

**SYNTHESIS AND CHARACTERIZATION OF SBA-15 AND Cu/SBA-15
CATALYSTS FOR PHOTOREDUCTION OF CARBON DIOXIDE**

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ABSTRACT

The greenhouse effect is a process by which thermal radiation from a planetary surface is absorbed by atmospheric greenhouse gases, and is re-radiated in all directions. The increasing concentrations of the greenhouse gases in the atmosphere, where the major contribution comes from carbon dioxide (CO₂). The result from a continued increase in CO₂ concentration will cause major changes in global climate. Due to high concentration of CO₂ in the environment, advanced oxidation process (AOP) was proposed. AOP is a process in which the oxidative capacity of a parent compound is modified to make oxidation-reduction reactions more rapid or complete. Due to the best properties that it can retain at high temperature and thermal stability SBA-15 has been chosen as catalysts. SBA-15 and Cu supported mesoporous siliceous SBA-15 catalysts have been prepared by direct synthesis methods and wetness impregnation method, respectively and are systematically characterized. The characterizations of the synthesized samples were done using Fourier Transforms Infrared Spectroscopy (FTIR), Scanning Electron Microscopy (SEM), Thermal Gravimetric analysis (TGA) and X-ray diffraction (XRD). The FTIR analysis shows that when SBA-15 was doped with copper, the % transmittance of the spectral had decreased. From the SEM analysis, the surface morphology of SBA-15 was changed from smooth to coarse and irregular structure due to existence of Cu in SBA-15. XRD measurement shows that the amorphous phase for pure SBA-15 was changed to crystalline phase when Cu was deposited into SBA-15 proving that Cu present in the SBA-15 structure. The TGA analysis shows that with existence of Cu in SBA-15, enhanced the thermal stability properties of catalysts. Thermo gravimetric analysis shows that the copper deposition on SBA-15 is stable up to a temperature of 515 °C and that the copper decomposes between 515 °C and 798 °C. The results of the FTIR, SEM, XRD and TGA testify completely that the Cu was incorporated into the framework sites of the SBA-15.

ABSTRAK

Kesan rumah hijau adalah satu proses oleh mana radiasi haba dari permukaan planet diserap oleh gas rumah hijau atmosfera, dan semula dipancarkan ke semua arah. Peningkatan kepekatan gas rumah hijau di atmosfera, di mana sebahagian besar datang daripada karbon dioksida (CO_2). Akibat daripada peningkatan berterusan dalam kepekatan CO_2 akan menyebabkan perubahan besar dalam iklim global. Disebabkan oleh kepekatan CO_2 yang tinggi dalam persekitaran, proses pengoksidaan lanjutan (AOP) telah dicadangkan. AOP ialah satu proses di mana keupayaan pengoksidaan sebatian diubahsuai untuk membuat tindak balas pengoksidaan-penurunan pesat atau lengkap. Disebabkan oleh sifat-sifat terbaik ia boleh dikekalkan pada suhu yang tinggi dan kestabilan terma SBA-15 telah dipilih sebagai pemangkin. SBA-15 dan disokong oleh Cu pemangkin telah disintesis oleh kaedah sintesis langsung dan kaedah kelembapan pengisitepuan, dan telah dicirikan secara sistematik. Pencirian sampel yang disintesis telah dilakukan menggunakan Fourier Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscope (SEM), Thermal Gravimetric Analysis (TGA) dan X-ray Diffraction (XRD). Analisis FTIR menunjukkan bahawa apabila SBA-15 telah dicampur dengan Cu, kadar % daripada spektrum infrared telah berkurangan. Daripada analisis SEM, morfologi permukaan SBA-15 telah berubah dari yang licin kepada kasar dan struktur yang tidak teratur disebabkan kewujudan Cu di dalam SBA-15. Penganalisaan XRD menunjukkan bahawa fasa yang asal untuk SBA-15 tulen telah ditukar kepada fasa hablur apabila Cu telah didepositkan ke dalam SBA-15 membuktikan bahawa Cu hadir di dalam struktur SBA-15. Analisis TGA menunjukkan bahawa dengan pemendapan Cu di dalam SBA-15, telah meningkatkan sifat-sifat kestabilan terma pemangkin SBA-15. Analisis gravimetrik menunjukkan bahawa pemendapan Cu pada SBA-15 adalah stabil sehingga suhu $515\text{ }^\circ\text{C}$ dan bahawa Cu mengurai antara $515\text{ }^\circ\text{C}$ dan $798\text{ }^\circ\text{C}$. Keputusan FTIR, SEM, XRD dan TGA membuktikan bahawa Cu telah dimasukkan ke dalam struktur SBA-15.

