

FISCHER-TROPSCH (FT) SYNTHESIS OF HYDROCARBON OVER MESOPOROUS  
CO/SBA-15 CATALYST: INFLUENCE OF COBALT AND ZINC PRECURSORS  
LOADING.

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Thesis submitted in fulfilment of the requirements  
for the award of the degree of  
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## BORANG PENGESAHAN STATUS TESIS\*

**JUDUL: FISCHER-TROPSCH SYNTHESIS OF HYDROCARBON OVER  
MESOPOROUS CO/SBA-15 CATALYST: INFLUENCE OF  
COBALT AND ZINC PRECURSORS LOADING**

**SESI PENGAJIAN : 2011/2012**

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## ABSTRACT

This research title is Fischer-Tropsch (FT) Synthesis Of Hydrocarbon Over Mesoporous Co/SBA-15 Catalyst: Influence Of Cobalt And Zinc Precursors Loading. The FT process is a set of chemical reaction that convert mixture of carbon monoxide and hydrogen into liquid hydrocarbons. The objectives are about to synthesis SBA-15 mesoporous silica, to synthesis Co-Zn/SBA-15 mesoporous catalyst and to determine the influence and effect of promoter on the catalytic properties. The synthesis of Co-Zn/SBA-15 catalyst is prepared by an impregnation method. Cobalt nitrate and Zinc nitrate will be used as precursors and promoter respectively and being introduced as metal to the catalyst. Fourier Transform Infrared (FTIR ) is used to identify types of chemical bonds in the catalyst where then Si-O-Si functional group is detected because of the present of silica from Tetraethyl-orthosilicate, TEOS. The morphology of the catalyst surface determined by Scanning Electron Microscope (SEM) and it is analyzed that the catalyst to have 'rope-like' structure and no change in morphology after modification. After Cobalt and Zinc is added, X-ray Diffraction (XRD) has detected that there are cobalt crystalline formed and the amorphous shape graph of Pure SBA 15 is changed with new peaks detected due to intensity changes. The best BET surface area analyzed is 375.9021 m<sup>2</sup>/g by the sample of 10%Co15%Zn-SBA15 catalyst which also poses big pore volume of 0.480953 cm<sup>3</sup>/g. Thermogravimetric Analyzer (TGA) measured the decomposition of the samples at temperature of 100°C, 250C, 300C and 450C which caused by decomposition of adsorbed water, organic functional group, dehydroxylation of silicate and nitrate group respectively. Thus, with all revenues collected from all the tests and compared with previous studies, this study found to be one small achievement in the catalyst industry.

## ABSTRAK

Tajuk penyelidikan ini adalah Fischer-Tropsch (FT) Sintesis Bagi Hidrokarbon Dari Pemangkin Liang Meso Co/SBA-15: Pengaruh Penambahan Cobalt Dan Zink. Proses FT adalah satu set tindak balas kimia yang menukarkan campuran karbon monoksida dan hidrogen ke dalam hidrokarbon cecair. Objektif untuk sintesis silika liang meso SBA-15, mensintesis pemangkin liang meso Co-Zn/SBA-15 dan untuk menentukan pengaruh penggalak sebagai pemangkin. Sintesis pemangkin Co-Zn/SBA-15 disediakan dengan kaedah impregnasi. Kobalt Nitrat dan Zink nitrat akan digunakan sebagai penggalak daripada logam untuk pemangkin. Fourier Transform Infrared (FTIR) digunakan untuk mengenal pasti jenis ikatan kimia dalam pemangkin di mana Si-O-Si kumpulan berfungsi dikesan kerana sekarang silika dari Tetraethyl-orthosilicate, TEOS. Morfologi permukaan pemangkin yang ditentukan oleh Pengimbasan Mikroskop Elektron (SEM) dan dianalisis bahawa pemangkin untuk mempunyai struktur 'seperti tali' dan tiada perubahan dalam morfologi selepas pengubahsuaian. Selepas Kobalt dan Zink ditambah, X-ray Difraction (XRD) telah mengesan bahawa terdapat kobalt kristal yang terbentuk dan graf bentuk amorfus untuk SBA 15 tulen bertukar bentuk dengan puncak baru dikesan disebabkan oleh perubahan keamatan. Luas permukaan BET terbaik dianalisis ialah  $375.9021 \text{ m}^2/\text{g}$  oleh sampel pemangkin 10%Co15%Zn-SBA15 yang juga meencatatkan isipadu liang besar iaitu  $0.480953 \text{ cm}^3/\text{g}$ . Thermogravimetric Analyzer (TGA) mengukur penguraian sampel pada suhu  $100^\circ \text{C}$ ,  $250^\circ \text{C}$ ,  $300^\circ \text{C}$  dan  $450^\circ \text{C}$  yang disebabkan oleh penguraian air yang terjerap, kumpulan berfungsi organik, dehydroxylation kumpulan silikat dan nitrat untuk setiap satunya. Oleh itu, dengan semua hasil yang dikutip dari semua ujian dan dibandingkan dengan kajian yang sebelumnya, didapati kajian ini dapat menjadi salah satu pencapaian kecil dalam industri pemangkin.

