

CHAPTER III EXPERIMENTAL

3.1 Materials

3.1.1 Catalyst Preparation Materials

Deoxycholic acid ($C_{24}H_{40}O_4$) of 98% purity was supplied from Aldrich Chemical Company (Steinheim, Germany).

Magnesium hydroxide ($Mg(OH)_2$) AR grade was supplied from APS Chemicals Limited (NSW, Australia)

Aluminum hydroxide ($Al(OH)_3$) AR grade was supplied from Carlo Erba Reagent Company (Michigan, U.S.A.).

Tungstophosphoric acid hydrate acid ($H_3[P(W_3O_{10})_4].xH_2O$) was supplied from Carlo Erba Reagent Company (Michigan, U.S.A.).

Tungstosilicic acid hydrate ($H_4[Si(W_3O_{10})_4].xH_2O$) was supplied from Fluka Co., Ltd. (Steinheim, Germany).

Ferric Nitrate hydrate ($Fe(NO_3)_3.9H_2O$) AR grade was supplied from Labscan Co.,Ltd. (Bangkok, Thailand).

Sodium Hydroxide (NaOH) AR grade was supplied from Labscan Co.,Ltd (Bangkok, Thailand).

Phosphoric acid (H_3PO_4) of 85% concentration was supplied from Labscan Co., Ltd. (Bangkok, Thailand).

3.1.2 Reactant Gases

1.31% Nitric oxide (NO) in helium was supplied from Air Products and Chemicals Inc.

1% Ammonia (NH_3) in helium was supplied from Thai Industrial Gases (Public) Co., Ltd.

Ultra high purity (UHP) oxygen (O_2) was supplied from Praxair (Thailand) Co., Ltd.

Ultra high purity (UHP) helium was supplied from Thai Industrial Gases (Public) Co., Ltd.

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

3.2 Catalysts Preparation

3.2.1 Synthesis of Pillared-clay Catalysts

Hydrotalcite-type clays intercalated with an organic compound and polyoxometalate were prepared by hydrothermal and anion exchanging method consecutively. The prepared pillared clays were calcined for 12 hours, then ground and sieved to 80-120 mesh before being used as catalysts for selective catalytic reduction of nitric oxide by ammonia.

3.2.1.1 *Deoxycholate-pillared Hydrotalcite-type Clay (DA-clay):*

1.28 g of $Mg(OH)_2$, 0.44 g of $Al(OH)_3$, 10.76 g of Deoxycholic acid and 0.1 g of NaOH were mixed in 100 ml of deionized water at room temperature with vigorous stirring (pH 8-10). Then, the suspension was transferred into an autoclave and heated at $150^\circ C$ for 48 hours. The solid precipitate was collected by filtration and washed with deionized water subsequently. The product was dried at $110^\circ C$ overnight, and calcined for 12 hours before being used as catalysts for selective catalytic reduction of nitric oxide by ammonia.

3.2.1.2 *Polyoxotungstophosphate-pillared Hydrotalcite-type Clay (PW_{12} -clay):*

A suspension of 1.0 g of dried DA-clay in 50 ml of deionized water was added to a solution containing 1.74 g of $H_3PW_{12}O_{40}$ and 0.1 g NaOH in 500 ml of deionized water (pH 8) at the temperature of $70^\circ C$. The reaction mixture was stirred for 12 hours, and then the precipitate was recovered by filtration and washed with deionized water. The product was then dried at $110^\circ C$ overnight, and calcined for 12 hours before being used as catalysts for selective catalytic reduction of nitric oxide by ammonia.

3.2.1.3 Polyoxotungstosilicate-pillared Hydrotalcite-type Clay

(SiW_{12} -clay):

A suspension of 1.0 g of dried DA-clay in 50 ml of deionized water was added to a solution containing 1.31 g $H_4SiW_{12}O_{40}$ and 0.15 g NaOH in 500 ml of deionized water (pH 8) at the temperature of 70°C. The reaction mixture was stirred for 12 hours and then the precipitate was recovered by filtration and washed with deionized water. The catalyst was dried at 110°C overnight, and calcined for 12 hours before being used as catalysts for selective catalytic reduction of nitric oxide by ammonia.

