

## CHAPTER III

### EXPERIMENTAL SECTION

#### 3.1 Materials

##### 3.1.1 Catalyst Preparation Materials

-Silver nitrate ( $\text{AgNO}_3$ ) of 99.9% purity was supplied from BDH Laboratory Supplies.

-Hydrogen tetrachloroaurate (III) ( $\text{HAuCl}_4 \cdot x\text{H}_2\text{O}$ ) of 99.9% purity was supplied from A Johnson Matthey Company.

-Aluminum nitrate nonahydrate ( $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ) of 99% purity was supplied from Fluka Co., Ltd.

-Sodium carbonate anhydrous ( $\text{Na}_2\text{CO}_3$ ) of 99.9% purity was supplied from BDH Laboratory Supplies.

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

-1,3 Butane diol anhydrous ( $\text{C}_2\text{H}_4(\text{OH})\text{C}_2\text{H}_4\text{OH}$ ) of 99% was supplied from Aldrich Chemical Company, Inc.

##### 3.1.2 Gas Reactants

-Nitric Oxide (NO) 5% in helium was obtained from Air Products and Chemicals.

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

-Ultra high purity (UHP) oxygen (O<sub>2</sub>) was obtained from Praxair (Thailand) Co., Ltd.

-Nitrogen (N<sub>2</sub>) 3.11% in helium used as a standard was obtained from Thai Industrial Gas (Public) Co., Ltd.

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

## **3.2 Catalyst Preparation**

In this work the catalysts were prepared at 5% loading of silver and gold on alumina by two methods, coprecipitation and sol-gel methods.

### **3.2.1 Coprecipitation Method**

Silver nitrate, hydrogen tetrachloroaurate and aluminum nitrate of known weight were dissolved in distilled water and put into a burette. This solution was added dropwise to a solution of sodium carbonate at a pH about 9-11. During the dropwise addition, the pH was kept in the range 9-11 by adding more sodium carbonate solution. The solution was stirred and kept at 60°C until the addition was complete. The precipitate and the supernatant were centrifuged to separate. The precipitates were washed by hot distilled water at 60°C to remove sodium ions. A conductivity meter was used to monitor the conductivity of water. Repeated washing were done until the conductivity was close to the conductivity of distilled water. The washed precipitate was dried at 110°C for 12 hours and calcined. The resultant catalysts were stored in a vacuum desiccator.

### 3.2.2 Sol-gel Method

Aluminum isopropoxide (AIP) of known weight was dissolved in hot water at 85°C with a small amount of nitric acid to form the fibrillar aluminum hydroxide sols. After vigorous stirring for a while, the fibrillar sol solution was slowly mixed with a solution of silver nitrate and hydrogen tetrachloroaurate (III) dissolved in 1,3-butanediol. The temperature of the mixed solution was controlled constantly at 85°C. After an hour of mixing, the heater was closed but the stirring of the solution continued. After one day of stirring, the solvents were eliminated by heating under reduced pressure to form a gel. The gel was dried at 110°C for 24 hours and calcined. The resultant catalysts were stored in a vacuum desiccator.

## 3.3 Catalyst Characterization

### 3.3.1 Surface Area Measurements

Brunauer-Emmet-Teller method (BET) was applied to determine the surface area of porous materials. The catalysts were out-gassed in flowing helium at 140°C for 16 hours before characterizing. The characterization was based on the physical adsorption of nitrogen (N<sub>2</sub>) at the liquid nitrogen temperature (77 K). The specific surface area was calculated from five points nitrogen adsorption isotherm. The average pore radius and average pore volume were calculated at P/P<sub>0</sub> ratios close to unity.

