunakan kaedah impregnasi lembap yang mempunyai komposisi kobalt (5, 10 dan 15%) dan zink (5, 10 dan 15%), seterusnya meneliti pengaruh sifat fizikal dan kimia ke atas aktiviti pemangkin dan selektiviti bagi proses penukaran gas sintesis H₂/CO₂. Pemangkin telah dianalisa dengan menggunakan Spektroskopi inframerah transformasi Fourier (FTIR), Pembelauan Sinar-X (XRD), Pengimbasan Mikroskop Elektron (SEM), N₂ Analisis Penjerapan (BET) dan analisa Termogravimetri (TGA). Gas yang digunakan ialah CO₂ menggantikan CO juga telah dianggap sebagai penyumbang kepada selektiviti produk berikutan pemangkin kobalt tidak berperanan dalam proses perubahan gas menjadi air (WGS), aktiviti dan akibat penghasilan CO₂ semasa sintesis Fischer Tropsch (FT) dengan pemangkin kobalt dan H₂/CO. Suatu penyiasatan penghidrogenan CO₂ sebagai pemangkin kepada bahan api yang berkualiti tinggi dan hidrokarbon yang berharga telah dijalankan menggunakan reaktor borosilikat kaca. Parameter yang digunapakai untuk eksperimen ini adalah pada 220 ° C dan 1 bar yang menggunakan nisbah H₂/CO₂ iaitu 3:1. Penghasilan produk bergantung kepada jumlah jujuk muatan logam serta campuran komposisi gas yang digunakan. Ia mendapati bahawa muatan logam yang lebih tinggi dengan muatan penganjur yang optimum adalah pemangkin terbaik sesuai untuk sintesis Fischer Tropsch. Hasil uji kaji daripada gas kromatografi, penukaran CO₂ dan selektiviti produk dapat ditentukan. Pemangkin yang paling berkesan untuk sintesis Tropsch Fischer adalah 15% Co/10% Zn-SBA-15. Keputusan ini telah dibuktikan melalui ciri-ciri pemangkin yang wujudnya kumpulan oksida kobalt, Si-O-Si, Si-CH₃, zink oksida, OH band, Si-C, dan sebagainya, beintensiti lebih tinggi yang menunjukkan bahawa penyebaran kobalt yang lebih tinggi, mempunyai kawasan permukaan yang besar serta saiz liang, kehilangan berat yang sedikit menunjukkan kestabilan terma dan mempunyai sejumlah besar zarah pemangkin yang bersusunan rapat antara satu sama lain yang membuat ia lebih berkesan semasa proses FT.

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LIST OF ABBREVIATION

BET	N ₂ Adsorption Analysis
Co	Cobalt
Co₃O₄	Cobalt oxide
FT	Fischer Tropsch
FTIR	Fourier Transform Infrared Spectra
GTL	Gas to Liquid
SEM	Scanning Electron Microscope
TGA	Thermogravimetric Analysis
WGS	Water Gas Shift
XRD	X-Ray Diffraction
Zn	Zinc

CHAPTER 1

INTRODUCTION

1.1 RESEARCH BACKGROUND

The increasing demand for high quality and environmentally friendly in transportation fuels together with the technology improvements in gas-to-liquid (GTL) processes making them more efficient and cost competitive. This latest innovation of technology has renewed the interest of using natural gas as a potential source of hydrocarbons (Fleisch, 2002). Often, in remote location of oil fields, a considerable amount of natural gas can be found, where the pipeline to transport the gas is not economically available. This condition has led natural gas to be flared, vented, or pumped undergrounds (Thayer, 2000). Therefore, the need to find an efficient process for utilizing natural gas receives considerable attention.

GTL is a technology that converts the gas (natural gas, biomass, and coal) to liquid fuel for easy to transport (Wilhelm et al., 2001). GTL process consists of three stages which are synthesis gas generation, production of heavy-chain hydrocarbons by Fischer-Tropsch synthesis and heavy fraction hydrocracking for production of useful products such as naphtha, lubricants and diesel (Aguiar et al., 2005). Particularly, diesel fuels made with GTL technology undergoes the Fischer Tropsch (FT) synthesis process offers significant environmental and efficiency benefits over those derived from crude oil, as they are mainly composed by liner paraffins having high cetane numbers as

higher cetane number gives higher speed diesel operation as well as free of sulfur and aromatics pollutants (Van der Laan and Beenackers, 1999). FT synthesis products have been practically used in worldwide as the alternative fuel to replace conventional diesel fuel in transportation by using syngas instead of crude oil which the source becomes crucial. The production process to obtain the FT synthesis product can be described as in Figure 1.1

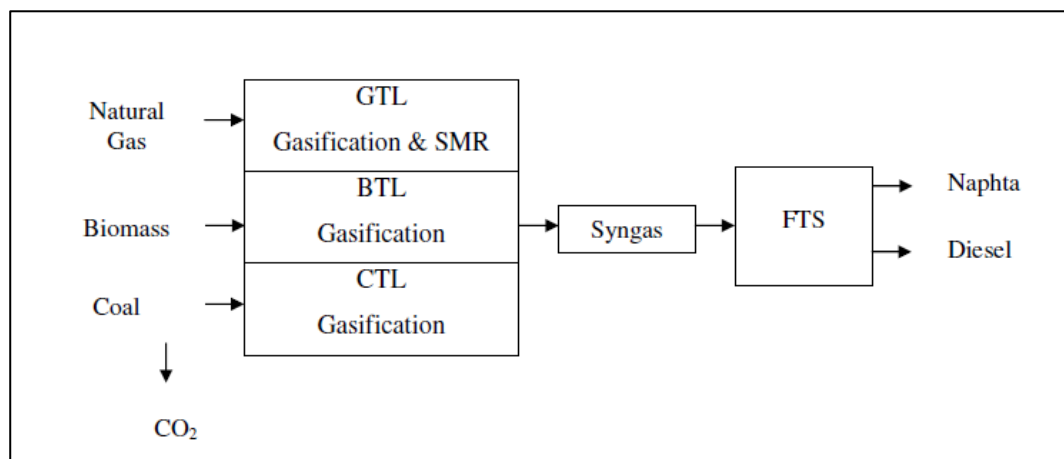


Figure 1.1: Potential routes to clean liquid fuels based on the Fisher Tropsch synthesis process (Wilhelm et al., 2001).

Fischer Tropsch (FT) synthesis proceeds through a polymerization-type mechanism where monomeric CH_3 species coming from the catalytic dissociation and hydrogenation of CO_2 are assembled in successive CH_3 insertion straight chain species (Brady and Pettit, 1980). The nature of product site requirements to selectively direct the CO_2 hydrogenation toward specific products and the structural and chemical changes experienced by the metal catalyst under working conditions (temperature of $200\text{-}350^\circ\text{C}$, relatively high pressures, CO_2 -rich environment and present of the by-product (Wilson, 1995).

The common catalyst that has been used in Fischer Tropsch industrial is metal that categorized as transition metals in group VIII. Their noticeable activities in the hydrogenation of carbon dioxide to hydrocarbon are greater than other metal group. The most active metals that used in catalytic conversion of syngas are ruthenium, iron,

nickel, and cobalt with the decreasing active metal. However, cobalt is the more suitable because it is more resistant to deactivation and cheaper than ruthenium which ruthenium reserves are insufficient for large scale industry. Cobalt supported on oxide supports is generally more resistant to attrition than iron precipitated counterparts as they are more suitable for use in slurry reactor. In addition, cobalt gives higher conversion of syngas due to large pore size that provide more surface area (Khadakov et al., 2007). Table 1.1 shows the detail comparison between cobalt catalyst and iron catalyst which are the common catalysts being used in industry.

Table 1.1: Comparison between Cobalt and iron catalysts in FT synthesis
(Khadakov et al., 2007)

Parameter	Cobalt	Iron catalyst
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 conversion	Lower, strong negative effect of water on the rate of carbon
Maximum chain growth probability	0.94	0.95
Maximum 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

On the other hand, the process also demonstrated that the larger pore size enhanced the activity and selectivity to C5+ products in the Fischer-Tropsch reaction on cobalt catalysts supported on periodic mesoporous silicas (SBA-15) (Khadakov et al., 2002). In this respect, SBA-15 metal displaying larger pore size which is 2–50nm in

diameter. The use of periodic mesoporous silica (SBA-15) as a Fischer-Tropsch catalyst support has witnessed a tremendous growth. The high surface area (500 - 1500 m²/g) of the SBA-15 gives higher metal dispersions due to providing more active sites. The dispersion gave better result after an amount of promoted noble metal zinc was promoted to the cobalt catalyst. It permits better control of the cobalt particle size and the distribution of hydrocarbon products from the FT synthesis. Thus, the best choice to recommend is SBA-15 as the catalyst to get higher catalytic activity and hydrocarbon selectivity in FT synthesis for cobalt based catalyst and Zn as promoter.

Fischer Tropsch synthesis is producing mostly fuel type products which are based on number of carbon such as wax, diesel, gasoline, naphtha, LPG and kerosene. But our main products are combined diesel and gasoline after product upgrading separation. But then, F-T synthesis is producing such as products below after going further to product upgrading section. Figure 1.2 shows the percentage of Fischer Tropsch product.

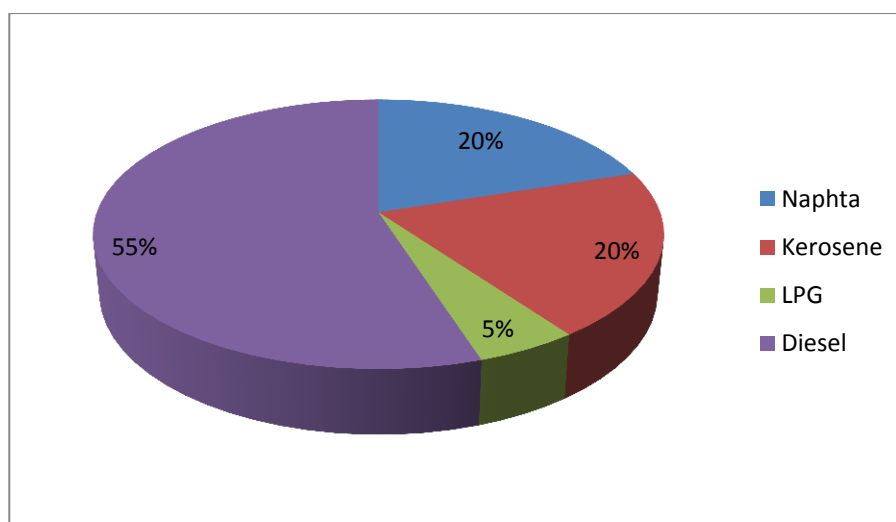


Figure 1.2: Percentages of the GTL products (Shalchi, 2006).

There are many factors that contribute on impact of the percentage of the either product increases or decreases. The percentage is rise or decline depending to the kind of technology employed nature of the catalyst, and the conditions of the reactions used. The properties of the GTL products are typical with respect of its combustion or its

environmental effects. Hence the important care of the properties of the products play a great part in the promotion of the GTL industry (Shalchi, 2006).

1.2 Problem Statement

The development of new catalysts is the necessity to improve better, cleaner manufacturing processes for the multitude of fine chemicals for daily life (Weitkamp, 2000). Catalyst is a vital part of any industrial Fischer Tropsch process. The synthesis products become highly demanded since the fuels are eco-friendly products which contain almost no sulphur. Several recent studies have revealed the feasibility of conversion of syngas into products of higher added values such as olefins, aromatics and oxygenous derivatives. These routes are possible if the reaction is carried out over a optimize catalyst.

In the industry application, iron, cobalt and ruthenium are the common catalysts for FT synthesis (Mukaddes, 2005). However, cobalt catalyst is being the preferred catalysts due to its high activity for FT synthesis, high selectivity to linear hydrocarbons, low activity for the water gas shift reaction, more stability toward deactivation by water and low cost compared to Ru (Tavasoli et al., 2007).

The application of SBA-15 which categorized in mesoporous silicas functions as a supports to the cobalt base catalysts. It has been chosen because the pores have very high surface area that will permit high dispersions at higher cobalt loading as compared to other silicas (Martinez et al., 2003).

Cobalt catalyst that promoted by noble metal like zinc has given strong impact on the catalyst structure and dispersion as well as FT reaction rates (Khodakov, 2009). Zinc promoter is used in this research in order to improve the reduction and reactivity of cobalt catalysts. In addition, it was commonly used in industry for hydrocarbon synthesis due to its lower price than other.

Numerous studies have shown that the catalytic conversion of syngas mixture into liquid hydrocarbons can be proceeding with high content of CO₂ in feed gas. Weatherbee et al. proposed that CO₂ hydrogenation process has follow the same reaction pathway with the formal process which is CO hydrogenation but different in product selectivity. So in this research, the investigation is about to see the how CO₂ affected the catalytic process that later will gives a large effect to the hydrocarborns produced.

1.3 Objective of Research

The objectives of this research are as follows:

- To prepare SBA-15 as supporter and to synthesis Co-Zn/SBA-15 with different cobalt and zinc loading
- To characterize of synthesized catalysts with different composition of cobalt and zinc loading by using several analytical techniques.
- To evaluate the effect of cobalt and zinc loading precursor on catalyst activity and product selectivity with influence of CO₂ fed.

1.4 Scope of Research

In order to accomplish the objectives, scopes of research have been identified in this research to manage the task within the frame work. The scopes of this research are divided into three. Firstly, synthesizing the optimize catalyst for FT synthesis which is SBA-15. The influence of different loading of cobalt and zinc precursor was investigated after synthesize Co-Zn/SBA-15 catalysts with different cobalt and zinc loading which range 5 to 15 wt% using incipient wetness impregnation method. The catalysts were then characterized for their properties by using Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), Thermogravimetric Analyzer (TGA) Scanning electron microscope (SEM), and N₂ adsorption analysis (BET). Lastly, the

catalysts have been tested in glass borosilicate reactor with furnace and connected to the online gas chromatograph to detect the hydrocarbon production and then analyzed the catalyst activity performance based on the selectivity.

