

CHAPTER III

EXPERIMENTAL SECTION

The experimental section can be divided into six different parts: (a) materials; (b) catalyst preparation; (c) catalyst characterization; (d) apparatus; (e) catalytic activity measurement; and (f) calculations for various conversions. The details for each part are respectively explained as follows:

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.

Silver nitrate (AgNO_3) of 99.9% purity was obtained from BDH Laboratory Supplies.

1,3-Butanediol anhydrous ($\text{C}_2\text{H}_4(\text{OH})\text{C}_2\text{H}_4\text{OH}$) of 99% purity was obtained from Aldrich Chemical Inc.

Manganese (II) nitrate hydrate ($\text{Mn}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$) of 98% purity was obtained from Aldrich Chemical Inc.

Sodium carbonate anhydrous (Na_2CO_3) of 99.9% purity was obtained from BDH Laboratory Supplies.

3.1.2 Reactant Gases

Nitric oxide (NO) 5% in helium used as a reactant gas was obtained from Air Products and Chemicals.

Propylene (C_3H_6) 0.91% in helium used as a reducing gas was obtained from Thai Industrial Gas Public Company Limited.

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

High purity (HP) helium used as a balancing gas was obtained from Thai Industrial Gas Public Company Limited.

Nitrogen (N_2) 3.11% in helium employed as a standard was obtained from Thai Industrial Gas Public Company Limited.

3.2 Catalyst Preparation

In this study the silver supported on alumina catalysts were prepared by the sol-gel method. The silver loading was varied in the range of 0, 1.0, 2.0, 4.0, 5.0, 6.0, and 10.0 wt % in order to clarify the effect of metal loading. The second catalyst, manganese oxide (Mn_2O_3), was prepared by precipitation method in order to study the cooperation effect when it was mixed physically as a promoter with the silver supported on alumina catalyst.

3.2.1 Sol-Gel Method

Fibrillar aluminum hydroxide sols were obtained by addition of a given weight of aluminum isopropoxide (AIP) to hot water at 85 °C with a small amount of nitric acid. After being stirred for a while, the solution of silver nitrate dissolved in 1,3-butanediol was slowly added to the fibrillar sol solution. During mixing, the temperature of this mixed solution was controlled constantly at 85 °C and continuously heated at this temperature for an hour after the completed addition of metal salt. Then the heating was stopped but the stirring of the mixed solution had been continued at room temperature for 24 hours. After vigorous stirring, the solvents were eliminated by heating under a reduced pressure to form a gel. The gel was dried at 110 °C for a day and calcined at 700 °C for 6 hours. The prepared catalyst was stored in a

dessiccator. Bare alumina, in the absence of Ag ion, was also prepared from the fibrillar aluminum hydroxide sols in the same procedure.

3.2.2 Precipitation Method

A given weight of manganese (II) nitrate was dissolved in distilled water at a total concentration of 0.1 M and put into a burette. This solution was added dropwise at the rate of 2-3 ml/min to a sodium carbonate solution of 1 M. During the dropwise addition, the pH was adjusted to be in the range of 9 to 11 by adding more sodium carbonate solution. The solution was stirred and controlled at 60 °C while precipitating. The precipitate was separated and washed thoroughly by hot distilled water in order to remove sodium ions. The washing was repeated until the change in conductivity of supernatant was insignificant. The washed manganese oxide precipitate was dried at 110 °C for 24 hours and calcined in air at 500 °C for 5 hours. The prepared catalyst was stored in a dessiccator.

3.3 Catalyst Characterization

3.3.1 Surface Area Measurement

The Brunauer-Emmett-Teller (BET) method was utilized for determining the surface area, total pore volume, and average pore diameter of the prepared catalysts. The characterization is based on the physical adsorption of an inert gas using Autosorb-1 Gas Sorption system (Quantachrome Corporation). It operates by measuring the quantity of gases adsorbed onto or desorbed from a solid surface at some equilibrium vapor pressures. Nitrogen gas with cross sectional area of $16.2 \times 10^{-2} \text{ m}^2/\text{molecule}$ was employed as an adsorbate at a liquefied nitrogen temperature (77 K).

The sample amount of 0.2 grams were dried and outgassed in the sample cell at 300°C for at least 2 hours before adsorption. The specific

surface area of each catalyst was evaluated from five points adsorption isotherm. The results were analyzed using Autosorb ANAGAS software Version 2.10.

3.3.2 X-ray Diffraction (XRD)

The XRD was utilized to identify the internal structure, bulk phases, and composition of crystalline catalyst. The XRD pattern was obtained by a Phillips X-ray diffractometer system (PW 3020) equipped with a graphite monochromator and a Cu tube for generating a CuK radiation (1.5406 \AA).

