

CHAPTER II

THEORETICAL BACKGROUND AND LITERATURE REVIEW

2.1 Sol-Gel Processing

Sol-gel technology is the preparation of ceramic, glass, or composite materials by the preparation of a sol, gelation of the sol, and removal of the solvent. In general, the sol-gel process is the synthesis of an inorganic network at low temperature by a chemical reaction in solution. This process involves the transition characterized by a relatively rapid change from a liquid (colloidal solution) into a solid (gel-like state). Generally, the precursor is dissolved in a suitable organic solvent in order to obtain a solution. The solvent must be carefully selected so that a solution with high concentration of the required component can be obtained. Sol-gel technique involves the following steps: hydrolysis of precursor, polycondensation, gel formation, organic pyrolysis by heat treatment (Thanabodeekij *et al.*, 2003).

2.2 Synthesis of TUD-1

TUD-1 mesoporous material is a random three-dimensional amorphous structure and interconnecting pores, providing a high surface area (400–1000 m²/g), an excellent hydrothermal stability, a tunable pore size, and a better accessibility of other molecules to diffuse into and out of them. These properties make the material interesting for catalyst development.

Angevine *et al.* (2008) reported that originally, synthesis of TUD-1 was based on the sol-gel methodology. The synthesis method involves a monomeric silica source, tetraethylorthosilicate (TEOS), mixing with triethanolamine (TEA) and optionally (tetraethylammonium hydroxide (TEAOH) acting as templates. Unlike the preparation of some mesoporous materials, no surfactant is added to form a regular pore structure. Desirable properties of the TUD-1 templates are: physically stable at elevated temperature (200°–250 °C), chemically interactive with the inorganic phase, and inexpensive. TEAOH serves as both a source of quaternary cation to generate some micropore and a basic environment to accelerate TEOS hydrolysis. Rate of the

reaction increased with pH: to a large extent, this acceleration can also be achieved by raising the temperature. The next step involves an ageing/drying phase to establish the primary pore structure. The last step is to remove a large quantity of organics by calcination. An optional step, between drying and calcination, is a pore modification step, employing elevated temperature. The pore diameter of TUD-1 in comparison to some major molecular sieves as ZSM-5, Zeolite Y, and MCM-41, is illustrated in Figure 2.1, while high resolution tunneling electron microscopic (HR-TEM) images of the 3-D structure of TUD-1 is shown in Figure 2.2. The results indicated that TUD-1 is clearly amorphous, which has the pore diameter varied from about 40 to 250 Å (Angevine *et al.*, 2008).

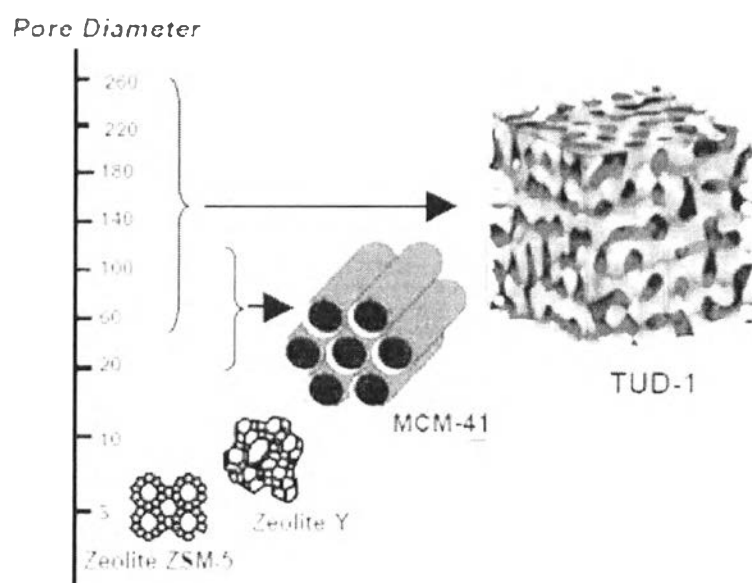


Figure 2.1 Pore diameters of TUD-1, MCM-41, and zeolites (Angevine *et al.*, 2008).