CHAPTER 2

LITERATURE REVIEW

2.1 Gas to Liquid Process

Gas-To-Liquids (GTL) processes have received wide spread attention as an economically viable route to convert natural gas to ultra clean liquid fuels. Recently, there has been an increasing interest in the conversion of remote and abundant natural gas into high quality fuels and valuable raw chemicals via synthesis gas. The GTL is the process of converting natural gas into transportable liquids and consists of three main steps, (i) the reforming of synthesis gas, (ii) the production of hydrocarbons from synthesis gas through Fischer Tropsch synthesis, and (iii) the optimization to upgrade and separate products (Shikada et al., 1983). There are several key factors that drive growth in the GTL industry (Fleisch et al., 2002):

- The need to monetize the large amount of existing stranded natural gas reserves.
- The market demand for cleaner fuels and new cheaper chemical feed stocks.
- Technological development by existing and new role players which is leading to cost effectiveness of FTS technology from development of more active catalysts and improved reactor systems.
- Increased interest from gas-rich host countries.
- The need to diversify economies and to create new employment opportunities.

The synthesis gas manufacturing and the product upgrading rely on established technologies. Synthesis gas manufacturing is applied widely in the production of methanol and ammonia. Future developments are expected in the field of catalytic partial oxidation and in membrane techniques for oxygen purification (Venkatarama et al., 2000). Product upgrading processes directly originate from the refining industry and are highly optimized. The three steps in GTL are schematically represented in the block diagram of Figure 2.1.

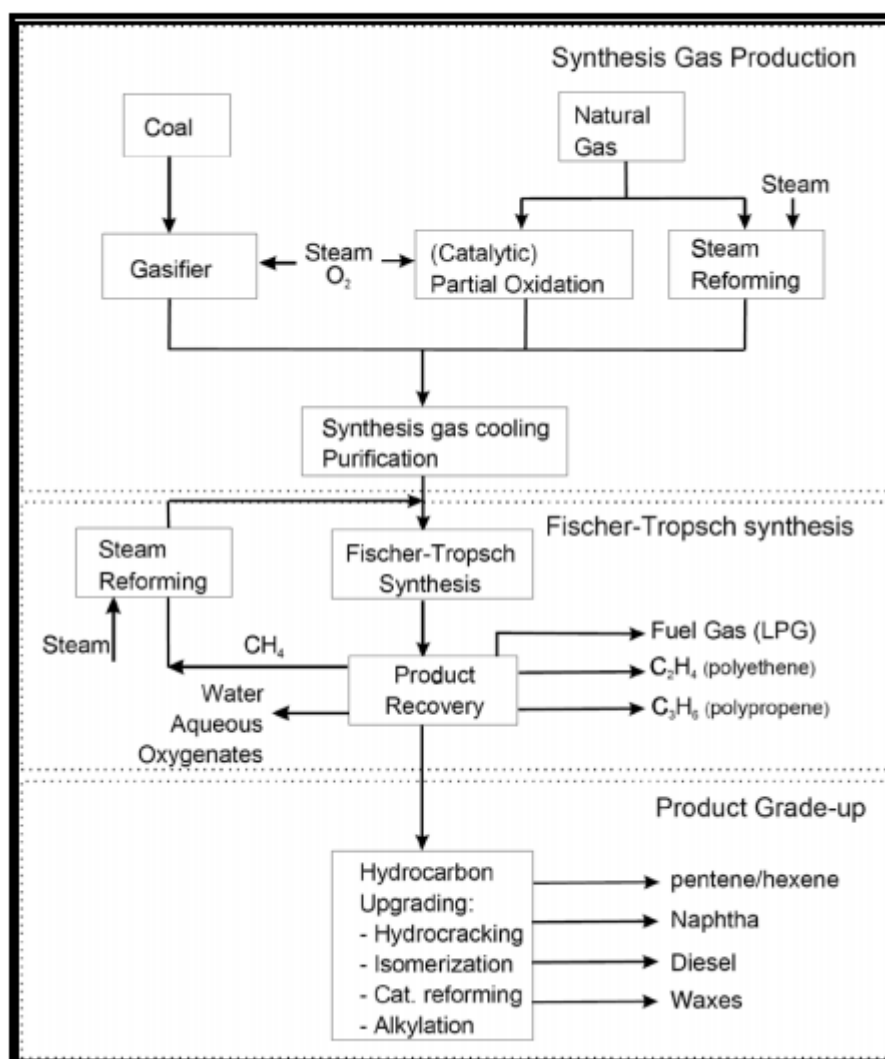


Figure 2.1: The main three processes present in Fischer-Tropsch synthesis (Tiefeng and Yong, 2007).

2.2 Synthesis Gas Manufacturing

Synthesis gas is a mixture of carbon monoxide (CO), carbon dioxide (CO₂) and hydrogen (H₂), which can be obtained from any carbon containing feedstock. Three basic methods of converting a feed stream into synthesis gas exist such as reforming, partial oxidation, and catalytic partial oxidation. Instead of natural gas, synthesis gas also can be produced by catalytic reaction or partial oxidation of fossil fuels such as coal, refinery residues, biomass or others. Table 2.1 below shows synthesis gas composition for different feedstock.

Table 2.1: Synthesis gas composition for different feedstock (De Smet, 2000)

Feedstock	Process	Component (vol%)			
		H ₂	CO	CO ₂	Other
Natural gas, steam	SR ¹	73.8	15.5	6.6	4.1
Natural gas, steam, CO ₂	CO ₂ - SR ²	52.3	26.1	8.5	13.1
Natural gas, O ₂ , steam, CO ₂	ATR ²	60.2	30.2	7.5	2.0
Coal/heavy oil, steam	Gasification ¹	67.8	28.7	2.9	0.6
Coal, steam, oxygen	Texaco gasifier ¹	35.1	51.8	10.6	2.5
Coal, steam, oxygen	Shell/Koppers gasifier ¹	30.1	66.1	2.5	1.3
Coal, steam, oxygen	Lurgi gasifier ³	39.1	18.9	29.7	12.3

SR= steam reforming, CPO= catalytic partial oxidation, ATR= autothermal reforming

In partial oxidation, the feed stream is mixed with steam and oxygen at high temperature (1573-1773 K). It is partially combusted followed by endothermic reforming steps and the water-gas shift reaction. Meanwhile, for the catalytic partial oxidation, a catalyst plays the function of the flame in the partial oxidation. The advantages of the catalytic partial oxidation of methane over steam reforming of methane are the low exothermicity of the process and the high reaction rates (De Smet, 2000).

2.3 Fischer-Tropsch (FT) Synthesis

Fischer-Tropsch synthesis is the process that converts synthesis gas that contains a mixture mainly of carbon monoxide, carbon dioxide and hydrogen, into a wide range of long chain hydrocarbons such as alkanes, alkenes, alcohols, aldehydes, ketones, ethers and acid as well as oxygenates (Gholami et al., 2009). Fischer-Tropsch synthesis provides alternative routes for the production of transportation fuels and petrochemical feedstock and it is the other way around to the classic refining of crude oil to produce the liquid fuel products.

Fischer Tropsch technology is seems to be increasing in these recent decades. The increasing importance of the Fischer-Tropsch synthesis for the near future is illustrated by four criteria:

- The world reserves of carbon-containing resources
- The geographic location of these reserves
- The demand for cleaner feedstock
- The reduction of CO₂ emissions.

The hydrocarbon and wax that produced by the low temperature FT process consists of linear paraffin with a small fraction of olefins and oxygenates. The FT mechanism is quite complex and it can be described in the following steps:

- 1) Initiation or C₁ compound formation.
- 2) Hydrocarbon chain growth by successive insertion of the C₁
- 3) Chain termination by: - desorption of unsaturated surface species, and
- Hydrogenation and desorption of saturated species.

The Fischer-Tropsch product spectrum consists of complex multi-component mixture of linear and branched hydrocarbons and oxygenated products. Main products are linear paraffin and α -olefins.

2.4 H₂/CO₂ Syngas

The synthesis gas or syngas that can be derived from coal, natural gas, or biomass primarily contains H₂, CO, and CO₂. The composition of syngas is reliant on many aspects such as gasifier type, operational conditions, and gasifying agents, causing the composition of CO₂ in the syngas varies from around 1 to 30% (Higman, 2007). Discharge control and utilization of CO₂ has received abundant of attention due to its large-scale availability and the harmful effect of carbon dioxide to the environment. Numerous approaches have been suggested to maintain the concentration of atmospheric CO₂ or to diminish and recycle it. Among these, the hydrogenation of CO₂ has conventionally been carried out on catalysts that are considered to be active and selective for the FT reaction (Rao et al., 1992)

The mechanism of CO₂ hydrogenation in FT synthesis is assumed to proceed in two steps; first, the reverse WGS (R-WGS) reaction takes place to produce CO, which is afterwards consumed in the FT conversion while the direct hydrogenation of CO₂ has also been suggested as an further reaction (Riedel et al., 2001) However, regardless of whether the conversion of CO₂ to hydrocarbons take place in one or many steps, the overall effect is that CO₂ is hydrogenated and being referred to the overall reaction as CO₂ hydrogenation. Figure 2.2 shows the mechanism of CO₂ hydrogenation that proposed in FT synthesis

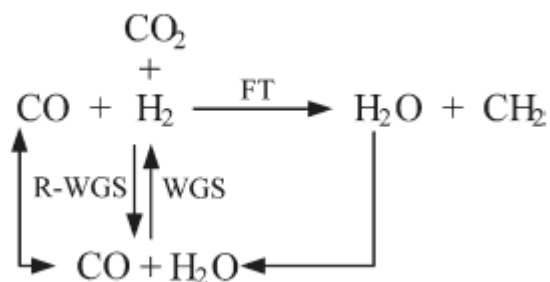


Figure 2.2: Reaction scheme proposed for H₂/CO or H₂/CO₂ feed gas for FT reaction (Riedel et al., 2001).

Cobalt based catalyst active in both WGS and R-WGS reactions would be ideal catalyst for use in the FTS for CO₂ syngas feeds. H₂/CO₂ can be converted into hydrocarbon products of a structure and composition similar to those obtained with H₂/CO over cobalt catalyst (Riedel et al., 2001). However, hydrogenation on cobalt-based catalysts shows that CO₂ hydrogenation has a higher selectivity for light hydrocarbon products with a low alpha distribution (Shi et al., 2005)

The CO₂ produced can be reduced by increasing the rate of the R-WGS reaction, with the potential addition of CO₂ as the WGS reaction is an equilibrium-controlled reaction. CO₂ creation could be significantly declined on cobalt catalysts when CO₂ was added to the syngas. The accumulation or recycling of CO₂ drops the net rate of CO₂ formation, and raises the fraction of the oxygen atoms in CO that are removed as H₂O. This is an essential practical concern when cobalt-based catalysts are used for H₂/CO mixtures derived from natural gas (Davis, 2007).

2.5 Fischer Tropsch Reactors

F-T reactor plays a main role in F-T plant which is considering the operating temperature, pressure and type of catalyst used. Currently there are three types of reactor that commercially used for FT synthesis. Figure 2.3 shows the schematic diagram of the reactor.

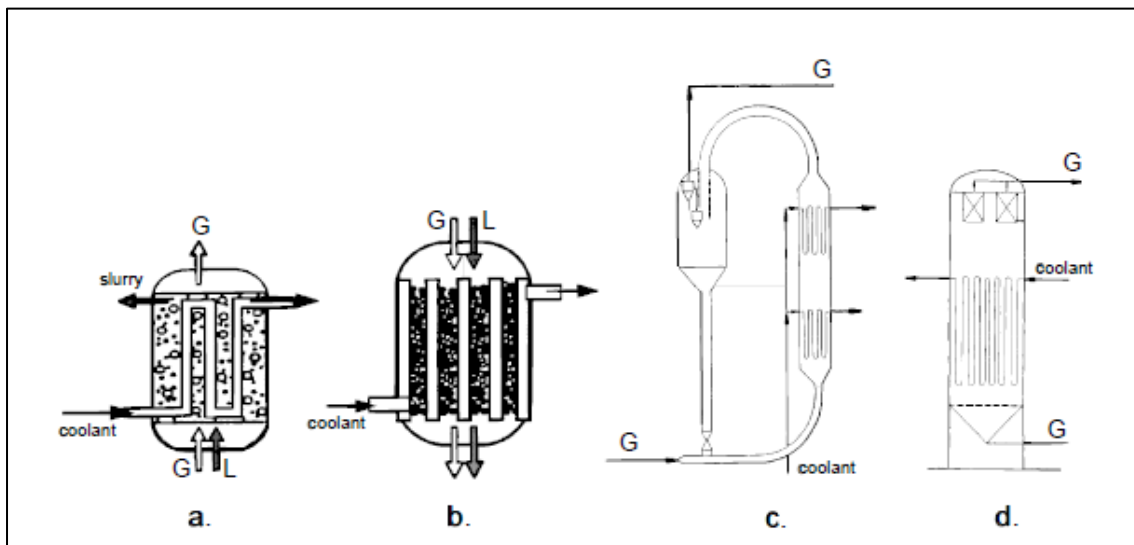


Figure 2.3: Possible reactors for Fischer-Tropsch synthesis a. Slurry bubble column reactor; b. Multi tubular trickle bed reactor; c. Circulating fluidized bed reactor; d. Fluidized bed reactor (Sie, 1998)

In a slurry-phase reactor, the feed syngas is bubbled through inert oil in which catalyst particles are suspended. Conversion by slurry-phase FT synthesis can achieve single-pass fractional conversion up to 80%. This compares to less than 40% conversion with traditional fixed-bed reactors. High single-pass conversion rates make slurry-phase reactors especially attractive from an overall cost perspective for operating temperature process designs. The slurry bed reactors operate in series and composed of 5 stages (Kreutz et al., 2008). The syngas is fed in the first stage of slurry bed reactors operating at 220°C and 21.4 bars can be converted into higher linear paraffin over cobalt catalyst. The bubble column slurry bed reactor eliminates extensive heat, released by FT synthesis reaction via steam generation and provides significant advantages over conventional fixed tubular reactor and fluidized bed reactors.

