

CHAPTER III

EXPERIMENTAL SECTION

3.1 Materials

3.1.1 Gases

All gases used in this study were supplied by Thai Industrial Gas Public Co., Ltd. (TIG)

a) Premixed 522 ppm carbon monoxide in helium was used as the reactant gas.

b) A cylinder of 5.30% carbon dioxide in helium was used to test the catalyst poisoning.

c) The high purity oxygen (99.8%) was used as the reactant gas and regeneration gas.

d) The ultra high purity hydrogen (99.999%) was used as regeneration gas.

e) The ultra high purity helium (99.999%) was used as diluted gas, purged gas, and carrier gas in gas chromatography and elemental analyzer.

f) The zero grade air was used as the driving gas for an auto injection valve in gas chromatography and combustion gas in elemental analyzer.

3.1.2 Chemicals

All chemicals used in catalyst preparation were analytical grade as described below.

a) Hydrogen tetrachloroaurate ($\text{HAuCl}_4 \cdot x\text{H}_2\text{O}$) was AR grade of 99.9 percent purity obtained from Johnson Matthey Company.

b) Silver nitrate (AgNO_3) was AR grade of 99.8 percent purity supplied by Merck.

c) Cobalt nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) was AR grade of 99.0 percent purity provided by Carlo Erba.

d) Manganese nitrate hydrate ($\text{Mn}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$) was AR grade of 98.0 percent purity supplied by Aldrich Chemical Company.

e) Sodium carbonate anhydrous (Na_2CO_3) was AR grade of 99.9 percent purity obtained from Merck.

3.2 Equipment

The experimental apparatus shown schematically in Figure 3.1 was divided into 3 main parts : (i) gas blending system, (ii) catalytic reactor, (iii) analytical instrumentation.

3.2.1 Gas Blending System

The reactant gas mixture consisted of CO and O₂ balanced in helium. Each gas was supplied from compressed gas cylinder at an initial pressure approximately of 2,000 psig. All gases were passed through micron line filters to remove particles and check valves to prevent reverse flow. The individual stream flow rate was controlled by Sierra instruments model 840 mass flow controller to achieve the desired composition. The mixed stream was adjusted to desired direction by three way valves, and delivered to the reactor.

3.2.2 Catalytic Reactor

The CO oxidation reaction was carried out in an 4 mm inside diameter Pyrex glass U-tube microreactor at atmospheric pressure. The catalyst was packed between quartz wool plugs in the middle of the reactor. The reactor was electrically heated in the heater. The temperature of catalyst bed was monitored and controlled by a PID temperature controller equipped with a chromel-alumel thermocouple. There were 2 reactors. The first reactor was used for reaction studies and was controlled by Shimaden model FP21 temperature controller with $\pm 0.6^{\circ}\text{C}$ deviation. The other one was used for the regeneration and was controlled by Yokogawa instruments model UT37 temperature controller with $\pm 0.3^{\circ}\text{C}$ deviation.

3.2.3 Analytical instrumentation

The effluent gas from the reactor was both qualitatively and quantitatively analyzed by autosampling with a Hewlett Packard 5890 series II gas chromatograph equipped with thermal conductivity detector (TCD). The column utilized in the chromatograph was Carbosphere, 80/100 mesh, 10 ft x 1/8 inch stainless steel packed column. The helium carrier flow rate was 40 ml/min. The temperature of oven, injector and detector were maintained at 95, 110 and 125°C respectively. The output of chromatograph was recorded by a Hewlett Packard 3365 series II Chemstation.

The observed peaks were identified by comparison with retention time of standard gases. The composition of the effluent gas was quantitatively determined by comparison of peak area with calibration curve obtained from known composition gases.

