

## CHAPTER III EXPERIMENTAL

### 3.1 Materials

Fumed silica ( $\text{SiO}_2$ , 99.8%) (Sigma-Aldrich, St. Louis, MO), titanium dioxide ( $\text{TiO}_2$ ) (Carlo Erba, Milan, Italy), ferric chloride ( $\text{FeCl}_3$ ) (Sigma-Aldrich, St. Louis, MO), molybdenum (VI) oxide (Fluka, Asia), triethanolamine (TEA) (Carlo Erba, Milan, Italy), tetraethylenetriamine (TETA) (Facai, Bangkok, Thailand), ethylene glycol (EG) (J.T. Baker, Philipsburg, NJ), acetonitrile (Labscan, Bangkok, Thailand), poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) ( $\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$ ) (Sigma-Aldrich, Singapore), hydrochloric acid (HCl) (Labscan, Asia), hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) (Labscan, Asia), and styrene monomer (Labscan, Asia) were used without further purification or treatment.

### 3.2 Materials Characterization

The products were characterized by powder X-ray diffraction with a PANalytical PW3830 instrument using  $\text{CuK}\alpha$  ( $\lambda_{\text{av}}=0.154$  nm) radiation generated at 50kV and 40 mA, over the  $2\theta$  range  $0.5\text{--}10^\circ$ , step size of  $0.01^\circ$  and dwell time of 10 seconds per step. Transmission electron microscopy (TEM) was conducted using a Hitachi H-7100FA machine operating at 125 kV with a large objective aperture. Field emission scanning electron microscopy (FESEM) was used to collect secondary electron images from powders mounted on double-sided carbon tape using a Zeiss Ultra plus, operating at 0.3-0.5 kV to minimize charging. Nitrogen adsorption and desorption isotherms were measured at  $-196^\circ\text{C}$  after outgassing at  $250^\circ\text{C}$  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. Diffuse reflectance UV-visible (DRUV) spectroscopic measurements were recorded on a Shimadzu UV-2550

spectrophotometer fitted with an ISR-2200 integrating sphere attachment and recorded from 190–600 nm and using BaSO<sub>4</sub> as a reference. The reflectance output from the instrument was converted using Kubelka-Munk algorithm.

### 3.3 Precursor Synthesis

#### 3.3.1 Silatrane Synthesis

The silatrane precursor was synthesized from fumed silica (SiO<sub>2</sub>) solubilized in triethanolamine (TEA) with ethylene glycol (EG) employed as the solvent, and acetonitrile used for silatrane purification. Following the method of Wongkasemjit *et al.* 0.125 mol TEA was refluxed with 0.1 mol silicon dioxide in ethylene glycol (100 ml) at 200 °C under nitrogen for 10 hr in an oil bath. Excess ethylene glycol was removed under vacuum at 110 °C to obtain a crude brown solid that was washed with acetonitrile to remove TEA and EG residues. The white silatrane product was vacuum dried overnight then examined by Fourier-transform infrared (FT-IR) absorption spectrometry (Bruker Optics EQUINOX55, Karlsruhe, Germany) at a resolution of 2 cm<sup>-1</sup>, and thermogravimetric analysis (DuPont 2950, Twin Lakes, WI) at a heating rate of 10°C/min from room temperature to 750 °C in a nitrogen atmosphere.

#### 3.3.2 Titanium Glycolate Synthesis

A mixture of titanium dioxide (TiO<sub>2</sub>) (0.025 mol, 2 g), triethylenetetramine (TETA) (0.007 mol, 3.7 g), used as a catalyst, and 25 ml of ethylene glycol (EG), used as a solvent were heated to the boiling point of EG for 24 h, followed by separating the unreacted TiO<sub>2</sub> from the solution part. The excess EG and TETA were removed by vacuum distillation to obtain the crude white solid product. The crude product was then washed with acetonitrile and dried in a vacuum desiccator before characterization using FTIR and TGA.

