

CHAPTER III EXPERIMENTAL

3.1 Materials

All syntheses were carried out with careful exclusion of extraneous moisture by purging under an atmosphere of nitrogen UHP grade nitrogen; 99.99% purity was obtained from Thai Industrial Gases Public Company Limited (TIG).

Titanium dioxide (TiO_2) as a starting material, with a surface area of $12.2 \text{ m}^2/\text{g}$, was purchased from Sigma-Aldrich Chemical Company. It was kept in a dry environment prior to use for preventing moisture adsorption.

Cerium (IV) hydroxide ($\text{Ce}(\text{OH})_4$) containing 87.4% CeO_2 was purchased from Aldrich Chemical Co. Inc. (USA) and used as received.

Triisopropanolamine (TIS) was purchased from Sigma-Aldrich Chemical Co. Inc. (USA) and used as a reaction starting material.

4-Nitrophenol was purchased from Sigma-Aldrich Chemical Co. Inc. (USA) and used as an organic pollutant for photocatalytic reaction.

Ethylene glycol (EG) was purchased from J.T.Baker Company Co., Ltd. and used as reaction starting material and solvent.

Commercial grade triethylenetetramine (TETA) was purchased from Facai Polytech. Co., Ltd. and used as catalytic base.

Acetonitrile was purchased from Lab-Scan Company Co., Ltd., used as received.

Hydrochloric acid, used as solvent, was purchased from BDH Laboratory Supplies and used as received.

Methanol and acetonitrile were purchased from Lab-Scan Company Co. Ltd., and purified by standard techniques.

All glassware is cleaned by soaking in a sodium hydroxide cleaning solution bath, followed by washing, rinsing with water and then drying in an oven at 120°C prior to use.

3.2 Instrumental

3.2.1 Thermogravimetric Analysis (TGA)

TGA thermograms were carried out on a Du Pont instrument, Du Pont TGA 2950. Approximately 5-10 mg of sample was placed into a platinum pan and heated under nitrogen atmosphere at a flow rate of 25°C/min. The temperature program was started from room temperature to 750°C, with a heating rate of 10°C/min.

3.2.2 Nuclear Magnetic Resonance Spectroscopy (NMR)

Solid state ^{13}C -NMR spectra were performed on Bruker 300 MHz spectrometer with cross polarization (CP) and magic angle spin (MAS) compatibility in order to study the structure of titanium glycolate. The sample was washed with acetonitrile for several times and vacuum dried for 1 day prior to use.

3.2.3 Elemental Analysis (EA)

The percent elements were obtained from Perkin Elmer PE 2400 Series II CHNS/O Analyzer with combustion and reduction temperatures at 975° and 500°C respectively and vial receptacle for 1000 runs. The sample was analyzed under air (flowing rate 60 psi) with oxygen as a combustion gas (flowing rate 15 psi) and helium as carrier gas (flowing rate 20 psi).

3.2.4 FAB⁺-MS Spectroscopy (MS)

Mass Spectra were obtained on a VG Autospec-ultima 707E from Fisons, using a direct probe of the positive fast atom bombardment (FAB⁺) mode. Cesium iodide (CsI) was used as a standard for peak calibration. The cesium gun beam, used as an initiator, was set at 2 μA for the optimum resolution. The range studied was set from m/e 20 to 1000.

3.2.5 Fourier Transform Infrared Spectroscopy (FTIR)

Infrared absorption spectra (IR) were recorded on a Bruker FT/IR (model EQUINOX 55) spectrometer using KBr pellets: 1-2 mg of the sample is crushed and mixed with 300 mg of KBr.

3.2.6 X-Ray Diffraction (XRD)

A Rigaku X-ray diffractometer (XRD) system equipped with a RINT 2000 wide angle goniometer and a Cu tube for generating a CuK α 1 radiation ($\lambda = 1.54 \text{ \AA}$) was used to obtain the X-ray diffraction patterns at a generator voltage of 40 kV and a generator current of 30 mA. Nickel filter was used as the K_{β} filter. The goniometer parameters were divergence slit = $1^{\circ}(2\theta)$; scattering slit = $1^{\circ}(2\theta)$; and receiving slit = 0.3 nm. Sample (0.1-0.2 g) was spread on a glass slide. A scan speed of $5^{\circ}(2\theta)/\text{min}$ with a scan step of $0.02^{\circ}(2\theta)$ was used during a continuous run in the 5 to $90^{\circ}(2\theta)$ range.

