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JUDUL: PREPARATION AND CHARACTERIZATION OF COBALT-ZINC CATALYST SBA-15 SUPPORTED FOR RISCHER TROPSCH SYNTHESIS : EFFECT ON ZINC LOADING

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SBA-15 SUPPORTED FOR FISCHER-TROPSCH SYNTHESIS: EFFECT ON
ZINC LOADING

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A thesis submitted in fulfilment of the
requirements for the award of the Degree of
Bachelor of Chemical Engineering (Gas Technology)

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I declare that this thesis entitled “Preparation and Characterization of Cobalt-Zinc Catalyst SBA-15 Supported for Fischer-Tropsch Synthesis” is the result of my own research except as cited in references. The thesis has not been accepted for any degree and is not concurrently submitted in candidature of any other degree.”

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Special dedicated to my beloved mother and father

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ABSTRACT

The influence of promoter (Zn) on the physiochemical and catalytic properties of mesoporous silica Co/SBA-15 catalysts for the Fischer-Tropsch (FT) synthesis was investigated. SBA-15 was synthesized as support. The mesoporous silica Co-Zn/SBA-15 catalysts were prepared by incipient wetness impregnation method. Cobalt nitrate and zinc nitrate were used as sources of metal that are introduced onto catalysts with same cobalt loading (15 wt %) and different zinc loading (5 wt %, 10 wt%, 15 wt %) The characterization of catalysts was performed by using Fourier transform infrared (FTIR), scanning electron microscopy (SEM) and thermogravimetric analysis (TGA). The results for FTIR were identification of Si-O-Si functional group indicating the absorption of silica inside SBA-15 support. Beside that, the identification of metal inside SBA-15 was determined by comparing the pure SBA-15 with the incorporated metal on SBA-15. For SEM analysis the image shows that the rope like domain aggregated to wheat-like microstructure. For this research, the characterization of the catalyst by selecting Zn as promoter have quiet similar characterization with noble metal that have been already investigate.

ABSTRAK

Pengaruh penggalak Zn kepada ciri-ciri fisiokimia dan pemangkin silica berliang meso Co/SBA-15 mangkin untuk sintesis Fischer-Tropsch adalah dikaji. SBA-15 disediakan sebagai sokongan. Silica berliang meso Co-Zn/SBA-15 mangkin dihasilkan melalui kaedah impregnasi basah. Kobalt nitrat dan zink nitrat digunakan sebagai sumber logam yang diperkenalkan kepada mangkin dengan kandungan kobalt sebanyak 15wt% dengan kandungan zink yang berbeza (5,10,15 wt%). Pencirian mangkin dilakukan menggunakan Fourier transform infrared (FTIR), scanning electron microscopy (SEM). Hasil dapatan untuk FTIR dikenalpasti sebagai kumpulan berfungsi Si-O-Si disebabkan oleh penyerapan silica yang terdapat dalam SBA-15. Selain itu, pengenalpastian logam dalam SBA-15 dikenalpasti dengan membezakan SBA-15 asli dengan SBA-15 yang digabungkan bersama logam. Analisis SEM terhadap imej menunjukkan bahawa domain seperti serat diaggregatkan kepada struktur mikro berupa seperti gandum. Untuk kajian ini, pencirian katalis dilakuklan dengan memilh Zn sebagai mangkin mempunyai pencirian yang sama dengan logam asli yang telah dikaji.

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LIST OF ABBREVIATION

FTS	Fischer-Tropsch synthesis
GTL	Gas to Liquid
LPG	Liquefied petroleum gas
XRD	X-Ray diffraction
HMS	Hexagonal mesoporous silica
FTIR	Fourier transform infrared
SEM	Scanning electron microscopy
TGA	Thermogravimetric analysis
Fe	Iron
Ru	Ruthenium
Pt	Platinum
Pd	Palladium
Rh	Rhodium
Zn	Zinc
CO	Carbon Monoxide
Co	Cobalt
O ₂	Oxygen
H ₂	Hydrogen
PNIPAAm	poly (<i>N</i> -isopropylacrylamide
CH ₃ OH	Methanol
P123	Triblock copolymer
TEOS	Tetraethyl orthosilicate
Co(NO ₃) ₂ ·6H ₂ O	Cobalt nitrate hexahydrate
Zn(NO ₃) ₂ ·6H ₂ O	Zinc nitrate hexahydrate
HCL	Hydrochloric acid
Co ₃ O ₄	Cobalt oxide

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CHAPTER 1

INTRODUCTION

1.1 Background of the study

1.1.1 Fischer Tropsch Synthesis

Fischer-Tropsch synthesis (FTS) is a chemical process that produces high hydrocarbons chain from synthesis gas (carbon monoxide & hydrogen) at an elevated pressure and temperature and in the presence of catalyst. In 1902 Paul Sabatier and Jean Sanderens discovered a way of converting carbon monoxide (CO) and hydrogen (H₂) to methanol (CH₃OH). During 1920s and 1930s, Franz Fischer and Hans Tropsch developed this synthesis to mainly oxygenated products and hydrocarbons using alkalized iron as a catalyst (Al-Shalchi, 2006).

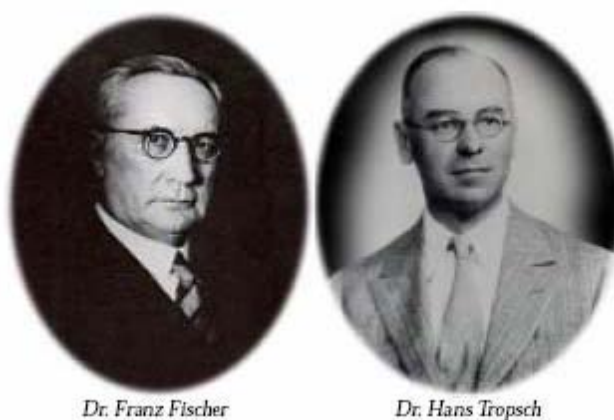


Figure 1.1: Developers of the Fischer -Tropsch Synthesis

By converting the mixture of CO and H₂, they further developed this reaction in a laboratory to oxygenated products and liquid hydrocarbons using cobalt and nickel catalysts at atmospheric pressures. As an assumption, they also found that at low pressure reaction, the product produced mainly hydrocarbons while high pressure produced oxygenates (Al-Shalchi, 2006). Synthesis gas can be made from any carbonaceous materials such as natural gas, biomass, coal and petroleum residues through Fischer-Tropsch synthesis. If liquid petroleum like fuel, lubricant, or wax is required, then the Fischer-Tropsch synthesis is the right process which can be applied. To obtain fuels and chemicals rather than the current dominant petroleum resources, this is an alternative route and Fischer-Tropsch synthesis and now is becoming competitive to petroleum due to its improved catalysts and processes (Al-Shalchi, 2006)

Gas to Liquid (GTL), where production of synthesis gas by using natural gas resources currently is the major focus on the Fischer Tropsch. However, coal to oil is still a vital solution for countries with abundant coal resources such as South Africa where their using coal to produce synthesis gas. In GTL process, paraffinic waxes are the majority of the product from FT synthesis based on following chemical Equation (1).