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**LIST OF ABBREVIATION**

BET	Bruno-Emmet-Teller
Co	Cobalt
FT	Fischer-Tropsch
FTIR	Fourier Transform Infrared Spectroscopy
LPG	Liquefied Natural Gas
NGL	Natural Gas Liquid
SEM	Scanning Electron Microscope
TEOS	Tetraethyl-Orthosilicate
TGA	Thermogravimetric Analyzer
XRD	X-ray diffraction
Zn	Zinc

## **CHAPTER 1**

### **INTRODUCTION**

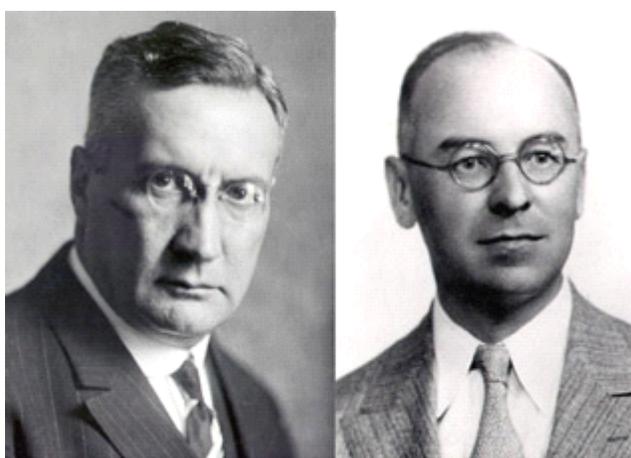
#### **1.1 Background of the study**

Recently the costs of crude oil have been increasing to well above US\$100 per barrel low and there were so much issues on the lacking of oil and fuel source (Heifeng, et al, 2008). Therefore, more interest has been developed in the production of liquid hydrocarbon using metal catalyst. In 1925, Professor Franz Fischer and Dr Hans Tropsch applied a patent describing process to produce liquid hydrocarbon which was synthesised in a process that made primilary of liquid alkanes (paraffins) which also known as Fischer-Tropsch (FT) synthesis. Figure 1.1, shows the potrait of both Professor Franz Fischer and Dr Hans Tropsch.

A set of chemical reactions that convert a mixture of carbon monoxide and hydrogen into liquid hydrocarbons is the basic explanation for FT synthesis. The chemical process for the production of liquid fuel has thus become more attractive because this synthesis could produce component of gas to liquids technology, produces a petroleum substitute from coal, natural gas or biomass for use as synthetic fuel.

