

CHAPTER III

EXPERIMENTAL SECTION

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 Fluka Co., Ltd.

Titanium (IV) butoxide ($\text{Ti}[\text{O}(\text{CH}_2)_3\text{CH}_3]_4$) of 98% purity was obtained from Aldirch Chemical Inc.

Ethanol ($\text{CH}_3\text{CH}_2\text{OH}$) of 99.9% purity was obtained from J. T. Baker.

Hydrogen hexachloroplatinate (IV) hydrate ($\text{H}_2\text{PtCl}_6 \cdot x\text{H}_2\text{O}$), A. C. S. reagent, was obtained from Aldirch Chemical Inc.

Nitric acid (HNO_3) of 65% purity was obtained from Riedel-de Haen AG.

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 reactant 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 (N₂) 3.11% in helium used as a standard was obtained from Thai Industrial Gas Public Company Limited.

3.2 Catalyst Preparation

In this study the silver supported on alumina (Ag/Al₂O₃), platinum supported on alumina (Pt/Al₂O₃), silver supported on titania (Ag/TiO₂), and platinum supported on titania (Pt/TiO₂) catalysts were prepared by the sol-gel method.

3.2.1 Sol-Gel Method for Ag/Al₂O₃ and Pt/Al₂O₃

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 solution of silver nitrate dissolved in 1,3-butanediol or hydrogen hexachloroplatinate (IV) hydrate dissolved in water 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 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 600°C for 6 hours. The prepared catalysts were stored in a dessicator. Bare alumina, in the absence of Ag and Pt ion, was prepared from the fibrillar aluminum hydroxide sols in the same procedure.

3.2.2 Sol-Gel Method for Ag/TiO₂ and Pt/TiO₂

Titanium (IV) butoxide was added to ethanol, which was then mixed with nitric acid. Nitric acid was added to form a clear sol. During mixing, the temperature of this mixed solution was controlled constantly at 0°C. After vigorous stirring for a while, the solution of silver nitrate dissolved in 1,3-butanediol or hydrogen hexachloroplatinate (IV) hydrate dissolved in water was slowly added to the solution. Then the solution became a transparent titania sol. A small amount of water was added to the solution to be cause gelation. The solvents were eliminated by evaporation at room temperature for 24 hours. The gel was dried at 110°C for a day and calcined at 400°C for 6 hours. The prepared catalysts were stored in a dessicator.

3.3 Catalyst Characterization

3.3.1 Surface Area Measurement

The characterization is based on the physical adsorption of an inert gas using Autosorp-1 Gas Sorption system (Quantachrome Corporation). It was utilized for determining the surface area, total pore volume, and average pore diameter of the prepared catalysts by using the Brunauer-Emmett-Teller (BET) method. It operates by measuring the quantity of gases adsorped onto or desorped from a solid surface at some equilibrium vapor pressures. Nitrogen gas with cross sectional area of 16.2×10^{-2} m²/molecule was employed as an absorbate at the liquid nitrogen temperature (77 K).

A small sample, between 0.05-0.1 g, was dried and outgassed in the sample cell at 300°C for at least 40 minutes before adsorption. The specific surface area of each catalyst was evaluated from the 5 point adsorption isotherm. The average pore radius and average pore volume were calculated at P/P₀ ratio close to unity. The results were analyzed using Autosorp ANAGAS software Version 2.10.

3.3.2 X-ray Diffraction (XRD)

X-ray Diffraction (XRD) was utilized to identify the internal structure, bulk phases, and composition of crystalline catalysts. The XRD pattern was obtained by a Rigaku X-ray diffractometer system equipped with a RINT 2000 wide angle goniometer and a Cu tube for generating a CuK α 1 radiation ($\lambda = 1.54 \text{ \AA}$) was used to obtain the X-ray diffraction patterns at a generator voltage of 40 kV and a generator current of 30 mA. Nickel filter was used as the K_{β} filter. The goniometer parameters were divergence slit = $1^{\circ}(2\theta)$; scattering slit = $1^{\circ}(2\theta)$; and receiving slit = 0.3 mm. The catalyst samples were filled on a glass slide, firmly pressed by another glass slide. A scan speed of $5^{\circ}(2\theta)/\text{min}$ with a scan step of $0.02^{\circ}(2\theta)$ was used during a continuous run in the 5 to $90^{\circ}(2\theta)$ range. 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.

