

SYNTHESIS AND CHARACTERIZATION OF Co/SBA-15 CATALYSTS FOR
FISCHER-TROPSCH SYNTHESIS

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ABSTRACT

Fischer-Tropsch synthesis (FTS) is one of the most promising ways for the conversion of syngas to hydrocarbon products. Supported cobalt is the preferred catalyst for FTS due to its high selectivity to heavy hydrocarbons, low activity for water-gas-shift reaction and comparatively low price. Cobalt loaded SBA-15 catalysts were prepared by two different techniques including wetness impregnation and direct-synthesis methods. The characterization of the synthesized samples was done by X-ray diffraction (XRD), scanning electron microscopy (SEM) and N₂ adsorption-desorption. XRD measurements showed that the calcined cobalt catalyst did not modify the structure of SBA-15, proving that Co was present under the form of Co₃O₄ in the catalyst. The hexagonal structure of pores of SBA-15 was confirmed by SEM images for all samples. BET surface area showed that Co/SBA-15 catalyst prepared by direct synthesis method was produced high surface area and pore volume compared prepared by wetness impregnation method.

ABSTRAK

Fischer-Tropsch sintesis (FTS) merupakan salah satu cara yang terbaik sebagai penukaran syngas kepada produk hidrokarbon. Kobalt telah digunakan sebagai pemangkin untuk FTS kerana dapat menghasilkan hidrokarbon yang tinggi dan aktiviti yang rendah bagi tindak balas air gas anjakan. Kobalt disokong oleh SBA-15 pemangkin telah disediakan oleh dua teknik yang berbeza iaitu penghamilan kebasahan dan kaedah langsung-sintesis. Pencirian sampel yang disintesis telah dilakukan oleh pembelauan sinar-X (XRD), imbasan imej elektron (SEM) dan N_2 penyerapan. Ukuran pembelauan sinar-X menunjukkan bahawa pemangkin kobalt dipanaskan tidak mengubah struktur SBA-15, membuktikan bahawa Co hadir di bawah bentuk Co_3O_4 pemangkin. Struktur heksagon liang-liang SBA-15 telah disahkan oleh imej SEM bagi kawasan permukaan semua samples. BET permukaan area menunjukkan bahawa Co/SBA-15 pemangkin yang disediakan dengan kaedah sintesis langsung menghasilkan luas permukaan yang tinggi dan luas permukaan isi padu liang yang tinggi berbanding kaedah yang disediakan oleh penghamilan kebasahan.

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CHAPTER 1

INTRODUCTION

1.1 Background of Research

Recently, the intensive concerns of fossil energy depletion, air pollution and global climate have encouraged many researchers to produce alternative energy. One of the promising alternative energy is synthetic fuels produced by the Fischer-Tropsch (FT) process, which have received increasing attention worldwide due to the compatibility with existing petroleum infrastructure and vehicles (Takeshita and Yamaji, 2008).

Fischer-Tropsch synthesis (FTS) is a well-known catalytic process that very clean alternative fuels can be produced from the conversion of synthesis gas (a mixture of carbon monoxide and hydrogen) which can be generated from natural gas, coal and biomass. FT synthesis has become a promising way to produce petroleum substitutes for renewable transportation fuels (Knottenbelt, 2002). Moreover, the synthesis gas which is used as reactant gas in FT synthesis can be produced from the reaction of carbon dioxide reforming of methane in present of catalyst, so called dry reforming reaction (Kodama *et al.*, 2001). By this process carbon dioxide and methane which are greenhouse gases can be reduced and converted into reactant gases in FT process in the same time.

According to the catalytic reaction of FTS, most of VIII group metals have measurable activity in carbon monoxide hydrogenation but yield different products, including hydrocarbons, acids, alcohols and esters. Generally, iron and cobalt metals are widely used as FT catalysts for larger hydrocarbon production (Iglesia, 1997).

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However, the supported cobalt catalysts are particularly suited for the FT synthesis since they give high yield of long chain hydrocarbons, low activity for the water-gas-shift reaction and have long active life time (Jacob *et al.*, 2002; Soled *et al.*, 2003; Davis, 2005).