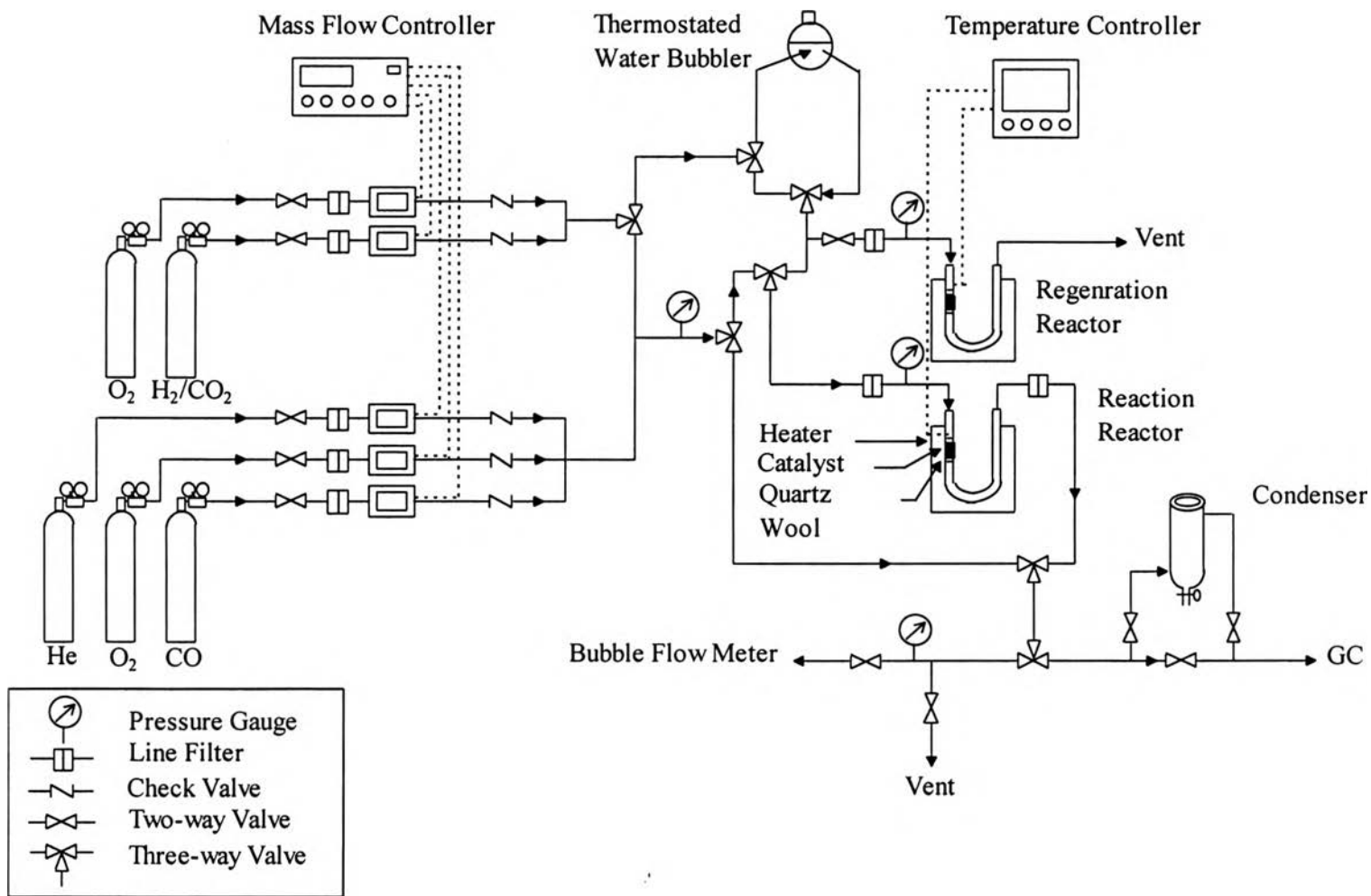


Figure 3.1 The schematic of diagram of experimental equipment.