Fluidized bed reactors are preferably suited for production of lower molecular weight long chain hydrocarbons from syngas. This reactor can operate only when all the reactants are in gaseous phase. Fixed fluidized bed reactor operates at a pressure at 24 bar and a temperature of 340°C while circulating bed reactor runs at 330-350°C and pressure of 25 bar. These types of reactor can be used for gasoline production. The chain growth probability (α) in fluidized bed reactor is less than 0.71 for stable bed

process since it is eliminating the production of heavy wax. For very high α , removal of hydrocarbon from the catalyst becomes a serious problem. Catalyst regeneration is frequent due to high condensable products in the fluidized bed process (Jager et al., 1996).

From the view point of precise controlling of reaction temperature and variably selectivity of the F-T catalyst by hanging operating conditions, reactor system was studied (Samiran, 2007). The summary of reactor studies is summarized in Table 2.2

Table 2.2: F-T synthesis reactors and their main feature, (Samiran, 2007).

Type of reactor	Status	Structural features	Operating Temp. (°C)	Approx. Heat Transfer coefficient (kcal/m ² .hr. °C)	Major product
Old fixed bed (German)	Industrial scale (ohsolate)	Shell & double tube (concentric)	220-260	30	Diesel oil and wax
Improved fixed bed (Arge)	Commercial	Shell & Tube	220-260	150	Diesel oil and wax.
Multi bed	Pilot scale	Shell & Tube and Tray		NA	
Tubular-cum Tray	Pilot scale	Shell & Tube and Tray	220-260	150-170 Tubular section & mainly as sensible heat from Tray	Diesel oil & Wax or gasoline & Diesel oil
Hot gas recycle	Pilot scale	Single catalyst bed (Cylindrical shell)	300-350	*	Gasoline
Oil recirculation	Pilot scale	Single catalyst bed. (Cylindrical shell)	220-270	*	Gasoline
Fixed fluidized bed.	Commercial	Cylindrical shell. Heat transfer through tube bundle in bed.	300-330	450	Gasoline & Chemicals
Circulating fluidized system	Commercial	Cylindrical shell with two cooling zones Top & bottom connected through piping loop	300-330	450	Gasoline & Chemicals
Slurry phase	Commercial	Cylindrical shell. Heat transfer through tube bundle in bed.	200-320	200	Gasoline/ Diesel oil/Eax.

The advantages and disadvantages of the two most common reactor systems; multitubular trickle bed reactor and the slurry bubble column reactor for the Fischer-Tropsch synthesis of high molecular weight products: that can be seen. Major drawbacks of the bubble column are requirements for continuous separation between catalyst and liquid products, a smaller scaling-up factor (500) in comparison to the multitubular reactor (max. 10,000), and possible attrition of the catalyst particles. However the advantages of multitubular reactor are;

- 1) Low pressure drop over the reactor.
- 2) Excellent heat transfer characteristics resulting in stable reactor temperatures.
- 3) No diffusion limitations.
- 4) Possibility of continuous refreshment of catalyst particles.

Disadvantages of the multitubular reactor are the larger catalyst particles, the required equal distribution of gas and liquid streams over all tubes, and the large reactor weight due to a large number of tubes for effective heat transfer area. However, the most important disadvantage of the multitubular reactor probably is in the high costs of 10 to 100,000 tubes, typical for commercial scale (Saxena et al., 1986).

2.6 Fischer-Tropsch Catalysts

Numerous of studies have been done on the influence of metallic based catalyst on CO₂ hydrogenation to hydrocarbons that occurred in the FT synthesis. In the periodic table, Group 8 transition metals are active for FTS but only Co, Fe or Ru; have sufficient CO₂ hydrogenation activity for commercial application (Davis, 2007). The selection of catalyst from active metal is very important as it gives large consequences for the selectivity of the catalyst and its cost.

2.6.1 Cobalt

Cobalt catalysts commonly used in FT synthesis because they produce the highest yields and have the longest life time, producing mainly linear alkanes (paraffins) among the metal based catalyst (Chaumette et al. 1995). While compared to other catalyst, cobalt was produced the lowest amounts of alcohols on the surface and water-gas shift (WGS) activity over cobalt catalyst is weak. This condition leads to improved carbon utilization and suitable for synthesis gas that produced via reforming of natural gas. They yield a high productivity for higher syngas conversion even though they are not inhibited by the water-gas-shift (WGS) (Van Berge and Everson, 1997). This give the large different between iron catalysts since it has high WGS activity. For each hydrocarbon formed during the synthesis, the cobalt catalyst will produce water while the iron catalyst will produce CO₂. Water vapor has been shown to influence the performance of the cobalt catalysts in a variety of ways meanwhile inhibition effect of water vapor on the catalyst's activity (Hilmena et al. 1999).

Cobalt catalytic systems are focused on improving the catalyst activity by increasing the number of active cobalt metal sites that are stable under reaction conditions. Cobalt catalysts are known to be sensitive to the reaction conditions, specifically pressure, as the product distribution of hydrocarbons varies with total pressure as shown in Figure 2.3. The density of produced hydrocarbons such as diesel fraction and paraffin components was found to be dependent on the pressure. Figure 2.4 also shows an existence of optimum pressure for those fractions for the low pressure operation (< 20 atm). As shown in the same figure light hydrocarbons and gasoline fractions were likely to decrease as the pressure increases (Pichler, 1952).

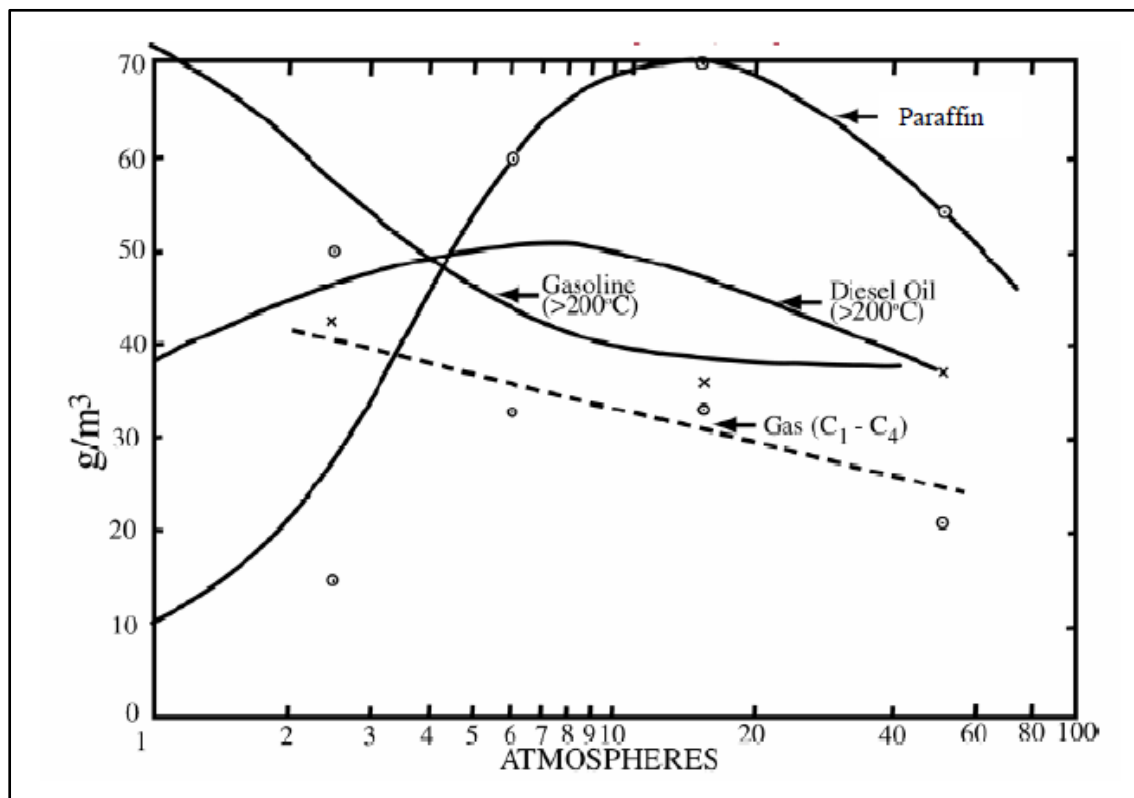


Figure 2.4: Effect of pressure on the cobalt catalyst selectivity in FT synthesis (Pichler 1952).

Cobalt catalysts yield mainly straight chain hydrocarbons. Since cobalt is much more expensive than iron, dispersing the ideal concentration and size of metal nanoparticles onto a support can help reduce catalyst costs while maximizing activity and durability. Supported cobalt catalysts are important for the FTS of high molecular weight, paraffinic waxes which can then be hydrocracked to produce lubricants and diesel fuels. Common support to cobalt that used widely is mesoporous and microporous silica due to small size in particle diameter. Cobalt is often present as dispersed clusters on a high surface area support. The loading of the metal on the support also influences the overall activity of the catalyst. A high degree of reduction is required as metallic cobalt is considered the active phase in the FTS. Small cobalt particles when supported on traditional oxidic carriers are difficult to reduce because of strong interaction with the support. Thus, catalysts are promoted with noble metals such as Ru, Pt or Pd; which lead to easier reduction of the cobalt oxide particles lead to the formation of bimetallic particles and alloys which then influence activity and selectivity,

enhance cobalt dispersion, inhibit catalyst deactivation by keeping the surface clean and allow easier regeneration of the cobalt surface (Morales and Weckhuysen, 2006).

At low metal loadings and relatively high dispersions, C5+ selectivity increases with decreasing dispersion and/or increasing metal loading (due to a decreasing metal-support interaction with decreasing dispersion, resulting in less methane formation and an increasing extent of olefin re-adsorption (Iglesia, 1997b).

2.6.2 Iron (Fe)

Ferum based catalysts have been used commercially in Fischer Tropsch (FT) synthesis in order to yield product variety of paraffin and olefin, ranging from ethane to high molecular weight waxes (Dry, et al. 1981). Fe catalysts offer an attractive complement and produced more olefinic compounds with inferior proportions of methane and paraffins than other metal based catalyst. Fe catalysts able to produce predominantly linear alpha olefins as well as a mixture of oxygenates such as alcohols, aldehydes and ketones. They tend to operate at relatively higher temperatures for a wide range of syngas feed ratios compared to the Co based which normally work under low temperature. The lower apparent FTS rates on Fe based catalysts have been affected due to the lower dispersion of their active components (Schulz, 1999). Thus, the increased surface area and density of active sites during synthesis and during the initial stages of use in synthesis gas have been assumed to bring Fe-based catalysts into the range of productivity and reaction conditions typical of Co-based catalysts (Li et al. 2002b).

Recent developments in Fe-based catalysts have focused on controlling the dispersion of the metals on the active sites to produce catalysts that are active at low temperatures and with low selectivity towards CO₂. Such active Fe based catalysts would also allow direct comparisons of FTS turnover rates on Fe and Co catalysts under similar conditions. Such comparisons require reliable measurements of the number of exposed active components in both catalysts (Li et al. 2002b).

However, this type of catalyst is known that can produce large amounts of carbon dioxide via the water gas shift (WGS) reaction and considered unsuitable for operation from natural gas derived syngas due to the environmental concern (Dry, 2001) On the other hand, the WGS activity of a Fe catalyst gives it flexibility for use with coal or biomass derived synthesis gas which has a low H_2/CO_2 ratio.

2.6.3 Periodic Mesoporous Silicas SBA-15 Catalyst Supporter

SBA-15 is the largest pore-size in mesoporous group with highly ordered hexagonally arranged mesochannels. SBA-15 possesses larger pores, thicker walls and higher thermal and hydrothermal stability compared to the other mesoporous silicas that may be used as a promising catalyst support especially for reactions occurring at high temperatures (Wang, et al., 2004). It uniform pore size is (4.6–30 nm) and pore wall thickness is (3.1–6.4 nm) (Xi and Tang, 2005). Formation of the triblock copolymer/mesostructured silica and mesoporous silica SBA-15 is shown as in Figure 2.5.

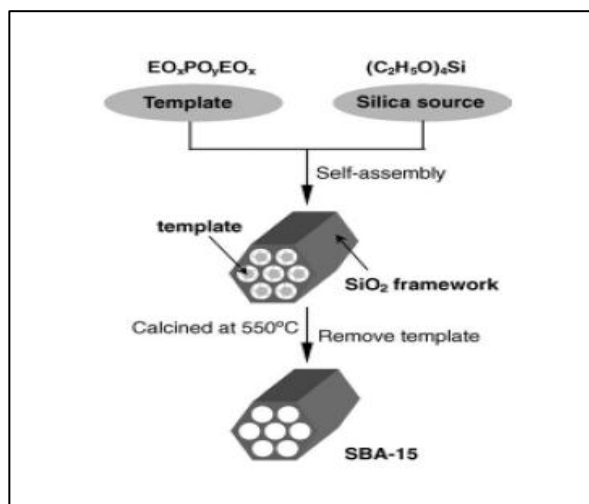


Figure 2.5: Formation of the triblock copolymer/mesostructured silica and mesoporous silica SBA-15 (Xi and Tang, 2005).

The synthesized 2D hexagonal mesoporous material has thicker walls. The thick walls significantly improve the thermal and hydrothermal stability compared to other related silicas (Taguchi and Schüth, 2005). Mesoporous materials also have involved significant attention in related fields of academia and industry, and have been widely used as catalysts in petrochemical industry. However, the low acidity and hydrothermal stability restricted their application in environmental catalysis, such as selective catalytic reduction (SCR) of NO in the presence of oxygen (Liang et al., 2007). SBA-15 has adjustable pore diameter, thick pore wall and excellent hydrothermal stability. Therefore, it is probably appropriate to be used in SCR of NO with ammonia (Liang et al., 2007).

