CHAPTER III

EXPERIMENTAL

3.1 Materials

3.1.1 Chemicals for Catalyst Preparation

- Hydrogen tetrachloroaurate (III) trihydrate ($HAuCl_4 \cdot 3H_2O$) was obtained from Aldrich.

- Nickel (II) nitrate hexahydrate ($Ni(NO_3)_2 \cdot 6H_2O$), purum p.a. grade, was obtained from Fluka.

- Yttrium (III) nitrate tetrahydrate ($Y(NO_3)_3 \cdot 4H_2O$), R&D grade with $\geq 99.99\%$ purity, was obtained from Aldrich.

- Ammonium hydroxide solution (28%) was obtained from Univar.

- Methanol solution (99.9%) was HPLC grade and was obtained from Merck.

3.1.2 Reactants for Oxidation Experiment

Carbon monoxide (CO) and methanol (CH_3OH) were used as the reactants in this research. Either 1% CO or 0.5% CH_3OH, both balanced by air, was fed into the system. Methanol was vaporized in a vapor generator and then was carried through the system by air. The composition of methanol in the feed was adjusted to the desired value by controlling the vapor saturator temperature and the air flow rate.

3.1.3 Gases for Oxidation Experiment

The gases used in this study were high purity hydrogen, helium, air zero, and 1% CO balanced in air, obtained from Thai Industrial Gas Public Co., Ltd. (TIG). The standard gas with the composition of 0.5% CO, 0.5% CO_2, 0.5% H_2, and 0.5% O_2 were all balanced by nitrogen supplied by Alltech.

3.2 Catalyst Preparation

In this research, the coprecipitation method was used to prepare the gold-doped oxide catalysts at 0.5% Au (Au/(Au+MO_x) = 0.5%) in nickle oxide (NiO) and yttrium oxide (Y_2O_3). A mixture of nickel (II) nitrate hexahydrate and hydrogen tetrachloroaurate trihydrate at 0.5% Au was dissolved in distilled water and the solution was heated to 60-70°C. 1 M ammonium hydroxide solution was then added drop-wise to the stirred solution until the pH of the solution was 8. After that the solution was left at 60-70°C for one hour for precipitation. The precipitate was seperated by centrifuge, washed with hot distilled water for several times, dried at 120°C overnight, ground into fine powder, and finally calcined for four hours in flowing air at different temperatures of 300, 400, 500, and 600°C for Au/Y_2O_3 and of 500°C for Au/NiO.

3.3 Catalyst Characterization

The characteristics of the prepared gold-doped oxide catalysts were determined with regard to their physical and chemical properties. The characterization techniques and equipments applied in this research were

Atomic Absorption Spectroscopy (AAS), BET surface area analyzer, X-ray Diffraction (XRD), and Thermalgravimetric Analysis (TGA). The details were described in the following sections.

3.3.1 Atomic Absorption Spectroscopy (AAS)

The actual contents of gold loadings in the prepared catalysts were determined by atomic absorption spectroscopy, VARIAN Model 300/400. The standard solution of 1,000 ppm of gold used in this work was manufactured by Merck. Firstly, a known weight around 0.02 g of a catalyst was completely dissolved in a mixture solution of aqua regia (hydrochloric acid and nitric acid with a ratio of 18:82). The solution was then diluted to the measuring range. The concentration of gold was obtained by comparing its absorbance with the calibration curve of the standard solution.

3.3.2 BET Surface Area Measurement

The surface areas of all prepared catalysts were determined by measuring the quantity of gas adsorbed onto or desorbed from their solid surface at some equilibrium vapor pressure by static volumetric method. The solid sample was maintained at a constant temperature below the critical temperature of the adsorbate. An adsorption or desorption causes the change in the pressure of the sample cell until the equilibrium is established. This volume-pressure data are used to calculate the BET surface area.

The BET surface area measurement was done by using Quantachrome Corporation Autosorb I. The catalyst sample was first outgased to remove the humidity and volatile adsorbents adsorbed on surface under vacuum at 300°C for three hours before starting the analysis to determine the surface area. Autosorb ANYGAS Version 2.10 was used to analyze the results.