### 3.3.2 X-ray Diffraction (XRD)

X-ray diffraction was used to identify the internal structure, bulk phases, and composition of crystalline material. An approximate crystallite size can be found from the broadening of an X-ray diffraction peak, measured

at one-half the height. An estimate of the dimension of the crystallites was calculated by the Scherrer formula.

$$d = k\lambda / (b \cos\theta)$$

where

d is the crystallite size ( $^{\circ}\text{A}$ )

k is a constant (frequency nearly unity)

$\lambda$  is a wavelength ( $^{\circ}\text{A}$ )

$\theta$  is the corresponding Bragg angle (degree)

b is the peak width at the middle height (radian)

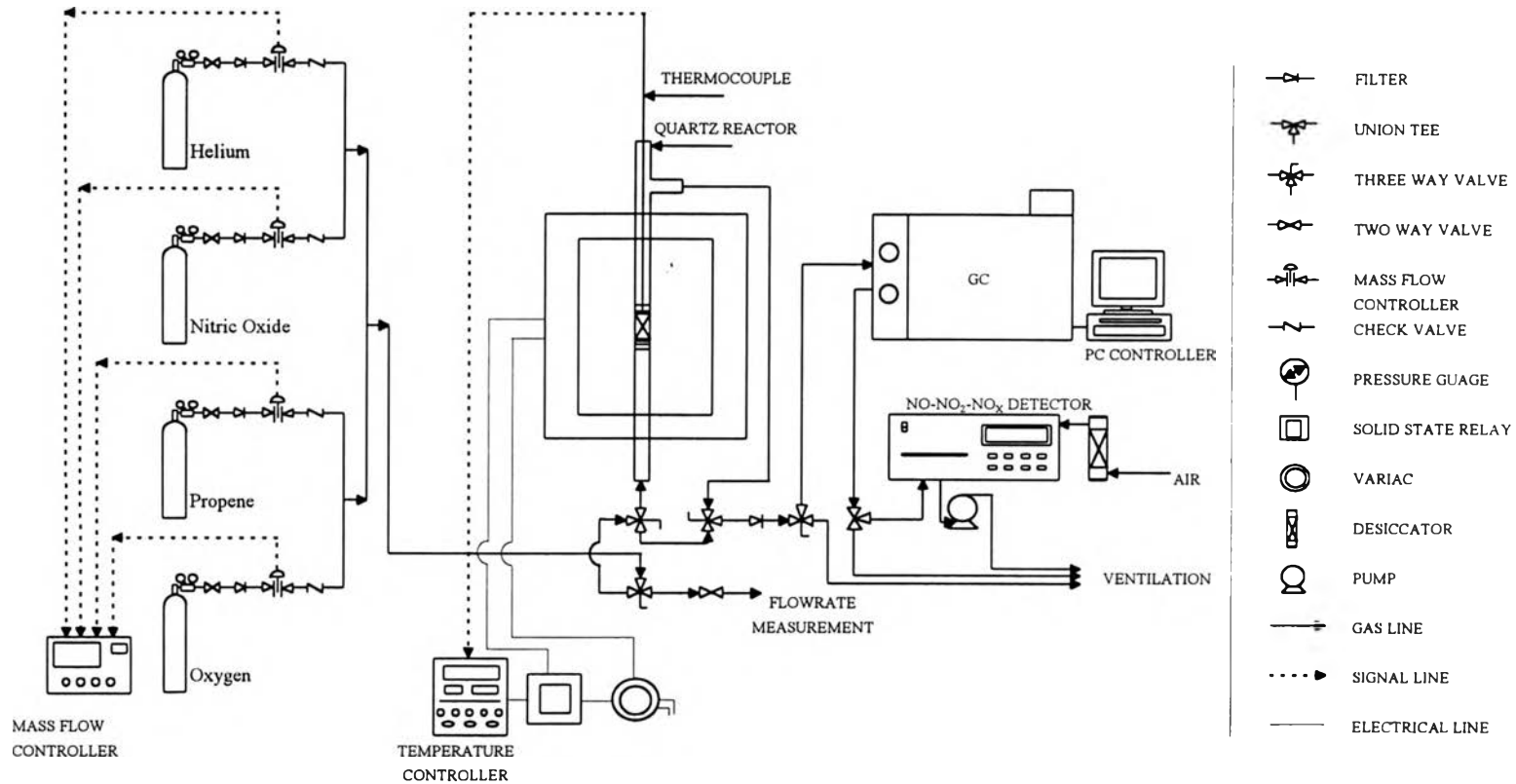
### 3.3.3 Thermogravimetric Analysis (TGA)

In a thermogravimetric analysis, the mass of sample in a controlled atmosphere is recorded continuously as a function of temperature or time as the temperature of the sample is increased (usually linear with time). A plot of mass or mass percent as a function of time is called thermogram, or a thermal decomposition curve (Skoog and Leary, 1992).

