

## CHAPTER III EXPERIMENTAL



### 3.1 Materials

#### 3.1.1 Catalyst Preparation Materials

Aluminum isopropoxide ( $\text{Al}(\text{OC}_3\text{H}_7)_3$ ) of 98% purity was obtained from Fluka Co., Ltd.

Hydrogen tetrachloroaurate (III) ( $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ ) of 99.99% purity was supplied from A Johnson Matthey Company.

Barium nitrate ( $\text{Ba}(\text{NO}_3)_2$ ) of 99% purity was obtained from Carlo Erba Reagent Company.

1,3-Butanediol anhydrous ( $\text{C}_2\text{H}_4(\text{OH})\text{C}_2\text{H}_4\text{OH}$ ) of 98% purity was obtained from Fluka Co., Ltd.

Nitric acid ( $\text{HNO}_3$ ) of 65% concentration was obtained from Riedel-deHaen AG.

#### 3.1.2 Reactant Gases

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

Propylene ( $\text{C}_3\text{H}_6$ ) 0.91% in helium was supplied from Thai Industrial Gas (Public) Co., Ltd.

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

Nitrogen ( $\text{N}_2$ ) 3.11% in helium was supplied from Thai Industrial Gas (Public) Co., Ltd.

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

## 3.2 Catalyst Preparation

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

### 3.2.1 Sol-Gel Method

#### 3.2.1.1 *Barium supported on alumina*

Aluminum isopropoxide (AIP) was dissolved in hot water at 85<sup>0</sup>C. After being stirred for a while, small amount of nitric acid was slowly added in order to form an aluminum hydroxide sol. The sol solution was then mixed with a solution of barium nitrate dissolved in water. After that, some 1,3-butanediol was added in mixed solution. During mixing, the temperature of solution was controlled constantly at 85<sup>0</sup>C. After an hour of mixing, the solution was continuously stirred at room temperature until all of solution formed gel. Then, the stirring was stopped in order to age the gel for 24 hours. The gel was dried at 110<sup>0</sup>C for 24 hours and calcined at 500<sup>0</sup>C for 6 hours. After calcination the catalysts were stored in a desiccator until needed. Bare alumina support, in absence of barium, was also prepared in same procedure described above.

#### 3.2.1.2 *Gold supported on alumina*

The catalysts were prepared in the same manner described above. However, hydrogen tetrachloroaurate dissolved in 1,3-butanediol was added instead of barium nitrate solution.

### 3.2.2 Impregnation

#### 3.2.2.1 *Gold impregnated on alumina and barium/alumina sol-gel support*

In order to obtain 0.5, 0.7 and 1% weight gold loading, the calculated amounts of hydrogen tetrachloroaurate solutions were added into Al<sub>2</sub>O<sub>3</sub> and Ba/Al<sub>2</sub>O<sub>3</sub> sol-gel supports. Then, the catalysts were dried at 110<sup>0</sup>C for overnight, followed by calcination at 500<sup>0</sup>C for 6 hours.

### 3.2.2.2 *Barium impregnated on gold/alumina sol-gel support*

To obtain 10% weight barium loading, the calculated amount of barium nitrate solution was added into Au/Al<sub>2</sub>O<sub>3</sub> sol-gel support. The catalyst was dried and calcined in the same manner described above.

## 3.3 Catalyst Characterization

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

### 3.3.1 Surface Area Measurement

Autosorb-1 Gas Sorption system (Quantachrome Corporation) 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 cross sectional area of  $16.2 \times 10^{-2}$  m<sup>2</sup>/molecule was considered to be an adsorbate at the liquid nitrogen temperature (77 K).

A small sample was dried and outgassed in the sample cell at 150<sup>0</sup>C for at least 4 hours before adsorption. The specific area of each catalyst was calculated from the 5 points adsorption isotherm. The average pore radius and average pore volume were determined at P/P<sub>0</sub> ratio close to unity. The results were analyzed by using Autosorb ANAGAS software version 2.10.

### 3.3.2 X-Ray Diffraction (XRD)

X-Ray Diffraction is widely used for characterizing supported metal crystallites. This analysis leads to an estimate 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 examined when an exact match is found between the pattern of unknown and an authentic sample. Furthermore, relative quantitative analysis can be done by comparing the intensity of

the diffraction lines. When comparing the same crystalline substance of two different samples, the higher intensity shows the higher content.

The XRD pattern was obtained from a Rigaku X-ray diffractometer system (RINT-2200) equipped with graphite monochromator and a Cu tube for generating  $\text{CuK}_\alpha$  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 =  $1^\circ(2\theta)$ ; scattering slit =  $1^\circ(2\theta)$ ; and receiving slit = 0.3 mm. The sample was ground to a fine powder. It was held on a glass slide holder and was examined between  $5$  to  $90^\circ(2\theta)$  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 online microcomputer to record the data and subsequent analysis.

