

CHAPTER III EXPERIMENTAL

3.1 Materials

Fumed silica (SiO_2), G4 PAMAM dendrimer amine-terminated and iron (III) chloride (FeCl_3) were purchased from Aldrich Chemical Co. Titanium dioxide (TiO_2) and hydrogen peroxide (H_2O_2) was purchased from Carlo Erba. Ethylene glycol (EG, $\text{HOCH}_2\text{CH}_2\text{OH}$), sulfuric acid, sodium hydroxide, acetonitrile (CH_3CN) triethanolamine (TEA, $\text{N}(\text{CH}_2\text{CH}_2\text{OH})_3$) and styrene monomer were supplied by Labscan Asia Co., and used as received. Alkyltrimethylammonium bromide (CnTMAB) was purchased from Sigma Chemical Co.

3.2 Materials Characterization

FTIR spectroscopic analysis was conducted using a Bruker Instrument (EQUINOX55) with a resolution of 4 cm^{-1} . The solid sample was prepared by mixing 1% of sample with anhydrous KBr. Thermal properties were analyzed using Du Pont Instrument TGA 2950 thermogravimetric analysis (TGA). The mesoporous product was characterized using a Rigaku X-ray diffractometer (XRD) with $\text{CuK}\alpha$ source at a scanning speed of 0.75 degree/sec . The working range was $2\theta = 1.5\text{-}10$. Electron microscope study (TEM micrographs and electron diffraction patterns) were carried out using JEOL 2010F. Surface area and average pore size were determined by BET method using a Quantasorb JR. (Autosorb-1). The product was degassed at 250°C for 12 hr prior to analysis. Diffuse reflectance ultraviolet spectroscopy was used to identify the location and the coordination of transition metal in hexagonal structure. The reflectance output from the instrument was converted using Kubelka-Munk algorithm. The metal content was characterized using SEM/EDS and XRF. Particle size analyzer was conducted using Malvern Instrument. The calcination was conducted using a Carbolite Furnace (CFS 1200) with the heating rate of 1°C/min .

3.3 Precursor Synthesis

3.3.1 Silatrane Synthesis

Wongkasemjit's synthetic method was followed by mixing silicon dioxide, and triethanolamine in a simple distillation set using ethylene glycol solvent. The reaction was done at the boiling point of ethylene glycol under nitrogen atmosphere to remove water as a by-product along with ethylene glycol from the system. The reaction was run for 10 hr and the rest of ethylene glycol was removed under vacuum (1.6 Pa) at 110°C. The brownish white solid was washed with acetonitrile for three times to obtain the final white powder product having theoretical ceramic yield of around 19%.

3.3.2 Titanium Glycolate Synthesis

A mixture of titanium dioxide (0.025 mol, 2 g), triethylenetetramine (0.007 mol, 3.7 g), used as a catalyst, and 25 mL of ethylene glycol, used as a solvent were heated to the boiling point of EG for 24 hr, followed by separating the unreacted TiO₂ 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.

3.4 Catalyst Synthesis

3.4.1 Synthesis of SBA-1

The synthesis procedure was as follows. Solution A was prepared by adding the required amount of C_nTMAB (n = 14, 16 and 18) to water (30 ml) and stirring for 0.5 h to obtain a clear solution. Solution B was prepared by adding silatrane (1.4g, 5 mmol) to 14 ml of H₂SO₄ (0.3 – 0.5 M) and NaOH (0.068g, 1.7 mmol), and stirring for 0.5 h to obtain a homogeneous solution. The pH values of the solution B is in the range of 1.5 – 2 around the isoelectric point (IEP) of silica. The solution B was then added to the solution A under vigorous stirring that was continued for 4 h. Before leaving the mixture at room temperature, water (30 ml) was added into the solution mixture. Then the mixture was allowed to age for 2 days at

the desired temperature to form white precipitates. The products were filtered and washed with distilled water and dried overnight in air. Template removal was achieved by calcination at 560°C for 6 h using a Carbolite Furnace (CFS 1200) with a heating rate of 0.5°C/min. The mixture composition in molar ratio was $1.0C_n\text{TMAB} : 5\text{SiO}_2 : 1.7\text{NaOH} : x\text{H}_2\text{SO}_4 : 3680\text{H}_2\text{O}$.

3.4.2 Synthesis of mesoporous silica by using dendrimer porogen template

Silatrane (1.4 g, 5 mmol) was suspended to a solution of 0.3 M H_2SO_4 (14 cm^3), and a solution of NaOH (0.068 g, 1.7 mmol) was added to the suspension. After stirring for 0.5 h, required amount of dendrimer was added to the suspension under vigorous stirring. After 0, 10 and 30 cm^3 of water was added, the mixture was stirred for 4 h and allowed to age for 2-5 days at room temperature. The white precipitates were filtered, washed with water, and dried overnight in the atmosphere (without removed the template). D1, D2, D3 and D4 labeled to the products were synthesized via four concentrations of dendrimer at 1.41, 2.81, 4.22 and 5.64 mM, respectively. The products that 0, 10 and 30 cm^3 of water were added were denoted DnH0, DnH10 and DnH30 ($n = 1 - 4$), respectively.

3.4.3 Synthesis of Fe-SBA-1

The synthesis procedure was as follows. Solution A was prepared by adding $C_{16}\text{TMAB}$ (0.44g) to water (30 ml) and stirring for 0.5 h to obtain a clear solution. Solution B was prepared by dissolving silatrane (1.4g, 5 mmol) in 14 ml of 0.3 M H_2SO_4 and NaOH (0.068g, 1.7 mmol) by stirring for 0.5 h. A required amount of FeCl_3 was added to the solution B and stirring continued for 0.5 h. Solution B was then added to the solution A under vigorous stirring that continued for 4 h. Water (30 ml) was added to this mixture before aging for 2 days at room temperature to form a white precipitate. The product was filtered, washed with distilled water, and dried at room temperature overnight. The template was removed by calcination (560°C / 6 h) in a Carbolite Furnace (CFS 1200) at a heating rate of 0.5°C/min.

3.4.4 Synthesis of Ti-SBA-1

The synthesis procedure was as follows. Solution A was prepared by adding $C_{16}\text{TMAB}$ (0.44g) to water (30 ml) and stirring for 0.5 h to obtain a clear solution. Solution B was prepared by dissolving silatrane (1.4g, 5 mmol) in 14 ml of 0.3 M H_2SO_4 and NaOH (0.068g, 1.7 mmol) by stirring for 0.5 h. A required amount

of titanium glycolate was added to the solution B and stirring continued for 0.5h. Solution B was then added to the solution A under vigorous stirring that continued for 4 h. Water (30 ml) was added to this mixture before aging for 2 days at room temperature to form a white precipitate. The product was filtered, washed with distilled water, and dried at room temperature overnight. The template was removed by calcination (560°C / 6 h) in a Carbolite Furnace (CFS 1200) at a heating rate of 0.5°C/min.

3.5 Catalytic Activity Testing

3.5.1 Catalytic Testing of Fe-SBA-1 and Ti-SBA-1

The epoxidation of styrene is carried out in a 50 ml glass flask to be heated with an oil bath. In a typical run, styrene (1.04 g, 10 mmol), an aqueous 30% H₂O₂ (1.14 g, 10 mmol), were mixed in 10 ml of CH₃CN. The catalyst (50 mg) was added in the reaction and heated at 80°C with continuous stirring. During the reaction, the products were analyzed (by withdrawing small aliquots after specific interval of time) using a gas chromatography (GC) equipped with a capillary column (DB-WAX, 30 Mx0.25 mm) and a FID detector.