

CHAPTER II

LITERATURE REVIEW

2.1 Silatrane

Silatrane was firstly discovered by Voronkov and Zelchan (1965). At that time, Bio-organosilicon which was a new branch of silicon chemistry was originated due to the specific biological activity of silatrane. Silatranes are cyclic organosilicon ethers of tris(2-oxyalkyl)amines and their derivatives (Voronkov *et.al*, 1982). A coordinate link from the nitrogen to the silicon results in a pentacoordinate silicon atom that shows a concavo-convex shape, as in Figure 2.1 (Harris *et al.*, 1978). High dipole moments (5.73-7.1 D) of silatranes were investigated as full electron transfer from the nitrogen to silicon atom. However, later research was found from the polarity calculation on silatrane using X-ray data that the polarity of N→Si bond is not great as previously reported. It was only the 0.1 \bar{e} charge transfer from the nitrogen to silicon atom. Many researchers have also confirmed this conclusion. (Ishmaeva *et al.*, 2008, 2009) Since silatranes exhibit a higher solubility than many atranes, applications of silatranes in various fields have been studied. (Puri *et al.*, 2011)

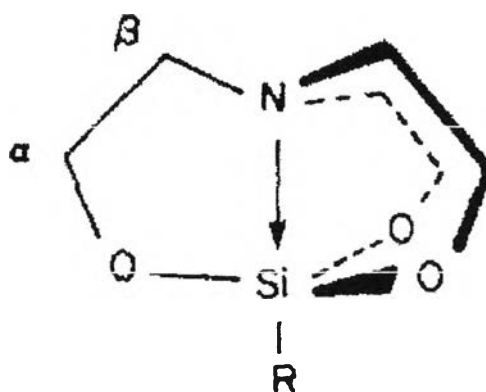


Figure 2.1 Chemical structure of silatrane which R = H, Me, CH₂=CH, Ph. (Harris *et al.*, 1978)

2.1.1 Biology Application

The discovery of silatrane was primitively studied of 1-arylsilatrane on biological activity. (Voronkov and Zelchan, 1965) Pilotropic activity (stimulating growth of hairs) of silaranes was explored by Voronkov and further researched in different reviews and papers. (Voronkov *et al.*, 1982; Bakhareva *et al.*, 1983) 1-chloromethylsilatrane shows pilotropic activity by an increase the permeability of connective tissues, blood vessels and hair follicles in skin at the drug application site. As some silatranes was introduced into an organism, it increases the resistance to the development of malignancies. (Sculimbrene *et al.*, 2001) It was also found that atranyl-nucleosides perform a great transition state analogs for phosphoryl transfer reactions and possess anticancer activity. (Puri *et al.*, 2011; Black *et al.*, 2002) Recently, silatranes exhibit antitumor activity by reducing tumor invasion and inhibiting tumor growth. (Wang *et al.*, 1988) The ferrocenyl containing silatrane moiety, *p*-FcC₆H₄COOSi(OCH₂CH₂)₃N is active against various bacteria such as *Gibberella saubinetii*, *Cladosporium fulvum*, *Bremia lactucae*, *Alternaria mali* and *Isariopsis clavispor*. (Chen *et al.*, 2003) 3-formylchromoniminopropylsilatrane (**66**) metal complexes perform high antimicrobial activity against *K. pneumoniae*, *S. aureus*, *E. coli* and *B. subtilis* bacterias. (Tharmaraj *et al.*, 2009) Silatrane-containing arylamide and acylthiourea compounds show good inhibition to fungi and pathogenic bacteria, respectively. (Li *et al.*, 2005) 1-Chloromethylsilatrane (CMS) posses wound healing properties in an alkaline or an acid burn area. CMS also prevents the loss of calcium from the bones of the skeleton. When CMS combined with zinc oxide, anti-inflammatory and biosynthetic activity were investigated. (Puri *et al.*, 2011; Kazimirovskaya *et al.*, 2001; Pisarskii *et al.*, 1987) Silatranes Not only show the application on human but also perform good activities on animal as reproductive agents. (Puri *et al.*, 2011)

