



CHAPTER III EXPERIMENT

3.1 Equipment and Materials

Equipment:

3.1.1 Fourier Transform Infrared Spectrophotometer (FT-IR)

Infrared spectroscopy provided functional groups information on the vibration of the precursors (silatrane, molybdenum glycolate and titanium glycolate). The spectra were obtained on a Nicolet, NEXUS 670 with a resolution of 4 cm^{-1} . The solid samples were mixed and pelletized with dried KBr.

3.1.2 Thermal Gravimetric Analyser (TGA)

TGA thermograms were carried out using TG-DTA (Pyris Dimond Perkin Elmer) with a heating rate of $10\text{ }^{\circ}\text{C}/\text{min}$ in a range of room temperature to $750\text{ }^{\circ}\text{C}$ under nitrogen atmosphere to determine the thermal stability of silatrane, molybdenum glycolate, and titanium glycolate.

3.1.3 Small-angle X-ray Scattering (SAXS)

SAXS patterns were carried out to characterize crystallinity of catalysts on a PANalytical PW3830 X-ray instrument with $\text{CuK}\alpha$ as a X-ray source. Samples were spread on adhesive tape and mounted on an aluminum frame. A 2θ range from 0.05° to 5° was investigated using a rate of $0.02^{\circ}/\text{min}$.

3.1.4 Transmission Electron Microscope (TEM)

TEM images were carried out to study the mesoporous order on a JEOL JEM-2100F TEM instrument. The sample's powder was lightly ground under ethanol, sometimes with the introduction of liquid nitrogen to enhance fracture and produce thin flakes that were dispersed ultrasonically. Two drops of the suspension were deposited on carbon-coated copper grid.

3.1.4 Diffuse Reflectance UV-VIS Spectroscopy (DR-UV)

DR-UV was extensively used to detect the framework and extra-framework of iron, molybdenum and titanium species using SHIMADZU UV 2550-VISIBLE spectrophotometer in a range of 200 to 600 nm.

3.1.5 Surface Area and Average Pore size Analyzer

Surface area and average pore size were measured by BET method using a Quantachrome JR. (Autosorb 1). The catalysts were degassed at 250 °C for 20 h before analysis.

3.1.7 Gas Chromatography (GC)

Products of the styrene oxidation reaction were analyzed using a GC equipped with FID detector.

Chemicals:

Fumed silica (SiO₂, 99.8%, Sigma-Aldrich, USA), triethanolamine (TEA, Carlo Erba), ethylene glycol (EG, J.T. Baker, USA), acetonitrile (Labscan, Asia), poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) (EO₂₀PO₂₀EO₂₀) (P123, Sigma-Aldrich, USA), hydrochloric acid (HCl, Labscan, Asia), ferric chloride (FeCl₃, Sigma-Aldrich, USA), titanium oxide (TiO₂, Sigma-Aldrich, USA), triethylenetetramine (TETA, Facai polytech, Thailand), and molybdenum oxide (MoO₃) (Fluka) were directly used without further treatment.

3.2 Methodology

3.2.1 Preparation of Silatrane Precursor (Wongkasemjit *et al.*, 2001).

Silatrane precursor was synthesized via Oxide One Pot Synthesis (OOPS) process by mixing SiO₂ and TEA in a simple distillation set using EG as solvent. Reaction was heated to 200 °C under N₂ atmosphere and kept running for 10 h. Then, EG was removed under vacuum to obtain crude solid product which was washed with acetonitrile and dried in desiccator.

3.2.2 Synthesis of Mesoporous SBA-15 (Samran *et al.*, 2008)

Mesoporous siliceous SBA-15 was prepared using silatrane and P123 as silica precursor and a template agent under acidic condition. A solution of P123:HCl:silatrane:H₂O = 1:20:2.25:5 (mass ratio) was prepared by dissolving 4 g of P123 in 80 g of 2 M HCl (part A) and 8.8 g of silatrane in 20 g of H₂O (part B) with continuously stirring for 1 h to ensure complete dissolution. Then, the part B solution was poured into the part A and stirred at room temperature for 24 h. The resulting

solid was recovered by filtration, washed with deionized water, and dried under ambient conditions. Then, it was calcined at 550 °C for 6 h in air to remove the residual organic template materials, yielding the final mesoporous SBA-15 materials. The product obtained was characterized using SAXS, SEM, TEM and BET.