The catalyst sample was ground to a fine homogeneous powder and held in the beam in a thin-walled glass container. Constructive interference could be achieved with monochromatic irradiation by varying the angle of incidence (5 to 70 degrees). The digital output of the proportional X-ray detector and the goniometer angle measurements were sent to an online computer to record and subsequently analyzed by PC-APD version 3.5B.

3.4 Apparatus

The experimental apparatus is schematically shown in Figure 3.1. It consists of three parts: (a) gas blending system; (b) catalytic reactor; and (c) analytical instruments.

3.4.1 Gas Blending System

Mass flow transducers and controller model 840 from SIERRA Instruments, Inc. were used for measuring and controlling the reactant gaseous flow rates before delivering them into the reactor. All fittings and tubing are made of stainless steel having outside diameters of 1/4" and 1/8" obtained from SWAGELOK Co., Ltd.

3.4.2 Catalytic Reactor

The quartz tube reactor was 0.25" in diameter. A catalyst sample of 0.1 gram was placed between quartz wool in the middle of the reactor. The catalyst temperature was monitored with a K type thermocouple and controlled by a PID temperature controller, YOKOGAWA Instrument model UP27. The heating rate was set at 10 °C/min and its variation in desired temperature was ± 1 °C.

3.4.3 Analytical Instrumentation

3.4.3.1 Gas Chromatograph (GC)

The main interested product, nitrogen, was analyzed using a gas chromatograph, a Hewlett Packard 5890 Series II model equipped with a thermal conductivity detector (TCD) and a column of Altech molecular sieve 13 X. The operating temperatures of oven, injector, and detector were set at 40 °C, 120 °C, and 210 °C, respectively. A sampling valve equipped with a 200 μ l sampling loop was applied to inject the reactor effluent gas every 15 minutes into the GC for analysis.

3.4.3.2 High Level Chemiluminescence NO-NO₂-NO_x Analyzer

Nitrogen oxides in the effluent gases which include NO and NO₂, were analyzed using a high level chemiluminescence NO-NO₂-NO_x analyzer, model 42C from Thermo Environmental Instrumental Inc. The operation is based on the principle that NO and ozone (O₃) react to produce a characteristic luminescence with an intensity linearly proportional to the NO concentration.