In order to make the product from Fischer-Tropsch synthesis suitable for using as fuels like gasoline, kerosene and diesel, upgrading process of the products is needed and the upgrading process here is similar to those carried on in refineries like hydrocracking, reforming, hydrogenation, isomerization, polymerization, and alkylation. Liquefied petroleum gas (LPG) and naphtha are typical byproduct from Fischer-Tropsch synthesis and for heavier hydrocarbons, it can be hydrocracked to produced distillate products, notably diesel and jet fuels (Tonkovich, 2008).

1.1.2 Catalyst for Fischer Tropsch Synthesis

The Fischer-Tropsch synthesis was shown to be catalyzed by certain transition metals, with cobalt (Co), iron (Fe) and ruthenium (Ru) presenting the highest activity (Martinez, 2003). Among them, cobalt based catalyst are the suitable catalyst used for Fischer -Tropsch synthesis. The product is primarily straight chain paraffin by reaction over cobalt based catalysts, whereas with iron catalyst, paraffin, alpha olefins, and primary alcohol are produced. Co based catalysts are preferred for their high activity compared to Fe catalysts and due to low activity of the water gas shift reaction. Beside that, cobalt catalysts are believed to deactivate less rapidly and yield high fraction of linear paraffin (Xiong, 2009). Ru based catalysts are highly active but the high cost and low availability of source are important concerns limiting their commercial application (Martinez, 2009).

In the Fischer-Tropsch synthesis, inert catalyst support plays two important roles. First, it serve to disperse the active metal which leads to higher metallic surface areas and therefore, higher catalyst activity. Second, and perhaps more importantly, it may provide a method of influencing the selectivity of the hydrocarbon products. For Fischer-Tropsch catalytic performance, MCM-41 and SBA-15 appear to be model systems to study the effect of support structure. They have ordered structure which can be observed by XRD, narrow pore size distribution, high surface area and pore volume.

The Fischer-Tropsch reaction mechanism is best described as being similar to a polymer chain reaction, although the exact steps may be somewhat different. Molecules of CO and H₂ adsorb to the surface of the catalyst and react to form an adsorbed of C=C species. Additional units of CO are then added at the C=C site and subsequently hydrogenated to form an adsorbed CH₂-C=C. The chain building process continues until the growing molecule desorbs from the surface. This process results in a wide distribution in the lengths of the resulting hydrocarbon chains and is difficult to influence by modifying the active catalytic metal. Recently, it has been shown that cobalt particle size can have an impact on product selectivity (Kim et al., 2006).

Cobalt based catalysts promoted with noble metals are typically prepared via co-impregnation of porous supports with an aqueous solution of a cobalt salt and noble

metal precursors such as ruthenium nitrosyl nitrate, etc. Besides the modifications of the catalytic performance in Fischer Tropsch synthesis, noble metal promoter produces a variety effects on the structure of cobalt catalysts (Diehl et al, 2009). These modifications could affect cobalt reducibility or cobalt dispersion, formation of bimetallic particles, formation of barely reducible cobalt support mixed compounds, decomposition of cobalt precursors and hydrogen activation (Diehl et al, 2009).

In the development of high active cobalt catalysts for Fischer Tropsch synthesis, one important issue need to be highlight is its improvement by increasing the number of active cobalt metal sites that are stable under reaction conditions. This is normally achieved by dispersing cobalt cluster on high area supports or hexagonal mesoporous silicas (HMS) such as SiO_2 , TiO_2 , SBA-15 or MCM-41. Usually, for catalysts support, silica-based mesoporous material such as MCM-41 and SBA-15 are the common catalyst support using in GTL plants. The catalysts supported by mesoporous silicas have exhibited good performance in Fischer-Tropsch synthesis (Khodakov, 2009).

1.1.3 Application of Fischer Tropsch Product

The Fischer Tropsch synthesis product consists mainly from the Figure 1.2. Diesel, naphtha, kerosene gasoline and liquefied petroleum gas (LPG) are the products that resulting from Gas to Liquid plant. Typical output yields for a Fischer-Tropsch process consist of about 55% ultra-clean diesel fuel, 20% naphtha, 20% kerosene and a few percent LPGs, lubes and waxes. The products had been formed by using natural gas as the raw material.

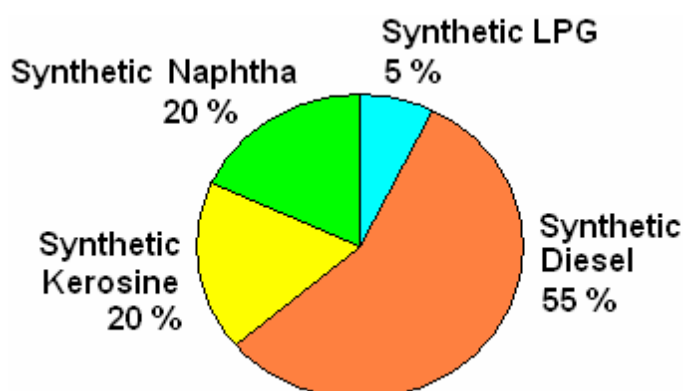


Figure 1.2: Products applications (Al-Shalchi, 2006)

Diesel is the main product of GTL plant where it contains a mixture of heavy hydrocarbon. It is a higher quality fuel than a diesel that is made from crude oil because of its advantages such as high in cetane number, low sulphur and aromatic, and good cold flow characteristic. Fischer-Tropsch diesel has been used as an alternative fuel to replace the conventional diesel fuel in transportation. All of the modern diesel engine in the vehicle can only use the Fischer-Tropsch diesel as the new driving force in vehicle after several modifications have been made on the engine. Furthermore, naphtha contributes to 25% of Fischer-Tropsch product.

Generally, naphtha can be described as a mixture of light hydrocarbon and it is also highly paraffinic. Naphtha is suitable to be used as a feedstock for producing certain chemicals. However, the most ideal usage of naphtha is in producing ethylene. Ethylene is synonymous in plastic industry which it provides polyethylene and polyvinyl chloride (Al-Shalchi, 2006). Liquefied Petroleum Gas or LPG consists of gaseous hydrocarbons or petroleum gases such as propane, butane and pentane that have been pressurized until they become a liquid form hydrocarbon. Basically, LPG is always being used as a heating source in commercial usage.

The benefits of Fischer-Tropsch reactions are not restricted to producing valuable light and mid petroleum derivatives, but it is also used to produce many valuable chemicals by only altering the operation conditions to change the growth of the hydrocarbon chains. Table 1.2 shows the typical uses and application of different types of Fischer-Tropsch product.