3.3 Catalyst Preparation

3.3.1 Dried Catalyst

The coprecipitation technique was employed to synthesize the noble metal on reducible oxide catalysts. There were 2 main types of catalysts used in this work, silver and gold on different reducible metal oxide supports. The catalyst compositions are shown in Table 3.1. The 1:4 ratio of Mn and Co was selected because from previous results in this laboratory it was shown to be the most active ratio (Butamjai, S., M.S. thesis, the Petroleum and Petrochemical College, 1996).

Table 3.1 The composition of catalysts

Catalyst type	Ag or Au (wt%)	Mn/CO (wt ratio)
Ag-Mn	0.10	-
Ag-Mn-Co	0.10	0.25
Au-Co	0.10	-
Au-Mn	0.10	-
Au-Mn-Co	0.10	0.25
Mn-Co	-	0.25

The preparation steps were as the following :

- a) The corresponding chemical compounds were dissolved in deionized water at a total concentration of 0.1M.
- b) The aqueous solution of 1 M sodium carbonate was prepared.

c) The precursor from first step was added to the basic solution from step b) at the rate of 2-3 ml/min.

d) This mixture was stirred and controlled at 60°C and pH 8-10 while precipitating.

e) The precipitates were separated and washed thoroughly by warm deionized water.

f) In order to eliminate the excess ions, washing procedure was repeated several times until the conductivity of supernatant change was insignificant.

g) The deionized precipitates were dried at 110°C for 12 hr and then ground to powder.

h) The powder was dried again at 110°C for 12 hr to ensure completely dry.

i) Dried powder was sieved into 80/120 mesh size and kept in a desiccator.

3.3.2 Pretreated Catalyst

Pretreatment had an enormous effect on the activity and performance of catalyst because this might be related to the oxidation state of the metal oxide surface (Tanielyan and Augustine, 1992). The previous work (Butamjai, S., M.S. thesis, the Petroleum and Petrochemical College, 1996) found that oxidation pretreatment increased the catalytic activity owing to active species formation. So this method was used to activate the catalyst by exposing to 50 ml/min of pure oxygen at a temperature of 120°C for 2 hr.

3.4 Catalyst Characterization

The catalysts were characterized by a number of techniques described below in order to understand the relation between the catalyst properties and its activity.

3.4.1 BET Surface Area Measurement (BET)

The Brunauer-Emmett-Teller method (BET) was used to determine the surface area and pore size. This method based on the physical adsorption of an inert gas by using Autosorb-1 Gas Sorption System (Quantachrome Corporation). Nitrogen gas with cross-sectional area of $16.2 \times 10^{-20} \text{ m}^2/\text{molecule}$ was used as the adsorbate at liquid nitrogen temperature (77 K). All samples were degassed at 140°C for 16 hr before measurement. The surface area of each catalyst was obtained from five point adsorption isotherm at P/P_0 ratio less than 0.3. The results were analyzed by Autosorb ANAGAS Software Version 2.10.

3.4.2 X-ray Diffraction (XRD)

Powder diffractometry both qualitatively and quantitatively investigated crystallographic phase form of the catalysts. X-ray diffraction is based upon the fact that an X-ray diffraction pattern is unique for each crystalline substance. Thus, if the observed diffraction pattern was exactly matched with that of reference samples, crystalline phase form could be identified (Baiker, 1985). With XRD it is also possible to make a relatively quantitative analysis by comparing the intensity of the diffraction lines. For the same crystalline substance, the higher intensity shows higher content of that phase.

A Phillips X-ray diffractometer system (PW 3020) equipped with a graphite monochromator and a Cu tube for generating a CuK radiation (1.5406 Å) was used to obtain the XRD patterns. The 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 (10 to 70 degrees). The digital output of the proportional X-ray detector and the goniometer angle measurements were sent to an on-line microcomputer to record and subsequently analyze by PC-APD version 3.5B.