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CHAPTER 1

INTRODUCTION

1.1 Background of Research

The greenhouse effect is a process by which thermal radiation from a planetary surface is absorbed by atmospheric greenhouse gases, and is re-radiated in all directions. Since part of this re-radiation is back towards the surface, energy is transferred to the surface and the lower atmosphere. As a result, the temperature there is higher than it would be if direct heating by solar radiation were the only warming mechanism (John, 1989). The increasing concentrations of the greenhouse gases in the atmosphere, where the major contribution comes from carbon dioxide (CO₂) has been claimed to cause the greenhouse effect with a significant atmospheric temperature rise, of 1.5 to 4.5 °C (Houghton et. al., 1990).

The result from a continued increase in CO₂ concentration will cause major changes in global climate. Because it is a greenhouse gas, elevated CO₂ contribute to an additional absorption and emission of thermal infrared in the atmosphere, which produce net warming. This is because CO₂ is a prominent greenhouse gas. It absorbs and emits infrared radiation at wavelength of 4.26 μm (asymmetric stretching vibrational mode) and 14.99 μm (bending vibrational mode) (Petty, 2004).

Recent research has shown that it will take centuries for natural removal of CO₂. Clearly, the effects of CO₂ emissions could be extremely far reaching and cause major problems if we delay about reductions in CO₂. Due to drawbacks of emission of CO₂, there are several methods proposed that can be uses to reduce the concentration

of CO₂ such as electrochemical, photochemical, photocatalytic and photoelectrochemical (Zhao, 1998).

However, advanced oxidation process was chosen. Advanced oxidation processes (AOPs) a process in which the oxidative capacity of a parent compound is modified to make oxidation-reduction reactions more rapid or complete. AOPs are near ambient temperature and pressure which involve the generation of hydroxyl radicals or others radicals to oxidize recalcitrant, toxic and non-biodegradable compounds to various by-products and eventually to inert end-products (Glaze, 1987). The hydroxyl radical ($\cdot\text{OH}$) is a powerful, non-selective chemical oxidant. AOPs are divided into homogeneous and heterogeneous systems in which hydroxyl radicals are generated with or without UV irradiation or solar visible irradiation, electrolysis, ozonation, the Fenton's reagent, ultra-sound and wet air oxidation. Due to its high reactivity, $\cdot\text{OH}$ can react with a great variety of organic compounds (Maria Klavarioti et. al., 2008).

Catalytic reduction of CO₂ to more valuable compounds has been investigated in many ways. However, this reaction often required a several condition of high pressure and high temperature. The reduction of CO₂ using photocatalysis is one of the most promising methods because CO₂ can be reduced by the UV radiation at room temperature and atmospheric pressure (Ondřej Kozák et. al., 2010). At the same time, this reaction is interesting from the view point of environmental protection, since it is a removal of a greenhouse effect gas under mild conditions (Weatherbee and Bartholomew, 1982).

Photoreduction is a reduction reactions induced by light. The processes are addition of one or more electrons to a photo excited species and the photochemical hydrogenation of a substance. Reactions in which the substrate is not electronically excited are sometimes called photo initiated reductions. The photocatalytic reduction of CO₂ to methanol has attracted much research attention in the past decades because it transforms greenhouse gas CO₂ to useful hydrocarbon resources (Fujishima, 1979).

In this study, SBA-15 and Cu/SBA-15 were prepared by direct synthesis method and impregnation method and will be used as a photocatalyst for photocatalytic reduction of CO₂. The prepared catalysts were characterized by X-ray Diffraction (XRD), Scanning Electron Microscope (SEM), Thermo Gravimetric Analysis (TGA) and Fourier Transforms Infrared Spectroscopy (FTIR).

1.2 Problem Statement

Due to high concentration of carbon dioxide (CO₂) in environment, advanced oxidation process (AOP) was proposed. The process chosen was photoreduction of CO₂ using SBA-15 and Cu/SBA-15 catalyst under visible light irradiation. Moreover, it is also a promising future technology since CO₂ can be reduced to useful compounds by solar energy at room temperature and ambient pressure.