2.1.3 Commercial Application

Silatranes and their derivatives can be used as coupling agents for curable silicone compositions which performed good adhesion to steel, glass, polycarbonate and polyester substrates. (Ishikawa *et al.*, 2001) Excellent flow ability and adhesion of substrate obtained when introduction of silatranes in curable organic

resin composition. These compositions are produced semiconductor device packaging. (Puri *et al.*, 2011; Shi, 2013) Carbasilatrane has found application as surface treatment agent for glass fibers and a material for electronic parts such as solar cells. (Wakita *et al.*, 2014) Application as a composite polymer for electric insulating coating films with uniform thickness short time curing, good dielectric constants and low moisture absorption was also observed. (Puri *et al.*, 2011)

2.1.4 Sol-gel Process Application

The sol-gel method demonstrates the generation of an adequate precursor, which requires good hydrolysis and condensation control in preparation step. The control of hydrolysis and condensation has played the important role in the synthesis of porous materials via sol-gel process. However, tetraethylorthosilicate (TEOS) which is commonly used as a silica source, is extremely sensitive in hydrolysis. Therefore, silatrane is an attractive material that shows more advantages over TEOS. Silatrane can be prepared in low cost by heating precursors in triethanolamine. Steric and chelate effects of silatrane control rates of hydrolysis and condensation process efficiently. Thus, silatrane is stable towards hydrolysis. Hydrolysis of silatrane generates triethanolamine molecules in the solution. Triethanolamine molecules act as co-template on the outer surface of surfactant micelle due to mesoporous formation. This reduced packing of micelle and also electrostatic repulsion between micelle head groups. According to these advantages of silatrane, it has been used to synthesize a variety of microporous and mesoporous solids. (Longloilert *et al.*, 2011; Puri *et al.*, 2011) Our research group also used silatrane as a silica precursor to synthesize porous catalysts such as zeolite, SBA-1, SBA-15, MCM-41 and MCM-48. (Sathupunya *et al.*, 2002; Tanglumlert *et al.*, 2008; Thitsartarn *et al.*, 2008; Longloilert *et al.*, 2011)

2.2 Three Dimensional Mesoporous Materials

Porous materials have been studied due to various applications such as catalysts and catalyst support. The International Union of Pure and Applied Chemistry (IUPAC) divides porous materials into three classes based on pore

diameter; microporous (pore size < 2 nm), mesoporous (2-5 nm), and macroporous (> 50 nm) materials. (Trong On *et al.*, 2003; Taguchi *et al.*, 2005). Large and bulky reactants can access into mesopores which overcome the limitation of microporous materials. Three-dimensional pore system is resistant to pore blocking and allow faster diffusion of reactant. (Logar and Kaučič, 2006) According to these abilities of 3D mesoporous materials, MCM-48 and TUD-1 were focused on this research.

2.2.1 MCM-48

In 1992, Mobil researchers discovered the novel type of mesoporous silica with large internal surface areas and narrow pore size distributions that was called M41S family. Three main members of this family consist of hexagonal MCM-41, cubic MCM-48 and lamellar MCM-50. Three-dimensional pore channel of MCM-48 prevents pore blockage and performs better diffusion of reactants than one-dimensional hexagonal pore of MCM-41. MCM-48 has a Ia3d symmetry. The structure of MCM-48 composes of the two identical cubes which separate compartment, creating two independent but intertwining enantiomeric 3D pore systems as shown in figure 2.2. (Meynen *et al.*, 2009; Sayari, 1996)

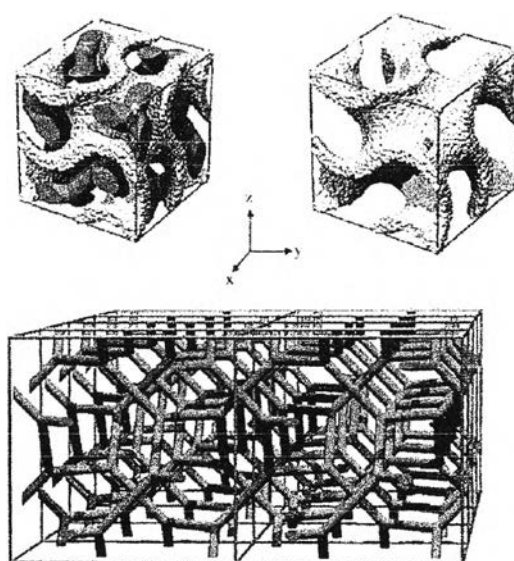


Figure 2.2 Cubic unit cell of MCM-48 with two independent micelle systems. (Meynen *et al.*, 2009)