The discovery of mesoporous silica opened up new possibilities in many areas of chemistry and material sciences (Kresge *et al.*, 2000). Therefore, SBA-15 material is a good choice to use as a catalyst support in larger hydrocarbon synthesis. The catalyst supporter is important in the Fischer Tropsch synthesis. Mesoporous silica (SBA-15) has high surface area and pore volume, much higher hydrothermal stability, especially due to its wide pores; it can diminish the diffusion resistance and provide pathways for rapid molecular transport. Thus, it can be used as the preferred support to study the catalytic behaviors in FT synthesis (Huo, *et al.* 1998). It is known that preparation methods have significant impacts on the physical properties of cobalt species, which leads to different reducibility and dispersion of catalysts. For obtaining more active and high selectivity towards C₅ + catalysts, many research groups did much work on this subject. Wetness impregnation method and, direct synthesis method are commonly used in order to obtain a broad range of particle size with relatively narrow particle size distribution.

The aim of this research is to increase the performance of cobalt catalyst in FT synthesis in order to obtain higher hydrocarbon selectivity in the range of diesel (C₁₀–C₂₀). The main goal of the present work is to prepare Cobalt-containing SBA-15 using two different preparation methods which is by wetness impregnation method and direct synthesis method to produce the high surface area of Co/SBA-15 catalysts.

1.2 Problem Statement

The major problem for this project is about sustaining future of fuel. The crude oil of fossil fuel is believed to deplete at the early decades of this century. According to this situation the Fischer Tropsch synthesis become a very good option as the alternative fuel. This is because the Fischer Tropsch synthesis is the process converting gas to liquid (GTL) from gas hydrogen and gas carbon monoxide to produced hydrocarbon. This process is used the coal, biomass, syngas as demand to produce of fuel.

In any industrial Fischer Tropsch synthesis, catalyst is a vital part and one of most important aspect 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. The preparation methods of Co/SBA-15 are important to produce heavier hydrocarbons selectivity and to synthesis the SBA-15 and Co/SBA-15 with high surface area.

1.3 Research Objectives

- a) To study effect of mesoporous silica (SBA-15) supporter to Co catalyst.
- b) To study the effects preparation of Co/SBA-15 using two different methods.
 - i. Wetness impregnation method.
 - ii. Direct synthesis method
- c) To identify the characterization of Co/SBA-15 for the Fischer Trops synthesis.
- d) To study effect surface area of Co/SBA-15 catalyst.

1.4 Scope of Study

Based on the objectives, the main scope of this project is to synthesis the mesoporous silica (SBA-15) and preparation Co/SBA-15 by wetness impregnation method and direct synthesis method. The characterization of SBA 15 and Co/SBA-15 catalysts will be identifying by Scanning Electron Microscopy (SEM), X-Ray Diffraction (XRD) and BET Surface Area.

1.5 Rationale and Significance

Fischer–Tropsch synthesis (FTS) is a process to convert synthesis gas H_2 and CO to water and hydrocarbons that can be used as liquid fuels or base chemicals. Feed stocks for the generation of synthesis gas can be natural gas, coal and biomass. A key element in the improved Fischer–Tropsch technology is the development of active catalysts with high wax selectivity. The productions of hydrocarbons depend on the catalysts used in the Fischer –Tropsch process. The supporter catalyst is important to produce long chain paraffin and heavier hydrocarbon.

The rationale of this study is to produce new catalyst that has quiet similar characterization with present catalyst that has been produce. There are several advantages by using SBA-15 as catalyst support. Particularly, for reaction occurring at high temperature, SBA-15 which possesses large pores, thicker walls and high thermal stability as compared other mesoporous silica, may be used as a promising support. Highly dispersed cobalt support SBA-15 mesoporous silica catalysts can be successfully synthesized via the direct synthesis method and high selectivity of long chain hydrocarbon products in the range of diesel in Fischer-Tropsch synthesis can be achieved over the catalysts prepared by direct synthesis method.