Photocatalytic reduction of CO₂ by UV light involves photocatalyst and UV radiation. Reduction process of CO₂ is difficult since it is inert and stable compound. Conventional process requires high pressure and high temperature. Hence, photocatalytic process by using photocatalyst is the most promising method because the reduction process can be preceded at room temperature and atmospheric pressure. Possible reduction products including CO, HCOOH, HCHO, CH₃OH or CH₄, have been obtained by photoreduction of CO₂ or aqueous carbonate. However, the SBA-15 and Cu/SBA-15 were chosen as a catalysts in photoreduction process, due to the best properties that it can retain high temperature and thermal stability.

1.3 Research Objectives

Based on the research background and problem statement described in the previously, the objectives of this research are as follows:

1. To synthesize photocatalysts, SBA-15 and Cu/SBA-15 that will be used in photoreduction process of CO₂.
2. To characterize the characteristic of pure SBA-15 and Cu/SBA-15 catalysts.

1.4 Scope of Research

Based on the objectives, the main scope of this study was to synthesis the mesoporous silica (SBA-15) by direct synthesis method and Cu/SBA-15 by impregnation method respectively. The characteristics of SBA-15 and Cu/SBA-15 catalysts were characterized by Scanning Electron Microscopy (SEM), Fourier transform infrared spectroscopy (FTIR), Thermal Gravimetric analysis (TGA) and X-ray diffraction (XRD).

1.5 Rational and Significance

Photocatalytic reduction process is purposely to provide an alternative method with low cost treatment because the process could be performed at room temperature under atmospheric pressure and also to form some useful products. The rationale of this study is to synthesize new photo-catalysts that have good properties with great performances compared with present catalyst available. The copper doped SBA-15 mesoporous silica catalysts were successfully synthesized via the impregnation method and the proposed heterogeneous photocatalyst that will provides high catalytic activity and easy separation at the end of the reaction process.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction to Carbon Dioxide (CO₂)

The amount of carbon dioxide (CO₂) in the air has been increasing during the recent years, which may adversely affect the environment in the future. CO₂ is the largest contributor to the greenhouse effect and is one of the gases in our atmosphere, being uniformly distributed over the earth's surface at a concentration of about 0.033 % or 330 ppm. In addition to being a component of the atmosphere, CO₂ also dissolves in the water of the oceans. At room temperature, the solubility of CO₂ is about 90 cm³ of CO₂ per 100 mL of water. When carbon-containing fossil fuels such as oil, natural gas, and coal are burned in air, CO₂ is released into our atmosphere. Some CO₂ is obtained from the combustion of coke or other carbon-containing fuels (Shakhashiri, 2008). One of the largest sources of CO₂ emission is coal fired power plants, which contribute to 36 % of the anthropogenic CO₂ emission in the United States, and a similar percentage is applicable worldwide (Halman, 1998).

As a result of the tremendous world-wide consumption of such fossil fuels, the amount of CO₂ in the atmosphere has increased over the past century, now rising at a rate of about 1 ppm per year (Shakhashiri, 2008). CO₂ is a greenhouse gas as it transmits visible light but absorbs strongly in the infrared and near-infrared, before slowly re-emitting the infrared at the same wavelength as what was absorbed. The resulting accelerating accumulation of CO₂ in the troposphere, with projections of continued warming in the absence of resolute changes in CO₂ management and this

will cause the greenhouse effect with a significant atmospheric temperature rise and which will produce net warming (Revkin, 2000).

CO₂ gas is formed from the combination of two elements of carbon and oxygen. The CO₂ molecule (O=C=O) contains two double bonds and has a linear shape. It has no electrical dipole, and as it is fully oxidized, it is moderately reactive and is non-flammable. Moreover CO₂ is very stable, linear molecule in which the oxygen atoms are weak Lewis bases and the carbon is electrophilic. Reactions of CO₂ are dominated by nucleophilic attacks at the carbon, which are result in bending of the O-C-O bond (Maria Jitaru, 2007).

CO₂ is colorless. At low concentrations, the gas is odorless. At higher concentrations it has a sharp, acidic odor. It can cause asphyxiation and irritation. The US National Institute for Occupational Safety and Health (2001) also state that amounts above 5,000 ppm are considered very unhealthy, and those above about 50,000 ppm (equal to 5 % by volume) are considered dangerous. The molecular weight of CO₂ is 44.01 g/mol and at standard temperature and pressure, the density of CO₂ is around 1.98 kg/m³. At atmospheric pressure and a temperature of -78.51 °C (-109.32 °F), CO₂ changes directly from a solid phase to a gaseous phase through sublimation, or from gaseous to solid through deposition. Solid CO₂ is commonly called "dry ice". It was first observed in 1825 by the French chemist Charles Thilorier. Liquid CO₂ forms only at pressures above 5.1 atm (Santoro et. al., 2006).