2.2.2 TUD-1

TUD-1 was explored by a joint research project between Lummus Technology and the Delft University of Technology which first reported in 2001. It has three-dimensional sponge-like structure, high surface area (400-1000 m²/g), tunable porosity (pore volumes of 0.3-2.5 cc/g and diameters of 4-25 nm) and excellent thermal, hydrothermal and mechanical stability. Because of large pore diameters (larger than MCM-48) and also 3D interconnecting pores of TUD-1 which give rise to a high accessibility for substrates. This mesoporous materials can be prepared using template like triethanolamine or tetraethyleneglycol instead of expensive surfactants. (Aquino and Maschmeyer, 2009; Angevine *et al.*, 2009; Telalović *et al.*, 2010; Telalović and Hanefeld, 2010)



Figure 2.3 Three-dimensional pore systems of TUD-1. (Angevine *et al.*, 2009)

2.3 Phenol Hydroxylation

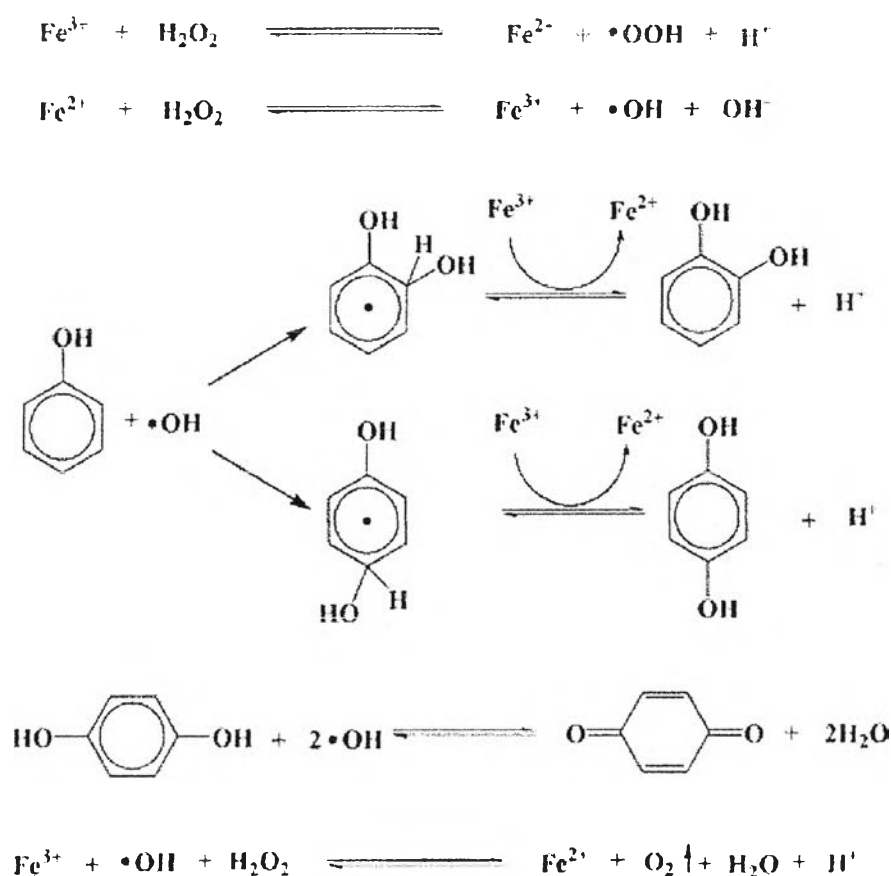
Despite promising properties of MCM-48 and TUD-1 in catalysis, adsorbent, catalyst support, template, etc, modification or functionalization of silica mesoporous materials is required to overcome the limitation of low acidity strength. Introduction of heteroatoms such as aluminum, boron and numerous transition metals into the frameworks also enhances the redox properties. (Zhao *et al.*, 2013)

Phenol is one of the most important representative of organic pollutants because of high toxicity at low concentration and leading to halogenated formation in natural water. (Molina *et al.*, 2006) Hydroxylation of phenol to catechol and

hydroquinone is a demanding reaction, as the products have a very wide range of applications such as photographic film developers, antioxidants, polymerization inhibitors, medicines and perfume. (Ray *et al.*, 2007; Parida and Rath, 2009) Recently, Cheng *et al.*, 2012, 2013 also reported the application of hydroquinone/benzoquinone as bio-inspired redox couple for dye-sensitized solar cells. Oxidation of phenol is interesting reaction for changing phenol in wastewater to valuable products.