Table 1.1: Typical uses and application of different type of Fischer –Tropsch product

Product	Typical uses and applications
Normal paraffin's	Production of intermediates (LAB, SAS, alcohols). Production of intermediates for plasticizers, Auxiliary chemicals, Additives, Cutting Fluids, Sealants, Manufacturing of Film and special Catalyst Carrier and low polar odor- free all purposes Solvents and Diluent
Mixed Paraffin's	Special low polar and odor-free solvent for paints, coating, dry cleaning, cleaners, insecticide and pesticide formulation, and drilling fluids
Synthetic Lubricants	Industrial and automotive lubricant applications including motor oils, compressor oils, hydraulic fluids, and grease
Paraffin Wax	Manufacturing of candies, crayons, printing inks, potting and cable compounds, cosmetics, pharmaceuticals, coatings, and packaging

1.2 Problem Statement

Nowadays, due to the new fuels regulation which require low sulphur content in diesel, deep hydrosulfuration is needed to remove sulphur from petroleum distillates and this will drive up the cost of petroleum-based fuels. Fischer-Tropsch synthesis has become more attractive approach in producing the hydrocarbon using syngas. In any industrial Fischer-Tropsch synthesis, catalyst is a vital part and one of the most important aspects during any chemical reaction. Supported cobalt catalysts have been

extensively used in Fischer-Tropsch synthesis when high molecular weight of hydrocarbon products is desired and represent the suitable choice. Numerous studies have shown that introduction of noble metal (Ru, Rh, Pt, Pd) has strong impact on the structure and dispersion of cobalt species but using the above type of noble metal, higher cost is needed due to lack of sources of the noble metal. Thus, this research will come out with new metal precursor which is using zinc metal.

1.3 Objective

- a) To synthesis SBA-15 mesoporous silica
- b) To synthesis Co-Zn/SBA-15 mesoporous catalysts
- c) To characterize Co-Zn/SBA-15 mesoporous catalysts : Effect on zinc loading

1.4 Scope of Study

The scope in this study is focusing on producing the new catalysts for Fischer-Tropsch synthesis which is Co-Zn/SBA-15 and investigate the influence of cobalt and zinc promoters loading need to be investigated. Co-Zn/SBA-15 catalysts with same Co contents which 15 wt % and different Zn contents which range 5 wt % until 15 wt % was prepared by incipient wetness impregnation of relative SBA-15 with the desired amount of aqueous cobalt nitrate and zinc nitrate. The Co-Zn/SBA-15 catalysts then were characterize by using FTIR analysis, scan electron microscopy (SEM) analysis.

CHAPTER 2

LITERATURE REVIEW

2.1 SBA-15

SBA-15 is the mesoporous materials which is a special type of nanomaterials with ordered arrays of uniform nanochannels that have been prepared in acidic conditions with triblock copolymer and tetraethyl orthosilicate. SBA-15 has an important application in a wide variety of fields such as separation, adsorption catalysis and advanced nanomaterials (Can et al, 2005). SBA-15 is silica based mesoporous material with uniform hexagonal channels and very narrow pore size distribution ranging 3 to 30 nm (Xiong, 2009). Comparing with other mesoporous silicas such as MCM-41, SBA-15 has enhanced hydrothermal stability and large surface area (600-1000 m²/g), allowing for the dispersion of large number of catalytically active species. Besides, the reducibility is favored for the SiO₂ supported Co catalyst because the strength of interaction between the cobalt and support is lower than the other commonly used (Xiong, 2009).

Pore size distribution, high surface area and pore volume of the SBA-15 make periodic SBA-15 mesoporous silica promising support for metal and oxide catalyst. Particularly, for reactions occurring at high temperature, SBA-15 may be used as promising catalysts support because it possesses larger pores, thicker walls and have higher thermal stability as compared to others mesoporous silica (Can et al, 2005). To improve their physical and chemical properties, the base mesoporous materials have often been modified by adding noble metals or metal oxides. Although some studies of the incorporation of Al and Ti in SBA-15, as active species were performed the

information is limited about the use of SBA-15 as host for the catalytic active specie. Anyway, this material presents a high potential in catalytic applications (Anunziata et al, 2007).

2.2 Co/SBA-15

The utilization of SBA-15 as a support for preparing cobalt based Fischer Tropsch synthesis has been explored. Recent study has shown that combination of Co/SBA-15 catalyst provide good performance and represent the optimal choice for low temperature Fischer-Tropsch process, because of higher stability, higher per single pass conversion (up to 60-70%), higher productivity, relatively smaller negative effect of water on conversion, and higher resistance to attrition especially in slurry bubble column reactors (Khodakov, 2009). The preparation of highly dispersed Co/SBA-15 catalysts from cobalt acetate and cobalt acetylacetonate precursor and found that the obtained exhibited low Fischer -Tropsch synthesis activity, which was ascribed to a low reductibility of Co species.

The effect of the average pore diameter (from 3.5 to 13 nm) of Co/SBA-15 catalysts on the Fischer–Tropsch Synthesis performance was examined and found that the catalyst with pore diameter around 8 nm showed the largest conversion. Due to large pores size, SBA-15 most suitable to use compared with cobalt loading in MCM-41 support, it has a limit due to cobalt loading which is the mesoporous structure starts to collapse when the cobalt loading exceeds 4 wt % (Wang et al, 2009). Lira et al., (2008) studied the loading effect of cobalt (10%-40% w/w) supported by SBA-15 showed that the maximum CO conversion was obtained for catalyst loaded with 30 wt% Co which presented the highest density of surface cobalt site.

According to Xiong et al, (2008), Fischer-Tropsch turnover rates are independent of the Co dispersion and support identity over the accessible dispersion range (0.01-0.12) at typical Fischer-Tropsch synthesis conditions. High productivity for supported cobalt based for Fischer-Tropsch synthesis catalysts requires small cobalt crystallites at high cobalt surface densities. It is well known that the smaller the cobalt particles size, the stronger interaction between the cobalt and support. Strong interaction between the cobalt support decrease both the catalyst reducibility and

activity for Fischer-Tropsch synthesis. To prepare highly active cobalt base catalyst, it is necessary to balance precisely between dispersion and reducibility (Xiong et al, 2008).

Zinc will use as promoter in term of finding the cheap sources of noble metals. Usually, the Pd, Rh, Ru and Pt are the common promoter that has been used for cobalt catalysts for Fischer Tropsch synthesis.

2.3 Effect on Zinc Promoter

The goal of promotion is to enhance cobalt Fischer Tropsch catalysts by the addition of small amount of noble metal and for this study, zinc are chosen for the catalysts promoter. Typically, the promoting of the metal for the catalysts in introduced via co-impregnation or subsequent impregnation (Khodakov, 2009). By introduced other noble metals as promoter, it could results in easing cobalt reduction, enhancement of cobalt dispersion and better resistance to deactivation. Beside that the promoter will result on formation of metallic alloys, high concentration of hydrogen activation site and resulting on modification of intrinsic of surface site (Khodakov et al., 2009).