2.2 Photoreduction Process Of Carbon Dioxide (CO₂)

International Union of Pure and Applied Chemistry (IUPAC) (1997) state that photoreduction is a reduction reactions induced by light. The processes are addition of one or more electrons to a photo excited species and the photochemical hydrogenation of a substance. Reactions in which the substrate is not electronically excited are sometimes called photo initiated reductions.

Catalytic reduction of CO₂ to more valuable compounds has been investigated in many ways. However, this reaction often required a several condition of high pressure and high temperature. The reduction of CO₂ using photocatalysis is one of the most promising methods because CO₂ can be reduced by the UV radiation at room temperature and atmospheric pressure (Ondřej Kozák et. al., 2010). At the same time, this reaction is interesting from the view point of environmental protection, since it is a removal of a greenhouse effect gas under mild conditions (Weatherbee and Bartholomew, 1982).

Photocatalytic reduction process is a method that can be used to reduce the concentration of CO₂ by using photosensitive semiconductor materials such as TiO₂, ZnS, ZrO₂, V₂O₅, ZnO, CeO₂ and NbO₅ as photocatalysts. Hoffman (1995) was reported about TiO₂ in photoreduction process that TiO₂ has been widely studied for its application as photocatalyst because of its excellent stability and strong oxidizing property. However, TiO₂ is a wide band gap semiconductor (3.03 eV for rutile and 3.18 eV for anatase) and can only absorb about 5 % of sunlight in the ultraviolet region, which limits its photocatalytic activity.

According to Anpo and Yamashita (1995), CuO/TiO₂ photocatalysts were prepared to enhance the rate of CO₂ photoreduction and the production of total organic carbon (TOC), including HCOOH, HCHO and CH₃OH. According to Ikeue (2002), in the presence of CO₂ and H₂O, Ti-containing porous silica thin films catalyzed will produce CH₄, CH₃OH and CO as a minor product under visible light

irradiation. Copper doping on TiO_2 promoted CO_2 photoreduction efficiency and improved the product selectivity toward methanol (Tseng et. al., 2002).

Akira Yoshida (2003) was reported that photoreduction of CO_2 with water into valuable organic compounds under concentrated sunlight as well as xenon (Xe)- or mercury (Hg)-lamp irradiation was investigated using a Pt-loaded potassium hexatitanate ($\text{K}_2\text{Ti}_6\text{O}_{13}$) photocatalyst or a composite catalyst in which the Pt- $\text{K}_2\text{Ti}_6\text{O}_{13}$ photocatalyst was combined with a CO_2 hydrogenation catalyst of Cu/ZnO. When the Pt/ $\text{K}_2\text{Ti}_6\text{O}_{13}$ photocatalyst was used under Xe- or Hg-lamp irradiation, H_2 , CH_4 , HCHO and HCOOH were formed. When the composite catalyst was used under concentrated sunlight, CH_3OH was successfully formed in addition to the above products (Tetsuya Kida, 2003). For the composite catalyst, H_2 resulting from the water decomposition over the photocatalyst serves as the reducing agent for the CO_2 hydrogenation over the Cu/ZnO catalyst. According to Shangguan and Yoshida (1999) in their previous research found that the photocatalytic production of H_2 from water over various metal oxides under sunlight and found that Pt-loaded potassium hexatitanate ($\text{K}_2\text{Ti}_6\text{O}_{13}$) which has a perovskite-type tunnel structure, showed the highest activity among the catalysts tested.

Fukuoka (2005) was reported that various metallic and semiconductor nanoparticles or nanowires have been prepared with SBA-15. Recent research had use the SBA-15 for the oxidation process of carbon monoxide (CO). Jernigan (1994) stated that catalytic CO oxidation is both of fundamental importance and has widespread applications in air purification, orbiting, closed-cycle CO_2 lasers and CO detectors (Minemura, 2005). The catalytic activity for CO oxidation over the resulting Cu/SBA-15 was evaluated with the focus on factors influencing the catalytic activity.

