

## CHAPTER III EXPERIMENTAL

### 3.1 Materials

Titanium dioxide ( $\text{TiO}_2$ ) (surface area  $12 \text{ m}^2/\text{g}$ ) was purchased from Sigma-Aldrich Chemical Co. Inc. (USA) and used as received.

Ethylene glycol (EG) was purchased from Malinckrodt Baker, Inc. (USA) and purified by fractional distillation at  $200^\circ\text{C}$  under nitrogen at atmospheric pressure, before use.

Triethylenetetramine (TETA) was purchased from Facai Polytech. Co. Ltd. (Bangkok, Thailand) and distilled under vacuum ( $0.1 \text{ mm/Hg}$ ) at  $130^\circ\text{C}$  prior to use.

Acetonitrile ( $\text{CH}_3\text{CN}$ ) was purchased from Lab-Scan Company Co. Ltd. and purified by distilling over calcium hydride powder.

Fumed silica ( $\text{SiOH}$ ) was purchased from Sigma Chemical and used as received.

Triethanolamine (TEA,  $\text{N}(\text{CH}_2\text{CH}_2\text{OH})_3$ ) was supplied by Carlo Erba reagent and used as received.

Sodium hydroxide ( $\text{NaOH}$ ) was purchased from EKA Chemicals and AJAX chemicals, respectively, and used as received.

Tetrapropyl ammonium bromide (TPA,  $\text{C}_{12}\text{H}_{28}\text{BrN}$ ) was obtained from Fluka Chemical AG and used as received.

### 3.2 Experimental Equipment

#### 3.2.1 Fourier Transform Infrared Spectroscopy (FT-IR)

Infrared spectroscopy provides important information on the vibrations of the TS-1 which the spectra are obtained using a Bruker instrument, model EQUINOX 55. The samples are pressed into pellet form with dried KBr.

### 3.2.2 Thermal Gravimetric Analysis (TGA)

TGA thermograms were carried out using a Perkin Elmer thermal analysis system with a heating rate of 10°C/min over 30-800°C temperature range.

### 3.2.3 FAB<sup>+</sup>-Mass Spectroscopy (FAB<sup>+</sup>-MS)

The mass spectrum was obtained on a Fison Instrument (VG Autospec-ultima 707E) with VG data system, using the positive fast atomic bombardment mode (FAB<sup>+</sup>-MS) with glycerol as the matrix, cesium gun as initiator, and cesium iodide (CsI) as a standard for peak calibration.

### 3.2.4 Scanning Electron Microscopy (SEM)

Crystal morphology was characterized using a JEOL 5200-2AE scanning electron microscope.

### 3.2.5 X-Ray Diffraction (XRD)

X-ray diffractometer is used to obtain XRD pattern. Sample (0.1-0.2g.) is ground using alumina morta and spread on a glass slide specimen holder. The CuK $\alpha$  ( $\lambda=0.154$  nm.) radiation is used as an X-ray source. Peak positions are compared with standard JCPDS files, to identify crystalline phases. The XRD patterns are used for average particle diameter estimation (West, 1989) by line broadening measurements in the debye-Scherrer equation,

$$T = K\lambda / B_d \cos\theta \quad (3.1)$$

Where  $\lambda$  is the wavelength (nm)

K is the Debye-Scherrer constant which is equal to 0.9

$B_d$  is the angular width of peak in the term of  $\Delta(2\theta)$ (radian)

$\theta$  is the Bragg angle of the reflection

T is the mean crystalline diameter (nm)

### 3.2.6 UV-Vis Diffuse Reflectance Spectroscopy (DR-UV)

UV-Vis diffuse reflectance spectroscopy is extensively used to detect the framework and extra-framework titanium species using Perkin-Elmer Lambda 800 spectrophotometer from 190 to 400 nm. DR-UV is used to probe the band structure, or molecular energy levels, in the materials since UV excitation creates photo-generated electrons and holes. The band at 220 nm is originated from the charge transfer of the  $p\pi-d\pi$  transition between titanium and oxygen of the framework titanium species, Ti-O-Si, in the zeolite. The tail of the band centered at 220 nm was actually extended to 330 nm due to the presence of extra-framework titanium species,  $TiO_2$ , in the TS-1 zeolite.

### 3.2.7 Microwave

Hydrothermal treatment by microwave heating technique was conducted using a MARS, CEM Corporation. The sample was heated in a Teflon tube using inorganic digestion mode with time-to-temperature programming.

## 3.3 Methodology

### 3.3.1 Silatrane Synthesis

Silatrane (tris(silatranyloxy-ethyl)amine or SiTEA) was synthesized following Wongkasemjit's method (Piboonchaisit *et al.*, 1999) by reacting 0.125 mol triethanolamine with 0.1 mol silicon dioxide using ethylene glycol as solvent at 200°C under nitrogen atmosphere. The reaction was complete within 10 h., and the reaction mixture was allowed to cool to room temperature before removing solvent by distilling under vacuum ( $10^{-2}$  torr) at 110 °C overnight. The resulting brownish white solid was washed three times with dry acetonitrile to obtain a fine white powder.

### 3.3.2 Titanium Glycolate Synthesis

The titanium glycolate was synthesized following Phonthammachai's method [11] by the OOPS method. A mixture of TiO<sub>2</sub> (2g, 0.025 mol) and TETA (3.65g, 0.0074 mol) was stirred vigorously in excess EG (25 cm<sup>3</sup>) and heated at the boiling point of EG under N<sub>2</sub> atmosphere. After heating for 24 h, the solution was centrifuged to separate the unreacted TiO<sub>2</sub> from the solution part. The excess EG and TETA were removed by vacuum distillation to obtain crude precipitate. The white crude solid product was washed with acetonitrile and dried in a vacuum desiccator.

### 3.3.3 TS-1 Synthesis

SiTEA equivalent to 0.21g SiO<sub>2</sub> was dispersed in 6.646 ml of water and continuously stirred before adding NaOH which both hydroxide and Na ion concentrations were controlled by adding calculated amounts of NaOH. The formulation SiO<sub>2</sub>: TPA: NaOH: H<sub>2</sub>O was fixed at 1: 0.1: 0.4: 114. All reaction mixtures were aged at room temperature for various times with continuously stirring prior to heating to the reaction temperature. Different heating and aging time, reaction temperature, ratio of Si/Ti, the effect of TPA and NaOH concentrations, and time period of adding titanium glycolate on morphology of TS-1 crystal are investigated.

### 3.3.4 Characterization

#### 3.3.4.1 *Characterization of titanium glycolate and silatrane precursors*

The obtained precursors were characterized using TGA, FAB<sup>+</sup>-MS and FTIR.

#### 3.3.4.2 *Characterization of TS-1 zeolite*

The crystal morphology of TS-1 was characterized using SEM. The crystal structure was determined using a Rigaku X-ray Diffractometer. The framework and extra-framework titanium species were detected using DR-UV.