**Table 1.1:** Malaysia energy overview reserves and consumptions (million Btu)

	<b>Reserves</b>	<b>Consumption (2009)</b>
<b>Coal</b>	4.4 millions short tons (2008)	2.3 millions short tons
<b>Crude Oil</b>	4 billion barrels (Jan,2010)	536, 000 bbl/d
<b>Natural Gas</b>	8.3 trillions cubic feet (Jan,2010)	1 trillions cubic feet

**Figure 1.1:** Developers of the Fischer -Tropsch Synthesis Process; Professor Franz Fischer and Dr Hans Tropsch.

## 1.2 Fischer-Tropsch Synthesis

The Fischer-Tropsch synthesis section consists of: FT reactors, recycle and compression of unconverted synthesis gas, removal of hydrogen and carbon dioxide, reforming of methane produced and separation of the FT products. The most important aspects for development of commercial Fischer-Tropsch reactors are the high reaction heats and the large number of products with varying vapor pressures (gas, liquid, and solid hydrocarbons).

Two main characteristics of Fischer-Tropsch synthesis (FTS) are the unavoidable production of a wide range of hydrocarbon products (olefins, paraffins, and oxygenated products) and the liberation of a large amount of heat from the highly exothermic synthesis reactions. Product distributions are influenced by temperature, feed gas composition ( $H_2/CO$ ), pressure, catalyst type, and catalyst composition. FT products are produced in four main steps: syngas generation, gas purification, FT synthesis, and product upgrading. Depending on the types and quantities of FT products desired, either low (200–240°C) or high temperature (300–350°C) synthesis is used with either an iron (Fe) or cobalt catalyst (Co).

Reactor plays a major role in order to produce a NGL products or liquid fuels. The main reactor which have been proposed and developed after 1950 are:

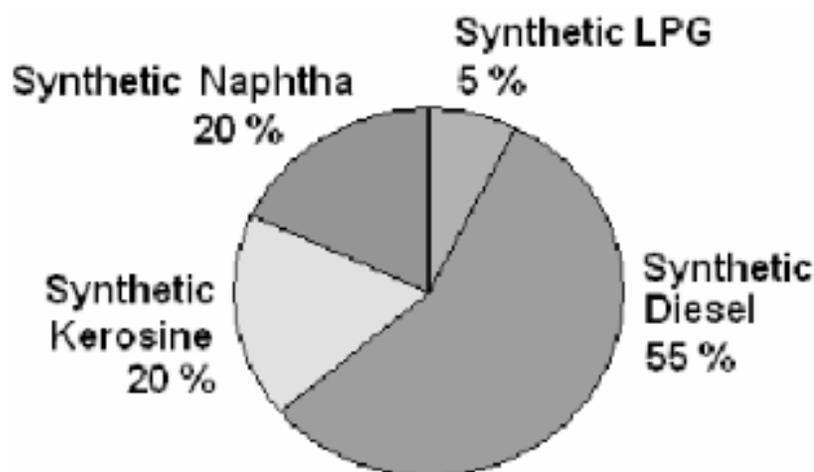
1. Three-phase fluidized (ebulliating) bed reactors or slurry bubble column reactors with internal cooling tubes (SSPD: Sasol; GasCat: Energy International, AGC-21: Exxon)
2. Multitubular fixed bed reactor with internal cooling (Arge: Sasol; SMDS: Shell)
3. Circulating fluidized bed reactor with circulating solids, gas recycle and cooling in the gas/solid recirculation loop (Synthol: Sasol)
4. Fluidized bed reactors with internal cooling (SAS: Sasol)

Based on the previous research done, most of main products yield from FT synthesis consist of 55% ultra-clean diesel fuel, 20% naphta, 20% kerosene and 5% LPG. (Shalchi, 2006). For industrial used, the product from FT synthesis have been applied as the alternative fuel to replace conventional diesel fuel in transportation. All of the modern diesel engine of vehicle nowadays can use FT diesel after some adjustment. Besides, the other product like naphta can be used as producing ethylene in plastic production and LPG as heating source in commercial use (Khadakov et al, 2007).