There are other factors influencing selectivity and efficiency of CO_2 photoreduction, including solvent, dissolved CO_2 concentration, pH and selection of sacrificial agent. Increasing the dissolved CO_2 concentration as a solvent led to the major reduction products of formate and carbon monoxide (Torimoto et. al., 1997). The pH will affect the carbonate photoreduction process and cause it to be faster in

acidic solutions than in alkaline solutions (Wang et. al., 2004). Concerning sacrificial agent, negative charges favored CO₂ photoreduction to formate, while positive charges favored CO production (Yoneyama, 1997).

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 non materials. These mesoporous materials exhibit high surface area (600–1300 m²/g), and large pore size exhibiting widely potential applications in industrial catalytic reactions (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) as illustrated in Figure 2.1. (Walcarius et. al., 2005)

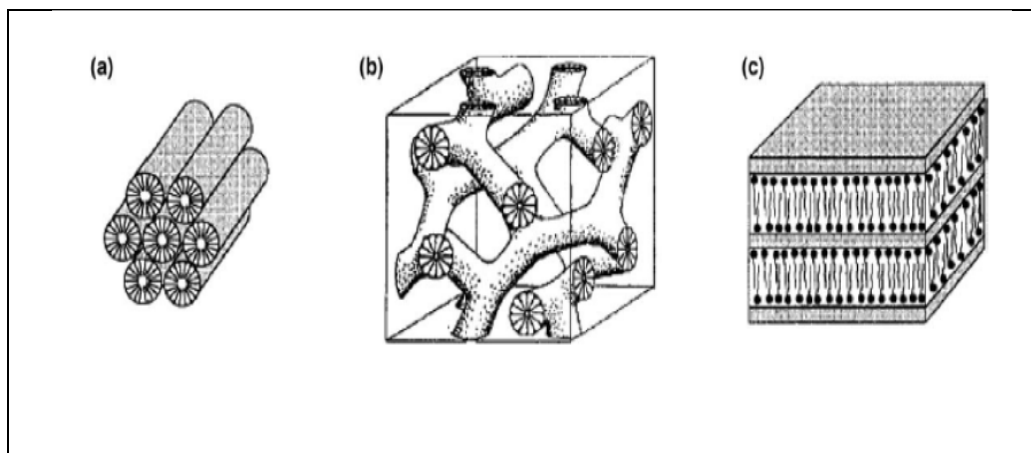


Figure 2.1 Three structure types for silica-surfactant mesophases
(a) hexagonal (b) cubic bi-continuous (c) lamellar

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 synthesis of ordered mesoporous materials (Xiao et. al., 2005).

2.3.2 (SBA-15)

SBA-15 is the most common type mesoporous of pure silica which is form of silica and a recent development in nanotechnology. Figure 2.2 shows the structure of SBA-15.