Crystallite size was estimated by using Scherrer equation in the following form:

$$d = K \lambda / b \cos\theta$$

where  $d$  = mean crystallite diameter ( $\text{\AA}$ )

$b$  = peak width at the middle height

$K$  = Scherrer constant which is equal to 1

$\lambda$  = X-ray wavelength ( $\text{\AA}$ )

$\theta$  = Bragg angle of the reflection (degree)

### 3.3.3 Atomic Absorption Spectroscopy (AAS)

A VARIAN Model 300/400 Atomic Absorption Spectroscopy was used to determine the actual content gold loading in the prepared catalysts. A known weight of catalyst was dissolved in an aqua regia solution (hydrochloric acid and nitric acid with a ratio of 3:1). The metal solution was diluted to the measuring range. The concentration of gold was obtained by comparing its absorbance with the calibration curve of the standard solution.

### 3.4 Apparatus

The experimental apparatus as shown schematically 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

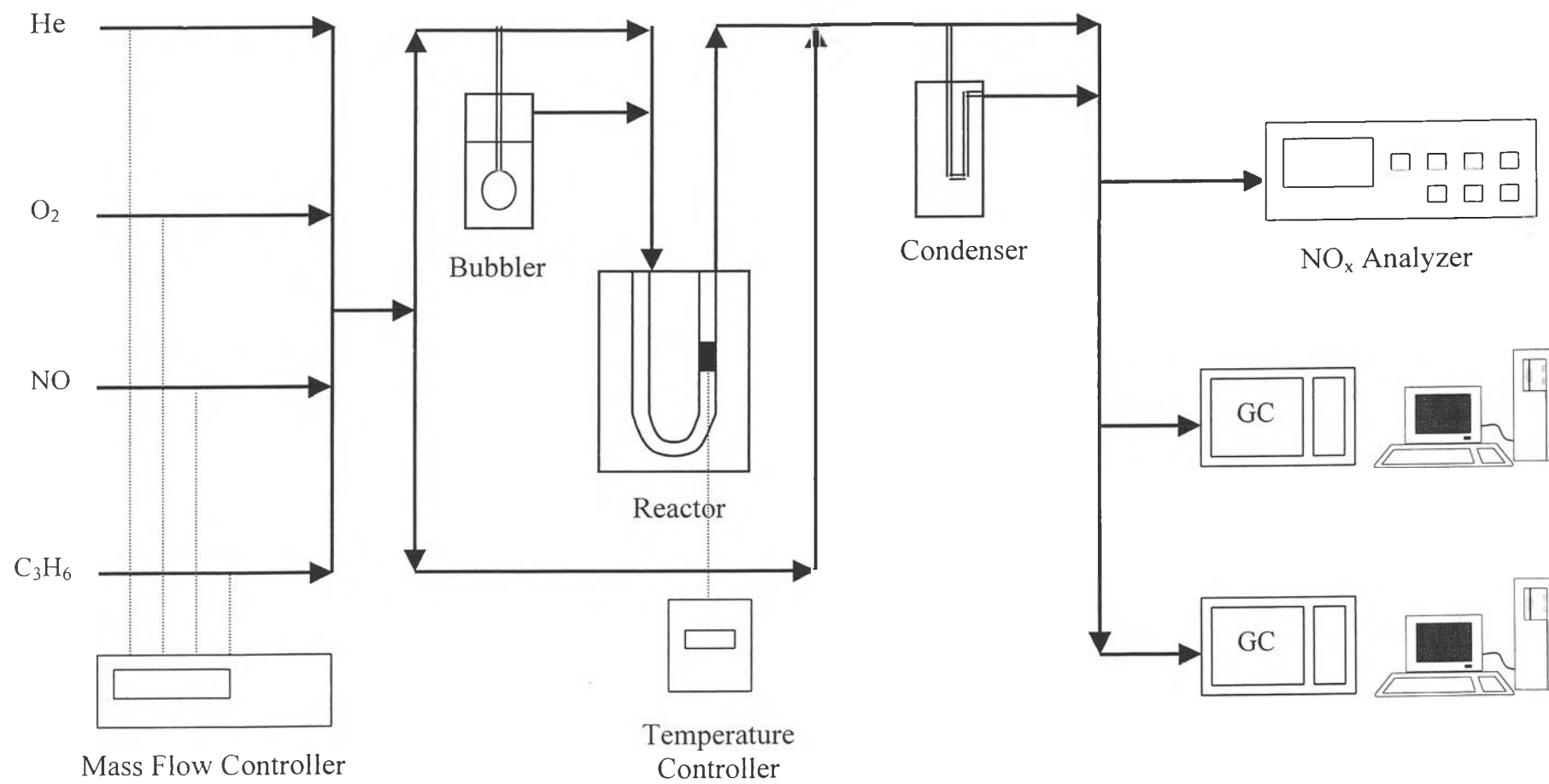
The reactant gas mixture was consisted of nitric oxide, propylene, oxygen balanced in helium. Each gas was passed through micro filter to remove small particles. The individual gas was controlled by mass flow controller (Sierra Instrument, Inc. model 840) to accomplish the desire composition and then passed through a check valve to prevent reverse flow. After that the mixed gas passed to reactor. In case of study the effect of water vapor, the mixed gas was passed through bubbler before flowing to a reactor.