3.2.2 Synthesis of Fe-loaded Pillared-clay Catalysts

To study the promoting effects of iron to pillared-clay, iron was loaded on the pillared-clay catalysts by an impregnation method. Appropriate amount of ferric nitrate ($Fe(NO_3)_3 \cdot 9H_2O$) solution was impregnated into the calcined pillared clays to obtain 5%wt Fe on clay. After that, the solid were dried at 110°C for overnight, and calcined for 12 hours before being used as catalysts for selective catalytic reduction of nitric oxide by ammonia.

3.3 Catalyst Characterization

The characteristics of the prepared catalysts were investigated by techniques described below.

3.3.1 Thermal Gravimetric Analysis (TGA)

Thermal Gravimetric Analysis (TGA) technique was employed to determine the transition weight loss of catalysts. Each sample was examined using the Du Pont TGA 2950 Thermogravimetric Analyzer. The chamber inside the analyzer was exposed to a flow of air zero (as a reactant gas) and air (as a purge gas) at a flow rate of 20 and 30 ml/min, respectively. The specimen was heated up from 30 to 800°C with the rate of 10°C/min, followed by cooling down to 30°C with the rate of 10°C/min. The mass changes during temperature increase were monitored and recorded using the TA instrument thermal analyst system.

Differential Thermal Gravimetric (DTG) plot ($-dm/dt$) was also employed to determine the mass change rate with temperature changes of catalysts.

3.3.2 X-Ray Diffraction (XRD)

The XRD pattern was obtained from a Rigaku X-Ray diffractometer system (RINT-2200) equipped with graphite monochromator and a Cu tube for regenerating CuK_α radiation ($\lambda = 1.5406 \text{ \AA}$) at a generator voltage of 40 kV and a generator current of 30 mA. Nickel filter was used as the K_α filter. The goniometer parameters were divergence slit = 0.5° , scattering slit = 0.5° , and receiving slit = 0.15mm. The samples were ground to a fine powder. It was held on a glass slide holder and was examined between 1.2 - $90^\circ(2\theta)$ range at a scanning speed of $5^\circ(2\theta)/\text{minute}$ with the 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 outline microcomputer to record the data and subsequent analysis.

3.3.3 Scanning Electron Microscopy (SEM)

Scanning Electron Microscopy (SEM) experiments were performed on the JOEL JSM-5200, with the magnification of 35-200,000. A catalyst powder was placed on a copper stub and coated with gold by ion sputtering device (JFC-1100E) at 10 mA for 4 minutes in order to prevent specimen charging. The examination was taken through this microscope at accelerating voltages of 20 and 25 kV with a magnification of 7500.

3.3.4 BET Surface Area

Autosorb-1 Gas Sorption system (Quantachrome Cooperation) was utilized for evaluation of surface area, total pore volume, and average pore diameter of catalysts. Brunauer-Emmett-Teller (BET) based on physical adsorption was applied in this characterization. Nitrogen gas with the cross sectional area of $16.2 \times 10^{-2} \text{ m}^2/\text{molecule}$ was considered to be an adsorbate at the liquid nitrogen temperature of 77K.

Before measurements, a sample was outgassed by heating at 250°C for overnight under vacuum in order to eliminate volatile adsorbates on the surface. The specific surface area of each catalyst was calculated from the 22 points adsorption isotherm. The average pore radius and average pore volume were determined at P/P_0 ratio close to unity. The results were analyzed by using Autosorb ANYGAS software.

3.4 Apparatus

The experimental apparatus was divided into 3 parts as shown in Figure 3.1: (i) gas blending system, (ii) catalytic reactor, and (iii) analytical instruments.