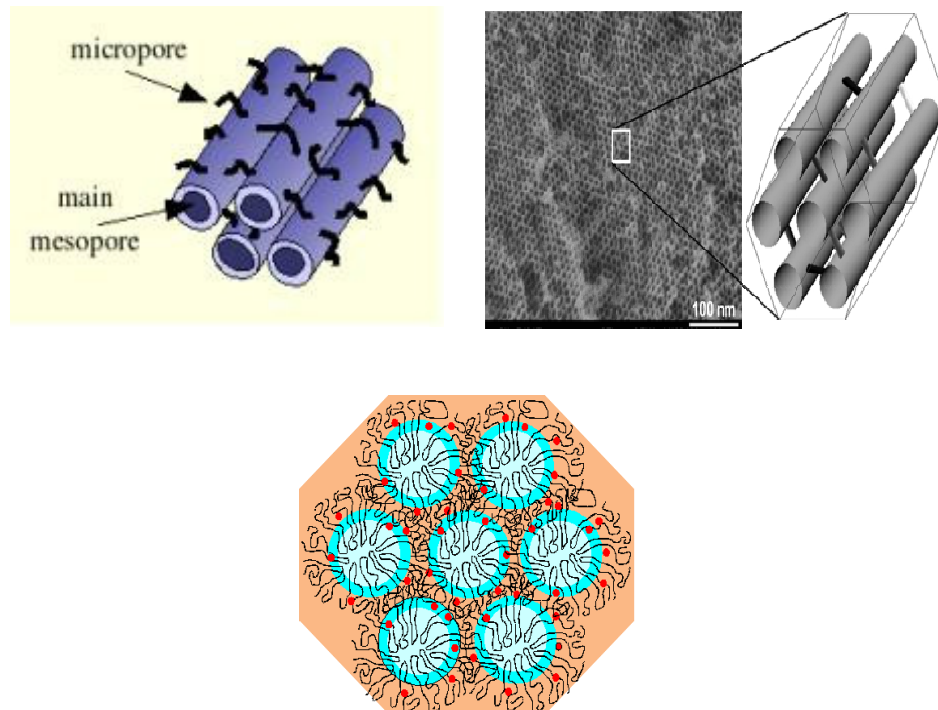


Figure 2.2 Structure of SBA-15

SBA-15 is a mesoporous silica sieve based on uniform hexagonal pores with a narrow pore size distribution and a tunable pore diameter of between 5 and 15 nm (Zhao, 1998). The thickness of the framework walls is about 3.1 to 6.4 nm, which gives the material a higher hydrothermal and mechanical stability than, for instance, MCM-41 (Cassiers, 2002). The high internal surface area of typically 400–900 m²/g makes SBA-15 a well suited material for various applications. It can be used in environmental analytics for adsorption and separation, advanced optics, as a support material for catalysts and as a template for the production of nano structured carbon or platinum replica (Thomas et. al., 2004).

According to Zhao (2007), mesoporous silica nanoparticles are synthesized by reacting tetraethyl orthosilicate with a template made of micellar rods. The result is a collection of nano-sized spheres or rods that are filled with a regular arrangement of pores. The template can then be removed by washing with a solvent adjusted to the proper pH. In another technique, the mesoporous particle could be synthesized using a simple sol-gel method or a spray drying method (Okuyama et. al., 2009).

The SBA-15 was many used in the recent research especially in Fisher-Tropsch synthesis (FTS). The recent experiment was on the use of different mesostructured material based on silica as cobalt support for the FTS (Gonzalez et. al., 2009). He published about the advantages of SBA-15 uses as cobalt supporter as saying that the use of SBA-15 as cobalt supporter for the FTS seems to be promising, since the Co/SBA-15 catalyst with diameter of 5 nm has shown the best catalytic reaction behavior in the comparison with the rest of the materials tested in the reaction such as Al-MCM-41 and INT-MM1 (Gonzalez et. al., 2009).

Gonzalez (2009) also stated that the larger surface-Co species anchored or encapsulated in the wide pore mesoporous supports showed a contrary tendency. As the conclusion of his statement that SBA-15 gave more great effect on the catalyst compared with other silica such as MCM-41 and INT-MM1 in his study.

2.3.3 Cu/SBA-15 catalyst

As far as we know, most of research works reported the metal containing SBA-15 materials prepared by wet impregnation method. Different strategies of synthesis may lead to major changes in bonding and environment of metal species within SBA-15 mesoporous silica (Li et. al., 2005). Generally, impregnation is the most common method for metal-containing mesoporous silica synthesis. By using this method, mesoporous catalyst supports are impregnated by various types of copper salt solutions, for example, copper nitrate and copper sulphate (Lou et. al., 2008).

Recent research was reported that copper nanoparticles were deposited onto mesoporous SBA-15 support via two different routes, post-grafting method and incipient wet impregnation method. X-ray diffraction spectroscopy reveals that the

impregnation method mainly forms large Cu particles on the external surface of SBA-15 (Zhang et. al., 2007).

Zhang et. al., (2007) was prepared with silica-supported copper (20 wt. %) catalysts by incipient-wetness impregnation. In order to study the effects of impregnation solvent on Cu/SiO₂ catalysts, different copper nitrate solutions including ethanol and aqueous solutions were used to prepare the copper catalysts. They found that the catalyst activity greatly depended on the type of impregnation solvent. The size of copper particles prepared from ethanol dehydration was smaller and more uniform than that of the aqueous solution at the same amount of copper loading. However, its reducibility was slightly poorer than that of copper catalyst impregnated by aqueous solution. The lower reduction degree of copper supported catalyst impregnated by ethanol solution could be ascribed to the decreased polarity of the solvent, which increased the interaction between copper complex and silica surface. Using ethanol as impregnation solvent promoted the distribution of Cu over the silica surface, resulting in higher dispersion of supported copper. For Cu/SBA-15 catalysts prepared from copper nitrate trihydrate, the dispersion of copper species was increased and the extent of copper reduction was increased with the amount of copper loading. A maximum CO₂ conversion was found for the catalyst in the photoreduction process (Zhang et. al., 2007).