Mesoporous materials incorporating various transition metals have been used as heterogeneous catalysts. Many iron-containing compounds have been reported to catalyze the selective oxidation of phenol. Adam *et al.* (2010) reported that the catalytic performance of rice husk increased with 10 wt % Fe^{3+} loading. As the iron content further increased, the reduction of the phenol conversion rate was observed. Higher Fe^{3+} loading ($>10\% \text{Fe}^{3+}$) resulted in smaller pore size and exhibited extra-framework of Fe^{3+} in the catalyst, leading to catalytic deficiency in phenol oxidation. Rice husk with 10% Fe^{3+} loading gave 95.2% conversion at 343 K with selective formation of 61.3% catechol and 38.7% hydroquinone. To synthesize Fe-MCM-41, Khieu *et al.* (2009) also achieved high iron content ($\text{Si/Fe} = 20$) by controlling initial pH. Activity and stability of the catalyst were evaluated on the wet peroxide oxidation of phenol under mild conditions ($<80^\circ\text{C}$, ambient pressure) with high organic mineralization, low sensitivity to leaching Fe out. and good oxidant efficiency. Lie *et al.* (2008) studied the hydroxylation of phenol over Fe-HMS. During the synthesis, they found that increasing the ratios of Fe/Si , $\text{H}_2\text{O/SiO}_2$, and EtOH/SiO_2 in the synthesis gel causes the pore diameter of Fe-HMS reduce. 21.7% conversion of phenol was obtained and Fe-HMS materials show a non-shape-selectivity for the hydroxylation of phenol since the pore size of Fe-HMS is much larger than dihydroxybenzene. Phenol hydroxylation of Fe-MCM-48 was firstly reported by Zhao *et al.* (2001). Fe-MCM-48 shows 43.6% phenol conversion and selectivity for catechol. Choi *et al.* (2006) investigated 60% conversion of phenol at 50°C over Fe-MCM-41 and also proposed phenol hydroxylation pathway of Fe ions as shown in Figure 2.3. Not only Fe silicates that can catalyze the oxidation of phenol but also the other transition metals that shows good catalytic properties. Pachamuthu *et al.* (2013) found that using copper nitrate as a copper source in Cu-

TUD-1 synthesis causes high Cu^{2+} active sites incorporated into the framework. That results in high catalytic activity which performed 72% conversion of phenol and selective with catechol product. Hydroxylation of phenol over Ti-SBA-12 and Ti-SBA-16 was also investigated by Kuma and Srinivas (2013). Conversions of Ti-SBA-12 and Ti-SBA-16 were 24.1% and 13.3%, respectively.



Scheme 2.1 Phenol hydroxylation reaction pathway of Fe ions. (Choi *et al.*, 2006)

For catalytic applications, the thermal stability of mesoporous materials is very important. Catalytic reactions require contact with water, especially in hot aqueous solution, and the lack of hydrothermal stability could be a serious barrier for the application of this material. Accordingly, the hydrothermal stability of pure silica

has been improved by heteroatom-substituted mesoporous materials. Shao *et al.* (2005) found that the incorporation of Ce into MCM-48 could enhance the thermal stability of MCM-48; however the addition of fluoride ions made it more efficient in improvement of hydrothermal stability. For Ce-SBA-15, the Si/Ce molar ratio of 10 had higher hydrothermal stability, and pH-adjusting hydrothermal method is an effective method to synthesize the well-ordered two-dimensional mesoporous materials (Selvaraj *et al.*, 2011). The thermal and hydrothermal stabilities of Zr-MCM-48 were also investigated by Jiang *et al.* (2011). The resulting Zr-MCM-48 still maintained cubic mesoporous framework even after calcinations at 800 °C for 4 h or hydrothermal treatment at 100 °C for 24 h.