Diehl et al. (2009) studied that the presence of noble metal can affect particle size of both cobalt oxide and metallic cobalt. Analysis of the literature data suggests that the promotion with noble metal primarily reduces the sizes of cobalt oxide particles in weakly interacting support such as silica. Promotion with noble metal can also affect the sizes of cobalt metal particles in the reduced cobalt catalysts. Beside that, promotion of with noble metals could also affect decomposition of cobalt precursor (Diehl et al. 2009). Recent report has shown that promotion with ruthenium using ruthenium nitrosyl nitrate could results in a lower temperature of decomposition of cobalt acetate in silica supported catalysts. It is however known that cobalt acetate usually decompose at 493 K in the presence of air while ruthenium nitrosyl nitrate decomposes at 423 K (Diehl et al 2009).

Nobuntu et al. (2005) investigated that the presence of zinc in the catalyst is anticipated to improve the dispersion of cobalt by forming a 'sandwich layer' between the cobalt and the support. It is expected by formation of big cobalt particle on top of

well dispersed zinc, can improve the stability of cobalt particle. By adding the other metal onto cobalt based catalyst, it displayed higher activity towards Fischer Tropsch synthesis when compared to single cobalt source precursors (Nobuntu et al., 2009). Researcher has been used cobalt and zinc as metal onto TiO_2 support. For Co10%/Zn5% impregnation onto TiO_2 , it has been found that they were more active and have higher CO conversion than catalyst prepared from single precursors of zinc and cobalt. The observed catalytic behaviour of Co/Zn TiO_2 when compared to Co/ TiO_2 catalyst could be attributed to the effect of zinc forming a 'sandwich layer' between cobalt and the support on the dispersion and stability of cobalt crystalline particles.

2.4 Catalyst Characterization

2.4.1 Fourier Transforms Infrared Spectroscopy (FTIR)

Fourier transform infrared (FTIR) is most useful for identifying chemicals that are either organic or inorganic. It can be utilized to quantitative analyze for some components of an unknown mixture. FTIR can be applied to the analysis of solids, liquids and gasses. It can be used to identify chemicals from spills, paints, polymers, coatings, drug and contaminants. FTIR is perhaps the most powerful tool for identifying types of functional group. The wavelength of light absorbed is characteristic of the chemicals bond as can see in this annotated spectrum. For most common materials, the spectrum of an unknown can be identified by comparison to a library of known compounds. To identify less common materials, IR will need to be combined with nuclear magnetic resonance, mass spectrometry, emission spectroscopy and X-ray diffraction

Figure 2.1 show the modification of SBA-15 support by introducing the aluminium (Al) and silica (Si). FTIR of Si-SBA-15 and Al-SBA-15, shows bands at 1069 cm^{-1} (T-O asymmetric stretching) and 800 cm^{-1} (T-O symmetric stretching). The bands are due to TO_4 vibrations (T = Si, Al), assigned to the bending Al-O-Si, that indicate the incorporation of Al into SBA-15 (Anunziata et al, 2007). Only one signal at 3740 cm^{-1} due to terminal Si-OH is observed in the case of SBA-15, a new band at

3630 cm^{-1} appears in Al-SBA-15, increasing from sample (a) to (b), assigned to Brönsted sites due $\text{Si}_3\text{-O-Al-OH}$. SBA-3 shows only a band at 3647 cm^{-1} , due to terminal silanol. Anunziata et al., (2007) studied on SBA-1 and SBA-3, show that a band at 3720 cm^{-1} for SBA-1 indicates a weaker acid site compared with SBA-3 and SBA-15. For this research, the present of several elements such as cobalt oxide and zinc oxide be determine due to the dispersion of the metal onto SBA-15.

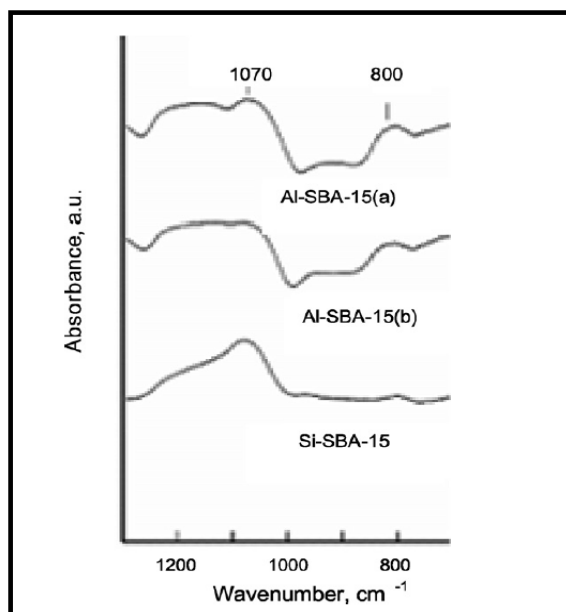


Figure 2.1: FTIR of Si-SBA-15 and Al-SBA-15 (Anunziata et al, 2007)

2.4.2 Scanning Electron Microscopy (SEM)

Scanning electron microscopy analyses are used to determine the morphology of the catalyst surface such as shape, size and crystallinity of the catalyst. Figure 2.2 show the example of SEM microphotograph.

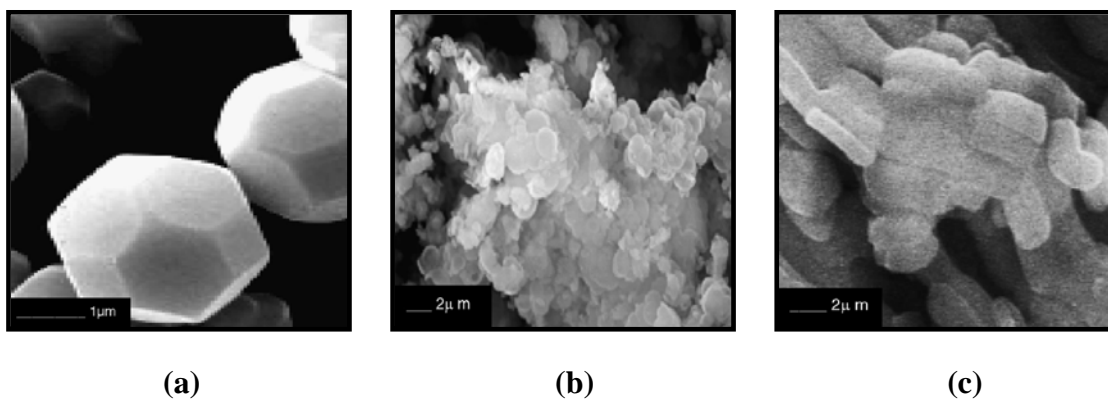


Figure 2.2: SEM microphotographs of (a) SBA-1, (b) SBA-3, and (c) SBA-15
(Anunziata et al, 2007)

The size and shape of the samples indicate good morphology of the crystals, without other phases, and typical of these materials. The pictures were shown in Figures 2.2a–2.2c. As shown in 2.2, separated almost spherical or spheroid crystals but have glass-like disorder in the walls observed for SBA-1 sample. The particle size of the siliceous SBA-1 was 1.5–2.2 μm in diameter, whereas for SBA-3 the crystal form was almost spherulitic with lower crystal size (0.8–1.3 μm). SBA-15 images reveal that it consists of many rope-like domains with relatively uniform sizes of 1.5–2 μm , which are aggregated into wheat-like macrostructures.