Transition metal copper substituted mesoporous silica (Cu/SBA-15) was synthesized using triblock copolymers surfactant as catalyst for the photoreduction process of CO₂. The result of Cu/SBA-15 was characterized with x-ray diffraction spectroscopy (XRD) and N₂ adsorption–desorption measurements, which prove that Cu (II) was mainly incorporated into the framework of Cu-SBA-15. Wu (1994) was reported that copper ion and the complexes containing copper ion have long been found to be effective catalysts and be used in a wide range of organic synthesis. Cu (II) substituted molecular sieves were found to be efficient catalysts in liquid phase oxidation of aromatic compounds, and the copper site in the framework of molecular sieves is active centre in phenol hydroxylation (Franco et. al., 2002).

2.4 Characterization of catalyst

2.4.1 Scanning Electron Microscope (SEM)

A scanning electron microscope (SEM) is a type of electron microscope that images a sample by scanning it with a high-energy beam of electrons in a raster scan pattern. The electrons interact with the atoms that make up the sample producing signals that contain information about the sample's surface topography, composition, and other properties such as electrical conductivity. There are many advantages to using the SEM instead of a light microscope. The SEM has a large depth of field, which allows a large amount of the sample to be in focus at one time. The SEM also produces images of high resolution, which means that closely spaced features can be examined at a high magnification. Preparations of the samples are relatively easy since most SEM only require the sample to be conductive. The combination of higher magnification, larger depth of focus, greater resolution, and ease of sample observation makes the SEM one of the most heavily used instruments in research areas today (Baghaei et. al., 2007).

The SEM analysis was carried out to specifically examine the topology of the catalyst surfaces and the morphology of the particles and crystals. Hunger et. al., (2007) was reported that the SEM images of SBA-15 with different tetraethylorthosilicate/triblockcopolymer (TEOS/TCP) ratios and pH values and the images were shown in Figure 2.3. Comparisons between the images of samples with different values for each synthesis variable were made to provide a clearer picture of the specific differences between structures. Again, the results suggest a strong dependence between SBA-15 formation and the synthesis conditions. The images of SBA-15 samples synthesized at a TEOS/TCP ratio of 3.15 showed more cavities compared to those synthesized with a TEOS/TCP ratio of 3.38. These results were attributed to the residual silica precursors that were hydrolyzed and preferentially condensed in the copolymer micelles. After surfactant removal through calcinations, the condensed amorphous silica deposited on the wall and subsequently covered the

pores. For the SEM images of SBA-15 samples synthesized below, the isoelectric point (below pH 2.0), and fewer cavities were observed (Hunger et. al, 2001).

