

CHAPTER III

EXPERIMENTAL

3.1 Materials

Fumed silica (SiO_2 , 99.8%, Nippon Aerosil, Japan), UHP grade nitrogen (N_2 , 99.99% purity, Thai Industrial Gases Public Company Limited (TIG), Thailand), ethylene glycol (EG, 99%, J.T. Baker, USA), TEA (QRĕc chemical, Thailand), acetonitrile (CH_3CN , 99.9%, Labscan, Thailand), methanol (CH_3OH , 99.9%, Labscan, Thailand), TEAOH (35% in water) (Sigma-Aldrich, USA), CAT (99%, Sigma-Aldrich, USA), HQ (99%, Sigma-Aldrich, USA), BQ (98%, Sigma-Aldrich, USA), phenol detached crystals (Fisher scientific, UK), hydrogen peroxide (H_2O_2 , 30% w/v, Fisher scientific, UK), iron (III) chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, Sigma-Aldrich, USA), and titanium (IV) isopropoxide (98%, Acros organics, USA) were used without further purification.

3.2 Precursor Synthesis

3.2.1 Synthesis of Silatrane

Wongkasemjit's synthetic method was followed by mixing fumed silica (0.1 mol), EG (100 ml), and TEA (0.125 mol) (Charoenpinijkarn *et al.*, 2001). The mixture was refluxed at 200 °C under N_2 atmosphere for 10 h in oil bath. The excess EG and water were removed under vacuum at 100 °C. The product was washed by acetonitrile to remove TEA and EG residue. The silatrane product was vacuum-dried overnight before characterization using TGA and FT-IR.

3.2.2 Synthesis of Fe,Ti loaded TUD-1

The synthesis of Fe,Ti-TUD-1 was carried out according to Wongkasemjit's method (Tanglumlert *et al.*, 2011). A desired amount of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ was dissolved in de-ionized water and the solution was stirred continuously, followed by adding silatrane precursor into the mixture. After that titanium (IV) isopropoxide was slowly added, the mixture was stirred for 1 h, followed by slow

introduction of TEAOH. The mixture was aged at room temperature for 4 h before drying at 100 °C for 24 h. The molar ratio of the mixture was 1.0 silatrane:14H₂O:0.7TEAOH:xTi,yFe, where 0.01 ≤ x, y ≤ 0.09. The resulting material was calcined at 600 °C for 10 h using a heating rate of 1 °C/min. Si-TUD-1, Fe-TUD-1 and Ti-TUD-1 were also synthesized using the same procedure as the bimetallic TUD-1, for comparison.

3.3 Materials Characterization

The phase of mesoporous products was characterized on a Rigaku TTRAX III Small Angle X-Ray Diffraction (SAXD) with a scanning speed of 1 °/min and CuK α source ($\lambda = 0.154$ Å) in a range of $2\theta = 0.4$ – 8° . Wide Angle X-Ray Diffraction (WAXD) was performed on a Rigaku Smartlab[®] with a scanning speed of 10 °/min and CuK α source ($\lambda = 0.154$ Å) in a range of $2\theta = 20$ – 80° to determine the metal nanocrystals. The specific surface area was measured by the Brunauer-Emmett-Teller (BET) method and the pore size distribution was calculated by the Barrett-Joyner-Halenda (BJH) on a Quantasorb Jr. (Autosorb-1). Prior to each analysis, the product was degassed at 250 °C for 12 h. Thermal properties were analyzed by Thermal gravimetric analysis-Fourier transform infrared spectrometry (TGA-FTIR) on Pyris Diamonds Perkin Elmer using a heating rate of 10 °C/min under N₂ atmosphere. FTIR analysis was conducted on a Perkin Elmer (Spectrum One) with a scanning resolution of 4 cm⁻¹ to investigate functional groups of the synthesized precursors. Powder specimens contained 1.0% sample with 99% potassium bromide (KBr). Identification of Fe,Ti loaded TUD-1 framework was observed by Diffused reflectance ultraviolet-visible spectrometer (DRUV) on a Shimadzu UV-2550 using BaSO₄ as the reference. The metal contents in samples were observed by X-ray fluorescence (XRF) on AXIOS PW 4400.

3.4 Activity Study

The study was followed Adam and coworkers' method (Adam *et al.*, 2010) for the oxidation of phenol by dissolving phenol (1.88 g, 20 mmol) in 10 mL of water. The mixture was then transferred into in a 50 mL double-necked round-bottom flask fitted with a water-cooled condenser, containing 30 mg of catalyst and immersing in an oil bath was added drop-wise to the vigorously stirred (600 rpm) reaction mixture. Aliquots of the reaction mixture (0.5 cm³) were periodically withdrawn using a syringe. The samples were analyzed by a UFLC Shimadzu high performance liquid chromatography (HPLC) equipped with a C-18 reverse-phase column (Inertsil ODS-3) and a UV detector (SPD-M20A Shimadzu). The products were further confirmed by comparing the HPLC of the respectively pure CAT, BQ, and HQ. All reactions were performed in triplicate and average values were used in the data presentation (Adam *et al.*, 2010).

3.5 Leaching and Reusable Study

Leaching of metal ions from the catalyst was determined by filtering off the catalyst from the reaction mixture after 30 min by using hot filtration technique. The hot filtrate was transferred without delay into a round bottom flask which had been immersed in oil bath at the same temperature. The reaction was allowed to continue for 1 h (without the catalyst) and the course of the reaction was monitored periodically by HPLC-UV to compare with the results before hot filtration (Adam *et al.*, 2010).

Reusability was studied by regenerating the catalyst by washing with distilled water, dried in an oven at 353K for 6 h and calcined at 500 °C for 2 h with a 0.5 °C/min heating rate. The catalyst was collected and reused for further runs, as described elsewhere (Adam *et al.*, 2010).