2.6.4 Promoted Zinc Catalyst

Promotion with noble metal like Zinc could result by cobalt can be reduced will be easier, formation of bimetallic particle and alloys, fraction of barely reducible mixed oxides will be lowered, enhancement in cobalt dispersion, catalyst deactivation will be inhibited, additional sites of hydrogen activation will be appeared and the intrinsic reactivity of surface site will be increased (Khodakov et al, 2007). Alkali metals such as Zn, Cu, Mn and Ce have been consumed widely as promoters to increase the activity and selectivity of the catalysts in the CO hydrogenation. Impregnated cobalt catalysts were less active than Co precipitated catalysts. Zinc is a better promoter than Cu or Cr (Yang and Oblad, 1978). Catalyst promoted with higher loading is more active than the other promoted catalysts. As example, analysis of the literature data suggest that introduction of noble metals could result on following phenomena (Khodakov, 2009):

- Ease cobalt reduction
- Improvement of cobalt dispersion
- Better resistance to deactivation.
- Alteration of activity of surface site.

The promotion with slight amount of noble metal does not usually have obvious effect on mechanical properties of cobalt supported catalysts. Thus, addition of small amounts of noble metal only changes the reduction temperature of cobalt oxides and cobalt species relating with the support to lower temperatures (Wei et al., 2001). Due to the added expense of the promoter, it is important to determine the appropriate loading of promoter to maximize the accessibility of active cobalt surface sites for involvement in the reaction, after catalyst activation.

2.7 Fischer Tropsch Operating Parameter

2.7.1 Temperature

The dominant operating parameter is the temperature. Temperature that operates at different reactor used give different product selectivity. In Fischer Tropsch process, the synthesis actually can be operated with two conditions of temperature. (Triantafyllidis and Lappas, 2007):

1. High-temperature process (HTFT):
 - 300-350°C, Fe catalysts, gasoline and light olefins
 - Circulating fluidized bed, Fixed fluidized bed reactors

2. Low-temperature process (LTFT):
 - 200-240°C, Fe or Co catalysts, linear paraffin (wax)
 - Multi-tubular fixed bed reactors, fixed slurry bed

The lower temperature operation (220°C) tends to form more primary products. This leads to longer straight chain paraffin and even waxed, much less oxygenates than the higher temperature and virtually no aromatics (the higher temperature yields around 7% aromatics) (Bukur et al, 1990). This product gives a very superior diesel with cetane number of about 75. However, the cut in the gasoline range is also highly paraffinic

with a low octane number. It is very good feedstock for a cracker, but would need extensive refining to meet gasoline specification (Manfred et al, 2002).

2.7.2 Pressure

The influence of pressure on the chain length is very complex. An increase in pressure indicates to increasing mass fractions of low molecular weight hydrocarbons, thus favoring the creation of lighter fractions rather than waxy products. Decreasing pressures favor an increase in liquid products of the range between C_{21} and C_{25} at high temperature. Waxy hydrocarbon products that increase were favored by mid-range pressures (between 24 and 27 atm). The temperature sensitivity for production of heavier hydrocarbons is at its peak where the partial derivative with respect to the temperature of the response surface reaches its maximum. Figure 2.6 shows mass fraction of hydrocarbons obtained under different operating pressure.

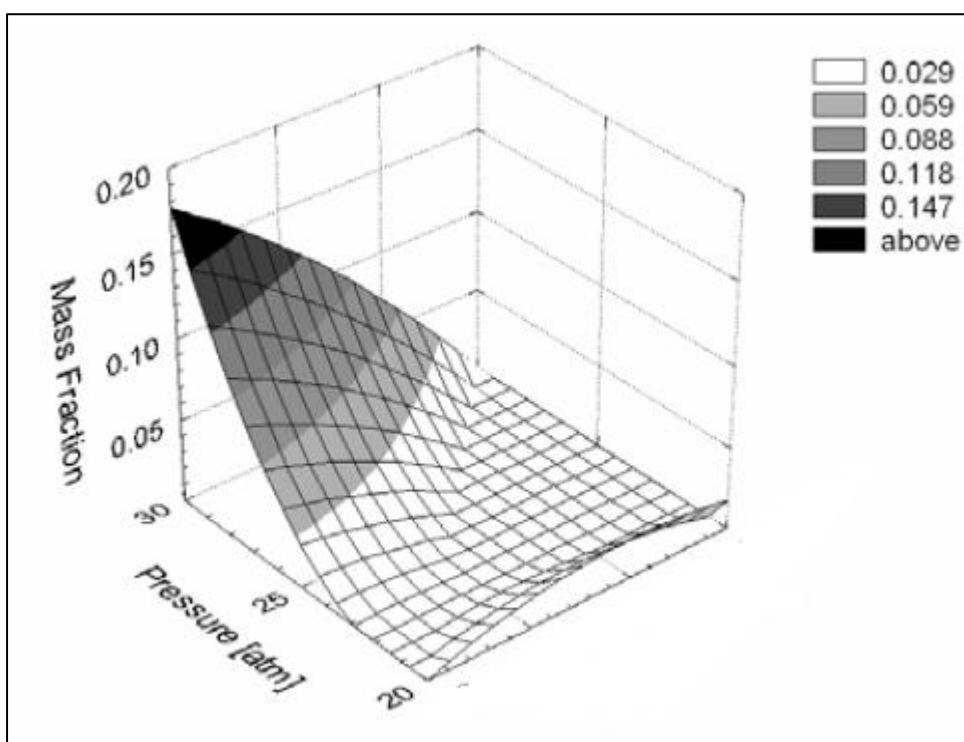


Figure 2.6: Mass fraction of hydrocarbons obtained under different operating pressure (Farias et al., 2007)

Depending on the optimal conversion for a required selectivity, it may be necessary to recycle tail gases from the reactor. This decreases thermal efficiency due to compression costs but serves the further function of acting as a mechanism for a temperature control. In the slurry bed and the advanced fluidized bed units, the latter function becomes less crucial. The ratio of hydrogen to carbon monoxide in the feed gas (combined syngas and recycle gas) is an important ratio from a kinetic point of view. The usage ratio of the gases as well as water gas shift activity of the catalyst has to be optimized in the light of feed gas hydrogen to carbon monoxide ratio. If reforming is used to produce the syngas, the recycle is especially important for the right hydrogen to carbon monoxide ratio.

The gas throughput of a reactor is proportional to the pressure, whereas the cost is more than proportional to the pressure. It is therefore a case of weighing up the advantages of higher throughput against higher costs. This affects the total system pressure and not merely the reactor (Fernandez et al., 2006)

2.7.3 H₂/CO₂ Feed Ratio

Total olefins selectivity affected by decreasing with an increase in H₂/CO₂ because of the increase in the rate of olefins hydrogenation to heavy hydrocarbons. The rise of the CO₂ amount in the synthesis gas dropped the activities of the catalysts. In fact the increasing feed H₂/CO₂ ratio will increase hydrogen concentration at the surface of catalyst and together with a decrease in CO₂ surface concentration would enhance termination reactions leading to a decrease in selectivity of heavier products (Tristantini et. al, 2007). Table 2.3 shows the effect of feed gas ratio on product selectivity.

Table 2.3: Product selectivity for different feed gas ratio (Li et al., 2002)

CO ₂ hydrogenation			
condition number	1	12	return to 1 ^c
CO ₂ /H ₂	3:1	1:1	3:1
CO ₂ conversion (%)	10.0	4.8	9.4
CO selectivity (%)	16.1	28.6	16.4
CH ₄ selectivity (%)	43.7	30.1	47.9
O ₂ /P ₂ ^a	0.007	0.010	0.007
O ₃ /P ₃ ^b	0.023	0.043	0.029
rate of FT (mol/(min·gcat))	3.8×10^{-5}	3.0×10^{-5}	3.6×10^{-5}
rate of R-WGS (mol/(min·gcat))	7.3×10^{-6}	1.2×10^{-5}	7.0×10^{-6}

^a Olefin to Paraffin ratio with chain length 2. ^b Olefin to Paraffin ratio with chain length 3. ^c Returning to the starting condition 1 at the end of the experimental series.

2.8 Products Separation and Upgrading

Conventional refinery processes still can be used in upgrading of Fischer-Tropsch liquid and wax products. A number of possible processes for FT products like wax hydrocracking, distillate hydrotreating, catalytic reforming, naphta hydrotreating, alkylation and isomerization (Choi *et.al.*, 1996). Fuels produced with the FT synthesis are of a high quality due to a very low aromaticity and zero sulfur content. The product stream consists of various fuel types: LPG, gasoline, diesel fuel, jet fuel. The definitions and conventions for the composition and names of the different fuel types are obtained from crude oil refinery processes and are given in Table 2.4 (Kroschwitz and Howe-Grant, 1996).

Table 2.4 Conventional of fuel names and composition (Kroschwitz and Howe-Grant, 1996).

Name	Synonyms	Components
Fuel gas		C ₁ - C ₂
LPG		C ₃ - C ₄
Gasoline		C ₅ - C ₁₂
Naphtha		C ₈ -C ₁₂
Kerosene	Jet fuel	C ₁₁ -C ₁₃
Diesel	Fuel oil	C ₁₃ -C ₁₇
Middle distillates	Light gas oil	C ₁₀ -C ₂₀
Soft wax		C ₁₉ - C ₂₃
Medium wax		C ₂₄ - C ₃₅
Hard wax		C ₃₅ +

The diesel fraction has a high cetane number resulting in superior combustion properties and reduced emissions. New and stringent regulations may promote replacement or blending of conventional fuels by sulfur and aromatic free FT products. Also, other products besides fuels can be manufactured with Fischer-Tropsch in combination with upgrading processes, for example, ethene, propene, O olefins, alcohols, ketones, solvents, specialty waxes, and so forth. These valuable by-products of the FT process have higher added values, resulting in an economically more attractive process economy. The value of Fischer-Tropsch products used as blending stocks for transportation fuels (kerosene and diesel) is higher than crude oil derived fuels due to their excellent properties. Table 2.5 shows properties of Fischer Tropsch product

Table 2.5 Fischer Tropsch (FT) Product properties (Gregor, 1990)

Product	Property	SMDS products	Hydrocracked Arge FT-wax	Specification
Diesel	Cetane number	70	> 74	min. 40
	Cloud point, °C	-10	-7	-20 to +20
Kerosene	Smoke point, mm	> 100	> 50	min. 19-25
	Freezing point, °C	-47	-43	max. -47 to -40

CHAPTER 3

RESEARCH METHODOLOGY & ANALYSIS

3.1 INTRODUCTION

The experimental method and procedure for the preparation and characterization throughout the research are summarized and description of rig setup is also explained in this chapter. Figure 3.1 shows the flow chart of overall experimental work. The first stage of this experimental work was preparation of catalysts. The catalysts which are Co/Zn/SBA-15 with cobalt loading 5 to 15 wt % and zinc loading also in the same range with cobalt loading which is 5 to 15 wt % were prepared. Then, the catalysts were characterized using Fourier Transform Infrared Spectroscopy (FTIR), X-Ray Diffraction (XRD), Scanning Electron Microscope (SEM), N₂ Adsorption Analysis (BET) and Thermogravimetric Analyzer (TGA). Finally, the catalysts have been tested using gas chromatograph (GC) to determine the activity performance and product selectivity.

3.2 Research Methodology

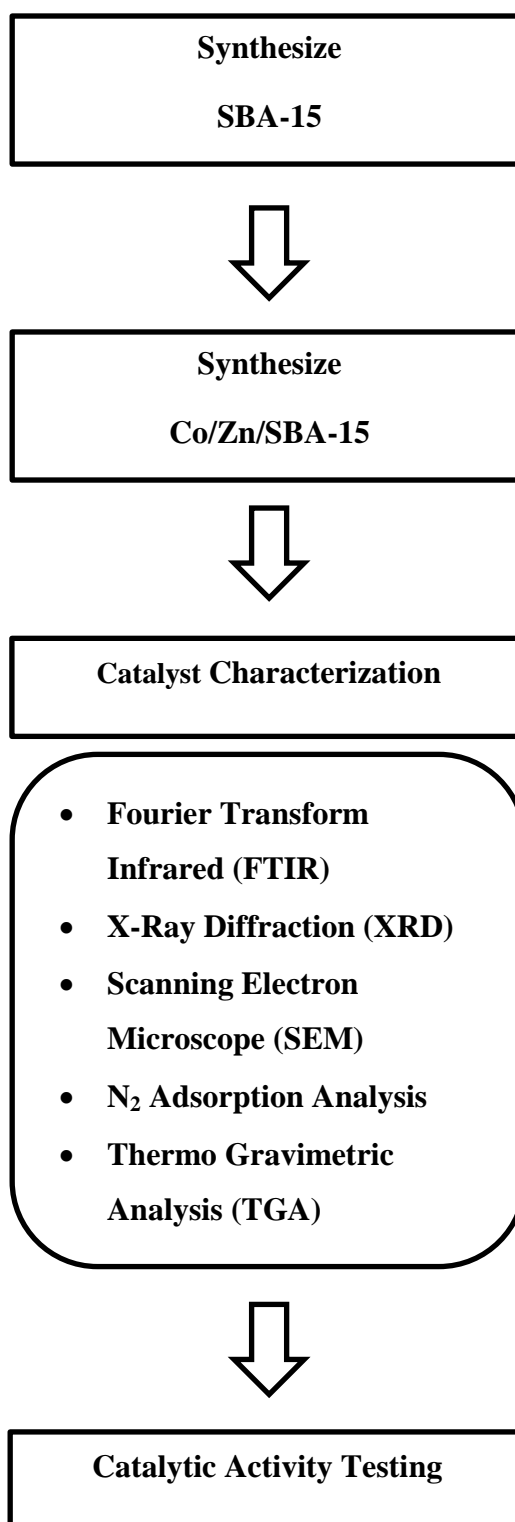


Figure 3.1: Flow chart of overall experimental work

3.3 Materials and Chemicals

All materials and chemicals used in this present research are listed in Table 3.1 as below:

Table 3.1: List of Chemicals

Chemical	Molecular Formula
Cobalt Nitrate	$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$
Zinc Nitrate	$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$
Pluronic P-123	$\text{HO}(\text{CH}_2\text{CH}_2\text{O})_{20}(\text{CH}_2\text{CH}(\text{CH}_3)\text{O})_{70}(\text{CH}_2\text{CH}_2\text{O})_{20}\text{H}$
Acid Hydrochloric	HCL
Tetraethylortosilicate TEOS	$(\text{Si}(\text{OCH}_3)_4)$

3.4 Synthesizing SBA-15

For preparing SBA-15, a specific amount of HCL with a certain concentration was shaken for an hour in the orbital shaker at 40°C. Then Pluronic P123, the triblock polymer was dissolved in the HCl solution with precise mass and shaken at the same temperature, 40°C for another two hours and then added with Tetraethyl orthosilicate (TEOS). As the gel start to develop, the solution was stirred under slow shaking for 24hours about 50 rpm at 40°C. Once the solid formed, it was filtered and washed with distilled water. Lastly, the sample was calcined at 500°C in a furnace for six hours.