3.2.7 Scanning Electron Microscopy (SEM)

The scanning electron micrographs were carried out to identify the microstructure of a sample. The samples are characterized using Jeol Scanning Electron Microscope, model JSM 5200.

3.2.8 Rheometric Measurement

A fluid rheometer, model ARES, from Rheometric Scientific., was used to determine the storage and loss shear moduli, $G'(\omega)$, $G''(\omega)$ and $\tan\delta$ as a function of angular frequency (varied from 0.2-6.4 rad/s). A 25 mm. diameter parallel plate was used, with 10 g transducer. The temperature was controlled and set to 30°C using a circulating fluid bath.

3.2.9 BET Surface Area Measurement

The surface areas of all samples were measured by the BET method using a Quantachrome Corporation Autosorb I gas sorption system (Quantachrome

Corporation) via the Brunauer-Emmett-Teller (BET) method. A gaseous mixture of nitrogen and helium was allowed to flow through the analyzer at a constant rate of 30 cc/min. Nitrogen was used to calibrate the analyzer and also as the adsorbate at liquid nitrogen temperature. The samples were thoroughly outgassed for 2h at 150°C, prior to exposure to the adsorbent gas.

3.2.10 Diffuse Reflectance Ultraviolet-Visible Spectroscopy (DR-UV)

The Diffuse reflectance ultraviolet-visible spectra were recorded under ambient conditions on a Shimadzu UV-240 spectrophotometer. The TS-1 samples were packed onto the Teflon holder prior to measure the absorbance of Ti-O-Si bond. The membranes were cut into the square shape and hold on the holder. The measurements were recorded from 500-190 nm.

3.3 Methodology

3.3.1 Synthesis of Titanium Alkoxides

3.3.1.1 *Preparation of Titanium Glycolate*

A mixture of TiO₂ (2g, 0.025 mol) and TETA (3.65g, 0.0074 mol) was stirred vigorously in excess EG (25 cm³) and heated to 200°C for 24 h. The resulting solution was centrifuged to separate the unreacted TiO₂. The excess EG and TETA were removed by vacuum distillation to obtain a crude precipitate. The white solid product was washed with acetonitrile, dried in a vacuum desiccator and characterized using FTIR, ¹³C-solid state NMR, EA, FAB⁺-MS and TGA.

3.3.1.2 *Preparation of Titanium Triisopropanolamine*

A mixture of TiO₂ (2g, 0.025 mol), triisopropanolamine (9.55g, 0.05 mol) and triethylenetetramine (3.65g, 0.0074 mol) was stirred vigorously in excess ethylene glycol (25 cm³) and heated to 200°C for 24 h. The resulting solution was centrifuged to separate the unreacted TiO₂. The excess EG and TETA were removed by vacuum distillation at 150°C to obtain a crude precipitate.

3.3.1.3 Preparation of Cerium Glycolate

Preparation of cerium glycolate complex was duplicated from previous work [17]. A mixture of 5 mmol (1.04 g) cerium hydroxide ($\text{Ce}(\text{OH})_4$), 18 mL of ethylene glycol (EG) and 5 mmol (0.73 g) triethylenetetramine (TETA) with sodium hydroxide (NaOH) at about 10 mole percent equivalent to cerium hydroxide were mixed, magnetically stirred and heated to the boiling point of ethylene glycol for 18 h under nitrogen to distill off ethylene glycol along with water liberated from the reaction. The reaction mixture was cooled overnight under nitrogen. The product was filtered and washed with acetonitrile (3x15 mL), followed by drying under vacuum (10^{-2} torr).

FT-IR bands used in the identification were: 2939 and 2873 cm^{-1} (ν C-H), 1080 cm^{-1} (ν Ce-O-C) and 550 cm^{-1} (ν Ce-O). ^1H NMR spectra of product recorded in deuterated DMSO: 3.4 ppm was assigned to chelated glycolate ligands. TGA showed one transition at 400°C and the percentage ceramic yield was 65.9%.

