

CHAPTER III

EXPERIMENTAL SECTION

3.1 Materials

Catalyst preparation materials

- Gamma alumina ($\gamma\text{-Al}_2\text{O}_3$) was analytical research grade (AR grade) and obtained from Aldrich Chemical Company. The size and surface area of this Al_2O_3 was 150 mesh and $155 \text{ m}^2/\text{g}$ respectively.

- Silver nitrate (AgNO_3) of 99.9% purity was from Fluka.

- Hydrogen tetrachloroaurate (III) trihydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$) was from Aldrich Chemical Company.

- Aluminum(III)-nitrate nanohydrate ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) of 98% purity was supplied from Fluka.

- Sodium carbonate anhydrous (Na_2CO_3) of 99% purity was from Fluka.

Gaseous reactant

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

- Carbon monoxide (CO) of 1.06 and 5.28% in helium was supplied from Thai Industrial Gas Public Co., Ltd. (TIG).

- Nitrogen (N_2) 3.16% in helium used as a standard gas was obtained from Thai Industrial Gas Public Co., Ltd. (TIG).

- Ultra high purified (UHP) helium were obtained from Thai Industrial Gas Public Co., Ltd. (TIG).

3.2 Catalyst preparation

The catalysts were prepared at 5 % loading of silver and gold on gamma aluminum oxide by two methods, impregnation and coprecipitation methods. The ratio of silver to gold was defined as the percentage of silver used in loading.

Impregnation method

Gamma alumina ($\gamma\text{-Al}_2\text{O}_3$) which was sieved in the range of 80-120 mesh of particle size was cleaned off volatile adsorbents by heating at 140 °C for 20 hours. The precursor solution for the catalyst was prepared by mixing hydrogen tetrachloroaurate (III) trihydrate and silver nitrate in distilled water. The ratio of the distilled water volume to the amount of catalyst was unity.

This precursor was slowly poured into the beaker of Al_2O_3 with stirring until Al_2O_3 powder wetted. The beaker of Al_2O_3 was heated to 60 °C and stirred during the addition. These catalysts were dried in air at 100 °C for 12 hours and calcined at varying temperatures. Finally, the catalysts were washed by distilled water to get rid of the undesired chlorine and sodium and dried again in air at 100 °C for 12 hours. After preparation, these catalysts were kept in a desiccator under vacuum.

Coprecipitation method

Silver nitrate, hydrogen tetrachloroaurate (III) trihydrate, and aluminium 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 pH about 9-11. During the dropwise addition, the pH was

kept in the range of 9-11 by adding more sodium carbonate solution. The solution was stirred and kept at 60°C until the addition was completed. The precipitate and the supernatant were separated by centrifuge. The precipitate was washed by hot distilled water to remove sodium ions. A conductivity meter was used to monitor the conductivity of water. Repeated washings were done until the conductivity was close to that of distilled water. The washed precipitate was dried at 100 °C for 12 hours and calcined. The resultant catalysts were stored in the desiccator under vacuum.

3.3 Catalyst characterization

3.3.1 Surface area measurements

Brunauer-Emmet-Teller (BET) method was applied to determine the surface area of porous materials. The catalysts were pretreated in He flow at 140 °C for 12 hours before characterizing. The characterization was based on the physical adsorption of nitrogen at the liquid nitrogen temperature (77 K). The specific surface area was calculated from five points of nitrogen adsorption isotherm. The average pore radius and average pore volume were calculated at P/P_0 ratios close to unity.

3.3.2 X-ray diffraction (XRD)

X-ray diffraction is usually used to identify the structure and composition of crystalline material. The 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 is calculated by the Scherrer formula :

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

where

d is the crystallite size (Å)

k is a constant (frequency nearly unity)

λ is a wavelength (Å)

θ is the corresponding Bragg angle (degree)

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

3.3.3 Transmission electron microscopy (TEM)

Transmission electron microscopy is used to identify the size of metal crystallites, the changes in the sizes, shapes, and position. JEOL 2000 Transmission electron microscope operated at an accelerating voltage of 200 kV was used in this study.

3.4 Apparatus

The experimental apparatus which is shown in Figure 3.1 can be divided into three parts: i) gas blending system; ii) the differential reactor and; iii) gas chromatograph for analysis of products.

3.4.1 Gas blending system

Gas flow rates were controlled by a mass flow transducer and controller model 840 from Sierra Instrument Inc.

Hydrogen was used for the reduction step to reduce the catalyst to the active form. Carbon monoxide and nitric oxide in helium were passed

through micro filters, and the mass flow controllers at a constant pressure. The gases were mixed before feeding the reactor.

3.4.2 Catalytic reactor (Differential flow reactor)

The reactor is made of a 1/4 inch diameter quartz tube and operated at 1 atm. The catalyst was packed in the middle of reactor between zirconia plugs. An electrical heater was used to heat the reactor. The reaction temperature was controlled by a PID controller using a type-K thermocouple inserted into the zirconia. The controller, connected to the thermocouple, was a model UP 27 Yokogawa Instruments. The deviation in temperature was ± 1 °C.