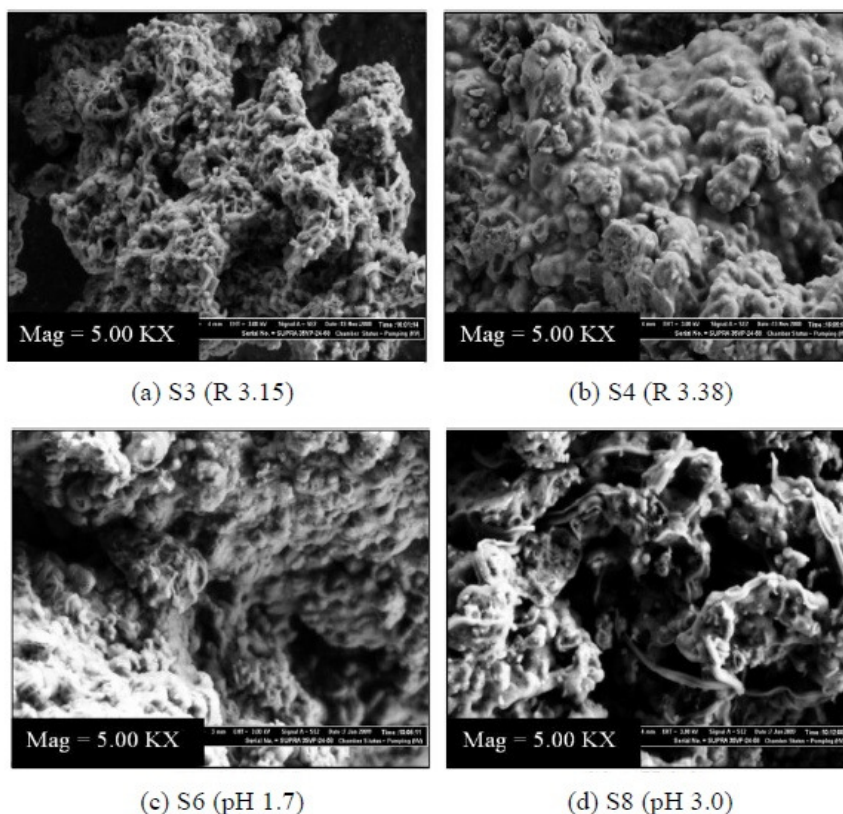


Figure 2.3 SEM images of mesoporous SBA-15 with different TEOS/TCP ratios and pH values

Fukushima (1996) was reported that the Cu/SBA-15 catalyst displayed highly dispersed copper particles which were homogeneously confined into the channels of SBA-15. It is surprising that the typical pore structure of SBA-15 sample cannot be clearly distinguished, presumably due to the presence of too much copper covered outside the channel. SEM images of Cu/SBA-15 show well defined wheat-like macro-structure and the rope-like domains with average size of 1 μm were still mostly retained and the images were shown in Figure 2.4. To confirm the presence of the mesoporous structure of SBA-15 with ultra- high copper content, the sample treated the Cu/SBA-15 sample in diluted hydrofluoric acid (HF) solution. The mesoporous structure was perfectly preserved, suggesting the well-preserved structure of SBA-15 with copper content. The remarkable difference in particle size and size

distribution of copper for the two samples indicates that copper species can be stabilized by the silica support that lead to a better dispersion of copper species into the channel of SBA-15 (Zhao, 1998).

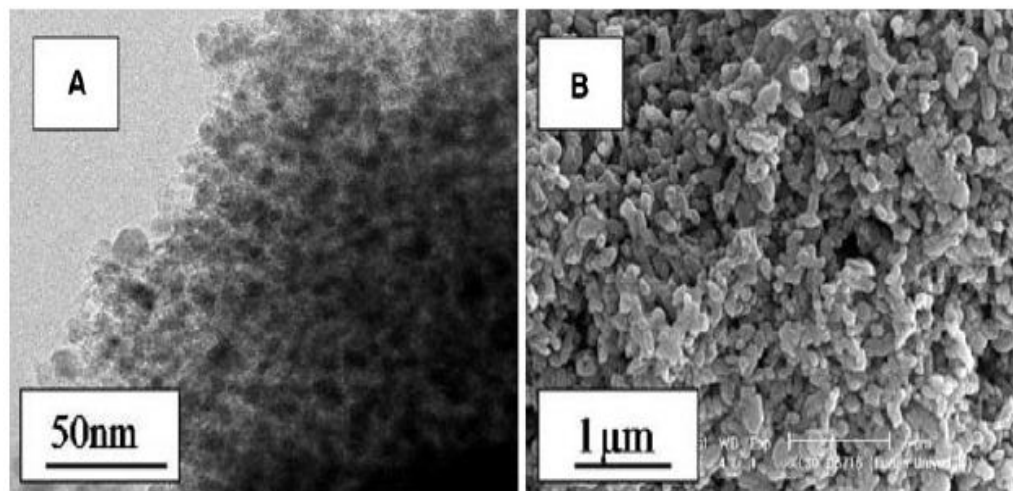


Figure 2.4 (a) TEM images of Cu/SBA-15 (b) SEM images of Cu/SBA-15.

2.4.2 Fourier Transforms Infrared Spectroscopy (FTIR)

Fourier Transform Infrared Spectroscopy (FTIR) identifies chemical bonds in a molecule by producing an infrared absorption spectrum. The FTIR generates an infrared spectral scan of samples that absorb infrared light. Metals do not absorb infrared light, but materials that contain metals can be scanned with FTIR. It covers a range of techniques, mostly based on absorption spectroscopy. As with all spectroscopic techniques, it can be used to identify and study chemicals (Paula, 2009).

A material's absorbance of infrared light at different frequencies produces a unique identification based upon the frequencies at which the material absorbs infrared light and the intensity of those absorptions. The resulting spectral scan is typically specific to a general class of material. Unknown spectral scans can be analyzed to determine the base material of the unknown by comparing their scan to spectral scans of known materials that are stored in a computer-based library. The resulting spectra produce a profile of the sample; a unique molecular "fingerprint"