

CHAPTER III

EXPERIMENTAL

3.1 Materials

Fumed silica (SiO_2 , 99.8%, Aerosil®380, Nippon Aerosil Co, Ltd. Japan), titanium(IV) isopropoxide (98%, Acros organics, USA), iron(III) chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, Sigma-Aldrich, USA), triethanolamine (TEA, synthesis grade, Carlo Erba, Milan, Italy), ethylene glycol (EG, 99%, AR grade, J.T. Baker, Philipsburg, NJ), UHP grade nitrogen (N_2 , 99.99% purity, Thai Industrial Gases Public Company Limited (TIG), Thailand), acetonitrile (CH_3CN , 99.9%, HPLC grade, Labscan, Bangkok, Thailand), poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) ($\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$, Pluronic123 or P123, Sigma-Aldrich, Singapore), hydrochloric acid (HCl, 37%, Labscan, Thailand), catechol (CAT, 99%, Sigma-Aldrich, USA), hydroquinone (HQ, 99%, Sigma-Aldrich, USA), 1,4-benzoquinone (BQ, 98%, Sigma-Aldrich, USA), phenol detached crystals (Fisher scientific, UK), hydrogen peroxide (H_2O_2 , 30% w/v, Fisher scientific, UK). All chemicals were used without further purification.

3.2 Materials Characterization

The products were characterized by Small-angle X-ray scattering (SAXS) spectroscopy for phase identification of a crystalline material and information on unit cell dimensions, using Rigaku TTRAX III equipped with $\text{CuK}\alpha$ ($\lambda_{\text{av}}=0.154$ nm) radiation generated at 50 kV and 30 mA over the 2θ range of $0.4-5^\circ$. Wide Angle X-Ray Diffraction (WAXD) was performed on a Rigaku Smartlab® with a scanning speed of $10^\circ/\text{min}$ and $\text{CuK}\alpha$ source ($\lambda=0.154$ Å) in a range of $2\theta = 20-80^\circ$ to determine the metal nanocrystals. Field emission scanning electron microscopy (FESEM, JSM-7001F) was used to collect secondary electron images from powder mounted on double-sided carbon tape using a Zeiss Ultra plus and operating at 0.3–0.5 kV to minimize charging. Nitrogen adsorption and desorption isotherms were

measured at -196 °C after outgassing at 250 °C for 12 h under vacuum (Quantasorb JR, Mount Holly, NJ) to determine the Brunauer–Emmett–Teller (BET) specific surface area. The pore size distributions were obtained from the adsorption and desorption branches of the nitrogen isotherms by the Barrett-Joyner-Halenda method. Thermal properties were analyzed by Thermal gravimetric analysis-Fourier transform infrared spectrometry (TGA-FTIR) on Pyris Diamond Perkin Elmer using a heating rate of 10 °C/min under N₂ atmosphere. FTIR analysis was conducted on a vector 3.0 Bruker Instrument (Equinox 55) 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). Diffuse reflectance UV-visible (DRUV) spectroscopic measurements were carried out on a Shimadzu UV-2550 spectrophotometer recorded from 200 to 900 nm and using BaSO₄ as a reference. It was used for identification and characterization of metal ion coordination in- or extra-framework of SBA-15 after calcination. The metal contents in samples were observed by X-ray fluorescence (XRF) on AXIOS PW 4400.

3.3 Precursor Synthesis

3.3.1 Silatrane Synthesis

The silatrane precursor was synthesized from fumed silica and TEA in EG solvent. By following the method cited elsewhere (Samran *et al.*, 2011), 18.6 g of TEA was refluxed with 6 g of fumed silica in 100 mL of EG at 200 °C under nitrogen atmosphere for 12 h using an oil bath as a heat source. Excess EG was removed under vacuum at 110 °C to obtain a crude brown solid, followed by washing with acetonitrile to remove unreacted TEA and excess EG. The white silatrane product was obtained and vacuum dried overnight in desiccator.

3.4 Catalyst Synthesis

3.4.1 Synthesis of SBA-15

SBA-15 was synthesized at room temperature from homemade silatrane using P123 as structural directing agent in acidic conditions. The P123 (4 g) was dissolved in 2M HCl (80 g, part A) and stirred for 1 h. For part B, silatrane (8.8 g) was dissolved in H₂O (20 g) and then continuously stirred for 1 h to obtain homogenous solution. The solution from part B was then poured into part A and stirred at room temperature for 24 h; the product was recovered by filtration, washed with deionized water, and dried overnight under ambient conditions. The obtained solid was calcined at 550 °C in air for 6 h with a heating rate of 0.5°C/min to remove the residual organics (Samran *et al.*, 2011).