#### 3.3.3 Molybdenum Glycolate Synthesis

Molybdenum glycolate was synthesized following the method of Sutara *et al.* by mixing molybdenum oxide (MoO<sub>3</sub>) and ethylene glycol (EG) with vigorous stirring and heating at the boiling point of EG under N<sub>2</sub> atmosphere for 15

min. The obtained solution was centrifuged to separate the unreacted  $\text{MoO}_3$ . The solution part was left at room temperature for 3 days to obtain molybdenum glycolate solid, followed by washing with acetonitrile and drying in a vacuum dessicator.

### 3.4 Catalyst Synthesis

#### 3.4.1 Synthesis of SBA-15

Mesoporous SBA-15 was synthesized from silatrane with poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) ( $\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$ ) (P123) employed as the template, and hydrochloric acid (HCl) as the catalyst in accord with the procedure of Stucky *et al.* A solution of  $\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}:\text{HCl}:\text{silatrane}:\text{H}_2\text{O} = 2:60:4.25:12$  (mass ratio) was prepared by dissolving 4 g of  $\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$  polymer in 80 g of 2 M HCl (part A) and 8.8 g of silatrane in 20 g of  $\text{H}_2\text{O}$  (part B) with stirring continued for 1 hr to ensure complete dissolution. For Route 1 synthesis, the solution of part B was then poured into part A, stirred at room temperature (RT) for 24 h, the product was recovered by filtration, washed with deionized water, and dried overnight under ambient conditions. For hydrothermally treated sample, the RT product was placed in a microwave oven at 300W for 1–2 h at 100 or 120 °C. After cooling to RT, the material was filtered, washed and dried. The obtained silicas were calcined at 550 °C in air for 6 hr using a tube furnace (Carbolite, CFS 1200, Hope Valley, U.K.) at a heating rate of 1 °C/min to remove the residual organics.

#### 3.4.2 Synthesis of Ti-SBA-15

Ti-SBA-15 materials were synthesized from silatrane and titanium-glycolate. The non-ionic triblock copolymer surfactant  $\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$  was used as the structure-directing agent and 2 M HCl was the acid catalyst. The preparation of Ti-SBA-15 with various  $n_{\text{Ti}}/n_{\text{Si}}$  molar ratios followed the method of Samran *et al.* A solution of  $\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}:\text{HCl}:\text{silatrane}:\text{H}_2\text{O} = 2:60:4.25:12$  (mass ratio) was prepared by dissolving 4 g of  $\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$  polymer in 80 g of 2 M HCl (part A) and 8.8 g of silatrane, in 20 g of  $\text{H}_2\text{O}$  (part B) with continuously stirring for 1 h to ensure complete dissolution. The solution of part B was then poured into part A. The

required amount of titanium glycolate was added into the homogenous solution with stirring. The resulting gel was aged at room temperature (RT) for 24 h and the product recovered by filtration, washed with deionized water, and dried overnight at ambient. Silicas were calcined at 550 °C in air for 6 h using a tube furnace (Carbolite, CFS 1200, Hope Valley, U.K.) at a heating rate of 0.5 °C/min to remove the residual organics. The catalysts were designated as (*x*) mol% Ti-SBA-15 where *x* denotes the percentage of the  $n_{Ti}/n_{Si}$  ratio. Ti-SBA-15 was also prepared by incipient wetness impregnation method to deposit Ti metal on the SBA-15 support, using 7 and 10 mol% titanium glycolate. The precursor was dissolved in water and dropped onto the catalyst supports. Drying was carried out at 100 °C for 12 h, followed by calcination (550 °C/6 h) in a Carbolite furnace (CFS 1200) at a heating rate of 0.5 °C/min.