3.5 Synthesizing Co/Zn/SBA-15

Incipient Wetness Impregnation (IWI) method was used in order to prepare the Co based catalyst with Zn as promoter. In this research, Zn and cobalt with specific loading was co-impregnated into SBA-15 where the weight of both Zn and Co was calculated. Co-Zn/SBA-15 catalyst was prepared with different amount of cobalt and zn which range between 5 wt% to 15 wt%. The catalysts then were dried for a night in oven at 60°C and calcined at 500°C. Table 3.2 shows the sample with different cobalt and zinc loading.

Table 3.2: Samples with different cobalt and zinc loading.

Sample	Metal Loading
A	15% Co/15% Zn-SBA-15
B	15% Co/10% Zn-SBA-15
C	15% Co/5% Zn-SBA-15
D	10% Co/15% Zn-SBA-15
E	5% Co/15% Zn-SBA-15

3.6 Catalyst Characterization

3.6.1 Fourier transform infrared (FTIR)

FTIR is used to identify chemicals that are either organic or inorganic. It can be utilized to quantitative some components of an unknown mixture can be applied to the analysis of solids, liquids, and gasses. FTIR is also can be considered as the most powerful tool to use for identifying types of chemical bonds (functional groups) and the

spectrum analysis. In the annotated spectrum, the wavelength of light absorbed is characteristic of the chemical bond can be seen. By interpreting the infrared absorption spectrum, the chemical bonds in a molecule can be determined.

3.6.2 X-Ray Diffraction (XRD)

X-Ray Diffraction techniques can determine the structures of the Co/Zn/ZSM-5 and Co/Zn/SBA-15 catalysts. This method explained that every crystalline material have their own characteristics diffractogram. All the samples were fully dried before diffractograms were measured.

3.6.3 Thermogravimetric Analysis (TGA)

Thermogravimetric analysis is an analytical technique used to determine a material's thermal stability and the fraction of volatile components. TGA monitors the weight change that occurs as a specimen is heated. Usually the measurement is carried out in air or in an inert atmosphere, such as Helium or Argon, and the weight is recorded as a function of increasing temperature. The samples were heated under the flow air which is 25 ml min^{-1} from ambient temperature (25°C) to 1000°C at the heating rate of $10^\circ\text{C min}^{-1}$.

3.6.4 N₂ adsorption analysis (BET)

Characterization using N₂ adsorption analysis was used to measure the physical porosities of the Co/SBA-15 samples and measured the outer surface of a solid sample on the molecular scale.

3.6.5 Scanning Electron Microscope (SEM)

Scanning Electron Microscope is used to provide data about the composition and electronic structure of heterogeneous catalyst with real space resolution down to the atomic level.

3.6 Catalyst Activity Testing

Glass borosilicate microreactor was used to test the catalytic activity on conversion of syngas to liquid hydrocarbons. This reaction equipment played the function just the same with fixed bed. It allowed for operating up to 4 bars and 1000°C. The micrometer is an isothermal fixed bed of 10 mm internal diameter, 300 mm length and volume of catalyst that can be loaded was up to 5 cm³. It was heated by an electric resistance and gases line that made from glass. Three mass flow controllers were equipped with a four-channel control panel that used to adjust the flow rate of inlet gases automatically. Simplified flow schematic of reactor used and representation of catalyst test was shown in Figure 3.2 as below

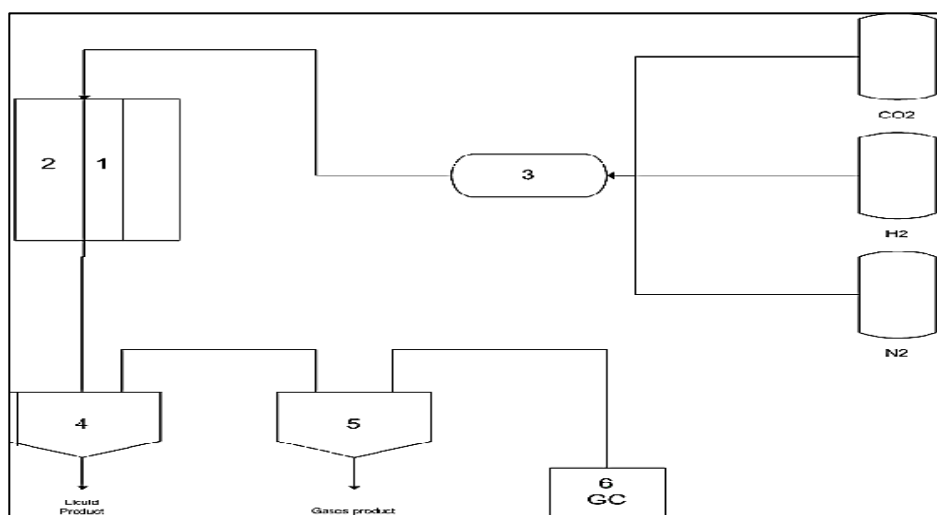


Figure 3.2: Simplified flow schematic of reactor used and representation of catalyst test: (1) reactor; (2) furnace; (3) inlet gas mixer; (4) cold condensable product trap; (5) hot condensable product trap; (6) online GC.

Catalyst tests were carried out at temperature of 220°C catalysts were activated (reduced) for 2 h period on line in pure hydrogen (1bar) and gas hourly space velocity (GHSV) of 1000 h⁻¹. A 1.0 g of each catalyst was loaded in the glass reactor on the glass wool. Glass wool was used to support the catalyst and prevented loss of the fine particles. Reactant and stream products were analyzed on-line using a gas chromatograph (GC) that basically was used to analyze hydrocarbons in the gas phase.

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 Fourier Transform Infrared Spectroscopy (FTIR)

Figure 4.1 (a), 4.1 (b), 4.1 (c), 4.1 (d), 4.1 (e) and 4.1 (f) show the selected FTIR spectra for 6 samples including the raw SBA-15. All support and promote catalyst samples were analyze using FTIR spectra to examine the existence of functional group were formed in the samples and provide surface information of materials for identification of chemical groups. Figure 4.2 (a) until figure 4.2 (f) show curves of catalyst with different loading composition of cobalt and zinc to the SBA-15 catalysts.

