

## CHAPTER III EXPERIMENTAL

### 3.1 Materials

#### 3.1.1 Catalyst Preparation Materials

Magnesium Nitrate-Hexahydrate ( $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ) AR grade was obtained from MERCK Co.,Ltd.

Aluminium Nitrate-Nonahydrate ( $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ) AR grade was supplied from Labscan Co.,Ltd.

Ferric Nitrate ( $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ) AR grade was obtained from Labscan Co.,Ltd.

Terephthalic acid ( $\text{C}_6\text{H}_4(\text{COOH})_2$ ) AR grade was supplied from Labscan Co.,Ltd.

Sodium Hydroxide (NaOH) AR grade was obtained from Labscan Co.,Ltd.

Sodium Molybdate-Dihydrate ( $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ ) AR grade was supplied from SM Chemical company.

Sodium Monovanadate ( $\text{NaVO}_3$ ) AR grade was obtained from SM Chemical company.

Phosphoric acid ( $\text{H}_3\text{PO}_4$ ) of 85% concentration was obtained from Labscan Co., Ltd.

Nitric acid ( $\text{HNO}_3$ ) of 70% concentration was supplied from Labscan Co., Ltd.

#### 3.1.2 Reactant Gases

Nitric Oxide (NO) 1.52% in helium was supplied from Air Products and Chemicals Co., Ltd.

Ammonia ( $\text{NH}_3$ ) 1.13% in helium was supplied from Thai Industrial Gases (Public) Co., Ltd.

Ultra high purity (UHP) oxygen ( $\text{O}_2$ ) was supplied from Praxair (Thailand) Co., Ltd.

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

Nitrogen (N<sub>2</sub>) 3.11% in helium was supplied from Thai Industrial Gases (Public) Co., Ltd.

## 3.2 Catalyst Preparation Procedure

In this study the catalysts were prepared by sol-gel and impregnation methods.

### 3.2.1 Sol-Gel Method

#### 3.2.1.1 *Terephthalate-pillared hydrotalcite-type clay: (TA-clay)*

33.3 g of Terephthalic acid, 143.8 g of 50% NaOH solution and 400 ml. of distilled water were mixed together in the three-neck round-bottom flask. This mixture was heated to 80°C, stirred and cooled to room temperature. 102.5 g of magnesium nitrate, 75 g of aluminium nitrate and 320 ml. of distilled water were mixed separately and, then, added dropwise to the vigorous stirring mixture. After complete addition, the gel-like mixture was digested at 75°C, which was controlled constantly for 18 hours. After that, the product was filtered and washed in order to remove excess ions. Finally, the slurry of clay was obtained (Drezdson, 1988).

#### 3.2.1.2 *Decavanadate-pillared hydrotalcite-type clay: (V-clay)*

A solution of sodium vanadate was firstly prepared by mixing 4.4 g of sodium vanadate and 29.8 ml. of distilled water and added to 100 g of terephthalate-pillared hydrotalcite-type clay with vigorous stirring. Nitric acid was slowly added to the mixture in order to adjust pH to 4.5 at which decavanadate was formed. Finally, the product was filtered and washed. The catalyst was dried at 110°C for overnight and calcined at 350°C for 12 hours.

#### 3.2.1.3 *Heptamolybdate-pillared hydrotalcite-type clay: (Mo-clay)*

A solution of molybdate was firstly prepared by mixing 8.5 g of sodium molybdate and 15 ml. of distilled water and added to 100 g of terephthalate-pillared hydrotalcite-type clay with vigorous stirring. Nitric acid was slowly added to the mixture in order to adjust pH to 4.5 at which heptamolybdate

was formed. Finally, the product was filtered and washed. The catalyst was dried at 110°C for overnight and calcined at 350°C for 12 hours.

#### 3.2.1.4 *Molybdate Vanadate-pillared hydrotalcite-type clay: (Mo-V-clay)*

A mixture of heptamolybdate and decavanadate solutions was prepared as by mixing 5.5 g of sodium molybdate and 1.5 g of sodium vanadate into 100 ml. of distilled water. The solution was added to 100 g of terephthalate-pillared hydrotalcite-type clay with vigorous stirring. Nitric acid was slowly added to the mixture in order to adjust pH to 4.5 at which heptamolybdate and decavanadate were formed. Finally, the product was filtered and washed. The catalyst was dried at 110°C for overnight and calcined at 350°C for 12 hours.