3.4.3 Elemental Analysis (CHNS)

The elemental analyzer was used to determine the basic elements in the catalysts which were carbon, hydrogen, nitrogen and sulfur. The amount of carbonaceous species deposited on the catalyst was evaluated from carbon content by Perkin-Elmer 2400 Series II CHNS/O Analyzer. The sample was burnt in an oxidizing atmosphere. The gas products were separated by chromatography column and then detected by the thermal conductivity detector (TCD). The operation conditions were carried out as the following.

Combustion furnace temperature = 975°C

Reduction furnace temperature = 501°C

Detector oven temperature = 82.6°C

3.4.4 Thermal Gravimetric Analysis (TGA)

Thermogravimetry investigation provided information about the thermal stability of catalysts (Baiker, 1985). The weight of a specimen in a controlled atmosphere was recorded continuously as a function of temperature or time. Thermograms obtained from Netzsch (TG 209) were recorded under nitrogen atmosphere at a heating rate of 10°C/min to 800°C.

Netzch (TG 209) consisted of (i) a sensitive microbalance with an analog-electronic display, (ii) a furnace with programmable temperature, (iii) a purge gas system providing nitrogen and oxygen gas, and (iv) a microcomputer for instrument control, data acquisition and display.

3.4.5 Transmission Electron Microscopy (TEM)

The image of catalyst was observed by transmission electron microscopy using a JEOL 1500X atomic resolution microscope. The catalysts were ultrasonically dispersed in ethanol for 30 min. The suspended composites were dropped onto copper grid coated with polyvinyl formvar desiccant. These samples were coated with carbon in order to enhance the conductivity.

3.5 Methodology

The CO oxidation reaction was carried out at atmospheric pressure in the fixed bed reactor as described previously. 100 mg of 80/120 mesh size catalyst was utilized. The reactant gas mixture consisted of 100 ppm CO and 20% O₂ balanced in helium. The total flow rate was 50 ml/min.

3.5.1 Temperature for 50% Conversion (T_{1/2}) Test

This study was carried out to identify the most active catalyst. Two main types, silver and gold on different metal oxide supports, shown in Table 3.2 were screened by continuously increasing the temperature from 40 to 250°C at a rate of 1°C/min. The catalytic activities were measured as a function of temperature. The temperature corresponding to 50% conversion of CO (T_{1/2}) was used as the index to determine the catalytic activity. The lower T_{1/2} showed relatively higher catalytic activity (Tanielyan and Augustine, 1992).

Table 3.2 The catalysts used for temperature for 50% conversion test

Silver catalyst	Gold catalyst
0.1%Ag-Mn	0.1%Au-Co
0.1%Ag-Mn-Co	0.1%Au-Mn
	0.1%Au-Mn-Co

3.5.2 Deactivation Test

After selecting the active catalyst in part I, this test was employed to observe the long term activity and stability of catalyst. The catalytic activities were measured as a function of time at different conditions.

Temperature : 40, 50 and 60°C

Amount of catalyst : 0.1, 0.2 and 0.3g

3.5.3 Regeneration Test

The deactivated catalysts were regenerated at various conditions to recover the activity. After regeneration procedure, the catalysts were reacted again to observe the recovery activity. There were 2 regeneration methods as described below.

3.5.3.1 Oxidation Regeneration The deactivated catalysts were exposed to 50 ml/min of pure oxygen at different conditions.

Temperature : 110, 200 and 300°C for 12 hr

Time : 12 hr and 2 days at 200°C

3.5.3.2 Reduction Regeneration The deactivated catalysts were exposed to 50 ml/min of pure hydrogen at different conditions.

Temperature : 110, 200 and 300°C for 12 hr

3.5.4 Effect of CO₂ Study

Carbon dioxide retention was a primary factor contributing to the decay of catalyst (Hoflund et al., 1995). Carbon dioxide was added to the reactant gas mixture to observe the catalyst behavior.