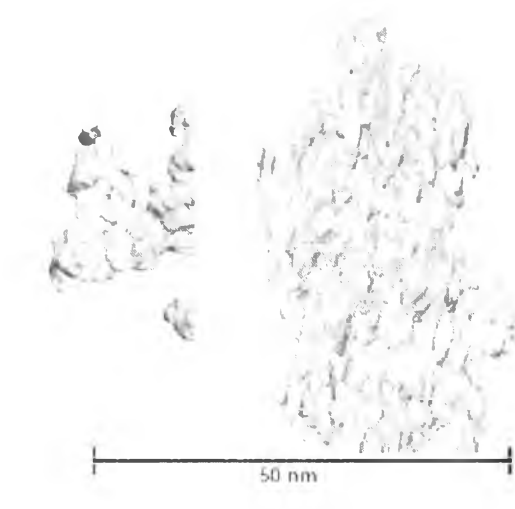


Figure 2.2 3-D TEM of TUD-1 irregular pore structure (Angevine, *et al.*, 2008).

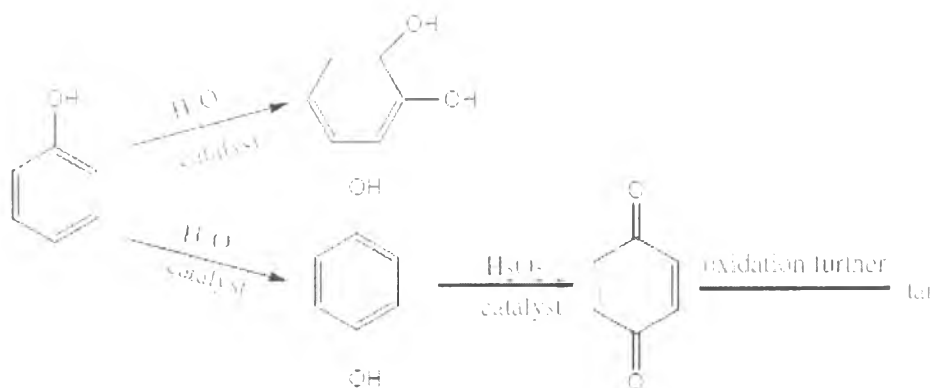
Zhang *et al.* (2006) reported the synthesis of mesoporous alumina TUD-1 with high thermal stability via the sol-gel process using tetraethylene glycol (TEG) as a directing agent and studied the effect of TEG and mixed solvents between EtOH:*i*-PrOH on the pore structure of the final products. They found that TUD-1 had amorphous framework, high surface area, large pore volume, and narrow pore size distribution, causing TUD-1 to have high thermal stability upon prolonged heat treatment at high temperatures. These properties are important for applications in adsorption and catalysis. When the amount of TEG increased, the pore size and the pore volume increased. The mixed solvents also played the role of pore-forming agents in the absence of TEG, but had no obviously direct effect on the mesopore structure in the presence of TEG (Zhang *et al.*, 2006).

Tanglumlert *et al.* (2011) reported facile synthesis of Ti-TUD-1 for catalytic oxidative desulfurization of model sulfur compounds. Ti-TUD-1 was successfully synthesized via the sol-gel process using silatrane as a silica source and titanium glycolate as a titanium source at room temperature within 4 h. The molar ratio of the mixture was 1.0 silatrane: x TiO₂: 14 H₂O: 0.7 TEAOH, where x was the molar ratio of TiO₂ varied from 0.02 to 0.08. After silatrane is hydrolyzed, it generates TEA molecule which acts as a template. The sample characterized by XRD, N₂

adsorption–desorption isotherms, and TEM showed disordered mesoporous structures with high surface area (715–824 m²/g) (Tanglumlert *et al.*, 2011).