CHAPTER 2

LITERATURE REVIEW

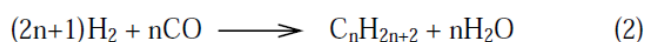
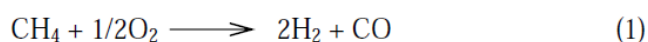
2.1 Fischer-Tropsch Synthesis

Fischer-Tropsch synthesis (FTS) is one of the major routes for converting coal based and/or natural gas-derived syngas into high quality chemicals and fuels. The main goal of FTS research is to develop FTS catalysts with high activity and selectivity by improving the selectivity of C₅₊ hydrocarbons while decreasing the selectivity of methane. In particular, liquid fuels in the range of diesel fuels produced by Fischer-Tropsch process (synthesis of hydrocarbons from CO and H₂) exhibit attractive potential as very clean alternative energy, relative to the conventional fossil petroleum. The products generated from FTS are mainly composed of linear paraffins with high cetane number and are free of sulfur and aromatic pollutants (Van der Laan and Beenacker, 1999). In order to improve the performances of FTS catalysts and increase the selectivity of the desired hydrocarbon products (C₁₀-C₂₀), informative research understanding is reviewed as the following description.

In the last decades, the interest in FTS has been increased as a result of change in fossil energy reserves, environmental demands and technological developments. FT syngas have become a key alternative fuel regardless of CO₂ policy because of their low transportation cost and compatibility with existing petroleum infrastructure and vehicles (Takeshita and Yamaji, 2008). In addition, FT syngas are virtually interchangeable with conventional diesel fuels and can be blended with diesel at any ratio without or with little modification. Concerning carbon monoxide and particulate matter, FT fuels offer important emission benefits compared with diesel.

2.1.1 The Fischer-Tropsch Process

Fischer-Tropsch (FT) process is a method for the synthesis of hydrocarbons and other aliphatic compounds principally for producing synthetic petroleum substitutes. FT process was discovered by Franz Fischer and Hans Tropsch, the German coal researchers, in 1923. This process was invented in petroleum-poor but coal-rich Germany to produce alternative fuels during the World War II. The original Fischer-Tropsch synthesis was described by the following chemical equations:



FTS reaction is regarded as a surface catalyzed polymerization process and a lot of heat is involved during reaction. The adsorbed CH_x monomers, formed by hydrogenation of adsorbed CO, react with the surface H atoms and hydrocarbon fragments to produce hydrocarbons with a broad range of chain lengths due to the limitation of the typical Anderson-Schultz-Flory (ASF) distribution (Iglesia, 1997). In this process, synthesis gas (a mixture of hydrogen and carbon monoxide) can be converted to large ranges of petroleum products such as methane, synthetic gasoline, waxes, alcohols, and water over heterogeneous catalysts (Van Der Laan *et al.*, 1999; Davis, 2001; Saib *et al.*, 2002). The mechanism of FT synthesis reaction is quite complex because there are many reactions occurred during the reaction (as shown in Table 2.1) and the product selectivity typically follows the Anderson-Schultz-Flory (ASF) distribution (Iglesia, 1997; Burton, 2001).

Table 2.1 major overall reaction in the Fischer-Tropsch synthesis

Main reactions	Chemical equations
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	$CO + H_2O \leftrightarrow CO_2 + H_2$
Side reactions	
4) Alcohols	$2nH_2 + nCO \rightarrow C_nH_{2n+2}O + (n - 1)H_2O$
5) Boudouard reaction	$2CO \rightarrow C + CO_2$

Source: Iglesia(2001)

2.2 Fischer Tropsch Catalysts

Fischer-Tropsch synthesis (FTS) process was shown to be catalyzed by certain transition metal, with cobalt (Co), iron (Fe) and ruthenium (Ru) presenting the noticeably high activity (Vannice, 1977). Cobalt and iron based catalysts were typically applied to FTS process. Moreover, ruthenium and nickel based catalysts also had good activity for FTS, however the availability of ruthenium was limited, thus it was not economically possible. The nickel based catalyst had high activity but methane selectivity was very high, and additionally the performance at high pressure was poor, due to production of volatile carbonyls. Consequently, the FTS reaction was catalyzed focusing on cobalt (Iglesia, 1997 and schultz, 1999) and iron (Luo and Davis, 2003 and Zhang *et al.*, 2006) as practical catalysts.