The adsorption data were calculated by using the Brunauer-Emmett-Teller (BET) equation.

$$\frac{P}{V(P_0 - P)} = \frac{1}{V_m c} + \frac{(c-1)}{V_m c}\frac{P}{P_0} \qquad (3.1)$$

where

V = the volume of gas adsorbed;

P = the pressure of gas;

P_0 = the saturated vapor pressure of the liquid at the operating

temperature;

V_m = the volume equivalent to an adsorbed monolayer; and

c = the constant related to the energy of adsorption in the

first adsorbed layer, the magnitude of adsorption in the

first adsorbed layer, and the magnitude of adsorbate/adsorbent

interaction, which is given by

$$c = \exp\left[\frac{H_1 - H_L}{RT}\right] \qquad (3.2)$$

where

H_1 = the fixed heat of adsorption;

H_L = the latent heat of evaporation;

R = the gas constant; and

T = the temperature

The surface area can be determined by using the following equation:

$$S_g = \frac{V_m}{0.0224}(6.02 \times 10^{23})(A) \qquad (3.3)$$

where

S_g = the specific surface area (m^2/g)

A = the area occupied by each adsorbate molecule (m^2)

3.3.3 X-ray Diffraction (XRD)

X-ray Diffraction (XRD) is based on the fact that an X-ray diffraction pattern is unique for each crystalline substance. Thus, if an exact match can be found between the pattern of an unknown and an authentic sample, chemical identity can be assumed. It is also possible to make a relatively quantitative analysis 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.

X-ray diffraction patterns of all catalyst samples were obtained by using a Phillips PW 1830/00 No. SY 1241 diffractometer equipped with a graphite monochromator and a Cu tube for generating a CuK radiation (1.5406°A). First, the sample was ground to fine powder by using a mortar. The powder was then spread on a glass slide specimen holder and was examined between 5-90° 2θ at a scanning rate of 1.5° 2θ/min in 0.02° 2θ increments. CuKα radiation with λ = 0.154 nm was used as the X-ray source and operated at 40 kV and 30 mA. The digital output of the proportional X-ray detector and the gonimeter angle measurements was sent to an online microcomputer for storing the data and the data were analyzed by PC-APD version 3.5B. Peak positions were compared with the standard files to identify crystalline phases.

The XRD patterns were used for the average particle diameter estimation by line broadening measurements in the Debye-Scherrer equation,

$$T = K\lambda \, / \, \beta\cos\theta \qquad\qquad (3.4)$$

where

λ = the wavelength (nm);

K = the Debye-Scherrer constant which to some degree
  depends on the shape of the peak (assume equal to 0.9);

β = the full width at half maximum (FWHM) of the broadened peak;

θ = the Bragg angle of the reflection (degree); and

T = the thickness of the crystal (nm)

3.3.4 Thermalgravimetric Analysis (TGA)

Thermogravimetric Analysis (TGA) technique was used to determine the phase transfer of yttrium oxide. Each sample was measured using the Du Pont TGA 2950 Thermogravimetric Analyzer. The chamber inside the analyzer was exposed to a continuous flow of nitrogen (as a protective gas) and air (as a purge gas) at a flow rate of 10 and 20 ml/min, respectively. The specimen was heated up from 30°C to 700°C with a rate of 10°C/min, followed by cooling down to 30°C with a rate of 10°C/min. The mass changes during temperature increase were monitored and recorded using the TA instrumental thermal analyst system.

