CHAPTER III
EXPERIMENTAL

3.1 Materials

The starting materials were slightly either moisture or air sensitive. Therefore, all glassware used in these experiments was dried in an oven at 110°c overnight. 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).

Cerium(IV) hydroxide($Ce(OH)_4$) containing 87.4% CeO_2 as determined by TGA were purchased from Aldrich Chemical Co. Inc. (USA) and used as received.

Ethylene glycol (EG) was purchased from Farmitalia Carlo Erba (Barcelona) and purified by fractional distillation under nitrogen at atmospheric pressure, 200°C before use. Sodium hydroxide was purchased from Merck Company Co., Ltd. (Germany) and used as received.

Triethylenetetramine (TETA) was purchased from Facai Polytech. Co., Ltd. (Bangkok, Thailand) and distilled under vacuum (0.1 mm/Hg) at 130 °C prior to use.

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

Hydrochloric acid solution (HCl) were diluted with deionized water at various concentrations

3.2 Equipment

3.2.1 X-ray Diffraction (XRD)

X-ray diffractometer was used to obtain the XRD pattern. Each sample (0.1-0.2g) was ground using an alumina morta and spread on a glass slide specimen holder. The CuKα (λ=0.154 nm) radiation was used as an X-ray source. Peak positions were compared with standard JCPDS files, to identify crystalline phases.

The XRD patterns were used for average particle diameter estimation (West, 1989) by line broadening measurements in the Debye-Scherrer equation.

$$T = K\lambda / B_d \cos\theta$$

Where λ is the wavelength (nm)

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

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

θ is the Bragg angle of the reflection, and

t is the mean crystallite diameter (nm).

3.2.2 BET Surface Area Measurement

The surface areas of all powder samples were determined by BET method. A gaseous mixture of nitrogen and helium using a gas mixer allowing the gas mixture flow through the system at constant rate. The nitrogen gas was used as the adsorbate.

The relationship between the average particle diameter and the specific surface area (assuming that all particles were spherical and of uniform diameter D) was shown in the form of

$$D = 6/ (\rho_s.A)$$

Where D is the diameter of particles (m),

ρ_s is the density of spinel, and

A is the specific surface area (m^2/g).

3.2.3 Scanning Electron Microscopy (SEM)

The scanning electron micrographs were taken to identify the microstructure of the sample. The samples were characterized using JOEL Scanning Electron Microscope, Model JSM 5200.

3.2.4 Fourier Transform Infrared Spectroscopy (FTIR)

The functional groups of precursor were identified by FTIR spectra obtained from a Bruker instrument, Model EQUINOX 55. The samples were pressed to form pellets with dried KBr.

3.2.5 Rheometric Measurement

The fluid rheometer utilizing cone and plate rheometer, Model ARES, from Rheometric Scientific Inc., was used to determine the storage and loss moduli, G'(ω), G"(ω) and the dynamic viscosity, $\eta^*(\omega) = (\eta'^2+\eta''^2)^{1/2}/\omega$ as a function of angular frequency varied from 0.2, 0.4, 0.8, 1.2, 1.6, 2.0, 3.2, and 6.4, using 10g. transducer. The rheometrics fluids spectrometer was operated with a 50 mm. diameter cone with 0.04 radian angle. Temperature was controlled by a circulating fluid bath.

3.2.6 Thermogravimetric analyses (TGA)

Thermogravimetric analyzer was used to determine the exact amount of ceramic content in precursor. The materials were loaded in an alumina crucible and heat under N_2.

3.3 Methodology

3.3.1 Precursor Synthesis

Preparation of cerium glycolate complex was duplicated from previous work.

A mixture of 5 mmol (1.04 g) cerium hydroxide ($Ce(OH)_4$), 18 mL of ethylene glycol(EG) and 5 mmol (0.73 g) triethylenetetramine (TETA) with sodium hydroxide (NaOH) at about 12 mole percent equivalent to cerium hydroxide were mixed, magnetically stirred, and heated to the boiling point of ethylene glycol for 18 hours under nitrogen to distill off ethylene glycol with removal of 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. The precursor obtained was identified using TGA and FTIR.

The identified precursor was pyrolyzed at 300°- 800°C to form cerium dioxide. The product after heat treatment was studied by using FTIR, XRD and SEM.

3.3.2 Sol-Gel Process

Cerium glycolate complex was mixed with hydrochloric solution, which acid-to-alkoxide and water-to-alkoxide molar ratio were varied at room temperature. After gel was formed, the gel was calcined at different temperatures to form cerium dioxide. The temperature was varied from 300-800^{0}C, and calcination time was varied from 1 to 7 hours. The calcined products were characterized using FTIR, XRD, TGA, SEM, and BET.

3.3.3 Sol-Gel Transition of Cerium Glycolate Complex

The cerium glycolate complex after removal of ethylene glycol was used to study sol-gel transitions. The material was dissolved in a hydrochloric solution. The solution was stirred until homogeneous, before being transferred to the rheometer for rheological analysis.

3.3.4 Characterization

The functional groups of precursor and sintered gels were characterized by FTIR. The crystallinity was examined using XRD. The morphology of both precursor and sintered gel were studied using SEM. Surface area, pore volume, and pore size distribution were evaluated using Autosorb-1. Sol-gel transition was studied using a fluid rheometer.