3.4.1 Gas Blending System

The typical reactant mixture consisted of nitric oxide, ammonia, oxygen balanced in helium. Each gas was controlled by a mass flow controller (Sierra Instrument, Inc. model 840) in order to accomplish the desired composition and then passed through a check valve to protect flow from reversing. After that the mixed gas was transferred to reactor.

3.4.2 Catalytic Reactor

Selective catalytic reduction of NO_x was carried out in a 1 cm. outer diameter borosilicate glass tube at atmospheric pressure. The catalyst was packed in the middle of reactor with glass wool. The temperature of catalyst bed was examined and controlled by PID controller equipped with K-type thermocouple (Yokohama, Model UP27). The product gases from reactor were then passed to analytical instruments.

3.4.3 Analytical Instruments

The product gases from reactor were passed to a water trapper to determine the amount of water in the product. Then, the effluent gas was separated into two parts. The first was sent to Hewlett Packard 5890 series II gas chromatograph in order to determine the concentration of Nitrogen (N_2) and Oxygen

(O₂). These compounds were separated by 6 ft x 1/8 inch x 0.085 inch column packed with the 80/100 mesh of Molesieve 13X. The GC was operated using injector, oven, and detector temperatures of 110, 40, and 175°C respectively. He (99.99% purity) was used as a carrier gas with the flow rate of 27 ml/min.

The second part was passed to the high level Chemiluminescence NO-NO₂-NO_x analyzer from ECO Physics Model CLD 700EL in order to determine the concentration of nitric oxide (NO) and nitrogen oxide (NO₂). Ammonia gas in the product was removed by 2 M phosphoric acid before the product effluent was passed to the analyzers.

3.5 Catalytic Activity Testing

The catalytic activity of selective catalytic reduction of NO_x with ammonia was carried out at atmospheric pressure. Either 0.1 or 0.2 g of catalyst was placed with glass wool in the fixed-bed flow reactor. The feed gas compositions were as follows: 1000 ppm NO, 1000 ppm NH₃, 2% O₂, and balanced in helium. The total flow rate for all experiments was 500 ml/min. The reaction temperature was varied from 150 to 450°C. The process flow diagram is shown in Figure 3.1.

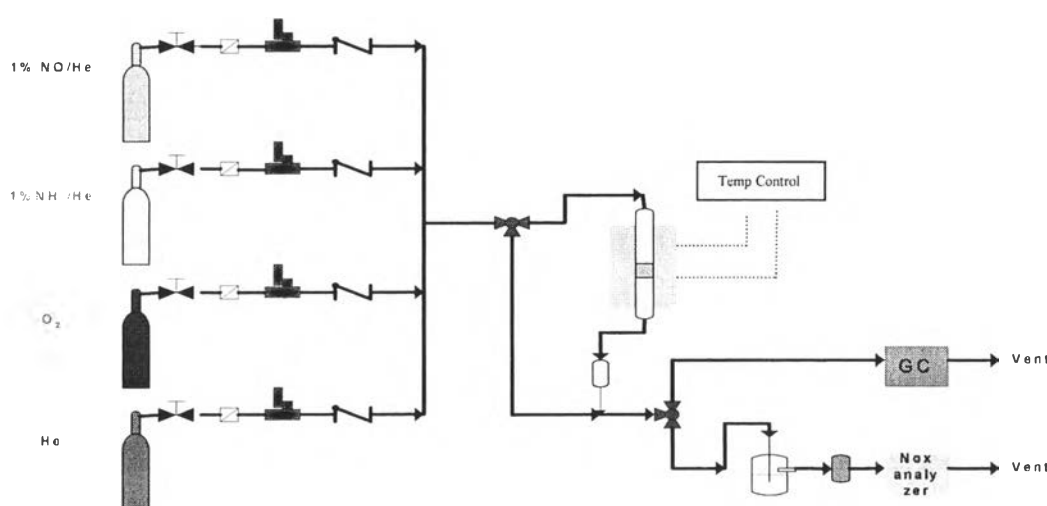


Figure 3.1 Schematic representation of SCR of NO with NH₃ process flow diagram (adapted from Rochanutama, 2003).