#### 3.4.3 Synthesis of Fe-SBA-15

Fe-SBA-15 was synthesized from silatrane and FeCl<sub>3</sub> as the silica and iron sources, respectively. The non-ionic triblock copolymer surfactant EO<sub>20</sub>PO<sub>70</sub>EO<sub>20</sub> was used as template and 2 M HCl was the acid catalyst. The preparation of Fe-SBA-15 with different  $n_{Fe}/n_{Si}$  molar ratios followed the method of Samran *et al.* A solution of EO<sub>20</sub>PO<sub>70</sub>EO<sub>20</sub>:HCl:silatrane:H<sub>2</sub>O = 2:60:4.25:12 (mass ratio) was prepared by dissolving 4 g of EO<sub>20</sub>PO<sub>70</sub>EO<sub>20</sub> polymer in 80 g of 2 M HCl (part A) and 8.8 g of silatrane in 20 g of H<sub>2</sub>O (part B) with continuous stirring for 1 h to ensure complete dissolution. The solution of part B was then poured into part A. The required amount of FeCl<sub>3</sub> was added to the homogenous solution with stirring. The resulting gel was aged at room temperature (RT) for 24 h and the product recovered by filtration, washed with deionized water, and dried at ambient overnight. This resin was calcined (550 °C/air/6 h) in a tube furnace (Carbolite, CFS 1200, Hope Valley, U.K.) at a heating rate of 0.5 °C/min to remove residual organics. The catalysts were designated as (*x*) mol% Fe-SBA-15 where *x* denotes the  $n_{Fe}/n_{Si}$  percentage used during synthesis. Fe-SBA-15 was also prepared by incipient wetness impregnation method by dropping an FeCl<sub>3</sub> solution (40 mg/ml) onto SBA-15 followed by oven drying (100 °C/12 h) and air calcination (550 °C/6 h) in a carbolite tube furnace (CFS 1200) at a heating rate of 0.5 °C/min.

### 3.4.4 Synthesis of Mo-SBA-15

Mo-SBA-15 was synthesized from silatrane and molybdenum glycolate as the silica and molybdenum sources, respectively. The non-ionic triblock copolymer surfactant  $\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$  was used as the structure directing agent and 2 M HCl was the acid catalyst. The preparation of Mo-SBA-15 with different  $n_{\text{Mo}}/n_{\text{Si}}$  molar ratios followed the method of Samran et al. A solution of  $\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}:\text{HCl}:\text{silatrane}:\text{H}_2\text{O} = 2:60:4.25:12$  (mass ratio) was prepared by dissolving 4 g of  $\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$  polymer in 80 g of 2 M HCl (part A) and 8.8 g of silatrane in 20 g of  $\text{H}_2\text{O}$  (part B) with continuous stirring for 1 h to ensure complete dissolution. The solution of part B was then poured into part A. The required amount of molybdenum glycolate was added to the homogenous solution with stirring. The resulting gel was aged at room temperature (RT) for 24 h and the product recovered by filtration, washed with deionized water, and dried at ambient overnight. This obtained product was calcined ( $550\text{ }^\circ\text{C}/\text{air}/6\text{ h}$ ) in a tube furnace (Carbolite, CFS 1200, Hope Valley, U.K.) at a heating rate of  $0.5\text{ }^\circ\text{C}/\text{min}$  to remove residual organics. The catalysts were designated as ( $x$ ) mol% Mo-SBA-15 where  $x$  denotes the  $n_{\text{Mo}}/n_{\text{Si}}$  percentage used during synthesis. For comparison, incipient wetness impregnation method was used to deposit molybdenum species on the SBA-15 support, using 1.0 and 1.25 mol% molybdenum glycolate. The precursor was dissolved in water and dropped onto the catalyst supports. Drying was carried out at  $100\text{ }^\circ\text{C}$  for 12 h, followed by calcination ( $550\text{ }^\circ\text{C}/6\text{ h}$ ) in a Carbolite furnace (CFS 1200) at a heating rate of  $0.5\text{ }^\circ\text{C}/\text{min}$ .

## 3.5 Catalytic Activity Testing

### 3.5.1 Catalytic Testing of Ti-SBA-15, Fe-SBA-15 and Mo-SBA-15

The catalytic activity of Ti-SBA-15, Fe-SBA-15 and Mo-SBA-15 towards epoxidation of styrene monomer was measured from data collected in a batch reactor. The catalyst (0.05-0.15 g), styrene (5 mmol), hydrogen peroxide (2.5-15 mmol of 30 wt% aqueous solution) and acetonitrile (5 ml) were introduced to a glass flask with closed cap (30 ml). The reactant mixture was stirred and heated for a

specific time and temperature in an oil bath. The products were identified and quantified by gas chromatography (GC) employing a capillary column (DB-Wax, 30 m x 0.25 mm) and flame ionization detector (FID). The conversion of styrene was calculated based upon the quantity of styrene monomer consumed.