3.4 Study of Carbon Monoxide and Methanol Oxidation Reactions

3.4.1 Equipment Setup

Figures 3.1 and 3.2 show the experimental setup for the studies of CO and methanol oxidations, respectively. The catalyst sample of ~0.2 g was packed into a Pyrex glass tube reactor between two plugs of glass wool. The reactor was placed in an electrical heater equipped with a PID controller. The temperature was controlled by Yokogawa temperature controller with a thermocouple inserted into the catalyst bed. The flow rate of each gas was controlled by Sierra Instrument mass flow controller to achieve the desired feed stream composition. A pressure gauge was installed at the end of the line near the needle valve which was used to ensure that the reaction was operated under atmospheric pressure.
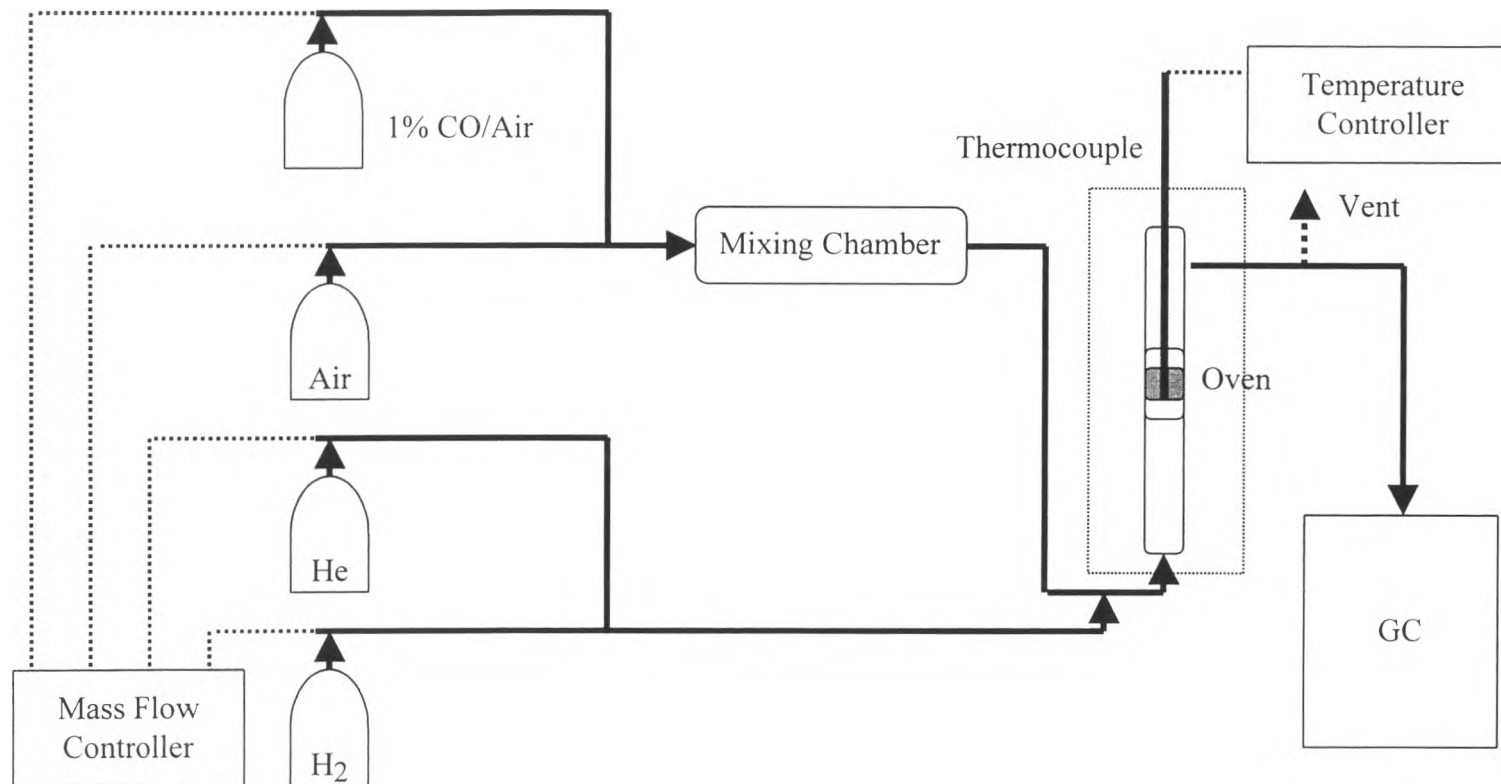
Figure 3.1 Schematic diagram of the experimental setup for carbon monoxide oxidation
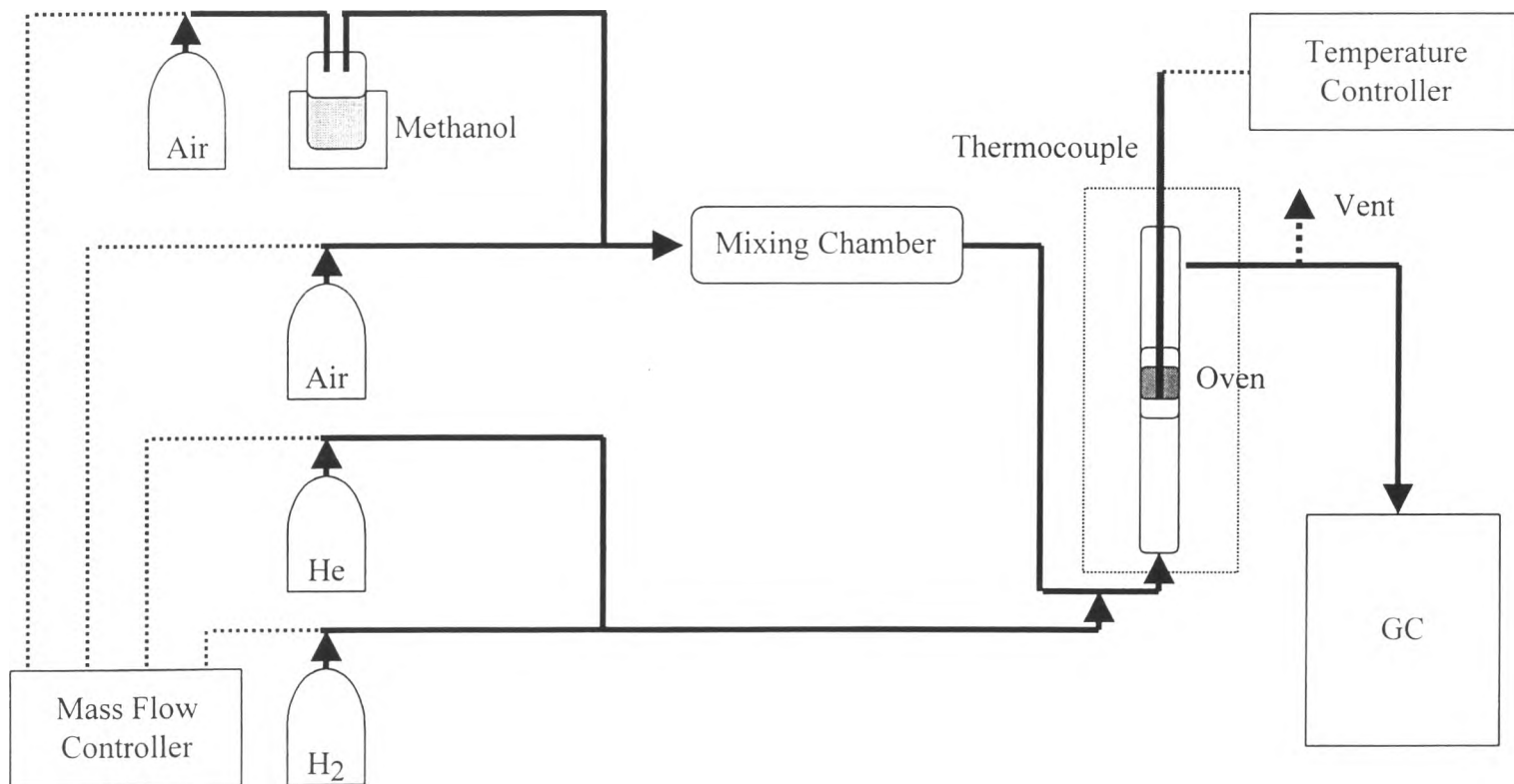
Figure 3.2 Schematic diagram of the experimental setup for methanol oxidation