3.4.2 Synthesis of Ti-SBA-15

Ti-SBA-15 was synthesized from silatrane as silica source, titanium(IV) isopropoxide as titanium source, P123 as the structure-directing agent, and 2 M HCl as the acid catalyst, using various Ti/Si molar ratios (0.01, 0.03, 0.05, 0.07 and 0.09). For part A, 4 g of P123 was dissolved in 80 g of 2 M HCl and stirred until it was completely dissolved. For part B, 8.8 g of silatrane was stirred in 20 g of H₂O for 1 h or until it became homogenous solution. The solution of part B was then poured into part A. The required amount of titanium(IV) isopropoxide was added into the homogenous solution with stirring. The resulting gel was aged at room temperature for 24 h and the product was recovered by filtration, washed with deionized water, and dried overnight at ambient temperature. The products were calcined at 550 °C in air for 6 h at a heating rate of 0.5 °C/min to remove the residual organics prior to characterization (Samran *et al.*, 2011).

3.4.3 Synthesis of Fe-SBA-15

Fe-SBA-15 was synthesized from silatrane and FeCl₃ as silica and iron sources, respectively. P123 as the structure-directing agent and 2 M HCl as the acid catalyst were added. Fe-SBA-15 with different Fe/Si molar ratios (0.01, 0.03, 0.05, 0.07 and 0.09) was prepared. For part A, 4 g of P123 was dissolved in 80 g of 2 M HCl. For part B, the required amount of FeCl₃ and 8.8 g of silatrane were added into 20 g of H₂O, and stirred until it was homogeneous. The solution of part B was

then poured into part A. The resulting gel was aged at room temperature for 24 h and the product was recovered by filtration, washed with deionized water, and dried at ambient condition overnight. The obtained solid was calcined at 550 °C in air for 6 h with a heating rate of 0.5 °C/min to remove residual organics before characterization.

3.4.4 Synthesis of Ti-Fe-SBA-15

Ti-Fe-SBA-15 was synthesized from silatrane, titanium(IV) isopropoxide, and FeCl₃ as silica, titanium, and iron sources, respectively, using P123 as the structure-directing agent and 2 M HCl as acid catalyst. Ti-Fe-SBA-15 with various molar ratios of Ti/Si and Fe/Si (0.01, 0.03, 0.05, 0.07 to 0.09) were prepared.

To synthesize Ti-Fe-SBA-15, 4 g of P123 was dissolved in 80 g of 2 M HCl (part A). For part B, 8.8 g of silatrane and a required amount of FeCl₃ were stirred in 20 g of H₂O for 1 h or until it became homogenous solution. The solution of part B was then poured into part A, followed by adding a required amount of titanium(IV) isopropoxide. The resulting mixture was aged at room temperature for 24 h to obtain crude product. The product was filtered, washed with deionized water, and dried overnight at ambient temperature, followed by calcination at 550 °C in air for 6 h at a heating rate of 0.5 °C/min to remove the residual organics before characterization.

3.5 Catalytic Activity

3.5.1 Phenol Hydroxylation Procedure

The procedure was followed Adam and coworkers' method for the oxidation of phenol by dissolving phenol (1.88 g, 20 mmol) in 10 mL of water (Adam *et al.*, 2010). Then, the mixture was poured into a bottle containing 30 mg of catalyst and immersed in an oil bath at 30°C with continuous stirring. After the reaction temperature was stabilized, H₂O₂ (2.27 ml, 20 mmol) was added into the reaction mixture. Aliquots of the reaction mixture (0.5 cm³) were periodically withdrawn using a syringe. All samples were investigated by HPLC. All reactions were repeated three times and average values were used in the data presentation.

3.5.2 Leaching and Reusability of the Catalyst

Leaching of metal ion from the catalyst was determined by filtering off the catalyst from the reaction mixture after 5 min. The filtrate was transferred without delay into the round bottom flask which had been controlled at the same temperature. The reaction was allowed to continue for an additional 20 min (without the catalyst) and the course of the reaction was monitored periodically by HPLC-UV to compare with the results before 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 heating rate at 0.5 °C/min. The catalyst was collected and reused for further runs, as described earlier (Adam *et al.*, 2010).