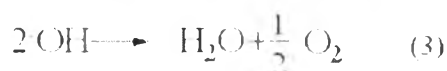
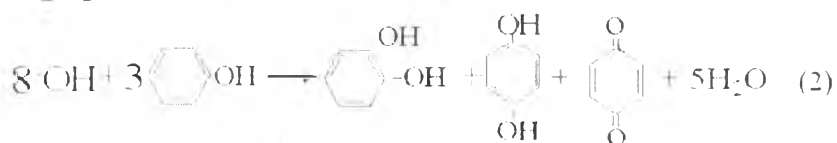
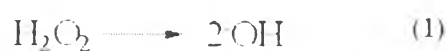
2.3 Oxidation of Phenol

Phenol is generally used in the production of phenolic resins for plywood application, construction, automotive, and appliance industries. It is also used in the production of caprolactam, and bisphenol A (ATSDR, 1998). Phenol is the one of pollutants in USEPA list which is highly irritating to the skin, eyes, and mucous membranes in human after acute inhalation or dermal exposures. Phenol is considered to be quite toxic to human via oral exposure. Anorexia, progressive weight loss, diarrhea, vertigo, salivation, a dark coloration of the urine, blood and liver effects have been reported in chronically exposed human (USEPA, 1999). Oxidation of phenol is an effective way to convert the phenol to the less toxic products, namely catechol (CAT) and hydroquinone (HQ) (Schemes 2.1 and 2.2) which are widely used as important precursors in the many valuable chemicals production, such as photographic chemicals (Ray *et al.*, 2007), polymerization inhibitors, antioxidants, and flavoring agents (Rives *et al.*, 2003; Kannan *et al.*, 2005). In addition, benzoquinone (BQ), which is the over oxidation product, as shown in Schemes 2.1-2.3, is an important precursor in hydroquinone production and used as a polymerization inhibitor, as an intermediate in the production of a variety of substances, including rubber accelerators and oxidizing agents (IARC, 1977). Hydrogen peroxide, H₂O₂, is the most powerful oxidizing agent and has become an important chemical in manufacturing plants due to its by-product, water, which is considered to be environmental friendly. Moreover, H₂O₂ is unstable and easy to lose oxygen when it contacts with active surfaces, such as high-surface-area substances (e.g., activated carbon, a transition or heavy metal or its oxide), by transferring electrons to the peroxide molecule (Rokhina *et al.*, 2011). Thus, many researchers attempt to oxidize phenol by aqueous H₂O₂ with a variety of heterogeneous catalysts (Adam *et al.*, 2013; Song *et al.*, 2011; Kumar *et al.*, 2013; Zhao *et al.*, 2010; Choi *et al.*, 2006; Liu *et al.*, 2008; Hu *et al.*, 2001; Yang *et al.*, 2012).



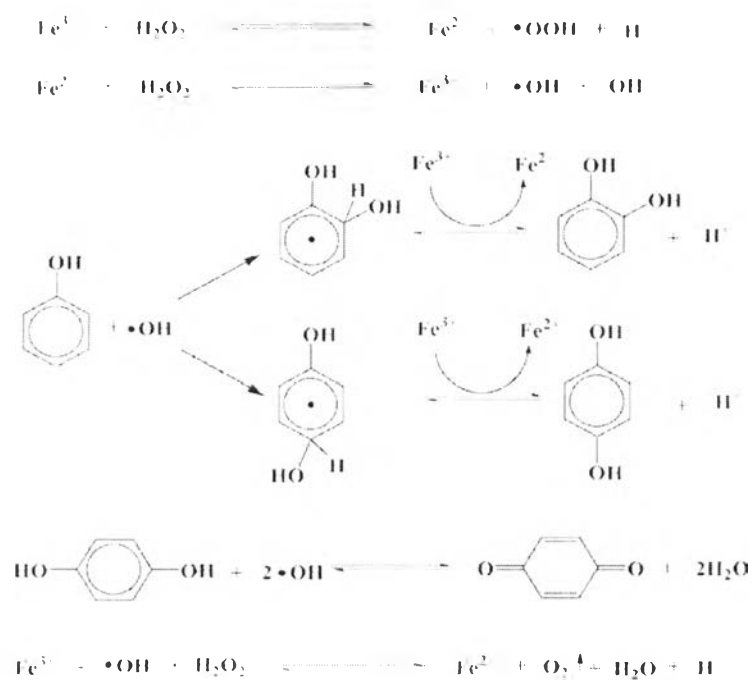
Scheme 2.1 Schematic presentation of oxidation of phenol (Qiao *et al.*, 2012).