The incorporation of two different metals can create materials with different redox and acid properties. Supported bimetallic catalysts are very attractive materials since one metal can modify the structural and electronic properties of the other. There are a few researches on bimetallic mesoporous materials. Fe-, Ce-MCM-41 was successfully synthesized under hydrothermal condition with excellent thermal stability (Ying *et al.*, 2006). Bimetallic Ce-Fe-SBA-15 was also synthesized through the hydrothermal treatment for the phenol hydroxylation catalysis. The incorporation of Fe promoted the incorporation or dispersion behavior of Ce into SBA-15 (Zhang *et al.*, 2008). Gao *et al.* (2007) reported the catalytic performance of V-Fe-SBA-15. High vanadium contents in the catalyst interact with H₂O₂ to form the peroxonium groups, which led to the higher selectivity for hydroquinone in the products. High iron contents in the sample lead to high OH· generation that results in high selectivity of catechol. The photocatalytic hydroxylation of phenol over Fe-Al-silicate was observed by Huixian *et al.* (2011). Fe-Al-silicate shows 64.9% conversion of phenol with a total selectivity of 95% and the yield of 39.3%, 22.3% for catechol and hydroquinone, respectively.

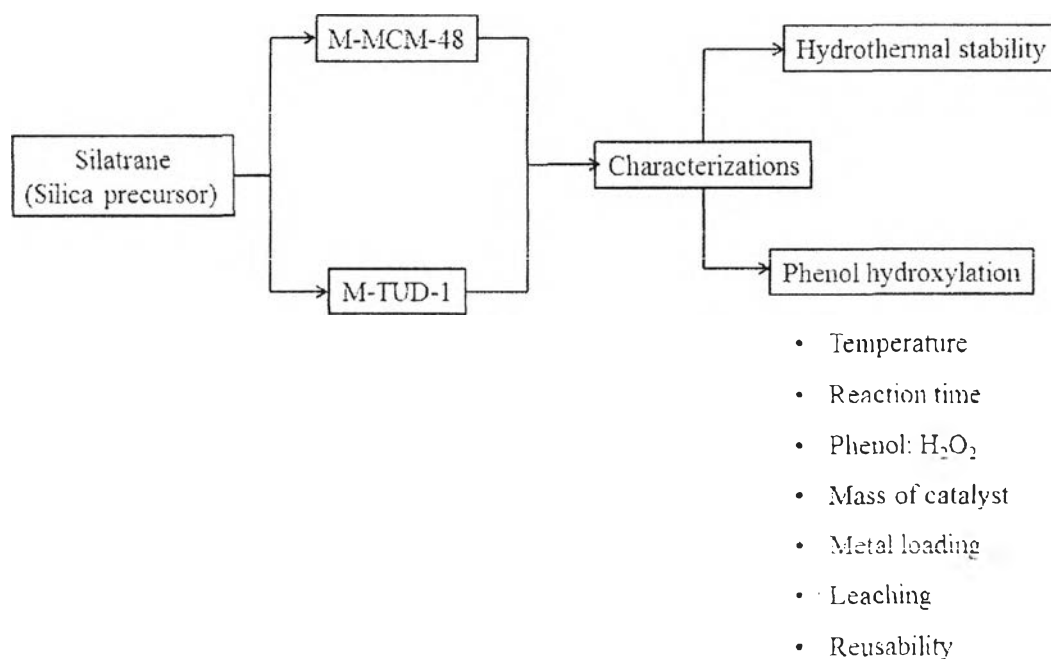
2.4 Points of Study

■ To synthesize silatrane which is an important silica precursor for the synthesis of catalyst.

■ To synthesize bimetallic MCM-48 and TUD-1 using silatrane precursor via sol-gel process.

■ To study the hydrothermal stability of bimetallic MCM-48 and TUD-1.

■ To study the effect of temperature, reaction time, amount of the oxidant, mass of catalyst, metal loading, leaching and reusability in phenol hydroxylation over bimetallic MCM-48 and TUD-1.



Scheme 2.2 Scope of research works.