2.4.3 Thermogravimetric Analysis (TGA)

Thermogravimetric analysis (TGA) is a technique which monitors changes in the mass of a sample as a function of time and temperature. The sample, usually a solid but liquids may be analyzed as well, is placed in an inert quartz sample vial inside a low volume, high temperature computer controlled oven. The quartz sample vial is suspended from one arm of a high sensitivity electro balance, which monitored along with the oven temperature during a TGA run..

Figure 2.3 show the quantitative analysis of the organic content of different types of poly (*N*-isopropylacrylamide)(PNIPAAm). Quantitative determination of the organic content was executed by TG analyses. It was reported that the pure PNIPAAm polymer suffered an initial minor weight loss at ~ 135 °C and a main decomposition in the range of 350-460 °C in the TG curve. It is seen from Figure 2.4.3a that no notable decrease in weight can be observed for pure SBA-15 in the temperature range of 100-800 °C except a lower weight loss below 100 °C due to removal of adsorbed water (Tian et al, 2009). For the PNIPAAm/SBA-15 composites, however, a remarkable loss in weight was found in the same temperature region. We also notice that the decomposition progresses as a gradual weight decline for 0.6-PNIPAAm/SBA-15 samples, which probably results from the high dispersion of monomer in the mesopores and formation of oligomers or polymers with different polymerizing degrees. As the dosages of monomer are increased in the syntheses, significant weight loss steps appear in TG curves of the samples, likely suggesting formation of polymer with relative uniform molecular mass in the channels (Tian et al, 2009). The reduction of cobalt and zinc inside SBA-15 at high temperature can be determined by using this analysis.

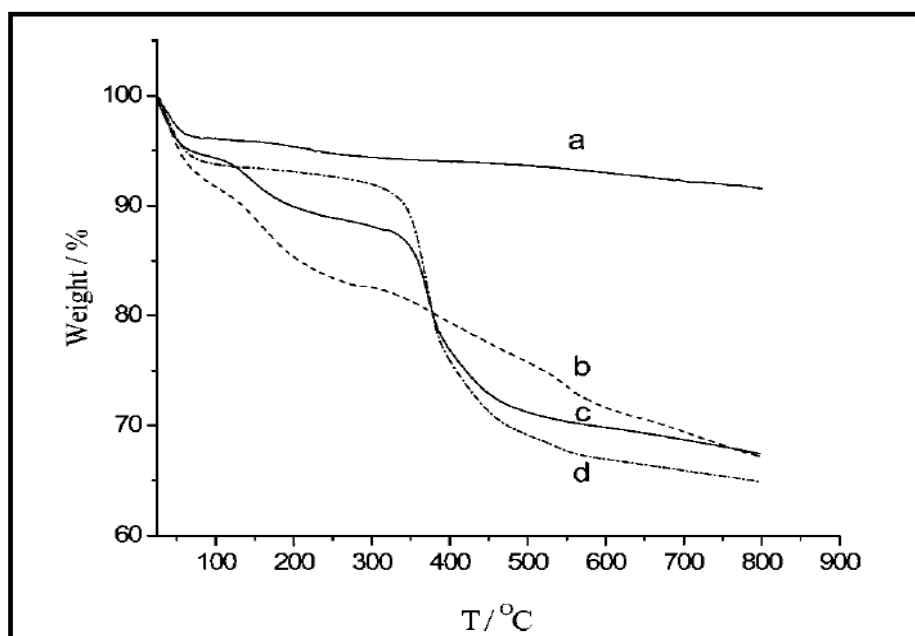


Figure 2.3: TG curves (a) SBA-15, (b) 0.6-PNIPAAm/SBA-15 (c) 1.2- PNIPAAm/SBA-15 and (d) 1.8-PNIPAAm/SBA-15 (Tian et al, 2009)

Girardon et al, (2007) studied on decomposition of cobalt precursor in the presence of Ru. Figure 2.4 show the DSC-TGA curves of the catalyst prepared from cobalt nitrate promoted with ruthenium. The decomposition profiles for the CoRu catalysts are similar and resemble the DSC-TGA curves of unpromoted cobalt silica supported catalysts. From the figure, two endothermic weight losses are observed at 323-328 K and 363-364 K. These losses can be attributed to the dehydration of cobalt nitrate and silica. An additional weight loss was detected at 431-432 K which can attribute to the decomposition of NO₃⁻ groups (Girardon et al., 2007)

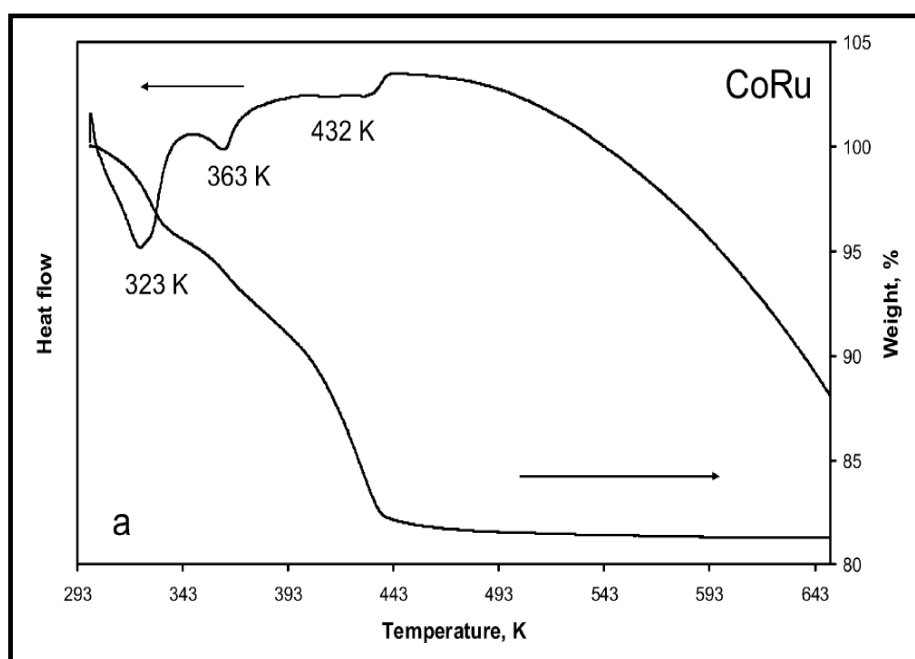


Figure 2.4: DSC-TGA curves of cobalt silica-supported catalysts promoted with ruthenium (Ru) (Girardon et al., 2007)

CHAPTER 3

MATERIALS AND METHODOLOGY

3.1 Introduction

In this chapter, the experimental techniques employed for the preparation and characterization through this research are summarized and descriptions of parameter calculated are also presented. The flow chart of the experimental work is shown in Figure 3.1. The first stage of this experimental work was preparation of catalysts. The catalyst which is Co-Zn/SBA-15 was prepared by using incipient wetness impregnation method. The characterization of the catalysts was performed by using Fourier Transform Infrared (FTIR), Scan Electron Microscopy (SEM).