#### 3.2.2 Ion exchange

Iron was loaded on the catalysts by an ion exchange method. Dried clay of V-clay, Mo-clay, and Mo-V-clay in the same amount were sunk in the appropriate amount ferric nitrate ( $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ) solution and stirred continuously for 6 hours to obtain 5% wt Fe on clay. After that, these catalysts were dried at 120°C for overnight and followed by calcination at 350 °C for 6 hours.

#### 3.2.3 Impregnation

Iron was also doped on the catalysts by an impregnation method. The impregnated catalysts were prepared by adding the appropriate amount of ferric nitrate ( $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ) solution to obtain 5% wt Fe on clay. After that the catalysts were dried at 120°C for overnight, followed by calcination at 350 °C for 6 hours.

### 3.3 Catalyst Characterization

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

#### 3.3.1 X-Ray Diffraction (XRD)

X-Ray Diffraction is widely used for characterizing crystallinity. This analysis leads to an estimation of a mean crystallite size, crystallite size distribution,

composition of crystalline catalysts and internal structure. XRD is based on the fact that an X-ray diffraction pattern is unique for each crystalline substance. Crystalline phase form can be assumed whether an exact match can be found between the pattern of unknown and an authentic sample. Searching and matching for the components was accomplished by comparing the XRD patterns with JCPDF files. The XRD pattern was obtained from a Rigaku X-Ray diffractometer system (RINT-2200) equipped with graphite monochromator and a Cu tube for regenerating  $\text{CuK}\alpha$  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  $\text{K}\alpha$  filter. The goniometer parameters were divergence slit =  $2^\circ(2\theta)$ ; scattering slit =  $2^\circ(2\theta)$ ; and receiving slit = 0.3 mm. The samples were ground to a fine powder. It was held on a glass slide holder and was examined between  $3\text{-}70^\circ(2\theta)$  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 outline microcomputer to record the data and subsequent analysis.

### 3.3.2 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 adsorptive at the liquid nitrogen temperature (77K).

Before measurement, sample was outgased by heating at  $250 \text{ }^\circ\text{C}$  for overnight under vacuum to eliminate volatile adsorbates on the surface. The specific of 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 ANAGAS software version 2.10.

### 3.3.3 Transmission Electron Microscopy

The size, shape, and morphology of catalysts were observed by using transmission electron microscope or TEM (Joel JEM-200 CX). The samples were prepared by grinding to fine particles and dispersing in epoxy resin. The samples were sheared into a thin section from the hardened epoxy block with a microtome. The catalysts were examined at a constant accelerating voltage of 100 kV.

### 3.3.4 Scanning Electron Microscopy

Each sample powder was placed on a copper stub and coated with gold at 10 mA for 8 minutes. The sample was, then, examined by using the SEM (Joel JSM-5200) at a constant accelerating voltage of 25 kV. The secondary electron images were taken for catalysts morphology.

### 3.3.5 Atomic Absorption Spectroscopy (AAS)

The AAS (VARIAN Model 300/400) was used to determine the actual content of iron loaded in prepared catalysts. A known weight of catalyst was dissolved in *aqua regia* solution (nitric acid and hydrochloric acid with a ratio of 2:1) to prepare the analysis solution. The metal solution was diluted to the measuring range. The concentration of iron was obtained by comparing absorbance with the calibration curve of the standard solution.

### 3.3.6 Thermal Gravimetric Analysis

Thermal Gravimetric Analysis (TGA) technique was used to determine the phase transfer of catalysts. Each sample was measured 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 °C to 700 °C with a rate of 10 °C/min, followed by cooling down to 30 °C with a rate of 10 °C/min. The mass changes during temperature increase were monitored and recorded using the TA instrument thermal analyst system.