Nevertheless, the supported Co-based catalysts have been widely used for the synthesis of long chain paraffins (Dry, 1990; Chanenchuk *et al.*, 1991; Iglesia, 1997) according to their high activity for syngas conversion and high yields of linear hydrocarbons in FTS reaction at medium reaction temperature and pressure (Iglesia, 1997; Ernst *et al.*, 1999). Moreover, Co-based catalysts were more stable toward deactivation by water (by-product of the FTS reaction), less active for the competing water-gas-shift (WGS) reaction and produced less oxygenates than the Fe-based systems. In order to achieve high amount of surface-active sites (Co₀), cobalt precursors were dispersed on porous carriers such as SiO₂, Al₂O₃ and TiO₂.

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In order to increase the conversion and product selectivity of cobalt catalyst, Martinez *et al.* (2003) studied the performance of FTS by investigating the influence of cobalt loading (10–40 wt. % Co) and type of cobalt precursor on catalytic properties of cobalt support SBA-15 mesoporous silica catalysts (Co/SBA-15). The performance of Co/SBA-15 catalysts were tested in a fixed-bed stainless-steel reactor at the reaction temperature of 220 °C (P = 20 bar, H₂/CO = 2). From the result, a maximum CO conversion of 33.1 % was obtained from the cobalt loading amount of 30 wt. % of which the highest amount of Co active sites were obtained. Moreover, the selectivity of hydrocarbon products was found influenced by the amount of cobalt loading attributed to the higher reducibility of metals with high degree of metal content.

Cobalt catalyst had been widely applied together with another metal. A lot of researchers worked on adding the promoters to enhance the performance of FTS reaction. In order to obtain higher selectivity of heavy hydrocarbons, FTS catalysts were modified to increase catalytic activity and FTS performances. Ruthenium and cobalt can also be applied as catalysts for FTS. Dunn *et al.* (2004) prepared cobalt and ruthenium loaded on a silica aerogel support. Ruthenium catalysts were considerably more active than cobalt catalysts at the same metal loading amount where the product distributions were similar. Hydrocarbon products from C₁ through C₁₅ were detected with the product distribution centered around C₉-C₁₀ at 265 °C and C₁₃ at 225 °C.

In 2008, Wan *et al.* investigated the effects of copper (Cu) and potassium (K) promoters on precipitated iron-based catalysts for FTS. The incorporation of Cu and K promoters to precipitated Fe catalyst was found to have significant role on the adsorption, reduction behaviors and catalytic performances of FTS. The addition of Cu metal promoted high dispersion of cobalt metal on SBA-15 support and the application of using both of Cu and K as promoters exhibited excellent stability and significantly improved the FTS and water-gas shift (WGS) activities as well as the chain growth reaction.

From the previous information, it is clearly seen that the performances of FTS reaction can be strongly promoted by selection of catalysts, mostly iron or cobalt catalyst where the reaction takes place.

2.2.1 Cobalt Catalyst

Nevertheless, the supported Co-based catalysts have been widely used for the synthesis of long chain paraffins (Dry, 1990; Chanenchuk *et al.*, 1991; Iglesia, 1997) according to their high activity for syngas conversion and high yields of linear hydrocarbons in FTS reaction at medium reaction temperature and pressure (Iglesia, 1997; Ernst *et al.*, 1999). Moreover, Co-based catalysts were more stable toward deactivation by water (by-product of the FTS reaction), less active for the competing water-gas-shift (WGS) reaction and produced less oxygenates than the Fe-based systems.

In order to achieve high amount of surface-active sites (Co), cobalt precursors were dispersed on porous carriers such as SiO₂, Al₂O₃ and TiO₂. In order to increase the conversion and product selectivity of cobalt catalyst, Martinez *et al.* (2003) studied the performance of FTS by investigating the influence of cobalt loading (10–40 wt. % Co) and type of cobalt precursor on catalytic properties of cobalt support SBA-15 mesoporous silica catalysts (Co/SBA-15). The performance of Co/SBA-15 catalysts were tested in a fixed-bed stainless-steel reactor at the reaction temperature of 220 °C (P = 20 bar, H₂/CO = 2). From the result, a maximum CO conversion of 33.1 % was obtained from the cobalt loading amount of 30 wt. % of which the highest amount of Co active sites were obtained. Moreover, the selectivity of hydrocarbon products was found influenced by the amount of cobalt loading attributed to the higher reducibility of metals with high degree of metal content.