**Table 1.2:** Major overall reaction in FT synthesis.

Main reactions	
1. Paraffins	$(2n + 1)H_2 + nCO \rightarrow C_nH_{2n+2} + nH_2O$
2. Olefins	$2nH_2 + nCO \rightarrow C_nH_{2n} + nH_2O$
3. Water gas shift reaction	$CO + H_2O \rightleftharpoons CO_2 + H_2$
Side reactions	
4. Alcohols	$2nH_2 + nCO \rightarrow C_nH_{2n+2}O + (n - 1)H_2O$
5. Boudouard reaction	$2CO \rightarrow C + CO_2$
Catalyst modifications	
6. Catalyst oxidation/reduction	a. $M_xO_y + yH_2 \rightleftharpoons yH_2O + xM$
	b. $M_xO_y + yCO \rightleftharpoons yCO_2 + xM$
7. Bulk carbide formation	$yC + xM \rightleftharpoons M_xC_y$

Source: Gholami et al. (2009)

**Figure 1.2 :** Percentages of the GTL products.

Source: Shalchi (2006)

### 1.3 Catalyst of FT synthesis

A lot of researches have been done on the effect of metallic based catalyst on CO hydrogenation to hydrocarbons that occurred in the FT synthesis. The choice of catalyst from active metal is very important as it contributes large implications for the selectivity of the catalyst and its cost. However, some parameters such as temperature, pressure, gas flow rate and H<sub>2</sub>/CO ratio in feed also could affect the distribution of catalyst products in term of their activity, selectivity, high temperature stability and long lifetime (Van der Laan et al, 1999).

Certain transition metals should be added as the catalyst in order for the FT synthesis to be successful. All group VIII (transition metals group) have noticeable activity in the hydrogenation of carbon monoxide to hydrocarbon. Ruthenium followed by iron, nickel, and cobalt are the most active metals for hydrogenation of carbon monoxide. But among these list, cobalt is the best to choose 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 are generally more resistant to attrition than iron co-precipitated counterparts which are more suitable for use in slurry reactor. Productivity at higher conversion of cobalt is also more sufficient compare to Iron. In the addition, for Co catalyst the amount of sulphur should not more than 0.2ppm (Khadakov et al, 2007).

Supporter is the main part of the catalyst. In this process, MCM-41 and SBA-15 are the common catalysts support that usually use in FT synthesis. Mesoporous silica MCM-41 has smaller pores in metal reduction with the average pores diameter is 3-7nm (Joongjai et al, 2002). But compared to MCM-41, SBA-15 posses big tubular channels ranging of 3-30nm in diameters and has thickness of pore walls as well as the hydrothermal stability that much higher than MCM-41 as discovered in previous research (Anunziata et al, 2007).

In the other hand, SBA-15 has large surface area (600 -1000 m<sup>2</sup>/g) allowing for the dispersion of a large number of catalytically active species (Haifeng et al, 2008). There was an obvious pore size effect on product selectivity probably due to the pores being

sufficiently large for the reaction easily to proceed. thus, SBA-15 is the better choice to be introduced as the support.

**Table 1.3 :** Comparison of Cobalt and Iron FT Catalysts.

Parameter	Cobalt catalysts	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 carbon monoxide conversion	Lower, strong negative effect of water on the rate of carbon
Maximal chain growth probability	0.94	0.95
water gas shift reaction $\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$	Not very significant, more noticeable at high conversion	Significant
Maximal sulphur content	<0.1 ppm	<0.2 ppm
Flexibility (temperature and pressure)	Less flexible, significant influence of temperature and pressure on hydrocarbon selectivity	Flexible, methane selectivity is relatively low even at 613K

Source: Khodakov et al. (2007)

To keep activity site at the right place to optimal dispersion for active component and stabilization against sintering and gives strong impact in enhancement of catalyst is called promoter (Wendelin et al, 2007). Nowadays, the common type of noble metals that usually used are manganese (Mn) and rhenium (Re). Besides, promoter are are also important as the substance that increase the catalytic activity (Chem et al, 2007). There were few cases like more reduction of cobalt oxide particles enhancement of cobalt dispersion and the increases of intrinsic reactivity of surface sites could be occurred when there are other noble metals being introduced as promoters (Hong et al, 2009). Therefore, Zn is chose as a new investigation in FT synthesis.

