

CHAPTER III EXPERIMENTAL



3.1 Materials

3.1.1 Preparation of Alkoxide (Sodium Tris(glycozirconate))

Zirconium hydroxide ($Zr(OH)_4$) of 97 % purity was obtained from Aldrich Chemical Company, and used as received

Sodium hydroxide (NaOH) of 98 % purity was obtained from Asia Pacific Specialty Chemicals Inc. Limited, and used as received

Ethylene glycol (dist. EG) was obtained from J T. Baker, and purified
Silicone oil was obtained from Dow Corning Cooperation U.S.A by fractional distillation

Acetronitril was obtained from Labscan Asia Co., Ltd., and purified
Methanol (dist. MeOH) of 99.97 % purity was obtained from F.E.R.O.S.A

Nitrogen (N_2) 3.11 % in helium was supplied from Thai Industrials Gas(Public) Co., Ltd.

3.1.2 Preparation of Zirconia (ZrO_2)

Sodium Tris(glycozirconate)

Oxalic acid, and used as received

Ammonium hydroxide (NH_4OH) 28-30 % by wt. was obtained from J.T. Baker, and used as received

Deionize water

3.2 Alkoxide Preparation Procedure

In this study alkoxide was prepared by the Oxide One Pot Synthesis (OOPS) process.

In a two neck, round bottom flash, a solution was prepared by mixing 10 mmol (1.59g) zirconium hydroxide ($Zr(OH)_4$), 20 mmol (0.80g) sodium hydroxide and 35 mL of ethylene glycol (EG.). The reaction mixture was vigorously stirred

using a magnetic stirrer bar. Then, the solution was heated to the boiling point of ethylene glycol (200°C) for 12 hours under nitrogen atmosphere in a thermostatted oil bath to remove by-product, water, formed from the reaction. The reaction mixture was cooled overnight under nitrogen. The products were isolated by the addition of 2-5% of dried methanol in acetonitrile to result in white solids. The product was filtered, and then washed with acetonitrile, followed by drying under vacuum (0.1 mmHg) at room temperature (Ksapabutr *et al.*, 2000).

3.3 Catalyst Preparation Procedure

In this study, catalyst was prepared by the sol-gel method.

ZrO₂ was prepared by adding a hydrolysis solvent into the precursor (Sodium Tris(glycozirconate)), and three preparation variables was examined : the pH condition, the amount of water, and the calcination temperature.

After the hydrolysis solution was mixed with the alkoxide precursor in a separate vial, the mixture was stirred with a magnetic bar at room temperature until homogeneity. Then, the gel was washed with deionized water to remove the Na content. After aging for 24 hours, the vials were transferred to an oven and dried at 110°C for 16 h. Finally, for gel stabilization and removal of organic residues, the gels were calcined at 600 °C for 4.5 h.

3.4 Catalyst Characterization

The characteristics of the prepared zirconia catalysts were determined regarding to their physical and chemical properties. The characterization technique and equipments applied in this research were BET surface area measurement, X-ray Diffraction (XRD), Atomic Absorption Spectroscopy (AAS), Scanning Electron Microscopy (SEM), Thermogravimetric Analysis (TGA) and Temperature Program Desorption (TPD) of ammonia and carbon dioxide.

3.4.1 Surface Area Measurement

Surface area, total pore volume, average pore diameter of all catalysts were determined by measuring the quantity of gas adsorbed onto or desorbed from their solid surface at some equilibrium vapor pressure by static volumetric method.

A solid sample was maintained at a constant temperature below the critical T of the adsorbate. The equilibrium of a adsorption or desorption causing the change in the pressure of the sample cell unit is established. This volume-pressure data are used to calculate the BET surface area.

Quantachrome Corporation Autosorb I, the BET surface area measurement were performed, each catalyst sample was first outgased to remove the humidity and volatile adsorbents adsorbed on surface under vacuum at 250 °C for three hours before starting the analysis to determine the surface area, total pore volume and average pore diameter. Nitrogen gas with cross sectional area of $16.2 \times 10^{-2} \text{ m}^2/\text{molecule}$ was considered to be an adsorptive at the liquid nitrogen temperature (77K). Autosorb ANYGAS Vession 2.10 was used to analyze the results.

3.4.2 X-ray Diffraction (XRD)

X-ray diffraction experiments utilizing $\text{CuK}\alpha$ radiation (Rikagu) were performed to determine the internal structure, bulk phase, and composition of the crystalline material. First, the sample was ground to fine powder by using a mortar. The powder was held on a glass slide specimen holder and was examined between 5 to 90 ° (2θ) range at scanning speed $5^\circ(2\theta)/\text{minute}$ with scan step of $0.02^\circ(2\theta)$. The digital output of proportional x-ray diffractor and the goniometer angle measurements were sent to an online microcomputer for storing the data and the data were analyzed by PC-APD version 3.5 B.

3.4.3 Atomic Absorption Spectroscopy (AAS)

The actual content of sodium in the prepared catalysts was determined using atomic absorption spectroscopy, VARIAN Model 300/400. Firstly, a known weight of catalyst was dissolved in an *aqua regia* solution (Nitric acid and hydrochloric acid with a ratio of 3:2) at 70-80 ° C for 30 min. The solution was diluted to the measuring range. The concentration of sodium was obtained by comparing its absorbance with the calibration curve of the standard solution (see in Appendix C 1).

3.4.4 Thermogravimetric Analysis (TGA)

Thermogravimetric Analysis (TGA) technique was used to determine the phase transfer of zirconia. Each sample was measured using the Du Pont TGA 2950 Thermogravimetric Analyzer. The chamber inside the analyzer was exposed to a continuous flow of air. The specimen was heated up from 30 to 800 ° C with a rate of 10 ° C/min. The mass changes during temperature increase were monitored and recorded using the TA instrumented thermal analyst system.

3.4.5 Scanning Electron Microscopy

Scanning electron microscopy was used particularly for examination of the topology of catalyst surfaces and the morphology of particles and crystals. It is particularly helpful to examine the characteristics of single particles and to determine particle size distribution.

Scanning electron microscopy (SEM) was performed on the JEOL 5200 with the magnification of 35-200,000 scanning electron microscope. The catalysts were stuck on the stubs and coated with gold by ion sputtering device (JFC-1100 E) for 4 minutes to prevent specimen charging. The examinations were taken through this microscope with the magnification range from 35 to 7500.

3.4.6 Temperature Program Desorption (TPD)

The acid-base properties of the catalysts were measured by temperature-programmed desorption (TPD) of ammonia and carbon dioxide, respectively. TPD experiments were conducted at atmospheric pressure. Typically, a 200-mg sample was loaded in a quartz reactor and activated in a helium stream by heating to 500 ° C at a rate of 5 ° C/min and maintaining at the final temperature for 30 mins. Afterthat, the sample was cooled down to ambient temperature and then it was absorbed by CO₂ or NH₃ for 30 min. Next, the oxide was flushed with helium at 50 ° C for 1 hour to remove physisorbed carbon dioxide or ammonia. TPD of CO₂ was performed from 50° to 470 ° C at a heating rate of 5 ° C/min, while TPD of NH₃ was performed from 80° to 650 ° C at 10 ° C/min rate. The effluent was monitored using a thermal conductivity detector.