Thermograms were obtained under an inert atmosphere heating from room temperature to 800°C at a rate of 5°C/min.

## 3.4 Apparatus

The experimental apparatus which are shown in Figure 3.1 can be divided into four parts: i) gas blending system, ii) the catalytic reactor, iii) gas chromatography, and iv) chemiluminescence NO-NO<sub>2</sub>-NO<sub>x</sub> analyzer for analysis of products.



**Figure 3.1** Schematic flow diagram.

### 3.4.1 Gas Blending System

Gas flow rates were controlled by a mass flow transducer and controller model 840 from Sierra Instruments. Helium gas was used for the pretreatment step to clean the surface of the catalyst. Nitric oxide, propylene in helium, and oxygen were passed through micron filters, and the mass flow controllers at constant pressure. Check valves were installed to prevent the back flow of gases. The gases were mixed and then fed to the inlet of the reactor.

### 3.4.2 Catalytic Reactor

The reactor was 0.25 inch diameter quartz tube operated at atmospheric pressure. The catalyst in the middle of reactor was packed between quartz wool plugs. An electrical heater was used to heat the reactor. The reaction temperature was controlled by a PID controller using a K-type thermocouple inserted into the quartz wool plug. The controller, connected to the thermocouple, was a Yokogawa Instruments model UP27. The variation in temperature was  $\pm 1^{\circ}\text{C}$ .

### 3.4.3 Gas Chromatography

A Hewlett Packard 5890 series II model gas chromatography with an Alltech Molecular sieve 13X, operated at 40, 210, 120°C for column, detector, and injector respectively, was used for measuring the composition qualitatively and quantitatively of feed and reactor effluent stream.

A sampling valve equipped with a 200  $\mu\text{l}$  sampling loop was used to inject the reactor effluent gas every 15 minutes into the gas chromatography for analysis.

#### 3.4.4 High Level Chemiluminescence NO-NO<sub>2</sub>-NO<sub>x</sub> Analyzer.

The effluent gases at a flow rate of more than 200 cm<sup>3</sup>/min from the gas chromatography were separated into two parts, the first part was sent to the high level chemiluminescence NO-NO<sub>2</sub>-NO<sub>x</sub> analyzer from Thermo Environmental Instruments Inc. Model 42C to measure the concentration of nitric oxide and nitrogen dioxide which are the major components in NO<sub>x</sub>, the excess was exhausted.

### 3.5 Activity measurements

The catalytic activity of NO reduction by C<sub>3</sub>H<sub>6</sub> on Ag/Au supported Al<sub>2</sub>O<sub>3</sub> was carried out at atmospheric pressure. The catalysts placed in a quartz tube with quartz wool plugs, were heated up to 300°C in a stream of helium at a rate of 100 cm<sup>3</sup>/min and heating rate about 10°C/min. The catalysts were left at this temperature for an hour and were then heated up or down to the designed reaction temperature. The catalysts were kept at the reaction temperature while the gaseous reactant was bypassed to the analysis equipment to check the composition of the feed stream. After feed stream checking, the activity-studies were started and the amount of N<sub>2</sub>, NO, and NO<sub>2</sub> were measured continually until steady-state was reached. The activities are defined in the terms of percentage conversion which are separated into 2 types

$$\% \text{ NO conversion to N}_2 = ((2 \times [\text{N}_2] \text{ produced}) / ([\text{NO}] \text{ feed})) \times 100$$

$$\% \text{ Conversion of NO} = (([\text{NO}] \text{ reacted}) / ([\text{NO}] \text{ feed})) \times 100$$

where

[compound] is the concentration of chemical compound.