General mechanism:

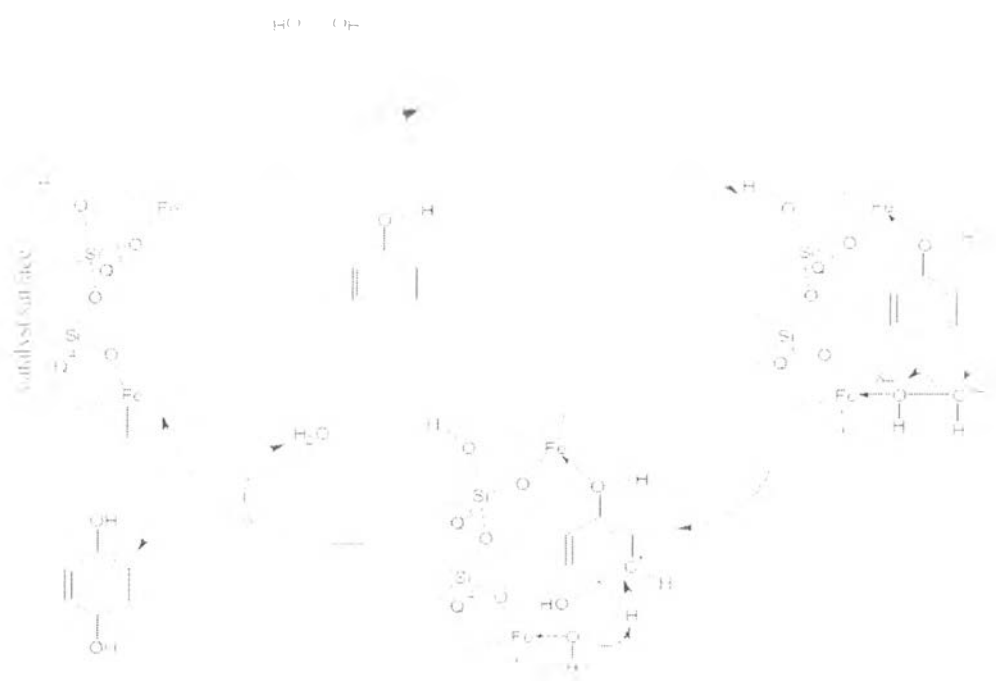


Scheme 2.2 Radical mechanism of phenol hydroxylation by H_2O_2 (Wu *et al.*, 2008).

Phenol hydroxylation has been known to proceed via a redox mechanism involving Fe(III)/Fe(II) redox pair, as described in Scheme 2.3, and the ability of the framework transition metal in zeolytic materials to change oxidation states between (II) and (III) is well-known (Choi *et al.*, 2006). However, Adam and coworkers proposed a non-free radical mechanism when the CAT/HQ ratio was found to be constant during the reaction and benzoquinone was not observed under the studied conditions, see Scheme 2.4. A similar mechanism may also be described for the formation of catechol (Adam *et al.*, 2010).