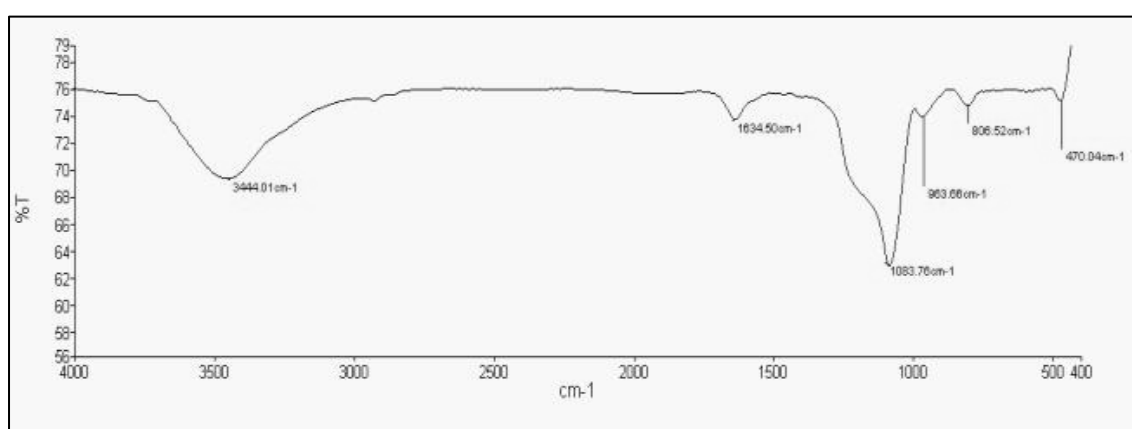


Figure 4.1 (a): FT-IR Spectra of SBA-15

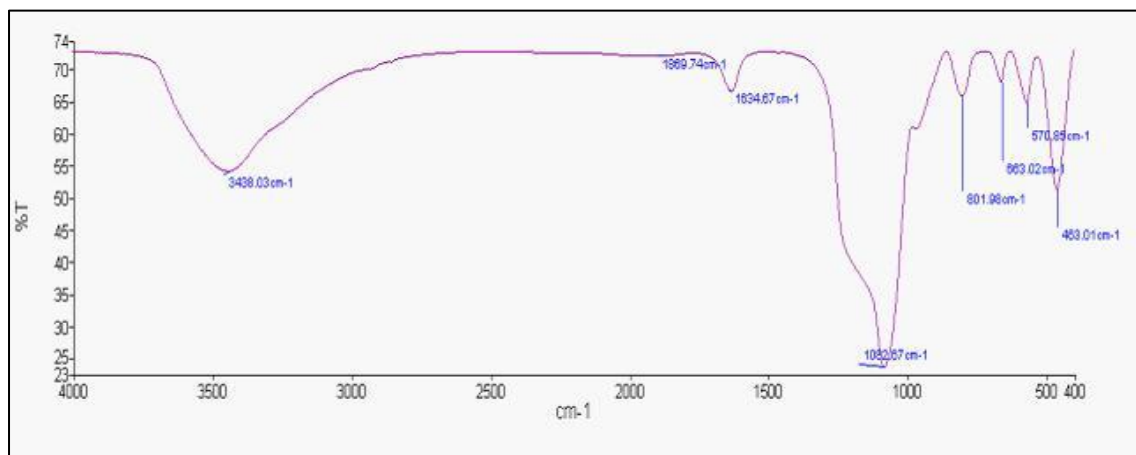


Figure 4.1 (b): FT-IR Spectra of 15% Co/15% Zn SBA-15

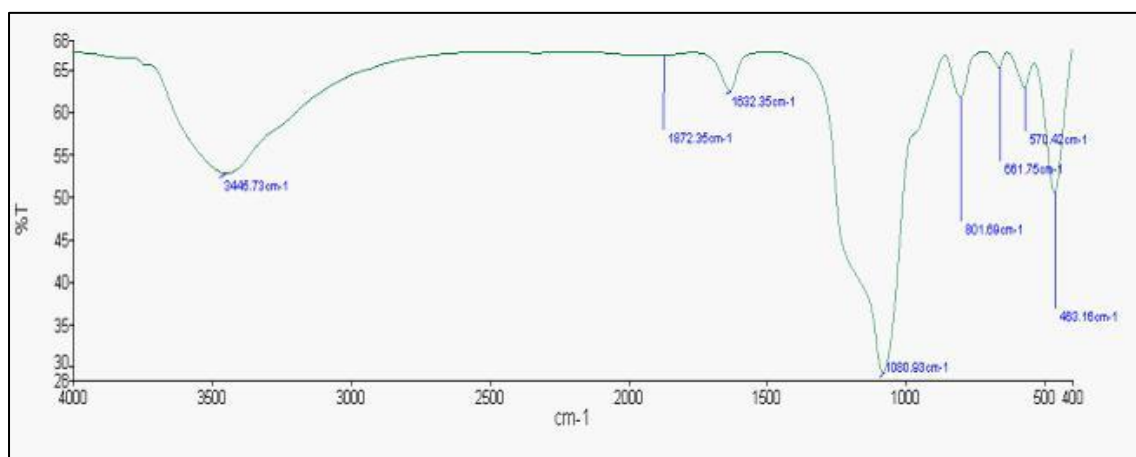


Figure 4.1 (c): FT-IR Spectra of 15% Co/10% Zn SBA-15

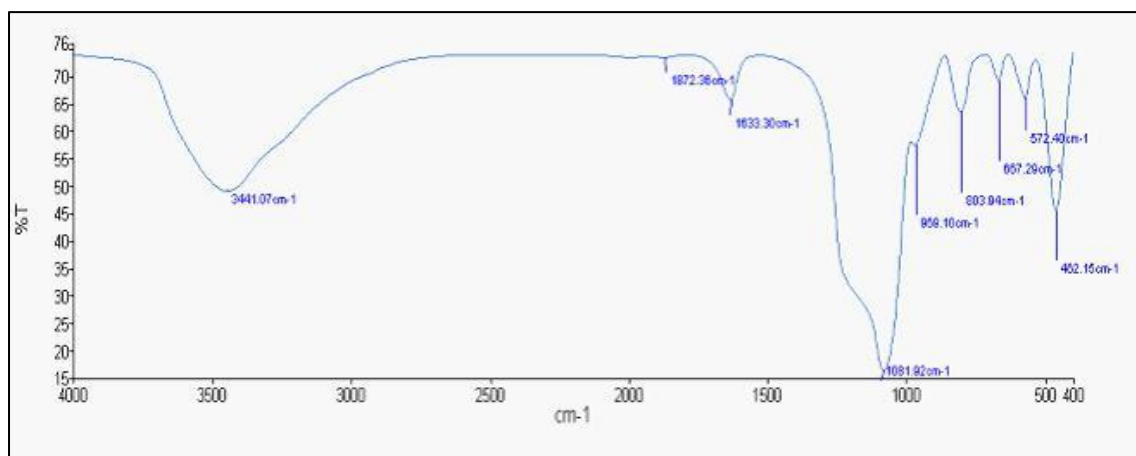


Figure 4.1 (d): FT-IR Spectra of 15% Co/5% Zn SBA-15

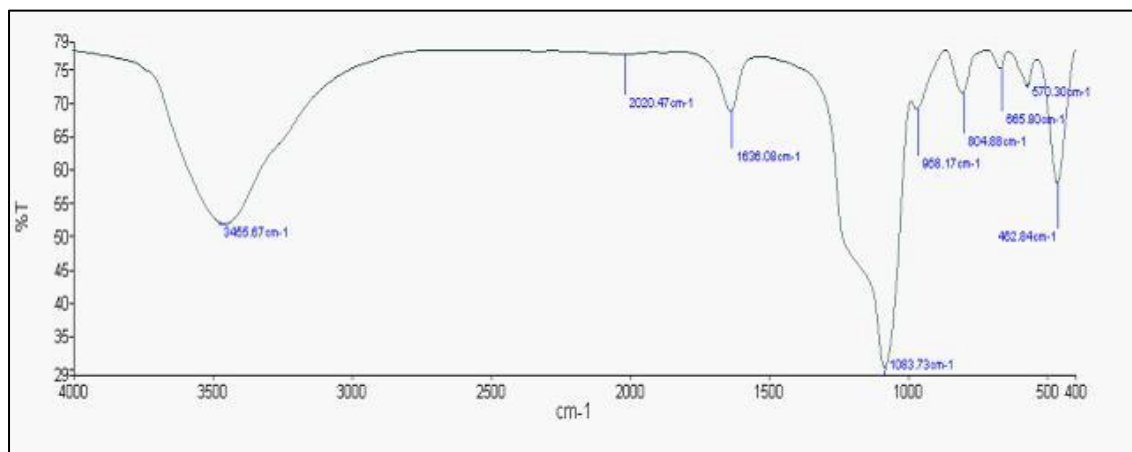


Figure 4.1 (e): FT-IR Spectra of 10% Co/15% Zn SBA-15

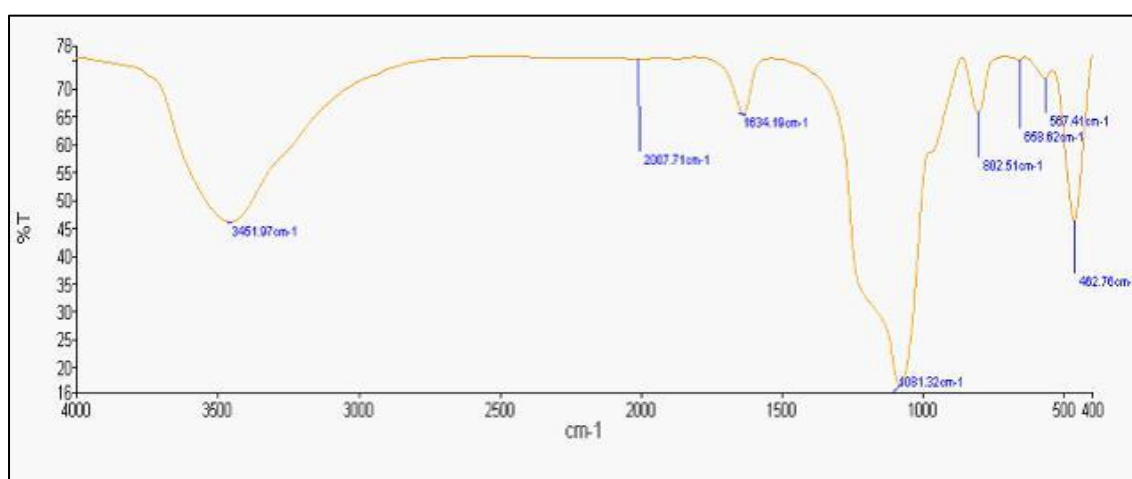


Figure 4.1 (f): FT-IR Spectra of 5% Co/15% Zn SBA-15

There are numerous functional groups identified with definite wavelength in the samples such as cobalt oxides, Si-O-Si, Si-OH, zinc oxide, OH band, nitrate group, and etc. In order to compare the curve of each sample, the major changes were studied at any peak showed. The changes on the curves showed were analyzed which promoted SBA-15 catalyst were detected at 3200-3800 cm^{-1} that contain of OH bond stretching's Si-O-Si and Si-OH. Silanol groups such as O-H bond on the silica surface happen in several forms such as isolated, hydrogen-bonded, and germinal types of silanol groups, IR absorption bands of which correspond to the peaks at 3738 cm^{-1} and 3200-3800 cm^{-1} due to Akcaet al. (2008).

Sample of raw SBA-15 as in figure 4.3 (a) didn't show any nitrate ion peak absorbencies because there is no nitrate group was added during conducting experiment. However, in other samples, a peak that detecting nitrate group was present. According to Kababji et al. (2009), this is happen because of possible interaction with hydrate silica at the higher surface and the ion nitrate during catalyst preparation.

The existence of SBA-15 resulted the formation of hydroxyl group that allocated around 1640 cm^{-1} . Spectrum of sample (c), (d), (e) and (f) that has more hydroxyl groups (SiOH) shown the higher intensity of the bands. The present of SiOH groups in spectrum in these samples possibly favors the formation of higher amount of tetrahedrally coordinated Co^{2+} ions, having interaction between silica supports (Agnes et al, 2009). The existence of silanol group (SiOH) on the silica surfaces also shows an important role in the formation of cobalt species (Kababji et al., 2009). As the modified of surface silanol groups of SBA-15 increasing by present of cobalt loading, the density of the surface silanol groups decreases. Thus, the O – H bond stretching bands of silanol groups decrease (Agnes et al, 2009).

FTIR spectrum of the samples except raw SBA-15 show there are zinc nitrate $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, which are the components of zinc nitrate are attended at OH stretching vibration area. The area of OH stretching vibrations contains three major absorption bands, at 3536 , 3483 , and 3184 cm^{-1} , in accordance with the existence of different OH situations as evidence from the structural data (Eriksson et al, 1989). The presence of water structure in this material is confirmed by the appearance of the H-O bending vibration at 1664 cm^{-1} (Biswick et al., 2007)

4.2 X-Ray Diffraction (XRD)

Most of the structural information about SBA-15 was obtained through XRD. It provides data about the average diameter of unit cell and the crystallinity of the catalyst based on the XRD diffractogram. Figure 4.2 (a), Figure 4.2 (b), Figure 4.2 (c), Figure 4.2 (d), and Figure 4.2 (e) show the intensity curve for each sample