#### 3.4.2 Catalytic Reactor

The experiment was carried out in an 8 mm. inside diameter pyrex glass U-tube reactor at atmospheric pressure. The catalyst was sealed in the middle of reactor with glass wool. Temperature catalyst bed was examined and controlled by PID controller equipped with K-type thermocouple (Yokohama, Model UP 27). The product gas from reactor was then passed to analytical instrument.

#### 3.4.3 Analytical Instruments

Before the effluent gas from reactor was passed to the analytical instrument part, it was passed through a condenser to get rid of water, in case of study the effect of water. Then, the effluent gas was analyzed both quantitatively and qualitatively. It was separated into 3 parts, the first two were sent to Hewlett Packard 5890 series II Gas Chromatographs equipped with thermal conductivity detector (TCD). The columns utilized in these chromatographs were Altech Molecular sieve 13X and Porapak N packed column. The output of chromatograph were recorded and analyzed by Hewlett Packard 3365 series II chemstation. The third part gas was passed to the high level Chemiluminescence NO-NO<sub>2</sub>-NO<sub>x</sub> analyzer from Thermo



**Figure 3.1** Schematic flow diagram of experimental equipment

Environmental Instruments Inc. Model 42C in order to determine the concentration of nitric oxide (NO) and nitrogen dioxide (NO<sub>2</sub>).

### 3.5 Catalytic Activity Measurement

The catalytic activity was carried out at atmospheric pressure. The catalyst 100 mg. sealed with quartz wool in the fixed-bed flow reactor was pretreated by heating to 300<sup>0</sup>C for an hour in a stream of helium at a rate 180 ml/min. Then, the catalyst temperature was set at a desired value. The total flow rate for all experiments was 180 ml/min. In case of studying the effect of water on the reaction, 3 vol% of water vapor generated by passing feed gas through the bubbler were added to the feed stream.

#### 3.5.1 NO<sub>x</sub> Storage-Reduction (NSR)

The feed gas compositions for NO<sub>x</sub> storage period under lean conditions (oxidizing conditions) were 1,000 ppm NO, 8 vol% O<sub>2</sub> and balanced helium. When the catalyst was saturated or the NO<sub>x</sub> outlet concentration was constant, the catalyst was then regenerated by reduction under rich conditions (reducing conditions) in 1,000 ppm NO, 0 vol% O<sub>2</sub>, 1,000 ppm C<sub>3</sub>H<sub>6</sub> and balanced helium for a short period. %NO<sub>x</sub> conversion was calculated as follow:

$$\% \text{NO}_x \text{ conversion} = \frac{[\text{NO}_x]_{\text{inlet}} * (t_2 - t_1) - \int_{t_1}^{t_2} [\text{NO}_x]_{\text{outlet}} dt}{[\text{NO}_x]_{\text{inlet}} * (t_2 - t_1)} * 100$$

where

t<sub>1</sub> and t<sub>2</sub> are the time at the beginning and end of each cycle

#### 3.5.2 Selective Catalytic Reduction (SCR)

The feed gas compositions were 1,000 ppm NO, 8 vol%, 1,000 ppm C<sub>3</sub>H<sub>6</sub> and balanced helium. %NO<sub>x</sub> conversion was calculated as follow:

$$\% \text{NO}_x \text{ conversion} = \frac{[\text{NO}_x]_{\text{inlet}} - [\text{NO}_x]_{\text{outlet}}}{[\text{NO}_x]_{\text{inlet}}} * 100$$

where

$[\text{NO}_x]_{\text{inlet}}$  and  $[\text{NO}_x]_{\text{outlet}}$  are the  $\text{NO}_x$  concentrations in the inlet gas and outlet gas, respectively

### 3.5.3 Effect of Pretreatment Gas

The fresh catalyst sealed with quartz wool in the fixed-bed flow reactor was treated with 1,000 ppm NO, 8 vol%, 1,000 ppm  $\text{C}_3\text{H}_6$ , 3 vol% of water and balance helium. The temperature was ramped with  $50^\circ\text{C}$  step size from 50- $500^\circ\text{C}$ . Each temperature was kept constant for an hour. After reaching  $500^\circ\text{C}$ , the temperature was cooled down to  $450^\circ\text{C}$  and stay for overnight. After pretreatment step was finished, this catalyst was performed in activity testing step as described above.