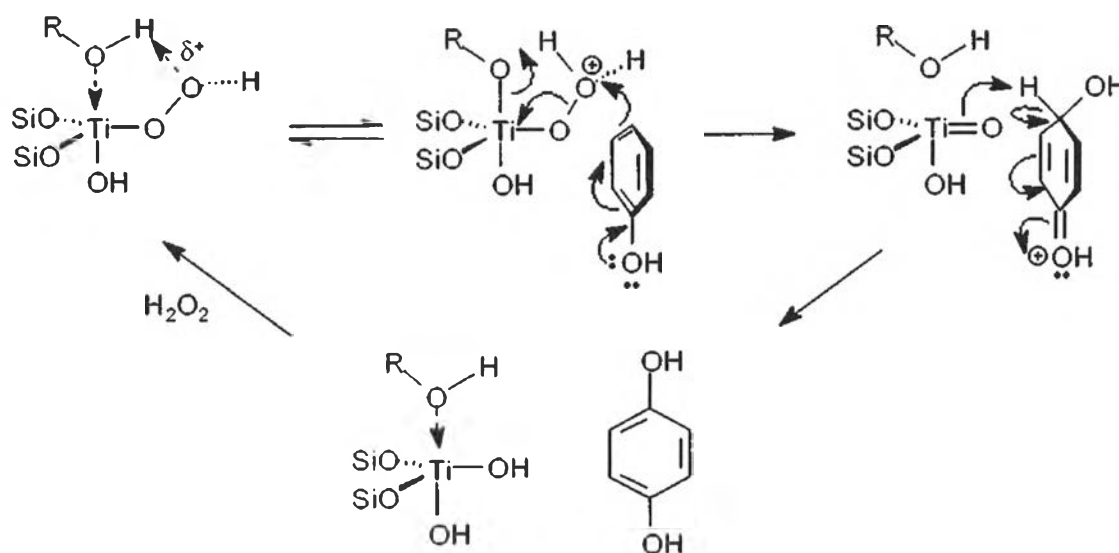


Scheme 2.3 Phenol hydroxylation reaction pathway of Fe ions (Choi *et al.*, 2006).