3.3.1.4 Preparation of Silatrane

A mixture of $\text{Si}(\text{OH})_2$ (6g, 0.1 mol) and TEA (18.648g, 0.125 mol) was stirred vigorously in excess EG (100 cm^3) and heated to 200°C for 10 h. The resulting solution was vacuum to remove EG to obtain a crude precipitate. The white solid product was washed with acetonitrile, dried in a vacuum desiccator and characterized using FTIR, FAB^+ -MS, and TGA.

FT-IR : 3422 cm^{-1} (ν O-H), 2986-2861 cm^{-1} (ν C-H), 2697 cm^{-1} (ν N-Si), 1459-1445 cm^{-1} (δ C-H), 1351 cm^{-1} (δ C-N), 1082 cm^{-1} (δ Si-O-C), 579 cm^{-1} (ν N-Si). FAB^+ -MS: approximately 100% of the m/e at 174 of $\text{N}[\text{CH}_2\text{CH}_2\text{O}]_3\text{Si}^+$, 11.3% intensity at 236 of $\text{H}^+\text{OCH}_2\text{CH}_2\text{OSi}[\text{OCH}_2\text{CH}_2]_3\text{N}$, 2.6% intensity at 323 of $\text{H}^+[\text{HOCH}_2\text{CH}_2]_2\text{NCH}_2\text{CH}_2\text{OSi}[\text{OCH}_2\text{CH}_2]_3\text{N}$ and 0.04% intensity at m/e 409 of $\text{N}[\text{CH}_2\text{CH}_2\text{O}]_3\text{H}^+\text{SiOCH}_2\text{CH}_2\text{OSi}[\text{OCH}_2\text{CH}_2]_3\text{N}$.

3.3.2 Sol-gel Processing of Titanium Glycolate

The hydrolysis of titanium glycolate (0.026 g) was carried out via addition of 160 μL of 1M HCl mixed with distilled water in volume ratios of HCl:H₂O 0.45, 0.39, 0.33 and 0.28. The mixtures were magnetically stirred and heated in a water bath at 50°C until a clear gel was obtained. The gels were calcined for 2 h at 600°, 700° and 800°C.

3.3.3 Rheological Measurement

3.3.3.1 *Rheological Study of Titanium Glycolate*

Gelation occurs when aggregation of particles or molecules takes place in a liquid, under the action of Van der Waals forces or via the formation of covalent or noncovalent bonds. The process can be conveniently monitored using rheological measurement techniques [13]. The rheometric measurements were conducted using an ARES rheometer with parallel plate geometry, 25 mm in diameter. The storage (G') and loss (G'') moduli were determined using oscillatory shear at frequencies in the range 0.2-6.4 rad/s. The strain amplitude was small enough to ensure that all experiments were conducted within the linear viscoelastic region, where G' and G'' are independent of the strain amplitude. Titanium glycolate 0.026 g was hydrolyzed at different HCl:H₂O volume ratios of 0.45, 0.39, 0.33 or 0.28. The hydrolysis temperature was selected to be 30°C. The mixtures were stirred until homogeneous before being transferred to the rheometer.

3.3.3.2 *Rheological Study of Cerium Glycolate*

The rheometric measurements were conducted using an ARES rheometer with parallel plate geometry, 25 mm in diameter. The storage (G') and loss (G'') moduli were determined using oscillatory shear at frequencies in the range 0.2-6.4 rad/s. The strain amplitude was small enough to ensure that all experiments were conducted within the linear viscoelastic region, where G' and G'' are independent of the strain amplitude. Cerium glycolate (0.026 g) was hydrolyzed in different HCl:alkoxide molar ratios of 0.8, 0.9, 1.0 or 1.1. The hydrolysis

temperature was selected to be 30°C. The mixtures were stirred until homogeneous before transferring to the rheometer.

3.3.4 Synthesis and Photocatalytic Reaction of Titanium Silicate-1 (TS-1)

Zeolite

3.3.4.1 Synthesis of TS-1 Zeolite

The hydrothermal syntheses were carried out using microwave irradiation. The TS-1 solution with the initial molar composition of gel equal to $\text{SiO}_2:0.1\text{TiO}_2:0.1\text{TPA}^+:0.4\text{NaOH}:114\text{H}_2\text{O}$. The effect of conditions was studied by varying the aging time (20, 60, 70, 90, 110, 130, 150 and 170 h), reaction time (5, 10, 15 and 20 h) and reaction temperature (120°, 150° and 180°C). The effect of conditions was studied by varied the TPA^+ , NaOH and H_2O . For the study of the Ti incorporated in the zeolite framework, the $\text{SiO}_2:x\text{TiO}_2:0.3\text{TPA}^+:0.4\text{NaOH}:114\text{H}_2\text{O}$ ($x = 0.1, 0.3, 0.5, 0.7, 1.0, 1.3, 1.7$ and 2.0) was used. The solution was then aging at room temperature for 110h. After aging, the solution was transferred into Teflon vessel and heated under microwave irradiation at 150°C and at varied reaction time. The TS-1 zeolite was washed several times with distilled water, dried at 60°C overnight and calcined at 550°C for 2h (0.5°C/min).