3.3.3 Atomic Absorption Spectroscopy (AAS)

Varian Specter AA300 was used to analyze the concentration of metal in catalysts.

3.4 Apparatus

The experimental apparatus is shown in Figure 3.1. It consists of four parts: (a) gas blending system; (b) catalytic reactor; (c) gas chromatography; and (d) chemiluminescence NO-NO₂-NO_x analyzer for analysis of products.

3.4.1 Gas Blending System

A mass flow transducer and controller model 840 from Sierra Instruments controlled gas flow rates. Helium gas was used for the pretreatment step to clean the surface of the catalyst. Nitric oxide, propylene in

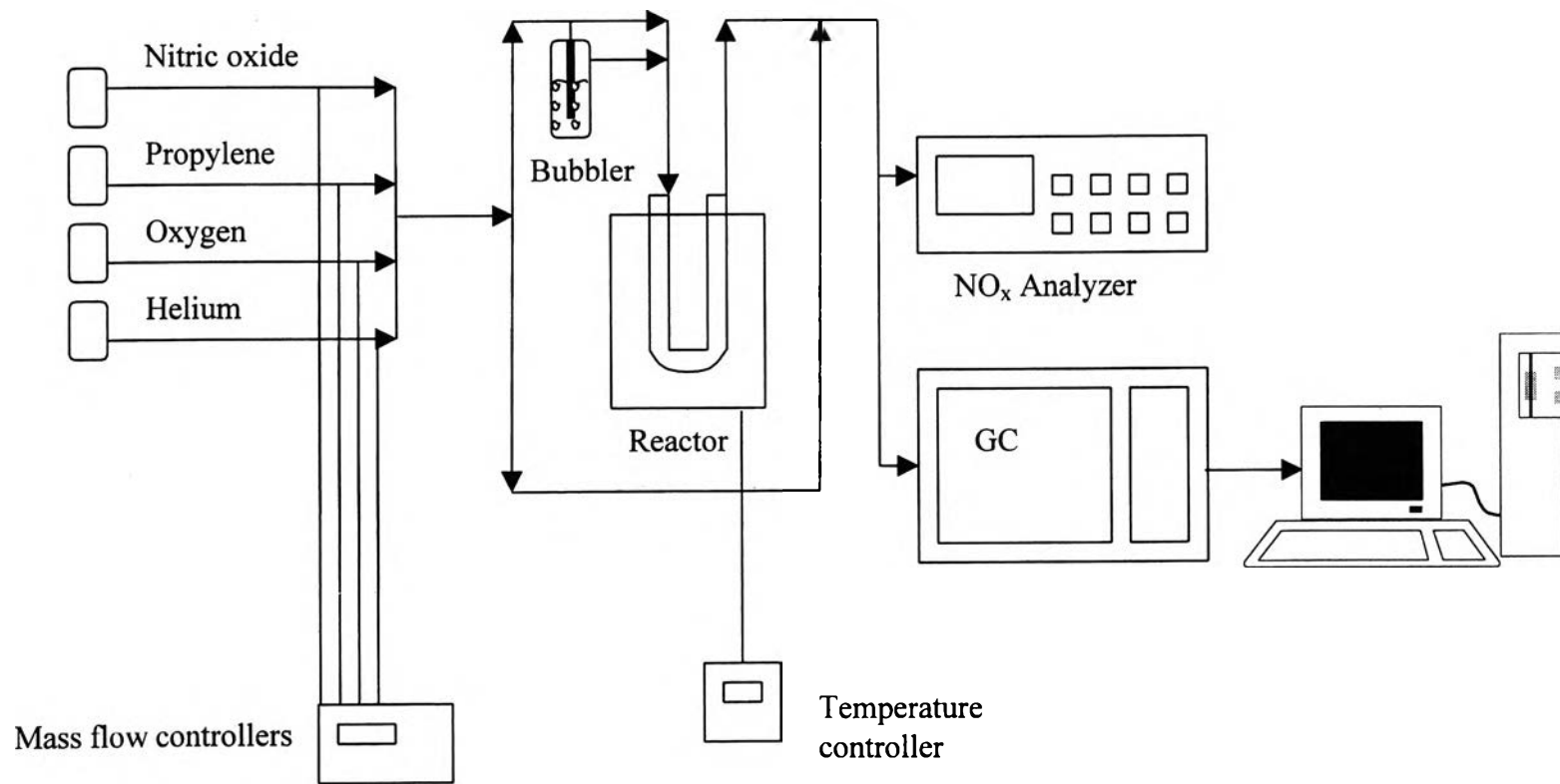


Figure 3.1 Schematic flow diagram.