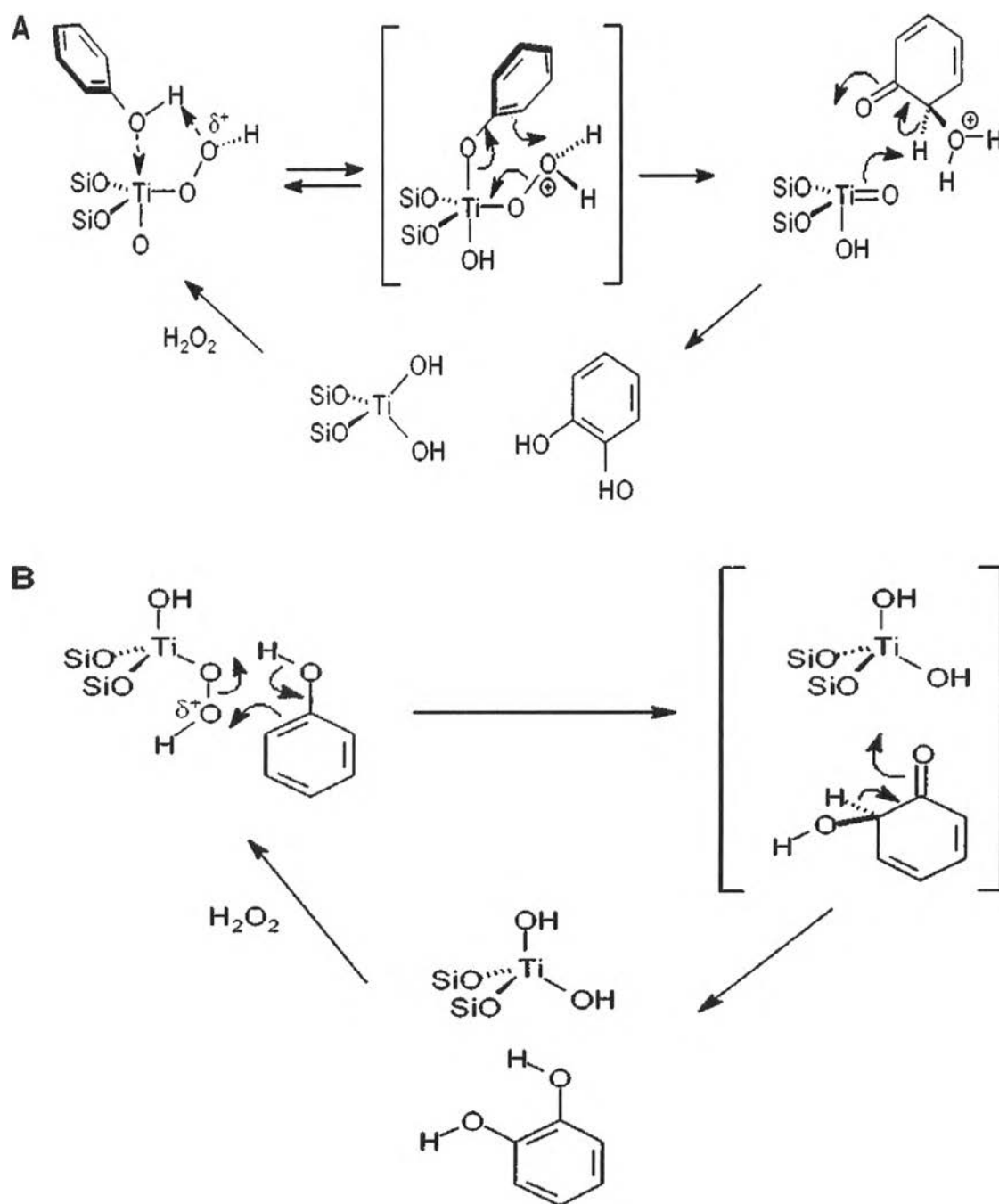


Scheme 2.4 The catalytic cycle for the oxidation of phenol by H_2O_2 in the presence of RH-10Fe. (Adam *et al.*, 2010).

Furthermore, it is generally agreed that protic solvents (alcohols, water) coordinate to titanium (the active center of the catalyst) to expand its coordination sphere to 5 or 6. In this way, five-membered ring, an active intermediate complexes catalyzed by titanium silicalite (TS-1) catalysts, is formed. The coordination of protic solvent molecules results in an increase of the size of the active titanium site, narrowing the TS-1 channels and leading to a geometric constraint for an approaching phenol molecule. Hydrogen bonds of the phenolic OH with solvent OH groups make the phenol molecule more bulky. Phenol, having hydrogen-bonded to the solvent OH groups, approaches the bulky titanium site with the OH group pointing away from the titanium site (Scheme 2.5), yielding HQ. Additionally, the presence of coordinated protic molecules close to the peroxy group could lead to hydrogen bond formation with the active site, destabilizing H-bonding with the phenol molecule assisting in *o*-hydroxylation (as shown in Schemes 2.6A and 2.6B). (Wilkenhöner *et al.*, 2001)



Scheme 2.5 Proposed reaction mechanism for the formation of HQ in phenol hydroxylation (Wilkenhöner *et al.*, 2001).



Scheme 2.6 Proposed reaction mechanism for the formation of CAT in phenol hydroxylation (Wilkenhöner *et al.*, 2001).

The ratio of HQ to CAT is always lower at the external surface than at the internal surface. It can be connected with the fact that at the external surface, the geometric strains are low and *o*-hydroxylation becomes more likely (Wilkenhöner *et al.*, 2001).

2.4 Phenol Hydroxylation Using Metal Loaded Mesoporous Silica

2.4.1 Monometallic Mesoporous silica

Song *et al.* (2010) reported one-step thermal synthesis of Ti-MSU and its catalytic performance on phenol hydroxylation. They studied on the role of addition time of a Ti source, which could effectively influence the structure and morphology of the product by adjusting the balance of hydrolysis–polymerization and nucleation–aggregation in different self-assembly steps. The optimum synthesized Ti-MSU sample showed a good catalytic performance on the phenol hydroxylation. Compared with Ti-MCM-41 and Ti-HMS, Ti-MSU showed the highest phenol conversion (close to the result of TS-1) due to its three-dimensional pore structure of Ti-MSU which might have a significant benefit in reducing the probability of pore blockage and increasing the number of reactive surface defect sites (Song *et al.*, 2010).