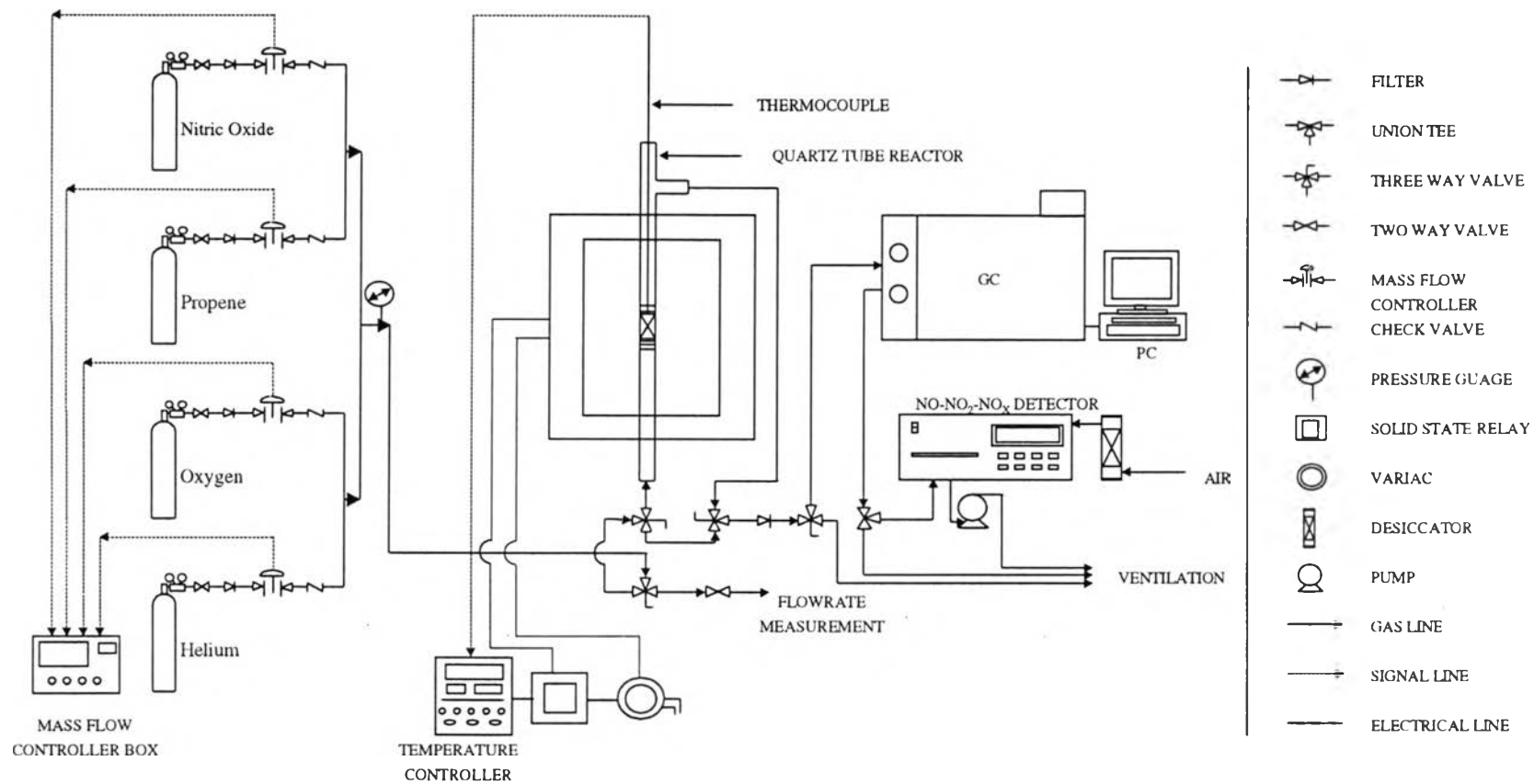


Figure 3.1 Schematic Flow Diagram



3.5 Catalytic Activity Measurements

3.5.1 The Dependence Study of Metal Loading

Catalytic activity measurements for selective reduction of NO with C₃H₆ in an oxidizing atmosphere over various silver supported on alumina catalysts were carried out by using a fixed-bed flow reactor. The procedure can be described as follows:

(a) The catalyst of 0.1 g was pretreated by heating from room temperature to 300 °C with a heating rate of 10 °C/min at a flowing He rate of 100 cm³/min. It was kept constant at this temperature for an hour and then heated up or down to the desired reaction temperature.

(b) The reactant gas mixture containing NO 1,000 ppm, C₃H₆ 1,000 ppm, O₂ 5.0 vol.%, and He was bypassed to the analytical instruments in order to check the composition of the feed stream before passing through the reactor.

(c) The mixture of reactant gases passed through the catalyst bed at a total flow rate of 200 cm³/min. The reaction temperature was varied in a range of 200 °C to 600 °C and the amount of N₂, remained NO, and NO₂ was measured every 50 °C when it reached steady state for each reaction temperature.

3.5.2 The Combination Study of Ag/Al₂O₃ and Mn₂O₃

From the dependence study of metal loading, the best catalyst was selected to study further on the cooperation study by mixing physically with the Mn₂O₃ catalyst.

The mixture of 5 %Ag/Al₂O₃ and Mn₂O₃ catalysts was prepared by grinding 5 %Ag/Al₂O₃ and Mn₂O₃ catalysts in a mortar for 30 minutes. This mixture was calcined in air at 500 °C for 5 hours. The resulting catalyst was ground again before being placed into the reactor. The procedure

performed in pretreatment, feed composition checking, and reaction steps was the same.

3.5.3 The Dependence Study of Oxygen Concentrations

From the dependence study of metal loading, the best catalyst was selected to study further on the dependence study of various oxygen concentrations.

The same procedure in pretreatment, feed composition checking, and reaction step was performed. The only change was the oxygen concentration which was increased from 5.0 vol.% to 10.0 and 20.0 vol.% while the total flow rate of reactant gases was kept constantly at 200 cm³/min for all runs.

3.6 Calculations for Various Conversions

In this study the percentage of conversions can be expressed in terms of conversion of NO, conversion of NO to N₂, and conversion of NO_x. All expressions are defined as follows:

$$\% \text{ Conversion of NO} = [\text{NO}] \text{ reacted}/[\text{NO}] \text{ inlet} \times 100 \quad (3.1)$$

$$\% \text{ Conversion of NO to N}_2 = 2 \times [\text{N}_2] \text{ produced}/[\text{NO}] \text{ inlet} \times 100 \quad (3.2)$$

$$\% \text{ Conversion of NO}_x = \{([\text{NO}] \text{ inlet} + [\text{NO}_2] \text{ inlet}) - ([\text{NO}] \text{ outlet} + [\text{NO}_2] \text{ outlet})\} / \{[\text{NO}] \text{ inlet} + [\text{NO}_2] \text{ inlet}\} \times 100 \quad (3.3)$$

where [compound] is the concentration of chemical compound.