3.2.3 Synthesis of Fe-SBA-15

Fe-SBA-15 was synthesized using silatrane and FeCl₃ as silica and iron precursors, respectively. Non-ionic triblock copolymer surfactant P123 was used as the structure directing agent. HCl was used as acid source.

The preparation procedure of Fe-SBA-15 material was described as follows: 2 g of P123 was dissolved in 40 mL of 2M HCl (solution A) and 4.5 g of silatrane was mixed with 10 mL of deionized water to get solution B. Solution A and solution B were stirred at room temperature for 1 h. Then, solution B and FeCl₃ (Fe/Si molar ratio = 0.01, 0.03, 0.05, 0.10, and 0.15) were added to solution A and kept stirring at room temperature for 24 h. After that, the resultant solid was filtered, washed with deionized water, and dried at ambient temperature overnight before further calcining at 550 °C for 6 h. The product was characterized using SAXS, DRUV, SEM, TEM and BET.

3.3.4 Synthesis of Titanium Glycolate (Wongkasemjit *et al.*, 2001)

Titanium glycolate was synthesized by mixing TiO₂ (2 g) and TETA (3.65 g) with stirring vigorously in excess EG (25 mL), and heating to 200 °C for 24 h. The resulting solution was centrifuged to separate the unreacted TiO₂. The excess EG and TETA was removed by vacuum distillation to obtain a crude precipitate. The white solid product was washed with acetonitrile 3 times, dried in a vacuum desiccator.

3.3.5 Synthesis of Ti-SBA-15

Ti-SBA-15 was synthesized using silatrane and titanium glycolate as silica and titanium precursors, respectively. Non-ionic triblock copolymer surfactant P123 was used as the structure directing agent. HCl was used as acid source.

The preparation procedure of Ti-SBA-15 material was described as follows: 2 g of P123 was dissolved in 40 ml of 2M HCl (solution A) and 4.5 g of silatrane was mixed with 10 mL of deionized water to get solution B. Solution A and solution B were stirred at room temperature for 1 h. Then, solution B and titanium

glycolate (Ti/Si molar ratio = 0.01, 0.03, 0.05, 0.07, and 0.10) were added to solution A and kept stirring at room temperature for 24 h. After that, the resultant solid was filtered, washed with deionized water, and dried at ambient temperature overnight and further calcined at 550 °C for 6 h. The product was characterized using SAXS, DRUV, SEM, TEM and BET.

3.3.6 Synthesis of Molybdenum glycolate (Sutara *et al.*, 2004)

Molybdenum glycolate was synthesized by mixing MoO₃ (4.29g) and EG (50 mL) with vigorously stirring and heating to 150 °C under N₂ atmosphere for 15 min. The obtained solution was centrifuged to separate the unreacted MoO₃. The solution part was left at room temperature for 3 days to obtain molybdenum glycolate solid, followed by washing with acetonitrile and drying in desiccator.

3.3.7 Synthesis of Mo-SBA-15

Mo-SBA-15 was synthesized using silatrane and molybdenum glycolate as silica and molybdenum precursors, respectively. Non-ionic triblock copolymer surfactant P123 was used as the structure directing agent. HCl was used as acid source.

The preparation procedure of Mo-SBA-15 material was described as follows: 2 g of P123 was dissolved in 40 mL of 2M HCl (solution A) and 4.5 g of silatrane was mixed with 10 mL of deionized water to get solution B. Solution A and solution B were stirred at room temperature for 1 h. Then, solution B and molybdenum glycolate (Mo/Si molar ratio = 0.0025, 0.005, 0.075, 0.010, and 0.0125) were added to solution A and kept stirring at room temperature for 24 h. After that, the resultant solid was filtered, washed with deionized water and dried at ambient temperature overnight and further calcined at 550 °C for 6 h. The product was characterized using SAXS, DRUV, SEM, TEM and BET.

3.3.8 Catalytic Activity Study of Ti-SBA-15

The catalytic activity of the catalyst was studied using the selective oxidation reaction of styrene. Ten mmol of styrene, 10 mmol of 30 % H₂O₂, (x) g of catalyst and 20 mL of acetonitrile were mixed in a 50 mL glass flask and heated to certain temperature. The products were analyzed using a GC equipped with FID detector. The studied factors were reaction temperature, reaction time, amount of

catalyst used, and amount of Ti loaded. The conversion of styrene were calculated on the basis of the amount of styrene monomer used.