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 1/4 inch diameter quartz U-tube operated at atmospheric pressure. The catalyst in the reactor was packed between quartz wool plugs. A PID controller (Yokogawa Instruments model UP27) controlled the catalyst temperature. It was connected to a K-type thermocouple inserted into the quartz wool plug.

3.4.3 Gas Chromatography

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

3.4.4 Chemiluminescence NO-NO₂-NO_x Analyzer

Thermo Environmental Instruments Inc. Model 42C was used for measuring the concentration of nitric oxide and nitrogen dioxide, which are the major components in NO_x.

3.5 Catalytic Activity Measurements

The activity of catalysts was studied by varying the metal loading and the reaction temperature in a range of 100°C to 550°C. The catalyst of 0.05 g was used. 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 bypassing through the reactor. The mixture of reactant gases passed through the catalyst bed at a total flow rate $100 \text{ cm}^3/\text{min}$. We then chose the catalysts which gave the highest nitric oxide conversion among other metal loading catalysts. Combining two catalysts, a two-stage catalyst in a reactor was also used to improve conversions. We also studied the effect of the water vapor. After feed stream checking, the activity studies were started and the amount of NO, NO₂ and NO_x were measured continually until steady state was reached. The activities are defined in the terms of percentage conversion of NO and NO_x

$$\% \text{ conversion of NO} = \left(\frac{[\text{NO}] \text{ reacted}}{[\text{NO}] \text{ feed}} \right) \times 100$$

$$\% \text{ conversion of NO}_x = \left\{ \frac{([\text{NO}] \text{ inlet} + [\text{NO}_2] \text{ inlet}) - ([\text{NO}] \text{ outlet} + [\text{NO}_2] \text{ outlet})}{([\text{NO}] \text{ inlet} + [\text{NO}_2] \text{ inlet})} \right\} \times 100$$

where [compound] is the concentration of chemical compound.

Table 3.1 Summary of experiments done.

Run number	Catalyst	Experimental condition*
1	Al ₂ O ₃	Dry reaction
2-7	1, 2, 4, 5, 6, 8% Ag/Al ₂ O ₃	Dry reaction
8-12	0.5, 1, 1.5, 2, 3% Pt/Al ₂ O ₃	Dry reaction
13	TiO ₂	Dry reaction
14-17	0.5, 1, 2, 3% Ag/TiO ₂	Dry reaction
18-23	0.5, 1, 1.5, 2, 3, 4% Pt/TiO ₂	Dry reaction
24	6% Ag/Al ₂ O ₃	Wet reaction
25	3% Pt/Al ₂ O ₃	Wet reaction
26	2% Ag/TiO ₂	Wet reaction
27	2% Pt/TiO ₂	Wet reaction
28	Ag/Al ₂ O ₃ → Pt/Al ₂ O ₃	Dry reaction
29	Pt/Al ₂ O ₃ → Ag/Al ₂ O ₃	Dry reaction
30	Ag/TiO ₂ → Pt/TiO ₂	Dry reaction
31	Pt/TiO ₂ → Pt/TiO ₂	Dry reaction
32	Ag/Al ₂ O ₃ → Pt/Al ₂ O ₃	Wet reaction
33	Pt/Al ₂ O ₃ → Ag/Al ₂ O ₃	Wet reaction
34	Ag/TiO ₂ → Pt/TiO ₂	Wet reaction
35	Pt/TiO ₂ → Pt/TiO ₂	Wet reaction
36	Mixing Ag/Al ₂ O ₃ and Pt/Al ₂ O ₃	Dry reaction
37	Mixing Ag/TiO ₂ and Pt/TiO ₂	Dry reaction
38	Mixing Ag/Al ₂ O ₃ and Pt/Al ₂ O ₃	Wet reaction
39	Mixing Ag/TiO ₂ and Pt/TiO ₂	Wet reaction

* 0.050 g catalyst, 100 cm³/min, 1,000 ppm NO, 1,000 ppm C₃H₆, 5% O₂, and ~3% water for wet reaction.