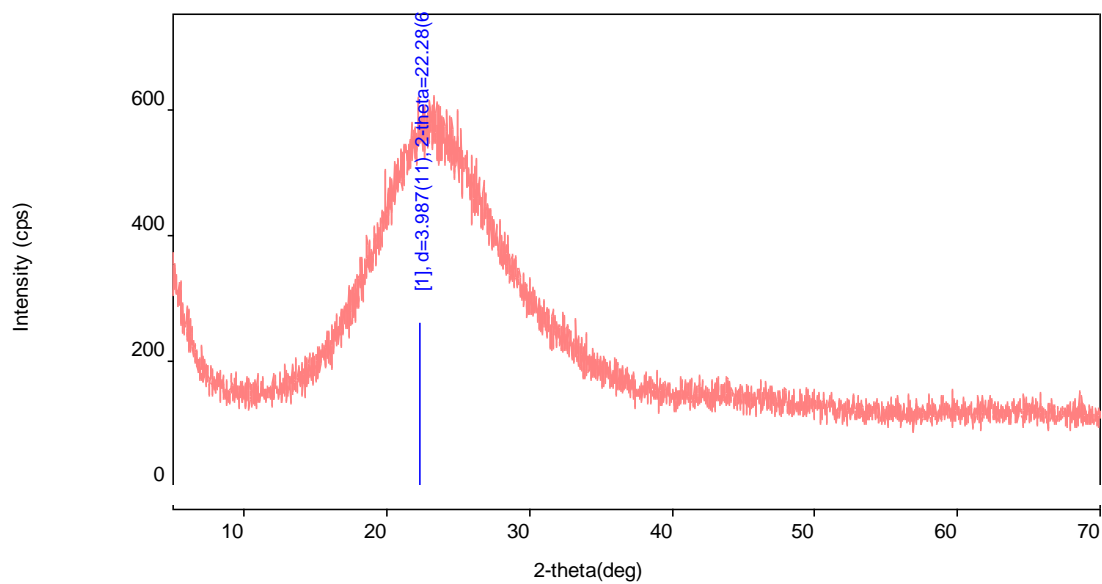


Figure 4.2 (a): X-ray diffractogram for raw SBA-15

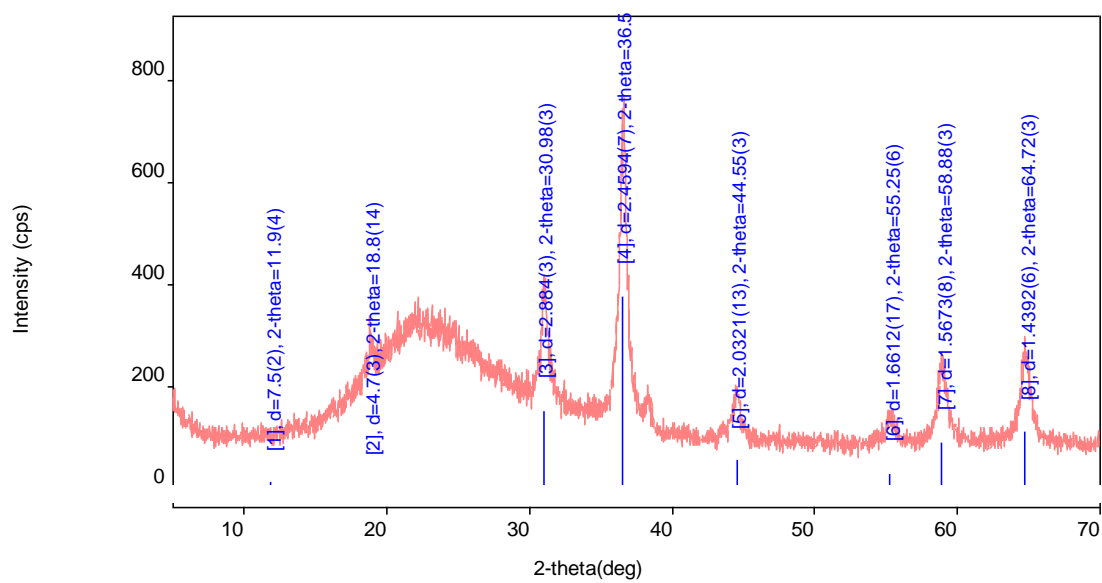


Figure 4.2 (b): X-ray diffractogram for 15% Co/15% Zn SBA-15

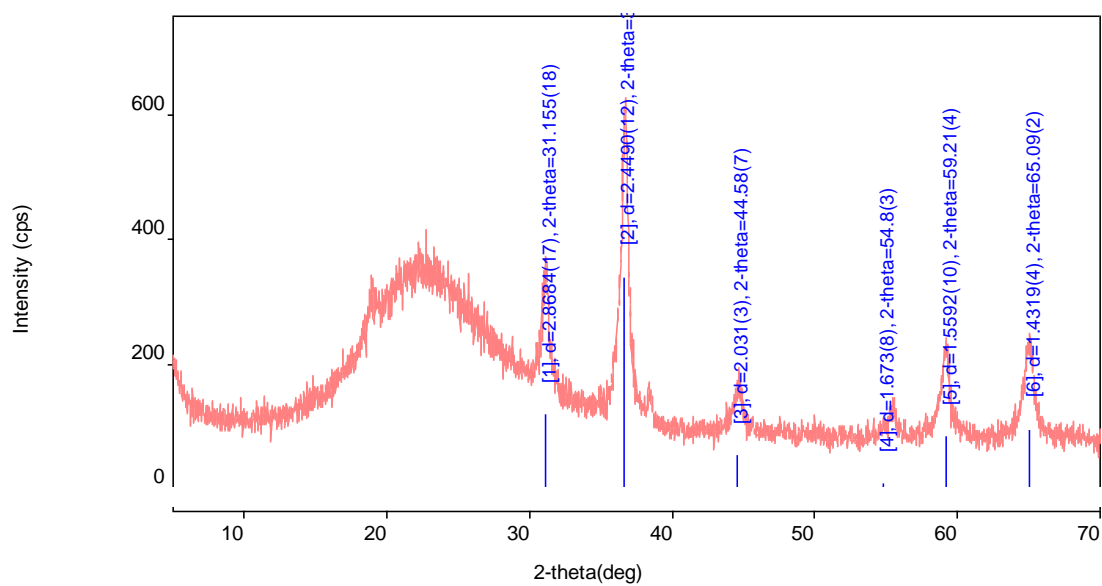


Figure 4.2 (c): X-ray diffractogram for 15% Co/10% Zn SBA-15

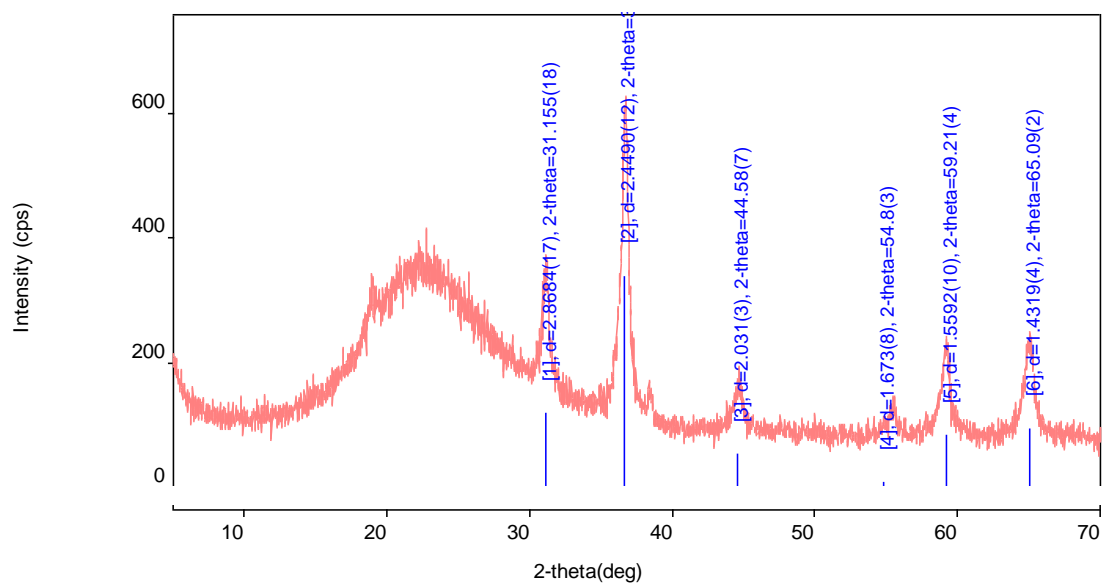


Figure 4.2 (d): X-ray diffractogram for 15% Co/5% Zn SBA-15

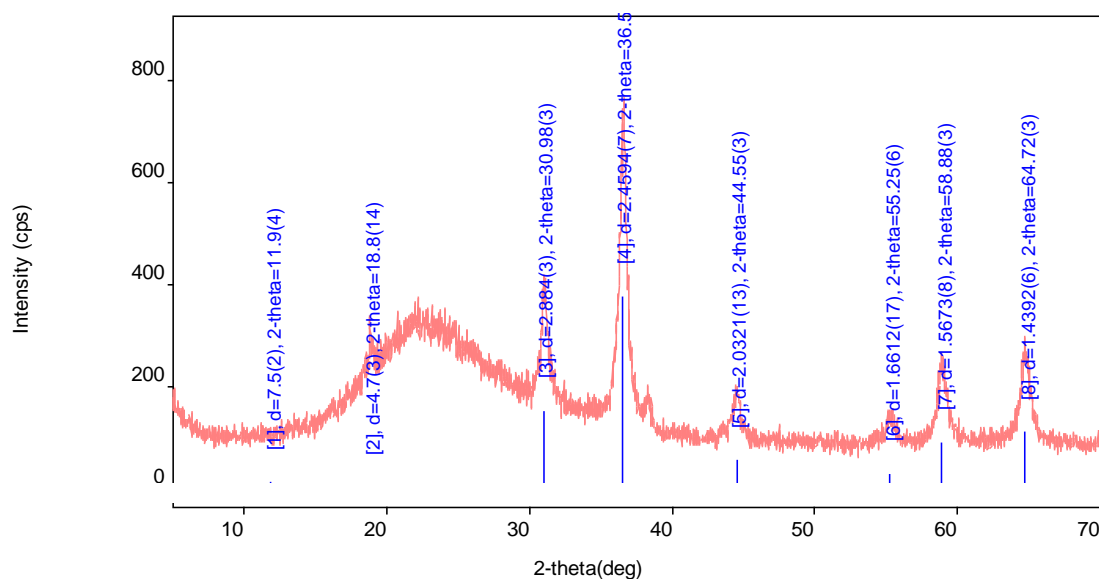


Figure 4.2 (e): X-ray diffractogram for 10% Co/15% Zn SBA-15

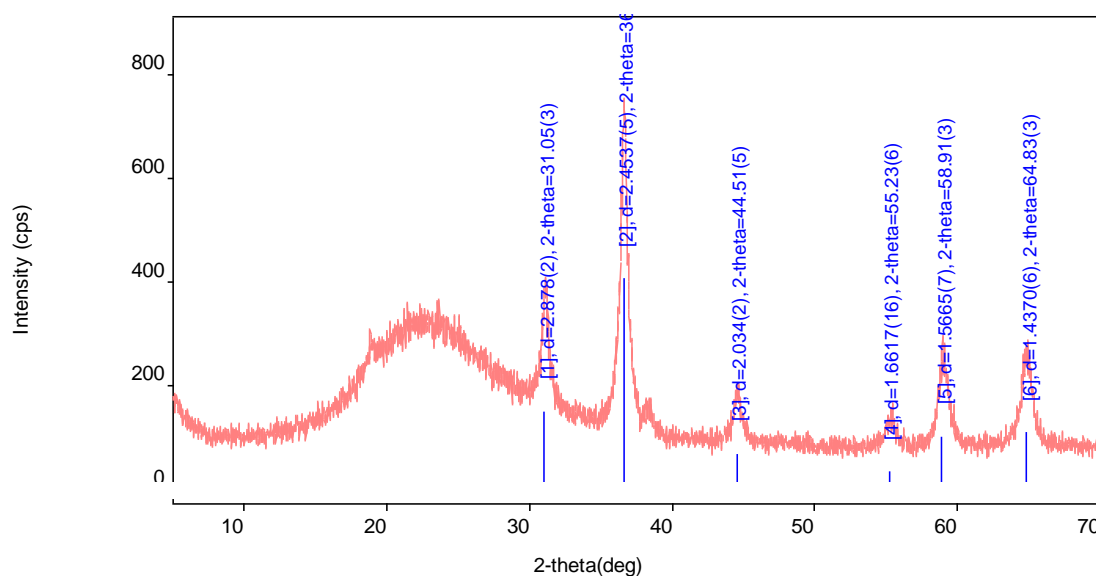


Figure 4.2 (f): X-ray diffractogram for 5% Co/15% Zn SBA-15

All the catalyst that prepared from cobalt nitrate precursor except for Figure 4.2 (a) has shown the reflexion of the characteristic of the Co_3O_4 spinel. In this series of samples, the peaks become narrower, specifying an increase of the mean Co_3O_4 crystallite size, when increasing the Co content. Sun et al. concluded that Co should be highly dispersed on the silica surface. However, the deficiency of Co_3O_4 reflexions in

supported Co catalysts does not certainly imply the presence of very small Co_3O_4 particles avoidance XRD detection, but could also be due to the formation of a noncrystallized cobalt phase induced by a strong cobalt–support interaction. The result indicates that the crystallinity of the cobalt loading on SBA-15 has increased the crystallinity. The change of the structure of the catalyst can be identifying as the cobalt and zinc loading was increased.

SBA-15 that categorized in mesoporous material has a single strong first-order peak that could be indexed to (100) plane (Tanev and Pinnavaia, 1995). This diffraction patterns characteristic still could be observed from Figure 4.2 (a). Diffraction peaks at higher order are not well resolved because these materials lack of long-range order. The absence of a long-range order can be attributed to the weak bonding forces between silicate species that govern the neutral templating pathway assembly (Tanev and Pinnavaia, 1996). However, characteristics of mesoporous SBA-15 material still could be observed form XRD patterns, which has unit cell, $a = 4.4 \text{ nm}$ ($a=2d_{100}/\sqrt{3}$) and d_{100} is 3.8 nm ($d=n\lambda/2\sin\theta$) (Tanev and Pinnavaia, 1995).

The effect of zinc and cobalt at different loading on SBA-15 is shown in Figure 4.2 (b-f). At variety composition from 5 wt % to 15 wt % loading, about 6 strong diffraction peaks around $2\theta = 30.1^\circ$, 36.5° , 44.4° , 58.7° , and 64.9° were detected. These peaks can be assigned to bulk zinc and cobalt nitrate. The presence of these peaks indicates that zinc and cobalt was highly dispersed on SBA-15. The metal has a striking effect on the width and intensity and this line becomes broader and weaker as the loading increases. This suggested that the structure of SBA-15 begin to collapse in the presence of zinc and cobalt and it also decrease in the dimensions of the scattering domain.

The effect on the intensity and width of mesoporous material with presence of inorganic compounds are similar to those reported earlier. It was claimed that hydrolysis of mesoporous material SBA-15 causes hexagonal framework to collapse. Further, this condition becomes more severe under acidic condition during impregnation (Chastain, 1992). On the other hand, another reason may be also due to the interaction between noble metal and SBA-15.

4.3 Scanning Electron Microscope (SEM)

Cobalt containing SBA-15 samples were tested using Scanning electron microscopy (SEM) in order to study surface morphology of structure of raw SBA-15 and metal loaded catalyst. The SEM images of SBA-15 particles before and after cobalt and zinc loading are shown in Figure 4.3 (a), Figure 4.3 (b), Figure 4.3 (c), Figure 4.3 (d), Figure 4.3 (e), and Figure 4.3 (f) as below

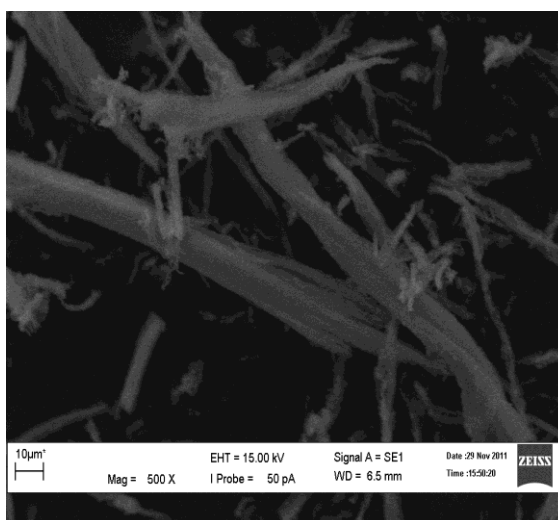


Figure 4.3 (a): SEM monograph of SBA-15

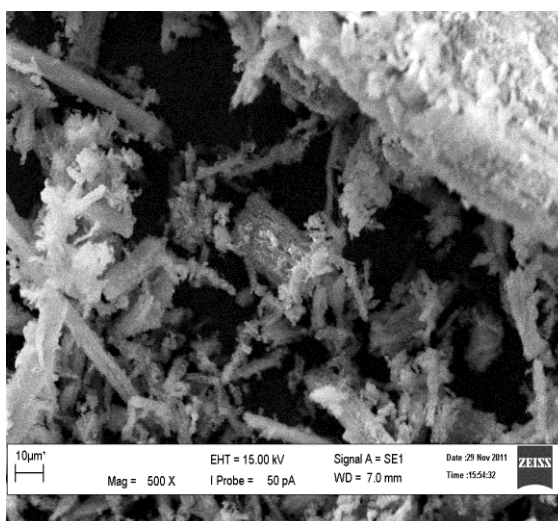


Figure 4.3 (b): SEM monograph of 15% Co/15% Zn-SBA-15

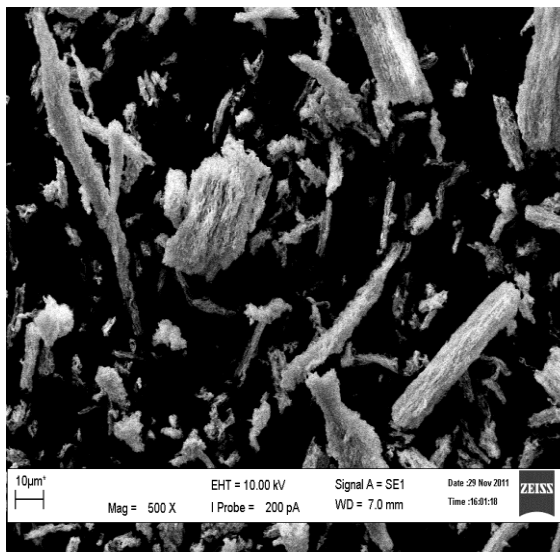


Figure 4.3 (c): SEM monograph of 15% Co/10% Zn-SBA-15

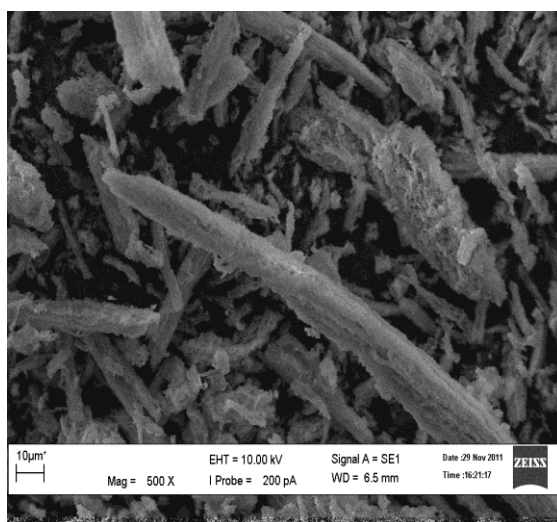


Figure 4.3 (d): SEM monograph of 15% Co/5% Zn-SBA-15

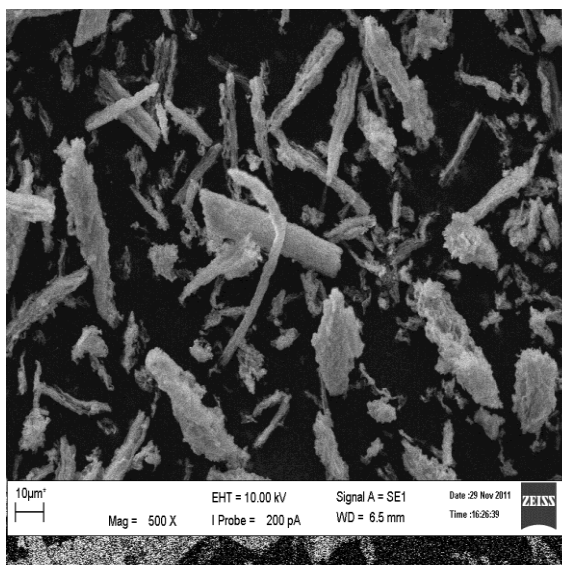


Figure 4.3 (e): SEM monograph of 10% Co/15% Zn-SBA-15

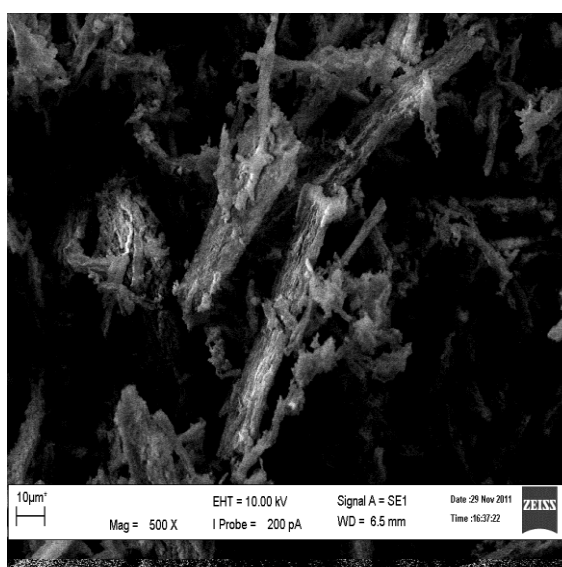


Figure 4.3 (F): SEM monograph of 5% Co/15% Zn-SBA-15

The structure of SBA-15 in Figure 4.3 (a) shows irregular cylindrical rod and clearly visible in agglomeration. After cobalt and zinc loading to the catalyst, the particles structure found to be closely attached to each other. SBA-15 reveals that it contains like a rope domain with relatively identical size of 1.5-10 μm , which are combined into wheat-like macrostructures mean that rod primary particles aggregated to form micron-sized fibers. Recently, Anunziata et al. (2007) mentioned the similar finding shows the spherical shape with agglomeration and homogeneous formed.