K.h Shuan, *et al.*, 1998 concluded that cobalt catalysts give the highest yields and longest life-time and produce predominantly linear alkenes. A precipitated cobalt catalyst on kieselguhr became the standard catalyst for commercial purposes in the Second World War in Germany. Disadvantages are the high costs of cobalt and low water gas shift activity. Therefore, cobalt catalysts are viable for natural-gas based

Fischer-Tropsch processes for the production of middle distillates and high-molecular weight products. Cobalt catalysts are not inhibited by water, resulting in a higher productivity at a high synthesis gas conversion.

According to E. Davids and H.L John,*et al*,1990 Cobalt based catalysts will produce heavier components which is tends to final product such as diesel and waxes. The optimal cobalt catalyst with a high H₂/Co ratio which is more hydrogen than carbon monoxide in the syngas , which happens when the syngas is produced with natural gas), such as in the gas to liquids process..Cobalt based catalysts and a lower operating temperature 200°C will produce heavier hydrocarbons, the final product will be mostly diesel.

Research article by E. Iglesia and S. L. Soled, 1992 the activity in the Fischer–Tropsch reaction is independent of the cobalt particle size, i.e., it is proportional only to the area of the metal surface, at least for particle sizes above 8 nm. However, both activity and selectivity are influenced by the particle size at high dispersion. Reoxidation by water might do not used on the cobalt catalyst, however be a major deactivation mechanism under normal Fischer–Tropsch conditions. The degree of reduction can also influence the selectivity: with decreasing extent of reduction the selectivity for shorter hydrocarbons increases. In addition to optimizing the reducibility and the particle size, one also needs to consider effects related, for example, to promoters and support properties. The pore diameter of the support has been shown to determine the cobalt particle size on impregnated catalysts and can therefore influence catalyst properties. Furthermore, isomerisation and other secondary reactions on the support can affect the selectivity.

2.2.2 Supported Cobalt Catalysts

Supported cobalt has been found to be a good choice of catalyst for FTS. A wide range of studies have been published on the interaction between metal and support on silica and alumina supported cobalt catalysts (G. Jacobs,*et al*,2002). Silica supported cobalt in some cases can form poorly reducible silicate-type compounds, for example during high temperature calcination, due to hydrothermal treatment,

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through reaction between CoO and silica during reduction , and following decomposition of cobalt nitrate in vacuum. Alumina supported cobalt readily forms poorly reducible aluminate-type species or a cobalt oxide phase that interacts strongly with the support. The degree of reduction has been found to decrease with decreasing cobalt crystallite size for particles below 15 nm on Al₂O₃, SiO₂ and TiO₂, due to increasing metal-support interaction. Production of a well-dispersed cobalt phase without the formation of large fractions of nondeductible cobalt species poses a difficult challenge.

The active catalyst metal is usually deposited on an inert support material like silica, alumina, titania, silicon carbide etc. Although inactive to the reactant gases, these supports can affect the overall synthesis by controlling the morphology of the active catalytic specie, its dispersion, and metal-support interactions. Silica and alumina supports are most commonly used due to the strength and porous nature of the material. Alumina, when used as support, decreases the reducibility of the catalyst. Silica, on the other hand does not appreciably produce irreducible compounds, however, the active metal dispersion is lower than that for alumina.(E.Iglesia and S. C. Reyes,*et al*,1993)

Synthesis of the active catalyst requires strong interaction between the metal and the support; however, if too strong, these interactions can lead to formation of irreducible mixed metal support oxides.D. M. Hercules,*et al*,1990 observed that the use of ethanol as a solvent (instead of water) for a cobalt nitrate precursor resulted in metal support interaction of sufficient strength to increase active metal dispersion while retaining a high extent of reduction.