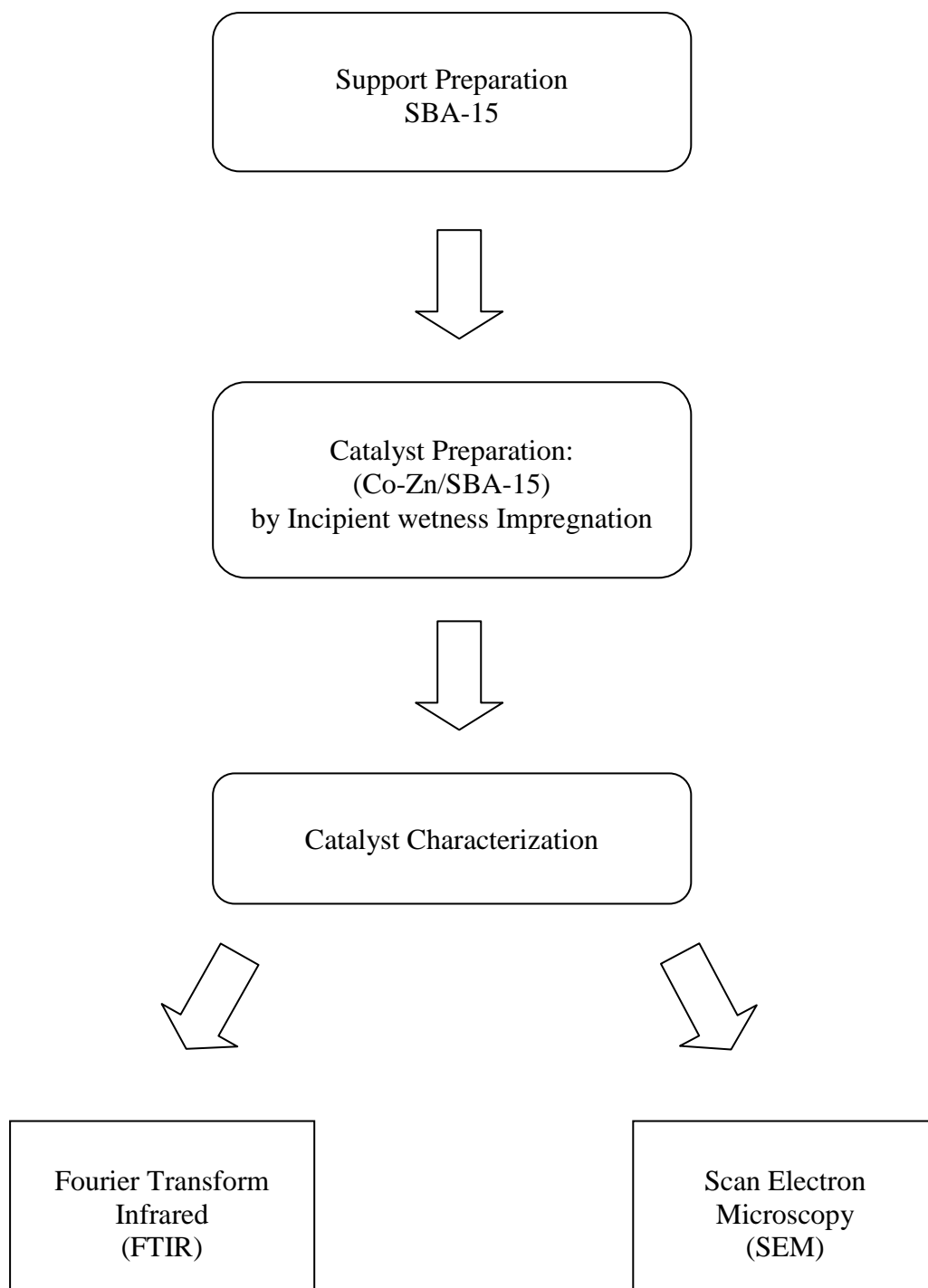


Figure 3.1: Flow chart of research work

3.2 List of chemicals

Table 3.1: List of Chemicals

Chemical	Supplier	Purity
Triblock copolymer (P123)	Sigma Aldrich	-
Tetraethyl orthosilicate (TEOS)	MERCK	> 9%
Cobalt nitrate hexahydrate, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	MERCK	> 99%
Zinc nitrate hexahydrate, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	R & M Chemicals	-
Hydrochloric acid (HCL)	Fischer Chemicals	37 %

3.3 Experimental procedures

3.3.1 SBA-15 preparation

150 ml HCL solution with 2M concentration was shaken in an orbital shaker at 40°C for half an hour. 4 ml triblock copolymer (P123) was dissolved in the HCL solution. Then the mixture was shaken at 40°C for an hour. 9 ml tetraethyl orthosilicate was added into the above solution and the mixture was stirred for two hours at around 40°C. As the gel started to develop, the mixture was heated at 40°C under slow shaking at 50 rpm for 24 hours. Then, the solid forms were filtered and wash for several times with distilled water. Finally, the sample was calcined at 500°C for 6 hour in furnace.

3.3.2 Metal deposition

Co-Zn/SBA-15 with same cobalt content (15 wt %) and different zinc content with range between 5 wt% until 15 wt% was prepared by incipient wetness impregnation of SBA-15 where the weight percent of cobalt and zinc loading was determined by calculate the amount of cobalt nitrate and zinc nitrate desired to use. The catalyst produced was dry overnight in oven at 60°C and calcined at 500°C for 6 hours. The Co catalyst with the addition of zinc promoter was labeled as Co-yZn/SBA-15 with y standing for zinc weight percent in the samples. The calculations are summarized in Table 3.1 and the detail calculations are shown in the Appendix A.