Kumar *et al.* (2012) reported the hydroxylation of phenol with hydrogen peroxide catalyzed by Ti-SBA-12 and Ti-SBA-16, which are ordered, three-dimensional, mesoporous titanosilicates. The catalysts of this work were more efficient than mesoporous Ti-MCM-41 and Ti-SBA-15. However, both Ti-SBA-12 and Ti-SBA-16 were highly active with their intrinsic catalytic activity lower than that of TS-1. Catechol and hydroquinone were the only products of the phenol hydroxylation. The para-selective hydroxylation was preferred more on Ti-SBA-12 to TS-1 and Ti-SBA-16. Moreover, the mesoporous Ti catalysts were reusable with little loss in activity and product selectivity even after the fifth recycle. Isolated framework Ti with tetrahedral geometry and 3D, ordered mesoporosity is the unique characteristic features which are responsible for the high efficiency of these titanium mesoporous catalysts on the phenol hydroxylation (Kumar *et al.*, 2012).

Zhao *et al.* (2000) reported on the synthesis of Fe-MCM-48 by the mixed templation method under low molar ratio (0.17:1) of mixed surfactants to silica and its catalytic performance in the phenol hydroxylation. The results showed that some Fe³⁺ ions have been successfully incorporated into the framework of MCM-48, causing the extension of the unit cell and the decrease of the framework connectivity. During the calcination, part of Fe³⁺ ions were removed from their

framework positions to form extra-framework species and the distortion of tetrahedrally coordinated framework isolated Fe^{3+} occurred. The active centers of the framework isolated Fe^{3+} were favorable for the phenol hydroxylation and had a good selectivity for catechol (Zhao *et al.*, 2000).

Choi *et al.* (2006) reported on the phenol hydroxylation using Fe-MCM-41 catalysts with 0.5–4 Fe/Si mol% loading and H_2O_2 as oxidant [phenol: H_2O_2 = 1:1, water solvent]. Fe-MCM-41 exhibited a high catalytic activity, giving phenol conversion of ca. 60% at 50 °C. Catechol to hydroquinone in the product ratio was close to 2:1 in accordance with a free radical reaction scheme involving $\text{Fe}^{3+}/\text{Fe}^{2+}$ redox pair. Increasing amount of Fe species always accomplished the given phenol conversion at a shorter reaction time. The performance of Fe-MCM-41 was compared with the other Fe-containing catalysts, such as Fe-salt impregnated MCM-41 or Fe_2O_3 nano-particles. The result showed that higher level of dispersion achieved in Fe-MCM-41 through the formation of Fe–O–Si bond in the mesoporous material was an advantage for the phenol hydroxylation (Choi *et al.*, 2006).

Liu *et al.* (2008) reported the synthesis and the catalytic properties of Fe-HMS materials in the hydroxylation of phenol. They revealed that both the conversion of phenol (X_{phenol}) and the selectivity to dihydroxybenzene (S_{DHB}) increased with an increase in the Fe amount in the Fe-HMS material when Fe/Si (mol) = 0.01–0.03 in the synthesis gel, but X_{phenol} and S_{DHB} slightly decreased when Fe/Si > 0.03. This result indicated that an appropriate ratio of Fe/Si was about 0.03. The results measured by DRS UV–Vis spectroscopy showed that Fe had incorporated into the HMS framework and formed the four-coordinated Fe species, that are the catalytic active sites for the hydroxylation of phenol by H_2O_2 . If Fe/Si > 0.03, some polymerized Fe species in the extra-framework could appear. Extra iron oxides can accelerate a decomposition of H_2O_2 , resulting in a decrease in the phenol conversion (Liu *et al.*, 2008).