After SBA-15 have been loaded by cobalt and zinc with different loading as referring to the Figure 4.3 (b), (c), (d), (e) and (f), it shows that catalyst seems to be attached very closely to one another. These occurrences observed both in microscopic and macroscopic scale due to alkyl chain like cobalt and zinc that growth in SBA-15. These chains of one SBA-15 particle may be caught on the chain of another SBA-15 where the bonding of large number of SBA-15 particles may take place (Mirji et al., 2006). The structural shown also can be resulted due to Van der Walls and electrostatic interaction of alkyl chain between cobalt and zinc of adjacent particles of SBA-15.

4.4 N₂ Adsorption Analysis (BET)

BET procedure using nitrogen adsorption was performed in order to analyze the specific surface area, pore size and pore size distribution of porous catalyst. Table 4.1 shows the textural properties obtained from N₂ adsorption isotherms for Co/Zn-SBA-15 catalysts sample.

Table 4.1: Textural properties obtained from N₂ adsorption isotherms for 5 samples of catalysts

Samples	BET surface area, m ² /g	Total pore volume, cm ³ /g
15% Co/15% Zn-SBA-15	375.02	0.74
15% Co/10% Zn-SBA-15	366.90	0.64
15% Co/5% Zn-SBA-15	246.99	0.43
10% Co/15% Zn-SBA-15	257.40	0.58
5% Co/15% Zn-SBA-15	305.97	0.63

All samples show a high surface area due to elimination of surface molecule in the material at the lower temperature which is less than 400°C. Increasing calcinations temperature up to 600°C causes a decrement of the surface area due to the

agglomerations process that increases the catalyst particle size. The increases of calcinations temperature also resulted pore diameter to increase. The reason came from the transformation of porosity system that categorized in mesoporous group material. This is due to sintering process to form a larger particle with higher crystallinity and at the same time reduced the pore volume (Sterenson et al., 1987).

From this analysis, the best catalyst is focused on the catalysts that have an isotherm of mesoporous material, open ended cylindrical pore with a uniform size and shape as well as pore diameter which is about 10nm for mesoporous. These surface conditions were expected to give an optimum active site for CO₂ and H₂ adsorption at the catalyst surface (Azelee et al., 1997)

The BET result of the catalysts that tested with H₂/CO₂=3/1 is compared base on the cobalt and zinc loading. The addition of cobalt loading will decrease the volume and surface area of the catalyst. BET surface area affected by impregnation of CO. This is happen also related to the partial blockage of SBA-15 pores by cobalt oxide clusters or partial collapse of SBA-15 (Therdthianwong et al., 2008)

4.5 Thermogravimetric Analyzer (TGA)

Thermogravimetric analysis was prepared using thermogravimetric analyzer. The analysis was done in order to detect the thermal stability of the catalyst with different composition of cobalt and zinc loading. Figure 4.4 shows the comparison of the analysis using 6 samples of catalyst including pure SBA-15.

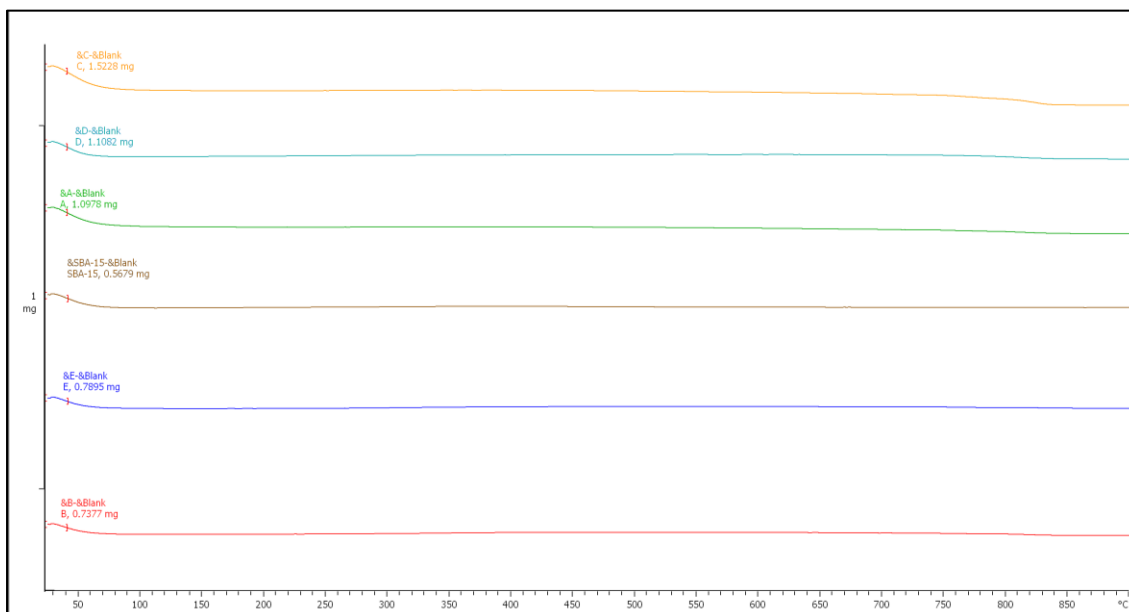


Figure 4.4: Weight loss against temperature for 6 samples with respective notation

The figure above is plotted by weight loss against temperature. The catalyst was heating starting at room temperature until 900°C with heating rate 10°C per minute. The maroon curve in the figure noted as pure SBA-15 without any metal loaded. The different color of curves indicates the different cobalt and zinc loading on the catalyst. A major weight loss for the sample six samples including pure SBA-15 experienced in a short time starting at room temperature until 100°C. At this stage, all the moisture that attached on the catalyst had been detached.

The second stage happens around 100°C until 800°C, the catalysts only experienced a slightly weight loss and the catalysts seem to be stable as the increasing in temperature. At the third stage which is temperature range of 800°C to 900°C, the weight loss of sample A, B, C, D and E consider no weight loss has occurred except for pure SBA-15 which the slighter loss of weight has been detected. This result shows that the catalytic reaction is can be take place at the second stage due to the stability of thermal of each catalyst especially sample B with 15% cobalt and 10% zinc loading.

The functional group of SBA-15 has higher thermal stability of the Cobalt supporter. The weight loss of Co/Zn-SBA-15 occurred at below 100°C which it was recognized to the evaporation of water, and to the combustion of catalyst sample

between 50°C to 375°C. According to Gonzalez (2009), the study shown that the weight loss was happened is about 16% from initial weight. After temperature at 375°C, no combustion occurred and the weight of catalyst sample becomes stable until 800°C (Gonzalez, 2009). For the samples Co/Zn/SBA-15 with composition loading of cobalt and zinc that varies from 5 to 15 wt % were performed at the temperature range between 20 - 220°C.

4.6 Catalytic Performance Analysis using Gas Chromatograph

Catalytic activity has been analyzed by detecting the gas trapped that yield throughout the reaction. The catalytic activity and product selectivity data were calculated after 5 hours of time on stream. Figure 4.5 shows variation of CO₂ conversion and number of active sites as a function of catalysts' compositions.

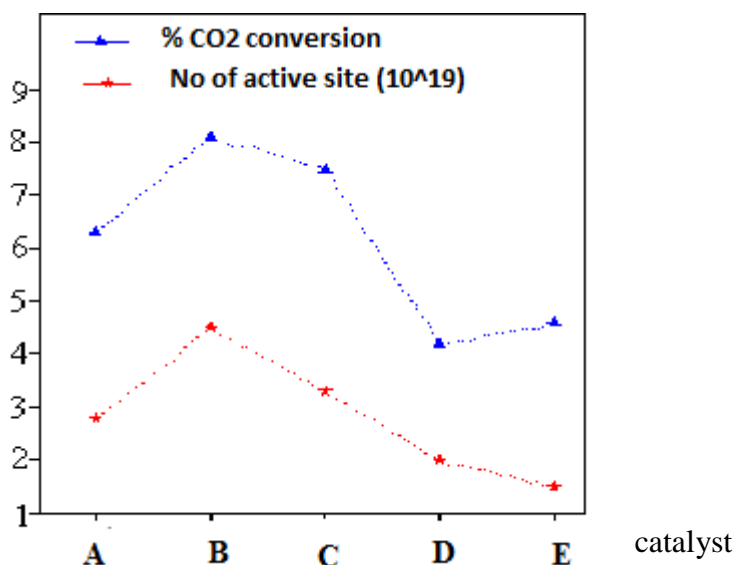


Figure 4.5: Correlation between the catalysts' compositions and the number of active sites and CO₂ conversions.

The product distribution for catalytic reaction was depending on the cobalt and zinc loading on the catalyst. The CO₂ conversion and product selectivities were calculated using the equation as stated follow:

$$\text{CO}_2 \text{ conversion (\%)} = \frac{\text{moles of CO}_2 \text{ (in)} - \text{moles of CO}_2 \text{ (out)}}{\text{moles of CO}_2 \text{ in}} \times 100$$

$$\text{HC selectivity (\%)} = \frac{\text{moles of HC produced}}{\text{Total moles of HC}} \times 100$$

$$\text{Olefinity} = \frac{\text{moles of olefin}}{\text{moles of paraffin}}$$

Through CO₂ hydrogenation, methane is detected as the major product with a very small quantity of short chain paraffins being formed. The CO₂ conversions and product selectivities over modified catalysts are summarized in Table 4.2

Table 4.2: CO₂ conversions and product selectivities over modified catalysts

Catalysts	% CO ₂ conversion	Product Selectivity (%)			Olefinity
		C ₁	C ₂ -C ₄	C ₅₊	
15% Co/15% Zn-SBA-15	6.3	80.7	15.6	3.5	0.4
15% Co/10% Zn-SBA-15	8.1	80.9	16.1	3.2	0.5
15% Co/5% Zn-SBA-15	7.5	79.4	18.4	2.2	0.6
10% Co/15% Zn-SBA-15	4.2	80.0	19.0	1.0	0.7
5% Co/15% Zn-SBA-15	4.6	70.9	27.5	1.6	1.0

Incorporation of zinc into SBA-15 resulted in an increase in the CO₂ conversion passing through a maximum for the 15% Co/10% Zn-SBA-15. The values of CO₂ conversion for other modified catalysts 15% Co/15% Zn-SBA-15, 15% Co/5% Zn-SBA-15, 10% Co/15% Zn-SBA-15 and 5% Co/15% Zn-SBA-15 were 6.3 %, 7.5%, 4.2% and 4.6%, respectively. This trend was in accordance with the results of catalyst

characterizations. Incorporation of zinc which up to 10% into the Co catalysts which is considered as optimized led to higher reducibility which in turn resulted in more metal active sites available for Fischer-Tropsch synthesis and thus enhanced catalytic activity (Jacobs et al., 2002). The highest CO₂ conversion was achieved using the 15% Co/15% Zn-SBA 15 which also among contributes to highest CO₂ adsorption capacity. Incorporation of cobalt on SBA-15 catalyst up to 15% resulted in an increase in the number of metal active sites which bring large impact in increasing the catalyst activity sequence to product selectivity of methane (Wilhelm, 2001).

From the result obtained, it can be seen that the olefinitivity selectivity approaches zero with using CO₂ as primarily feed gas mixed with H₂. This shows that CO₂ is predominantly converted to methane, and to some extent C₂–C₄. CO₂ reacts to form hydrocarbons only when the CO₂ conversion approaches maximum limits. Yao et al. claimed that at a high content of CO₂, the gas is not functioning as a diluted (inert) gas but is converted to hydrocarbon products using Co/Zn-SBA-15 catalyst in a borosilicate glass fixed-bed micro reactor.

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

The result shows that zinc loading improved the surface area of the catalyst while cobalt loading increased the thermal stability. Both of this metal desired in order to have higher conversion and selectivity of hydrocarbons yield. However, the cobalt loading should not more than the zinc loading on catalyst since because it will reduce the thermal stability. Cobalt functions by increase the thermal stability but decrease the surface area of the catalyst. However the zinc loading promoted can improves the surface area by larger the area for reaction to occur. The most efficient catalyst that could be used in Fischer Tropsch is sample B with 15% Co 10% Zn- SBA-15. This is because it shows the optimized combination of zinc and cobalt loading. This result was proven by the characteristic of catalyst which is the existance functional groups of cobalt oxides, Si-O-Si, Si-CH₃, zinc oxide, OH band, Si-C, and others, higher intensity that indicates higher cobalt dispersion, possess large surface area as well as pore size, small weight loses that indicate thermal stability and having large number of catalyst particles attaching closely with one another that make it more effective during FT process.

5.2 Recommendations

As a recommendation to improve the research for further and future improvement, the research should be performed by using analytical equipment which is NH_3 -Temperature Programmed Desorption (TPD) in order to characterize the catalyst. This equipment is used to identify the acid site of the catalyst such as bronsted and lewis acid site. The existence of acid site in catalyst will affect the catalytic activity by increasing the conversion of syngas.

Another recommendation is the characterization of the catalyst should be done before and after the catalyst activity testing. This is significant in order to check the characteristic that belong to catalyst in term of how it can affect the catalyst performance and what the effect on the catalyst after the reaction process has taken place.

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