### 3.3.7 Temperature Programmed Desorption

A micrometrics TPD/TPR 2900 was employed as an analyzer for temperature programmed desorption (TPD). Helium was selected as a carrier gas with a flow rate of 50 ml/min. Nitric oxide was adsorbed at room temperature for 15 minutes before being purged with helium with a flow rate of 30 ml/min for 30 minutes. The furnace controller was set to increase the furnace temperature up to 900 °C at the linear ramp rate of 10 °C/min in the desorption step. As temperature increased, the surface species began to be desorbed. The signal from the thermal conductivity detector was displayed as a function of temperature, and the mass spectrometer Model ThermoStar PEIFFER VACUUM reported qualitatively and quantitatively the desorbed components.

## 3.4 Apparatus

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

### 3.4.1 Gas Blending System

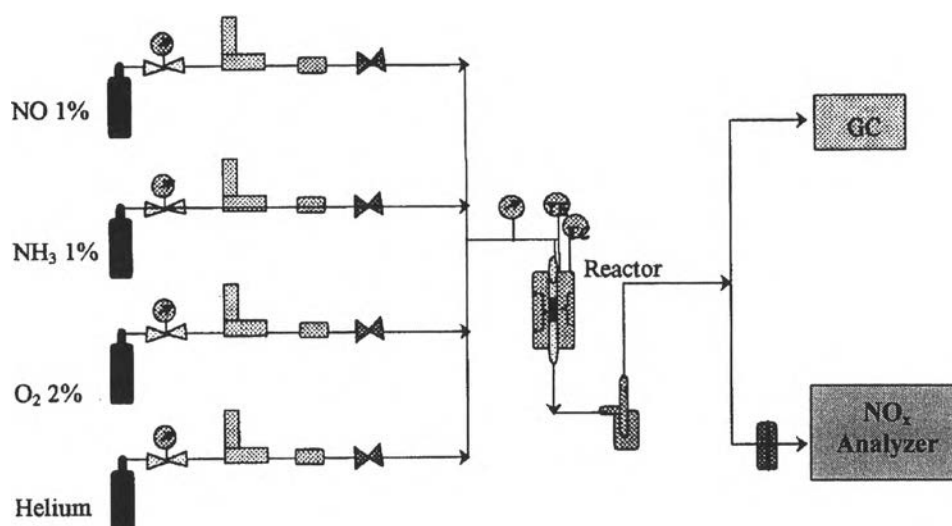
The typical reactant mixture consisted of nitric oxide, ammonia, oxygen balanced in helium. Each gas was controlled by a mass flow controller (Sierra Instrument, Inc. model 840) to accomplish the desired composition and, then, passed through a check valve to protect reverse flow. After that, the mixed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

### 3.4.2 Catalytic Reactor

Selective catalytic reduction of NO was carried out in a 1 cm. outside diameter borosilicate glass tube at atmospheric pressure. The catalyst was packed in the middle of reactor with glass wool. The temperature 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 section.

### 3.4.3 Analytical Instruments

Before the product gas was passed to the analytical instruments, it was passed through water traps for water removal. Then, the effluent gas was analyzed both quantitatively and qualitatively. A sample was separated into two parts. The first was sent to Hewlett Packard 3365 series II chemstation in order to analyze the concentration of  $O_2$  and  $N_2$  using a molecular sieve 13X column. The second part was passed through a bubbler for ammonia removal and, then, passed to the high level Chemiluminescence NO-NO<sub>2</sub>-NO<sub>x</sub> analyzer from ECO physics Model CLD 700 EL in order to determine the concentration of nitric oxide (NO) and nitrogen oxide (NO<sub>2</sub>). N<sub>2</sub>O was calculated from mass balance.



**Figure 3.1** Schematic flow diagram of experimental equipments.

### 3.5 Catalytic Activity Measurement

The catalytic activity of selective catalytic reduction of NO with ammonia was carried out at atmospheric pressure. 100 mg. of catalyst packed over glass wool in the fixed-bed flow reactor was heated to 350 °C for an hour in a stream of helium at a rate 420 ml/min. Then, the reactants were fed to the reactor. The feed gas compositions were as the followings: 1000 ppm NO, 1000 ppm NH<sub>3</sub>, 2 vol% O<sub>2</sub>, and balanced helium. The total flow rate for all experiments was 500 ml/min.

The activity of the catalyst was defined in terms of percent conversion as display in Appendix B.