## **1.2 Problem statement**

Problem of pollution and the lacking stock of fuel source worldwide is getting narrowed. Nowadays there are regulations on fuels that required diesel to be low in sulphur content. Deep hydrosulfuration is a method to remove sulphur from fuels but it cost a high number of amount. Therefore, FT synthesis has become an alternative way in order to produce good and clean hydrocarbon by using syngas. In any FT synthesis for industrial application, catalyst is the main aspect and the most important part to complete the synthesis and chemical reaction.

In active metal site, cobalt is the best to choose among Ru, Fe, and Co because it is more resistant to deactivation and cheaper than ruthenium. The productivity at higher conversion of cobalt is also more sufficient compare to Iron (Khadakov et al, 2007).

For the supporter, SBA-15 posses big tubular channels ranging of 3-30nm in diameter, thicker of pore walls and higher hydrothermal stability compare to MCM41(3-7nm). So it is the best supporter to choose since there was an obvious pore size effect on product selectivity probably due to the pores being sufficiently large for the reaction easily to proceed. (Anunziata et al, 2007).

In the other hand, huge number of studies have been done on noble metal like Ru, Rh, Pt and Pd and proof there is strong impact on the structure and dispersion of cobalt by using stated noble metal. Therefore, this research now looking for effect with using Zn as promoter together with Co and SBA-15 since it is rarely use and cheap.

### **1.3 Objectives**

- a) To synthesis SBA-15 mesoporous silica
- b) To synthesis and characterize Zn-Co/SBA-15 mesoporous catalyst
- c) To study the effect of Zn ad Co loading on the characterization of catalyst.

### **1.4 Scope of Study**

Production of new catalyst for FT synthesis which is Co-Zn/SBA-15 is the main focus on this study. Such a higher quality and cheaper catalyst is expected to be produce while conducting this research. In the other hand, it is also being focused on characterization and investigation for the effect of zinc precursor loading on the catalyst enhancement. In order to characterize, the SBA-15 is prepared at first and has been synthesized. Then, by using impregnation method, the catalyst of Co-Zn/SBA-15 is prepared. The catalyst consist of maximum 15 wt % of cobalt and zinc. The Co-Zn/SBA-15 catalyst then again been characterized by using Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), Scanning electron microscope (SEM), N<sub>2</sub> adsorption analysis (BET) and Thermogravimetric Analyzer (TGA).

## **CHAPTER 2**

### **LITERATURE REVIEW**

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

Fischer-Tropsch (FT) synthesis is a set of chemical reactions that convert a mixture carbon monoxide and hydrogen into liquid hydrocarbons. Franz Fischer and Hans Tropsch developed this synthesis to mainly oxygenated products and hydrocarbons in 1923 using alkalized iron as a catalyst. The production of raw hydrocarbons can be refined and upgraded to different fuels like gasoline, diesel, and other products. In the mid 1930s a number of Fischer-Tropsch plants were constructed, and by 1938 over 590,000 tons of oil and gasoline were being produced annually in Germany from synthesis gas manufactured from coal gas became available (Nebeker et al, 2005).

FT Synthesis converts synthesis gas which can be made from carbonaceous materials to long chain hydrocarbons. This process is a master component of gas to liquids technology, produces a petroleum substitute, typically from coal, natural gas or biomass for use as synthetic fuel. If liquid petroleum-like fuel, lubricant, or wax is required, then the FT synthesis is the right process to be applied (Heifeng et al, 2008).