Thermal treatment of the catalyst precursor (drying, calcinations and reduction) also impacts the dispersion. The calcination atmosphere changes the arrangement of the surface molecules to some degree and affects the metal support interaction(B Earnest,*et al*,1999) showed that during the reduction process the reaction of CoO and SiO₂ results in the formation of irreducible cobalt ortho-silicates. This formation of silicates increases the dispersion.

2.2.3 Catalyst Reactor

The low temperature reactors are either fixed -bed type or slurry type, whereas fluidized bed reactors, fixed bed or circulating bed reactors can be used for the high temperature Fischer Tropsch process. It should be noted that a large number of downstream operations are needed for both the high temperature and low temperature Fischer Tropsch process before the final product is ready(R. Krishna and S. T. Sie,*et,al* 2000).

The focus of Fischer Tropsch research has recently shifted to product distribution, with the aim of maximizing the yield of gasoline, diesel and commercially-valuable chemicals. Most of these efforts are on the catalyst level (K. Jalama, N. J. Coville,*et,al* 2000).Although some researchers are trying to change the product distributions on a micro scale by changing the reactor or process design(S. Sharifnia, Y. Mortazavi and A. Khodadadi,*et,al* 2005). Figure 2.1 presents Fischer Tropsch synthesis reactors.

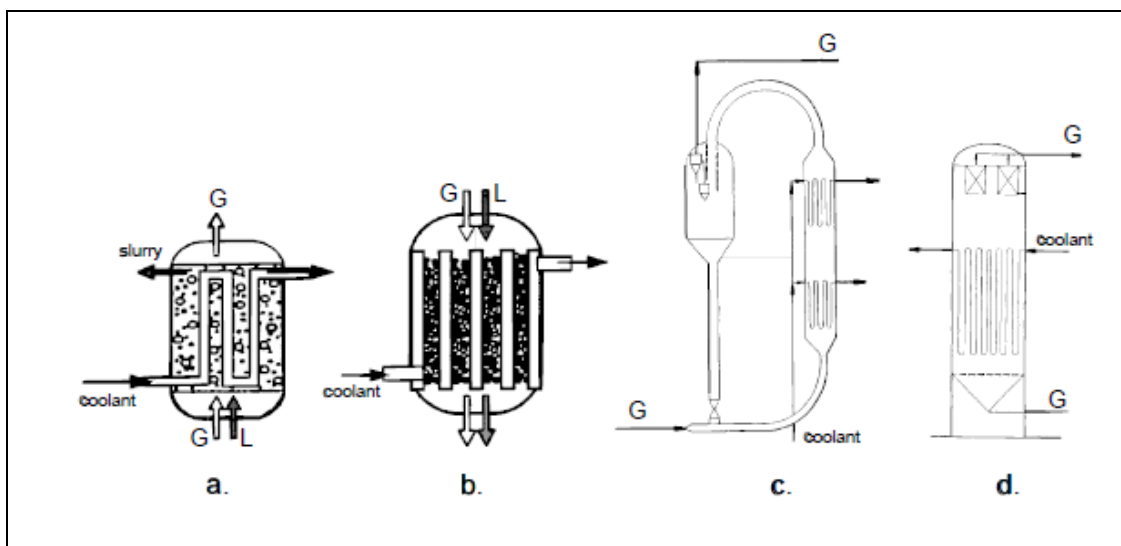


Figure 2.1 Fischer Tropsch synthesis reactors; a)Slurry Bubble Column ;b) Multitubular Trickle Bed Reactor;c) .Circulating fluidized bed reactor; d) Fluidized bed reactor

Source: A. Khodadadi,*et,al*(2005)

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2.3 Mesoporous Materials

Mesoporous materials are one of the types of porous materials with pore diameters in the range of 2-50 nanometers. The mesoporous silicas are made up of frameworks (pore walls) which are crystallographically amorphous. These materials are special types of nanomaterials with ordered arrays of uniform nanochannels. They have important applications in a wide variety of fields such as separation, catalysis, adsorption and advanced nonmaterials. These mesoporous materials exhibit high surface area (600–1300 m²/g), and large pore size exhibiting widely potential applications in industrial catalytic reactions (Xia, Y. and Mokaya, *et al*, 2003)