3.4.2 Oxidation Experiment Procedure

After loading the catalyst sample in the tube reactor, the catalyst bed temperature was raised to 573K in hydrogen stream at a flow rate of 20 ml/min and was held for two hours at this temperature to reduce the catalyst sample. After completing the reduction step, the catalyst was cooled down to room temperature and was then heated up again to 473K in helium stream at a heating rate of 10 K/min. Then helium was switched to air and the temperature was raised to 773K and held for 30 min. After the pre-treatment step, the catalyst was cooled down to the desired temperature by air stream.

For CO oxidation, 1% CO balanced in air was fed into the reactor. In the case of methanol, a vapor generator to generate methanol vapor was applied. The temperature of the vapor generator was kept constant at 278K by immersing it in a water bath. The air stream with a flow rate of ~6.65 ml/min was flown into the vapor generator (bubble reactor) to carry the methanol vapor into the system. The concentration of methanol vapor in the feed stream was kept constant at 5,000 ppm (0.5% by volume) by controlling the temperature of the vapor generator. The total flow rate was 70 ml/min and the space velocity (SV) was 21,000 ml/h g_{cat}.

The compositions of the reactants and the products were analyzed by Autosystem Perkin Elmer ARNEL 5653V gas chromatography equipped with a thermal conductivity detector (TCD) and a flame ionization detector (FID). The sample was injected into the packed columns by 10-port valve with 10 μl sampling loop. A 60-80 carboxen 1000 column to analyze oxygen, carbon monoxide, and carbon dioxide for TCD and a 80/120 carbopack column to analyze methanol, formaldehyde, and formic acid for FID were both used at isothermal condition.