Adam *et al.* (2010) reported on the synthesis of iron silica catalyst with 5–20 wt.% Fe^{3+} by solvent extraction and sol-gel technique using rice husk (RH) as silica source. These catalysts were applied for the oxidation of phenol using H_2O_2 as an oxidant. Catalytic activity increased, using the catalysts containing up to

10 wt.% Fe³⁺ loading. Further increase in the iron content was found to decrease the phenol conversion rate. Higher Fe³⁺ loading (>10% Fe³⁺) resulted in smaller pore size and exhibited extra-framework Fe³⁺ in the catalyst, leading to the lack of catalytic activity. Phenol oxidation by RH-10Fe gave 95.2% conversion at 343K with selective formation of 61.3% catechol (CAT) and 38.7% hydroquinone (HQ). Reusability studies with RH-10Fe resulted in only 16% loss in catalytic activity. However, no leaching of iron was detected. The CAT/HQ ratio was found to be constant during the reaction which suggested a non-free radical catalytic mechanism to be operative (Adam *et al.*, 2010).

2.4.2 Bimetallic Mesoporous Silica

Zhang *et al.* (2007) reported on a series of Ce and Fe incorporated SBA-15 mesoporous materials synthesized through a direct hydrothermal method. The results indicated that: (1) all the samples exhibited typical hexagonal arrangement of mesoporous structure with high surface area, (2) the heteroatoms were, at least in some extent, incorporated into the framework of SBA-15, (3) high utilization of the Fe and Ce could be achieved through the hydrothermal treatment, and (4) the incorporation of Fe could efficiently promote the incorporation/dispersion behavior of Ce into the SBA-15. Catalytic performances of the obtained materials were evaluated in the hydroxylation of phenol with H₂O₂. Catalytic tests showed the different selectivity with different incorporated Ce/Fe ratios, and the results suggested that an appropriate Ce/Fe ratio would be the optimal catalyst for the reaction (Zhang *et al.*, 2007).

Timofeeva *et al.* (2009) reported on iron-containing mesoporous mesophase materials Fe,Al-MMM-2 synthesized according to a sol-mesophase route under mild acidic condition (pH 2.3–4.4) using Keggin type cation [Fe₃Al₁₂O₄(OH)₂₄(H₂O)₁₂]⁷⁺ (FeAl₁₂⁷⁺) as Al and Fe sources. Fe,Al-MMM-2 materials were tested as catalysts for wet phenol oxidation with H₂O₂. Insertion of Al species into the framework of the silicate matrix increased the activity, comparing to a reference Fe, Al-pillared clay, due to both higher surface acidity and lower diffusion limitations that corresponded to Fe,Al-MMM-2 (Timofeeva *et al.*, 2009).

Chumee *et al.* (2009) reported on the synthesis of mesoporous material RH-MCM-41 using rice husk (RH) as silica source by a hydrothermal

method. The material was used as a support for bimetallic platinum-iron catalysts Pt-Fe/RH-MCM-41 by co-impregnation with Pt and Fe at amounts of 0.5 and 5.0 wt.%, respectively, for phenol hydroxylation using H_2O_2 as the oxidant at phenol: H_2O_2 mole ratios of 2:1, 2:2, 2:3, and 2:4. The first three ratios yielded only catechol and hydroquinone as products, while the last one also produced benzoquinone. The 2:3 ratio gave the highest phenol conversion of 47% at 70 °C. The catalyst prepared by co-impregnation with Pt and Fe was more active than a physical mixture of 0.5Pt/RH-MCM-41 and 5Fe/RH-MCM-41. The catalytic performance of 5Fe0.5Pt/RH-MCM-41 was better than that of 5Fe0.5Pt/RH-SiO₂ because the RH-MCM-41 support had a significant higher surface area, resulting in a better metal dispersion (Chumee *et al.*, 2009).