3.3.4.2 Photocatalytic Reaction of 4-Nitrophenol

The photocatalytic reactions were carried out in the 250 ml batch reactor with a gas inlet and outlet at the flow rate of O_2 gas 20 ml/min. The cooling water jacket was used to control the temperature at 30°C. The suspensions were illuminated by using a Hg Philip UV lamp. The concentration of 4-NP was 40 ppm and the solution was continuous magnetically stirred. The TS-1 zeolite at Si/Ti molar ratios 100.00, 14.29, 7.69 and 5.00 was added in the solution with the concentration of catalyst 0.8 g/l, after that the 10 mmol/l H_2O_2 was dropped. The samples were taken out and analyzed the concentration of 4-NP by Shimadzu UV-240 spectrophotometer.

3.3.5 Photocatalytic membrane reactor

3.3.5.1 *Membrane Preparation*

Polyacrylonitrile Membrane

A 10 wt% mixture of polyacrylonitrile powder in dimethyl formamide (DMF) was vigorously stirred at 50°C until homogeneous solution was obtained. A specified amount of TiO₂ was added to the stirred polymer solution. Partial vacuum was applied for a brief duration to ensure the removal of air bubbles. The mixture was then coated on a clean glass plate using a casting knife. The resulting membrane was allowed to set for 2 min before being dried in a vacuum oven at 40°C overnight following by 60°C for 2h and 80°C for 2h. The prepared membrane was cut into a circular shape with a diameter of 6 cm and thickness of 15 μm.

Cellulose Acetate Membrane

The membrane preparation followed Kunprathippanja's method [31]. A suspension of TiO₂ in acetone was formed, to which cellulose acetate was subsequently added. A partial vacuum was applied for a brief duration to ensure the removal of air bubbles, while the suspension was stirred to obtain a homogeneous suspension. The solution was then coated on the surface of a clean glass plate. The membrane was allowed to set for 2 min, followed by submersion in an ice water bath for 2 min. The membrane was then soaked in a hot water bath at 90°C for 1h before being dried. The membrane was cut into a circular shape with a diameter of 6 cm and thickness of 15 μm.

Polyvinyl Acetate Membrane

The polymer was dissolved at 50°C in tetrahydrofuran (THF) and stirred until all the polymer had dissolved in the solvent. TiO₂ was then added to the stirred polymer solution, followed by degassing to remove air bubbles. The mixture was transferred to a teflon flat sheet and cast to the desired thickness. The prepared membrane was left overnight at room temperature to slowly evaporate solvent and then dried in a vacuum oven at 40°C for 2h. The membrane was cut into a circular shape with a diameter of 6 cm and thickness of 15 μm.

3.3.5.2 Stability Test of Prepared Membranes

The prepared polymeric membranes (PAN, CA and PVAc) were placed in the membrane reactor and irradiated under UV irradiation for 15 h. The concentration of 4-NP used was 140 ppm. The samples were withdrawn and analyzed for total organic carbon (TOC) to verify that the organic components were released from the prepared membrane. SEM was used to investigate the presence of defects in membranes before and after the stability test.

3.3.5.3 Photocatalytic Decomposition of 4-Nitrophenol

The photocatalytic reactions were carried out in a 500 ml continuous batch glass reactor, figure1, with a gas inlet and outlet at an O₂ flow rate of 20 ml/min. A cooling water jacket was used to maintain the temperature at 30°C. The suspensions and membrane were illuminated using a 100 Watt Hg Philip UV lamp. The concentration of 4-NP used was 140 ppm and the solution was continuously stirred. The obtained permeate was removed at 1h intervals and analyzed to determine the concentration of 4-NP using a Shimadzu UV-240 spectrophotometer.