Table 3.2: Summarize of metal loading to SBA-15

Sample	Ratio of Co:Zn (% wt)	Mass of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (gram)	Mass of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (gram)
Co-15Zn/SBA-15	15 : 15	2.863	2.152
Co-10Zn/SBA-15	15 : 10	2.863	0.835
Co-5Zn/SBA-15	15 : 5	2.863	0.294

3.4 Catalysts characterization

3.4.1 Fourier Transform Infrared (FTIR)

FTIR is an analytical instrument for identifying chemicals that consist inside either organic or inorganic compound. It can be utilized to quantitative some components of an unknown mixture. It can be applied to the analysis of solids, liquids, and gasses. FTIR is perhaps the most powerful tool to use in this research for identifying types of chemical bonds (functional groups) and the spectrum analysis. The wavelength of light absorbed is characteristic of the chemical bond as can be seen in this annotated spectrum. By interpreting the infrared absorption spectrum, the chemical bonds in a molecule can be determined. For this experiment there is a booklet for FTIR which is work as reference for determination of substance that lying at the particular wavelength that produce from the analysis. The FTIR analysis was performed in clean room Universiti Malaysia Pahang

3.4.2 Scanning Electron Microscopy

Scanning electron microscopy analyses are used to determine the morphology of the catalyst surface such as shape, size and crystallinity of the catalyst. This analysis was performed at Faculty of Manufacturing Universiti Malaysia Pahang.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Fourier transform infrared (FTIR)

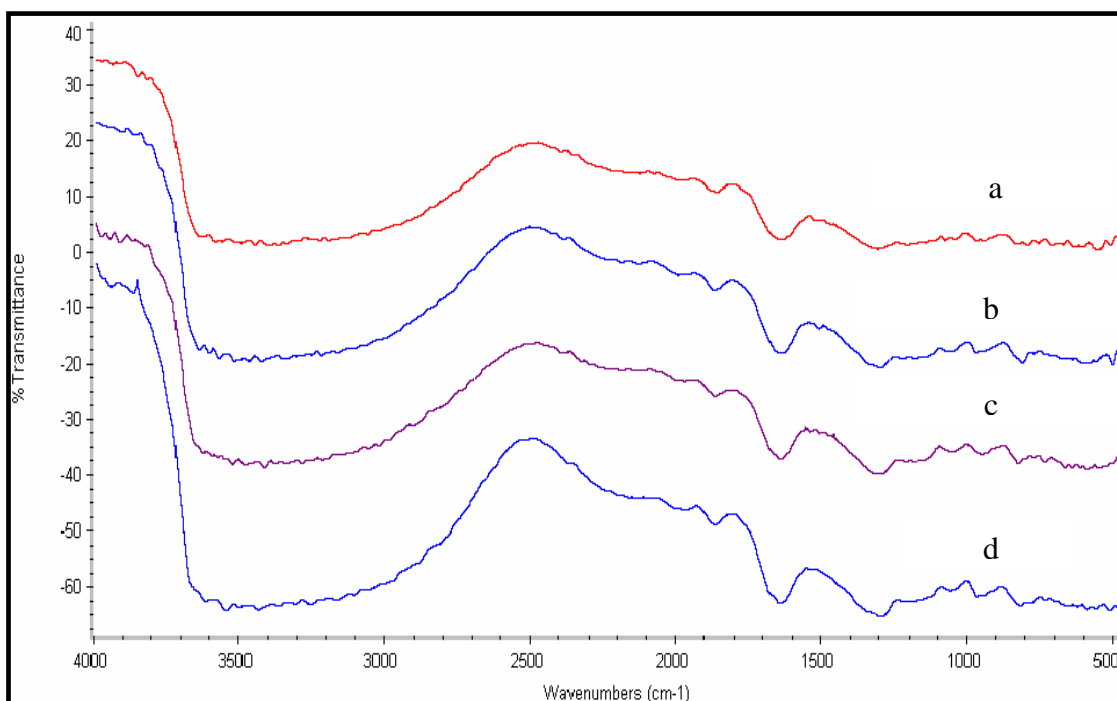


Figure 4.1: FTIR spectra of a) Co-5Zn/SBA-15 b) Co-10Zn/SBA-15 c) Co-15Zn/SBA-15 d) SBA-15

The modification of SBA-15 support was investigated by Fourier transform infrared (FTIR) spectroscopy for four different type of catalyst as shown in Figure 4.1. In these four spectra, the absorption peak of Si-OH bond appeared at 860 cm^{-1} and the absorption peak of Si-O-Si bond appeared at 1090 cm^{-1} . Li et al., (2006) found that the Si-OH bond appeared around 960 cm^{-1} . Previous investigation also revealed

that the absorption of silica shown around 800-1000 cm^{-1} . In the hydroxyl region all spectra show a band at 3745 cm^{-1} assigned to isolated OH in silanol groups (Mazaj et al., 2009). It seems like by introducing the metal onto SBA-15, the curve length becomes less due to dispersion of cobalt and zinc onto pure SBA-15. Wang et al., (2006) studied that the incorporation of organic functional groups in the silica framework was also confirmed by FTIR spectra as shown in Figure 4.1. The typical Si–O–Si bands around 1200- 1400 cm^{-1} associated with the condensed silica network are observed on the as-synthesized and all the extracted samples. The Si-O-Co bond assigned at 1020 -1036 cm^{-1} which this peak determines the cobalt silicate (Kababji et al. 2009)

From the results, the weak Co-O absorbance peaks exist around 580 cm^{-1} probably due to small amount of CoO formation. The spinel Co-O bond absorbance peak corresponding to $\text{Co}^{3+}\text{O}^{4-}$ is clearly visible around 667 cm^{-1} . By using infrared spectroscopy, previous study found that much less than expected Co_3O_4 formation upon calcinations when silica was used as support. This is also explained by reaction between CoO and SiO_2 during calcinations which prevented large amount of CoO from further oxidation to form Co_3O_4 (Kababji et al., 2009). To explain why some catalysts samples contain more cobalt oxide species, it starts when the initial mixing of cobalt precursor and the various surface area of silica support. The cobalt positive ions are attracted to the silica support pores after mixing process by adjusting the pH using aqueous ammonia to maintain a negative charge through the silica surface. The preferable pH is around 4.5 and if the pH value is 2-5, the surface is negatively charged and cobalt ions are dragged to the pores by capillary action. If the pH value is less than 2 then the silica surface is positively charged, thus repulsing the bulk of cobalt cations from the porous silica surface. Cobalt cations at pH less than 2 and higher than 5, can react with SiOH group to form cobalt silicate. These cations can react with the nitrate ions and surface SiOH group forming complexes that could hinder the deposition of cobalt ions in the pores thus affecting the dispersion of cobalt ions and ultimately upon drying and calcination the amount of cobalt oxide species formed (Kababji et al., 2009).

The FTIR spectrum of all samples shows that the characteristic set of stretching vibrations attributed to nitrate anions appears at 1420, 1338 cm^{-1} (Biswick et

al.2007). By increasing the nitrate composition onto the support, it seem that the band curves at the particular wavenumbers become decrease. This changed can be described due to existence of zinc nitrate that are not really clearly remove when calcination process. The spectrum also confirms the absorbance of nitrate group at 1610, 975, 800 cm^{-1} and indicate the existence of cobalt nitrate residue due to low drying temperature (Kababji et al., 2009)

The figures are also in agreement with the established structure of the materials. The spectrum for $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ contains OH stretching vibrations of the layer hydroxyls and water molecules in the region 3660-2900 cm^{-1} with the upper limit corresponding to the free OH group and the lower limit to OH groups involved in significant hydrogen bonding (Biswick et al.,2007). By introducing $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ onto the support, they are several finding that can determine due to three types of structurally different hydroxyls. The stretching vibrations of OH groups not substantially involved in hydrogen bonding can be assigned at band 3500 cm^{-1} . The band 3460 cm^{-1} may be assigned to vibrations of OH groups hydrogen bonded to nitrate groups whereas the band at 3280 cm^{-1} may be assigned to stretching vibrations of OH groups of the water molecules.