Currently, Gas to Liquids (GTL) is the major focus on the FT synthesis. Even coal to oil is still a vital solution for countries with abundant coal resources but, the product from FT synthesis have been applied as the alternative fuel to replace conventional diesel fuel in transportation for industrial used. This is such an alternative route for fuels to be obtained rather than the current dominant petroleum resources (Nebeker et al, 2005). All of

the modern diesel engine of vehicle nowadays can use FT diesel after some adjustment. Besides, the other product like naphtha can be used as producing ethylene in plastic production and LPG as heating source in commercial use (Khadakov et al, 2007). Based on the previous research done, most of main products yield from FT synthesis consist of 55% ultra-clean diesel fuel, 20% naphtha, 20% kerosene and 5% LPG (Shalchi, 2006).

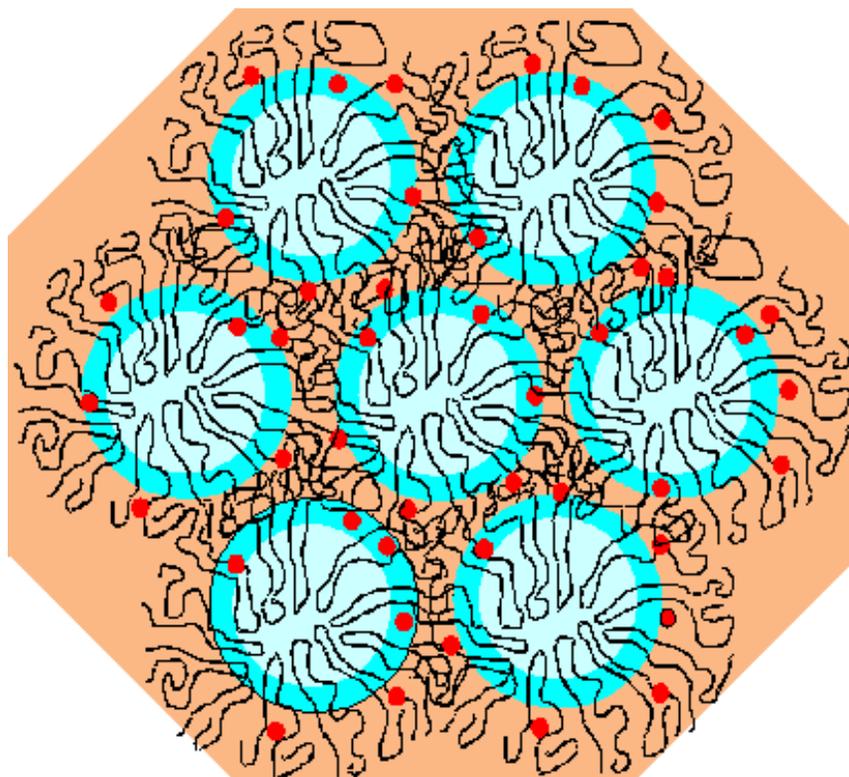
Chemically the GTL in FT synthesis process is a series of catalyzed chemical reactions in which carbon monoxide and hydrogen are converted into liquid hydrocarbons of various forms. Therefore, in any FT synthesis, catalyst is the main aspect and the most important part to complete the synthesis and chemical reaction and it is shown to be catalysed by certain transition metals (Khadakov et al, 2007).

## **2.2 SBA-15**

Silica that can be either crystalline or amorphous is usually in the form of  $\text{SiO}_4$  monomer blocks. Nature has perfected silica architectures on the nano-scale in the form of zeolites, which possess an open porous framework ( $< 20 \text{ \AA}$ ) ideal to host small guest molecules. The size and uniformity of the internal porous network of channels and cavities gives rise to shape selectivity and thus determines which molecules diffuse through or form within. Microporous zeolites are very effective in transformations of molecules which are too large to access the internal channels.