3.4.3 Product analysis

A model 5890 series II Hewlett Packard gas chromatograph coupled with an Alltech 13X Molecular Sieve column operating at 50 °C was used for product separation. The helium carrier flow was 10 ml/min and the temperatures at the injection and detector ports were 120 °C and 210 °C respectively. GC peaks were calibrated by using known standards.

3.5 Activity measurements

The NO reduction and CO oxidation on Ag/Au/Al₂O₃ catalysts were carried out at atmospheric pressure. The catalysts were pretreated 6 hours in 40 ml/min of H₂ at 200 °C after heating at 10 °C /min to the desired temperature. After the pretreatment, the activity studies were started. Measurements of N₂ and CO were continued until the steady-state condition was reached.

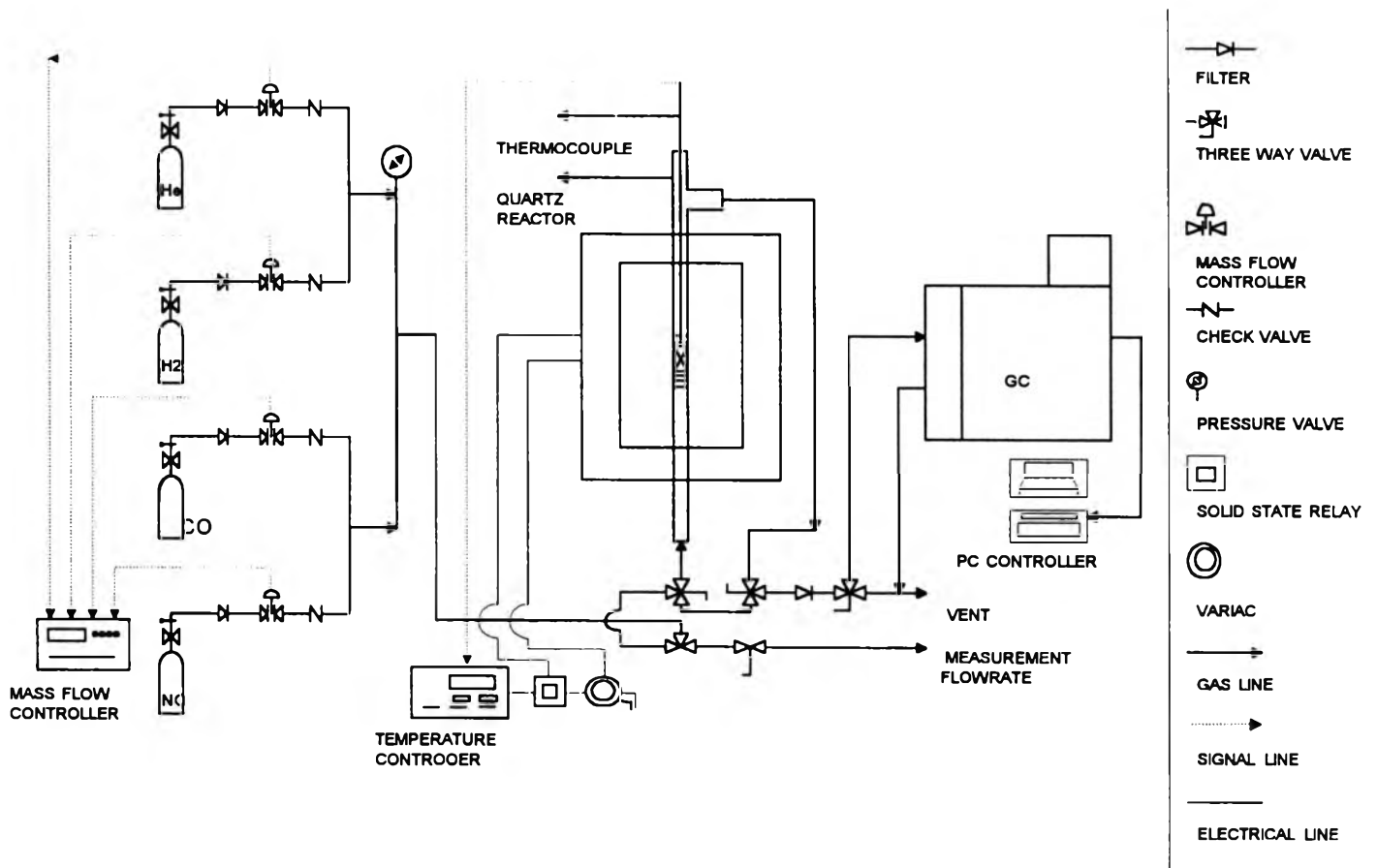


Figure 3.1 Schematic flow diagram.