

CHAPTER III

EXPERIMENTAL

3.1 Materials

Fumed silica (99.8% SiO₂) from Nippon Aerosil, iron (III) chloride hexahydrate (FeCl₃·6H₂O), tetraethylammonium hydroxide (35%, TEAOH), catechol (CAT, 99%), hydroquinone (HQ, 99%), 1,4-benzoquinone (BQ, 98%) from Sigma-Aldrich, USA, titanium (IV) isopropoxide (Ti(OCH(CH₃)₂)₄) from Acros Organics, cetyltrimethylammonium bromide (CTAB) from Fluka, ethylene glycol (EG) from J.T. Baker, triethanolamine (TEA, (HOCH₂CH₂)₃N) from QREC, acetonitrile (CH₃CN, 99.9%), methanol (CH₃OH, 99.9%), and sodium hydroxide (NaOH) from Labscan, phenol detached crystals and hydrogen peroxide (H₂O₂, 30% w/v) from Fisher scientific, UK, were used without purification.

3.2 Characterization

The mesoporous product is characterized using a Rigaku X-ray diffractometer (XRD) a scanning speed of 1°C/min. and a CuK α source ($\lambda = 0.154$ Å). An X-ray source in the range of $2\theta = 0.5\text{--}6^\circ$ for TUD-1 product and $2\theta = 2\text{--}8^\circ$ for MCM-48 product. The specific surface area is measured by the Brunauer-Emmett-Teller (BET) method and the pore size distribution is calculated by the Barrett-Joyner-Halenda (BJH) on a Quantasorb Jr. (Autosorb-1). Prior to each analysis, the TUD-1 product is degassed at 250 °C for 12 h. and the MCM-48 product is degassed at 200 °C for 16 h. Scanning electron microscope (SEM) is obtained on JOEL Model 5200 for identification of product microstructure. The order of mesopores is observed by a transmission electron microscope (TEM) on JEOL JEM-2010. Thermal properties are analyzed by Thermogravimetric analysis (TGA) on TG-DTA, Pyris Diamond Perkin Elmer with a heating rate of 10°C/min under nitrogen atmosphere. For the identification and characterization of metal ion coordination in framework, diffuse reflectance UV-visible spectra is recorded on a shimadzu UV-2550 using BaSO₄ as the reference. XRF was carried out on a

PANalytical AXIOS PW 4400. High performance chromatography (HPLC, SPD-M20A Shimadzu) equipped with a C-18 reverse-phase column (Inertsil ODS-3) using 10 vol% acetonitrile and 10 vol% methanol in water as a mobile phase at a flow rate of 1.0 ml/min and a UV detector operating at 254 nm was used to analyze the activity study products.

3.3 Precursor Synthesis

3.3.1 Synthesis of Silatrane

Wongkasemjit's synthetic method (Charoenpinikarn *et al.*, 2001) is followed by mixing 0.1 mol fumed silica, 0.125 mol TEA and 100 ml EG. The mixture is refluxed at 200 °C under nitrogen atmosphere for 10 h in oil bath. The excess EG and water are removed under vacuum at 100 °C. The product is washed by acetonitrile to remove TEA and EG residue.

3.3.2 Synthesis of Cerium glycolate

Cerium glycolate was synthesized according to Ksapabutr *et al.* (2004). Cerium hydroxide (1.04 g, 5.3 mmol of CeO₂), 18 ml of ethylene glycol and 5 mmol (0.73 g) triethylenetetramine with sodium hydroxide at about 12 mol% equivalent to cerium hydroxide was mixed, stirred and heated to the boiling point of ethylene glycol for 18 h under nitrogen. Excess ethylene glycol and water by-product were distilled out during this process. The reaction mixture was cooled overnight under nitrogen. The precipitated product was filtered, washed with acetonitrile and dried under vacuum.

3.4 Catalysis Synthesis

3.4.1 Synthesis of MCM-48, Fe-Ce-MCM-48 and Fe-Ti-MCM-48

Fe-Ce-MCM-48 and Fe-Ti-MCM-48 was synthesized according to Longloilert *et al.* (2011). The molar ratio of gel composition was 1.0SiO₂:0.3CTAB:0.5NaOH:62.0H₂O:xFe:yTi (or yCe). where 0.01 ≤ x, y ≤ 0.09. A desired amount of metal precursors was dissolved in water, followed by addition of 2 M NaOH while the solution was continuously stirred. The solution was slightly

heated at 323 K and simultaneously added CTAB. Then silatrane was added and stirred for 1 h. The mixture was transferred into a teflon-lined stainless steel vessel and autoclaved at 413 K for 16 h. The solid product was filtered and washed with distilled water. The sample was calcined at 823 K for 6 h with a heating rate of 274.5 K/min after drying. MCM-48, Fe-MCM-48 and Ti-MCM-48 were also prepared using the same procedure.

3.4.2 Synthesis of TUD-1 and Fe-Ti-TUD-1

Synthesis of Fe-Ti-TUD-1 followed the work done by Tunglamert *et al.* (2011) who synthesized Ti-TUD-1. The molar ratio composition was $\text{SiO}_2:0.7\text{TEAOH}:14\text{H}_2\text{O}:x\text{Fe}:y\text{Ti}$, where $0.01 \leq x, y \leq 0.09$ was prepared by adding a required amount of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ in 0.90 g of water, followed by dissolving 4.50 g of silatrane and stirring for 1 h. 4.21 g of TEAOH was added dropwise into the mixture, followed by adding a desired amount of $\text{Ti}(\text{OCH}(\text{CH}_3)_2)_4$. After aging for 2 h at room temperature, the synthesized solution was dried at 373 K for 24 h. The organic residue was removed by calcination at 873 K for 10 h using a heating rate of 1°C/min. TUD-1, Fe-TUD-1 and Ti-TUD-1 were also synthesized using the same procedure for comparison.

3.5 Catalytic Activity Study

Phenol hydroxylation was carried out in two systems: thermal and photocatalytic systems. In the thermal reaction, a 50 ml reaction flask fitted with a water condenser was heated at 303–363 K. Phenol (1.88 g, 20 mmol) and 30% aqueous H_2O_2 (2.28 g, 20 mmol) were mixed in 10 ml of water before heating the mixture in an oil bath with vigorous stirring. (Adam *et al.*, 2010) For the photocatalytic study, the same solution as the hydrothermal study before heating was exposed to UV light from a UV lamp (100 W Hg Sylvania UV lamp). The reaction products were analyzed by HPLC. All reactions were repeated three times and average values were used in the data presentation.

3.6 Leaching and Recycling of the Catalysts

Leaching of metal ions from the catalyst was investigated at 363 K. The catalyst sample was filtered off after 30 min reaction time and allowed the reaction mixture to undergo further reaction in the oil bath at the same temperature for 1 h. The solutions before and after filtration were analyzed by HPLC. The filtered catalyst was washed with distilled water, dried, and calcined at 773 K for 2 h before carrying out the next run.

3.7 Hydrothermal Stability Test

After running the reaction at 363 K for 1 h, the catalysts were recovered by filtration, washed with distilled water, and calcined at 773 K for 2 h. The stability of the samples was analyzed using XRD and nitrogen adsorption.