SBA-15 is silica-based mesoporous material with uniform hexagonal channel ranging from 3 to 30 nm and very narrow pore size distribution (Anunziata et al, 2007). It enhanced hydrothermal stability at higher rate as compared to other mesoporous silica like MCM-41. SBA-15 also has large surface area (600 -1000  $\text{m}^2/\text{g}$ ) for allowing the dispersion of a large number of catalytically active species (Haifeng et al, 2008). Therefore, among the various structures of mesoporous silica materials, SBA-15 which synthesized by Pluronic P123 is noted to be the most extensively investigated due to its mesostructural diversity as well as larger uniform pore size, thicker silica wall, and better stability than mesoporous silicas MCM-41.

Previous study, Zhang et al, have obtained to pictured a model for SBA 15 based on their study in 2006 of "Pore size design of ordered mesoporous silicas by controlling micellars properties of triblock copolymer  $\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$ ". In Figure 2.1, it show a proposed model for SBA15 synthesized with P123 where the presents of polyethylene oxide (PEO) bond and the one central poly-propylene oxide (PPO) chain are detected.



**Figure 2.1 :** Model for SBA15 synthesized with P123. The beige color represented silica network, turquoise represented the part of the PEO chains in the mesopores and the blue color represented the PPO chains.

Source: Zhang et al. (2006).

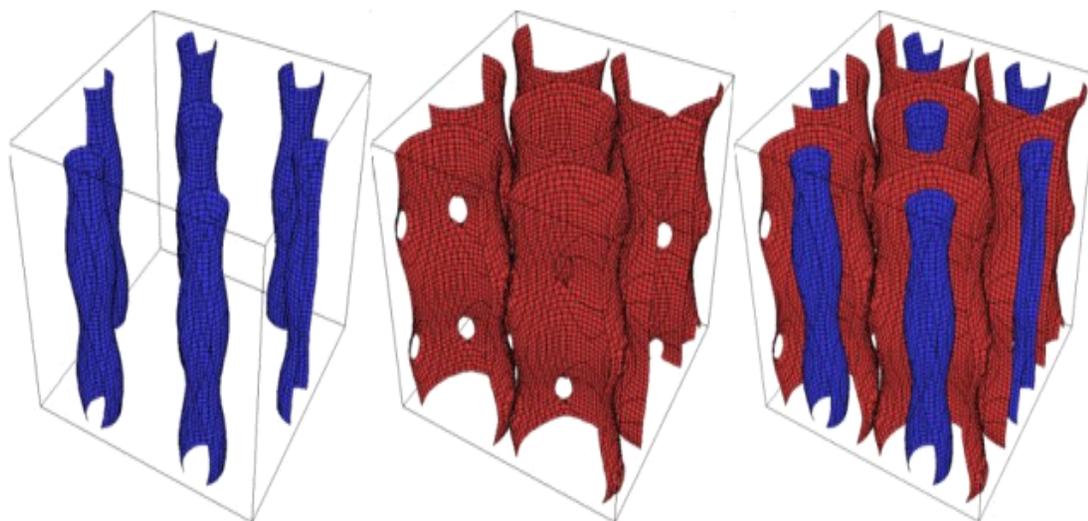
In the other hand, ordered mesoporous silicas with large pores and the ability to functionalise such molecular sieves uniformly throughout the internal surface render such materials to adopt great potential in materials chemistry, for applications in fields as diverse as gas adsorption, catalysis, microelectronics and drug release with the large apertures of

such solids readily permitting ingress of reactant and egress of product species (Robert et al, 2001).

For instance, the larger pores make it an attractive host for the insertion of large amounts of guest molecules with functional properties, and better stability makes it very suitable for immobilization of functional molecules. There is also differences of SBA-15 and MCM-41 as the host materials of luminescent lanthanide complexes, and it is observed that the SBA-15-supported materials show an overall increase in relative luminescent intensity and lifetime compared to the MCM-41-supported materials (Jing et al, 2007).