4.2 Scanning Electron Microscopy (SEM)

The SEM microphotograph of mesoporous SBA-15 particles before and after surface modification is shown in Figure 4.4a and Figure 4.4b respectively. Figure (a) is pure SBA-15 while Figure (b) is SBA-15 with incorporated with 15wt% of cobalt and 10wt% of zinc promoter. The SBA-15 particles are something like spherically shape with approximately 187x magnification and these particles seem like to agglomerate. Both images show that the rope like domain aggregated to wheat-like microstructure (Anunziata et al., 2007). The size and shape are indicating good morphology of the support with incorporation of Co and Zn did not change the morphology of the SBA-15 support.

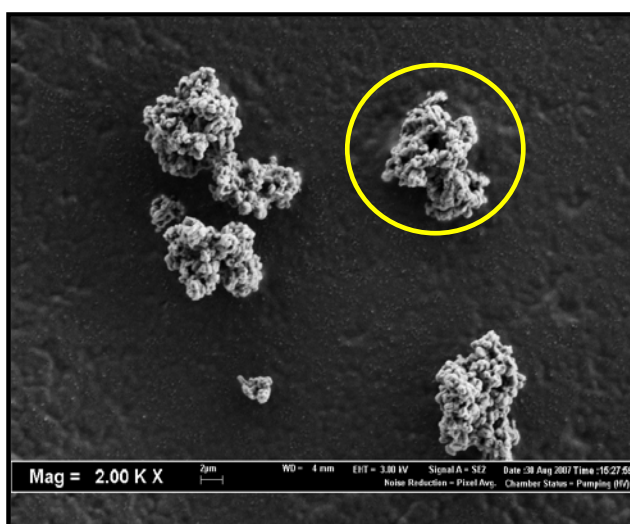


Figure 4.2: SEM microphotograph of SBA-15

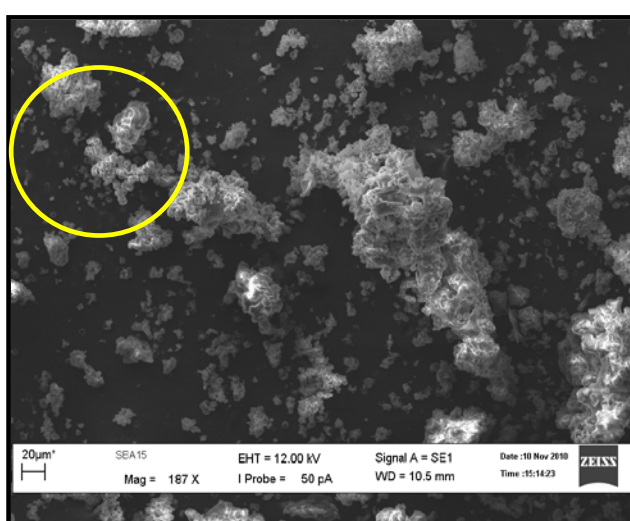


Figure 4.3: SEM microphotograph of %Co-10%Zn/SBA-15

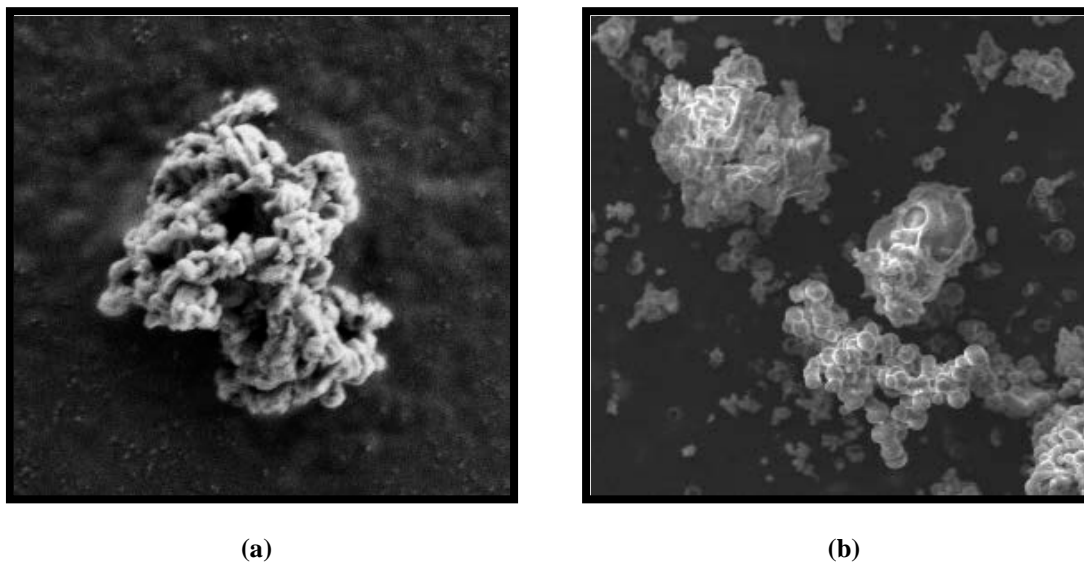


Figure 4.4: SEM microphotograph of (a) SBA-15 and (b) 15%Co-10%Zn/SBA-15

Mazaj et al.(2009) studied the incorporation of Ti-Beta nanoparticles onto SBA-15 that the SEM image of pure SBA-15 shows curved rod-like aggregates of SBA-15 particles with a relatively smooth surface. The SEM image of sample shows that the morphology and size of the particles does not change after the deposition of Ti-Beta nanoparticles on the SBA-15 matrix.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusions

A series of same cobalt loading (15 wt%) with different zinc loading as promoter (5wt%,10wt%,15wt%) on Co/SBA-15 catalysts have been prepared using incipient wetness impregnation method and were characterize using Fourier transform infrared and scanning electron microscopy. From this research, it can be conclude that they are several similar characterizations between Co-Zn/SBA-15 catalysts with previous catalyst studied. This characterization was an important analysis and it was the first step to determine the quality of the catalyst. In addition, studies on adsorption on Co-Zn/SBA-15 catalyst by using FTIR revealed that the cobalt and zinc were finely dispersed onto SBA-15. By comparing with previous study, this characterization analysis was a few of achievement in catalyst industry.

5.2 Recommendation

In this research, the novel technique of characterization by using FTIR, SEM had been well demonstrated. In order to get the precise results and specific characteristic of the catalyst, it is recommended that further work on adding other techniques of catalyst characterization such by using XRD, N₂ adsorption, transmission electron microscopy, DSC-TGA.

Another recommendation is by furthering the studies on reaction analysis by using the prepared catalysts. Analyzing the catalytic reaction can determine the ability of prepared catalyst especially the conversion rate of the reaction and the performance of Fischer-Tropsch synthesis basically.

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