Pure silica mesoporous molecular sieves exhibit three structure types: hexagonal (1D regular hexagonal packing of mesopore channels), cubic (3D bicontinuous system of pores), and lamellar (2D system of silica sheets interleaved by surfactant bilayers), (Walcarius, *et al* 2005) as illustrated in Fig. 2.2

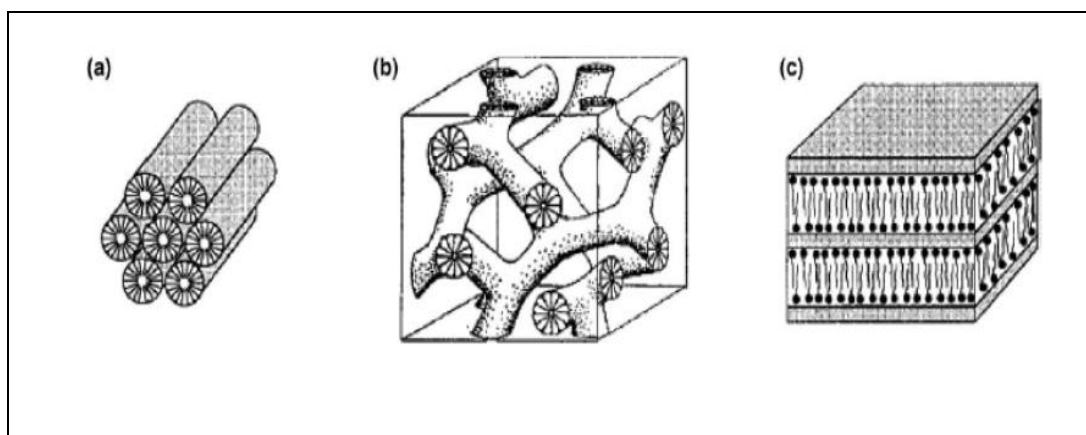


Figure 2.2 Three structure types for silica-surfactant mesophases
; (a) hexagonal; (b) cubic bi-continuous; (c) lamellar

Source : Walcarius, *et al* (2005)

2.3.1 Usage of Mesoporous Materials in Catalysis

Mesoporous materials have several possible applications within heterogeneous catalysis, due to their high surface area and ordered pore structure. The advantage of using ordered mesoporous solids in catalysis are the relatively large pores which facilitate mass transfer and the very high surface area which allows a high concentration of active sites per mass of material. In recent years, environmental and economic considerations have raised strong interest to redesign commercially important processes so that the use of harmful substances and the generation of toxic waste could be avoided. In this respect, heterogeneous catalysis can play a key role in the development of environmentally benign processes in petroleum chemistry and in the production of chemicals (Taguchi, *et al*,2005).

The amorphous pore walls give mesoporous silica a great deal of flexibility in terms of their composition and pore channel structure and allow post-synthesis modifications which may be performed for pore size control framework stabilization, compositional modifications or the formation of mesoporous/zeolite composite materials .But unfortunately, these mesoporous materials have relatively low catalytic activity and hydrothermal stability, which severely hinders their practical applications in catalysis. The relatively low catalytical activities of mesoporous materials such as can be typically attributed to the low acidity or low oxidation ability of catalytically active species, which is strongly related to the amorphous nature of the pore walls. Therefore, increasing acidity, oxidation ability, and hydrothermal stability are great tasks for rational syntheses of ordered mesoporous materials (Xiao and F. S,*et al*,2005).