The samples templated by Pluronic P123 ( $\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$ ) shows the internal surfaces were functionalised adopting a co-condensation approach with various organo trialkoxysilanes including 3-mercaptopropyltriethoxysilane during the sol-gel syntheses and the resulting solids rendered porous by solvent extraction. Specifically controlling the levels of the thiol-siloxane in the sol-gel synthesis (as well as temperature) results in changes to the meso-product. At lower levels (2% thiol - based on total silicon), SBA-15 (p6 nm) results. SBA-15 (and other mesoporous solids) is not crystalline in the conventional way but rather contains amorphous silica walls with a 2-dimensional well-defined regular hexagonal array of 1-dimensional pores (Robert et al, 2001). The internal surface template and silica walls of SBA 15 image is shown in Figure 2.2.

Preparation of SBA-15 is done based on impregnation method where HCl and P123 is stirred together with TEOS and followed by filtration and calcination under certain temperature and condition as stated in journal of previous study done before.



**Figure 2.2:** From left to right; Simulation of SBA-15 surface shows solid surfactant rods and the silica walls showing both mesopores & complementary micropore then finally the permeation of hydrolysed silica around the voids of the surfactant rods.

Source: Robert et al. (2001)

### 2.3 Co/SBA-15

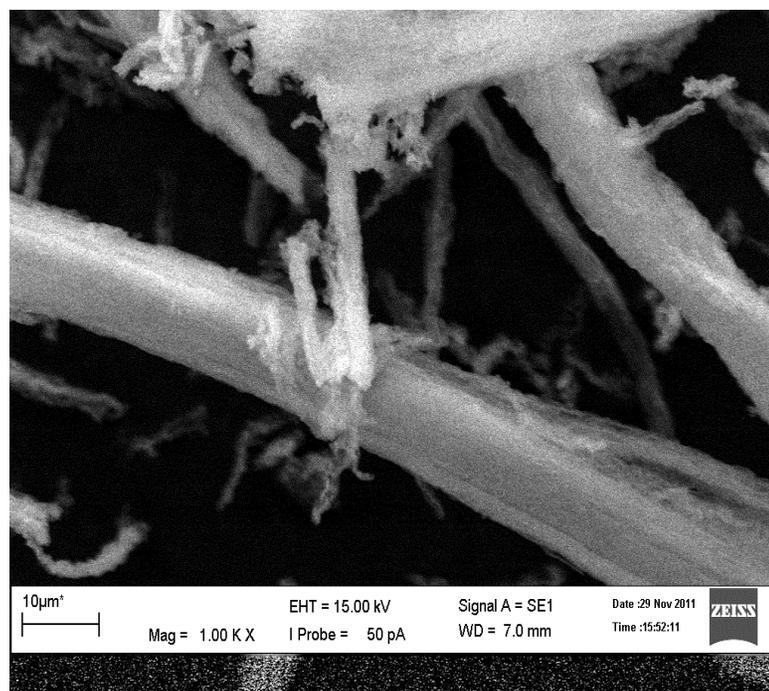
Recently, SBA-15 utilization as a support for preparing cobalt for FT synthesis has been studied and the result obtained stated that the dispersion performance of Co/SBA-15 is high. Cobalt catalytic systems are focused on improving the catalyst activity by increasing the number of active Co metal sites that are stable under reaction conditions.

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 WGS

### 4.3 Scanning Electron Microscopy (SEM)

Detailed information about the composition and electronic structure of heterogeneous catalyst with real space resolution down to the atomic level is provided by the analysis using SEM. In SEM, the microscope resolution is limited by the size of the electron probes. For long time, SEM has been considered to have only the modest resolution. With development of novel instrumentation, the resolution of SEM has been also considerable improved.

Figure 4.3 until 4.8 shows the result of SEM analysis done on each of the catalyst with different percentage of Co and Zn respectively.



**Figure 4.3** : SEM spectra for pure SBA-15