CHAPTER III
EXPERIMENTAL

3.1 Materials

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

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.

All glassware was 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 Equipment

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 glycolato titanium. 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 was crushed and mixed with 300 mg of KBr.

3.2.6 X-Ray Diffraction (XRD)

A Rigagu X-ray diffractometer (XRD) system equipped with a RINT 2000 wide angle goniometer and a Cu tube for generating a CuK α 1 radiation (λ = 1.54 A°) 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°(2Θ); scattering slit = 1°(2Θ); and receiving slit = 0.3 nm. Sample (0.1-0.2 g) was spread on a glass slide. A scan speed of 5°(2Θ)/min with a scan step of 0.02°(2Θ) was used during a continuous run in the 5 to 90°(2Θ) range.

3.2.7 Scanning Electron Microscopy (SEM)

The scanning electron micrographs were carried out to identify the microstructure of a sample. The samples were 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. 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 five-point BET method using a Quantachrome Corporation Autosorb I. Before the measurement, a sample was outgased by heating at 473 K for 2 h under vacuum to eliminate volatile adsorbents on the surface. The quantity of gas adsorbed onto or desorbed from a solid surface at 5 equilibrium vapor pressure (P/P_o) values (0.1115, 0.1615, 0.2115, 0.2615 and 0.3115) was measured by the static volumetric method. The data were obtained by admitting or removing a known adsorbate gas, nitrogen, into or out of a sample cell containing the solid adsorbent maintained at a constant temperature below critical temperature of the adsorbate, that is 77 K for nitrogen.

The adsorption data were calculated using the Brunauer-Emmett-Teller (BET) equation.

$$1/[W((P_o/P)-1)] = 1/[W_mC] + [(C-1)/(W_mC)]*(P/P_o) \qquad (3.1)$$

where W = weight of gas adsorbed at relative pressure P_o

W_m = weight of adsorbate constituting a monolayer of surface coverage

C = constant related to the energy of adsorption in the first adsorbed layer and magnitude of adsorbate/adsorbent interaction.

The surface area can be obtained from the following equation.

$$\text{Surface area of sample} = W_mA_{nitrogen}(6.02*10^{23})/M_{w,nitrogen} \qquad (3.2)$$

where $A_{nitrogen}$ = Cross-sectional area of one molecule nitrogen
= 0.162 nm^2 (at 77 K)
$M_{w,nitrogen}$ = molecular weight of nitrogen

3.3 Methodology

3.3.1 Synthesis of Glycolato Titanium via Oxide-One-Pot-Synthesis (OOPS) Process

Synthesis of glycolato titanium was carried out by placing 8.00 g (100 mmol) of TiO_2, 14.6 g (100 mmol) of TETA and 100 mL of EG into two-necked round bottom flask. The reaction took place in a simple distillation set up. The reaction mixture was stirred and heated at 200 °C under N_2 atmosphere in a thermostatted oil bath for 24 h. The mixture was allowed to cool down and then centrifuged to remove out unreacted TiO_2. The remain solution was further distilled for approximately 15 h. at 110 °C under vacuum (10^{-2} torr) to remove most of unreacted EG residue. The white solid product occurred during the vacuum reaction. After the reaction cooled down, the product was washed with acetonitrile and dried under vacuum at room temperature.

3.3.2 Sol-Gel Processing of Glycolato Titanium

Glycolato titanium precursor was dissolved in water containing 1 M HCl to form a colloidal solution. The amount of HCl and water were varied by x μL of 1 M HCl: y μL of water, where x: y = 35: 125, 40: 120, 45: 115 and 50: 110. The total volume was equal to160 μL. The gel was formed in a close system and the controlled temperature at 50 °C using water bath. After the gel was formed and aged at 50 °C, the gel was calcined for 2 h at different temperatures to obtain titania powder. The temperature used was varied from 600°-800 °C.

3.3.3 Rheological Study of Glycolato Titanium

Gelation occurs when aggregation of particles or molecules takes place in a liquid, under the action of Van der Waals force or via the formation of covalent or noncovalent bonds. The process can be conveniently monitored using rheological measurement technique. The rheometric measurements were conducted using an ARES rheometer with the parallel plate geometry, 25 mm in diameter. The storage (G') and loss (G") moduli were determined using oscillatory shear at frequency 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" were independent of the strain amplitude. Glycolato titanium 0.026 g was hydrolyzed at different HCl: H_2O ratios of 50: 110, 45: 115, 40: 120 or 35: 125. The hydrolysis temperature was selected to be 30 °C. The mixtures were stirred until homogeneous before being transferred to the rheometer.

3.3.4 Characterization

3.3.4.1 Characterization of Glycolato Titanium Precursor

The obtained precursor was characterized using TGA, NMR, EA, FAB^+MS and FT-IR. The identified precursor was calcined at 300°-1100 °C for 2 h to obtain titania powder. The morphology and phase transition of glycolato titanium at different calcination temperatures were studied using SEM and XRD, respectively.

3.3.4.2 Characterization of Glycolato Titanium Gel

During the gelation process, gelation time and rate of transformation reactions of glycolato titanium were determined using fluid rheometer.

3.3.4.3 Characterization of Titania Powder

After titania powder was prepared by sol-gel process, it was characterized using XRD and SEM. The surface area was also measured using BET.