2.3.2 SBA-15 Mesoporous

SBA-15 is by far the largest pore-size mesoporous material with highly ordered hexagonally arranged mesochannels. SBA-15, which possesses larger pores, thicker walls and higher thermal and hydrothermal stability as compared with other mesoporous silicas may be used as a promising catalyst support, particularly for reactions occurring at high temperatures(Wang,*et al* 2004).SBA-15, with uniform

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tubular channels is one of the most widely studied mesoporous silica. It can be readily prepared over a wide range of uniform pore size (4.6–30 nm) and pore wall thickness (3.1–6.4 nm), by using a variety of poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide) triblock copolymers ($\text{EO}_x\text{PO}_y\text{EO}_x$) as templates, as shown in Fig. 2.3

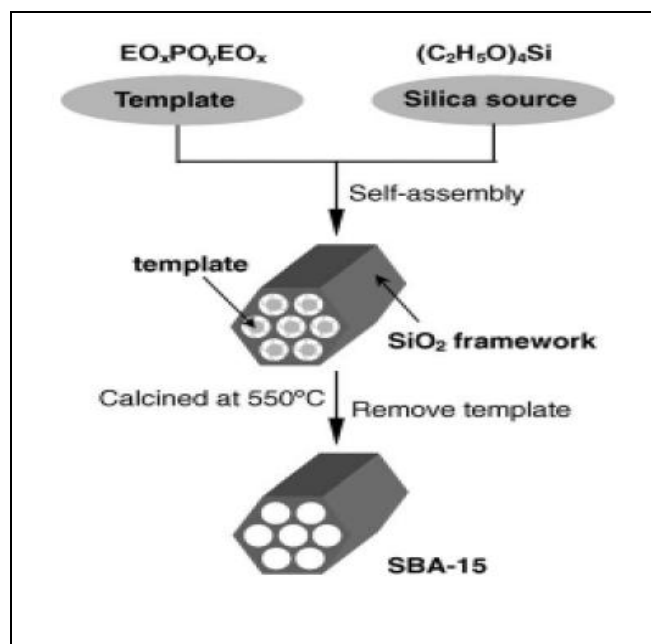


Figure 2.3 Formation of the triblock copolymer/mesoporous silica and mesoporous silica SBA-15

Source: Xi, *et al* (2005)

The 2D hexagonal mesoporous material formed via this pathway has thicker walls. The thick wall of this material significantly improves the thermal and hydrothermal stability compared to mesoporous MCM-41 and related silicas (Xi, *et al*, 2005)

The utilization of SBA-15 as a support for preparing cobalt based FT synthesis has recently explored (Wang, *et al*, 2007) and the result shows that it was highly dispersed of Co/SBA-15. It was also found that Co/SBA-15 exhibited low FT synthesis activity which was ascribed to a low reducibility of the Co species

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(Haifeng, et al, 2008). Nevertheless, combination of Co/SBA-15 provided of good performance and represent the optimal choice for low temperature FT synthesis process due to the higher stability, higher per single pass conversion that up to 60%-70% and higher productivity. Besides, cobalt performed high resistance to attrition especially in slurry bubble column reactor (Khodakov A.Y, et al 2007).

As another example, impregnation of Co into MCM-41 and SBA-15 were implemented. It is observed that catalysts supported by SBA-15 are 5-10 times more active than supported by MCM-41. While MCM- 41 structure collapsed after impregnation and BET-surface area decreased with adding much amount of Co impregnation, SBA-15 structure leaded to no destruction of ordered structure (R. M. Rioux,et,al 2005).

2.4 Effect of Catalyst Preparation on FTS Performances

The selectivity towards the desired products is the main subject in FT synthesis. One of the most important product selectivity is the selectivity of C₅₊ hydrocarbon products. Because the ultra clean liquid fuels are of industrial interest, it is significant to improve the performances of FT synthesis by increasing the C₅₊ selectivity and suppress the formation of undesired methane in FT products. Either the properties of synthesized catalyst support or the methods or chemicals used in catalyst preparation have direct influence on FTS catalytic performance.

2.4.1 Effect of Catalyst Support on FTS Performance

In fact, it was well-known that the catalytic conversion of carbon monoxide occurred on the surface of porous catalyst. For this reason, the structure of catalyst support greatly affected the orientation of metal particles locating on the surface of catalyst support. Many studies have been carried out on Fischer-Tropsch synthesis using different supports for cobalt loading, including alumina (Bechara *et al.*, 2001 and Hosseini *et al.*, 2004), titania (Zennaro *et al.*, 2000)