

CHAPTER III

EXPERIMENTAL SECTION

3.1 Materials

3.1.1 Reactant Gases

The gases used in this work were research grade carbon monoxide (0.102 percent balanced in helium), oxygen (HP, 99.8 percent purity), helium (UHP, 99.999 percent purity), and hydrogen (UHP, 99.999 percent purity) supplied by Thai Industrial Gas (TIG). All of these gases were obtained at an initial pressure approximately 2000 psig.

3.1.2 Catalyst Preparation Materials

Silver nitrate (AgNO_3) used in this research was AR grade of 99.8 percent purity obtained from Merck.

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.

Manganese nitrate hexahydrate ($\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) was AR grade of 98.0 percent purity supplied by Aldrich Chemical Company.

Sodium carbonate (Na_2CO_3) was AR grade of 99.0 percent purity provided by Carlo Erba.

The composite oxides supported silver catalysts were synthesized by the co-precipitation technique described below.

3.2 Catalyst Preparation

In this research, co-precipitation technique was employed in preparing the composite silver oxide catalysts of transition metals (Ag-Mn-Co). Silver nitrate, cobalt nitrate hexahydrate and manganese nitrate hexahydrate at the selected ratios were first dissolved in distilled water to prepare a solution of total metal concentration of 0.1M and the Ag:Mn:Co molar ratios were varied to change the percent atom of silver (0.1, 1, and 5 percent) in the composite catalysts. These solutions were added to sodium carbonate solution (1M) stirring continuously at a rate of 2-3 ml/min. The temperature of the precursor solution was controlled at 60 °C and kept the pH in the range of 8-10. The resultant precipitates were separated by a centrifuge and washed thoroughly with boiling deionized hot water and then separated by a centrifuge again. This washing was repeated many times in order to remove excess ions. To ensure the removal of the excess ions completely, conductivity of the supernatant was measured until changes were insignificant. The washed co-precipitates were dried in air at 110 °C overnight and ground into a fine powder and then calcined in air at two different temperatures (ranging from 200 to 300 °C). The catalysts were kept in a desiccator before being used.

3.3 Equipment

The experimental apparatus shown in Figure 3.1 can be classified into 3 parts: i) Gas Blending System, ii) The Quartz U-tube Reactor, and iii) Gas Chromatograph.

3.3.1 Gas Blending System

Carbon monoxide specifically used as a reactant gas diluted in helium, oxygen, and remainder being helium passed through micron filters.

Flow was controlled directly by the mass flow controllers, model 840 of Sierra Instruments. The check valve prevented reverse flow of gases.

3.3.2 Catalytic Reactor

The CO oxidation was carried out in a 3.8 mm diameter quartz U-tube microreactor at atmospheric pressure. The silver oxide catalysts were packed in the reactor and sandwiched by quartz wool. The quartz U-tube reactor was heated by a furnace controlled by a PID temperature controller, A Shimaden FP 21, and reactor temperature was controlled to within ± 1 °C. The temperature in the catalysts bed was measured by a chromel-alumel thermocouple type K inserted into the center of the catalyst bed.

3.3.3 Analytical Instrumentation

The effluent gases leaving from reactor were detected by an autosampling valve and analyzed by 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, 10ft x 1/8 inch stainless steel. The helium carrier flow rate was 40 ml/min and the temperature of oven, injector, and detector port were maintained at 40, 110, and 125 °C respectively. The output of the chromatograph was recorded by a Hewlett Packard 3365 series II Chemstation.

The observed peaks were identified by comparing with the retention times obtained from injection of standard gas sample. The composition of carbon monoxide in the effluent gases was determined by comparison of the peak area with a calibration curve obtained by using gas mixtures of known composition.

3.4 Activity Studies

The catalytic activity of the catalysts synthesized was measured by running the steady state CO oxidation in a fixed bed quartz U-tube reactor with the mixture of 0.01% (100 ppm) CO, 20 vol% O₂ and remainder being helium. The experiments were carried out at the atmospheric pressure with a total gas flow rate 50 ml/min using 100 mg of catalyst in the reactor system shown in Figure 3.1.

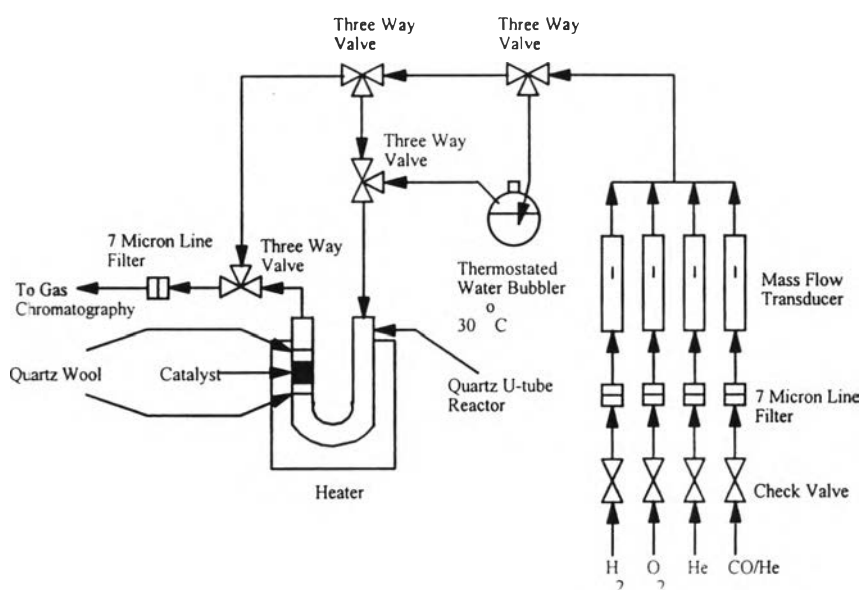


Figure 3.1 The Schematic of Carbon Monoxide Oxidation

3.4.1 Temperature for 50 percent Conversion ($T_{1/2}$) Tests

In this work, we used catalysts containing 0.1 percent atom silver and various ratios of cobalt and manganese (before pretreatment) and applied a heat at a rate of one °C/min. The temperature of the catalysts was increased continuously from 35 to 200 °C. The catalytic activity was measured in terms of the temperature corresponding to 50 percent conversion of CO ($T_{1/2}$). The lower the temperatures for 50 percent conversion, the higher the catalytic activity is (Tanielyan and Augustine, 1992).

3.4.2 Deactivation Tests

Deactivation tests were conducted to determine the long term stability of catalysts. The studies were conducted at 50 and 40 °C.

3.5 Catalyst Pretreatment Tests

Pretreatment can have an enormous impact on the activity and performance of catalysts because these variations may be related to the oxidation state of the metal oxide surface (Tanielyan and Augustine, 1992).

For this research, catalysts prepared and calcined at 200 °C were subjected to the various pretreatment procedures described below.

i) The calcined silver oxide catalysts without any pretreatment were placed in the reactor.

ii) The calcined silver oxide catalysts were oxidized by oxygen at a flow rate of 50 ml/min and the catalyst bed was maintained at 200 °C for 8 hours.

iii) The calcined silver oxide catalysts were humidified by H₂O saturated helium (30 °C) obtained by passing helium through a water bubbler at a flow rate of 50 ml/min. The catalyst bed was maintained at 200 °C for 8 hours.

iv) The calcined silver oxide catalysts were reduced by hydrogen at a flow rate of 50 ml/min at 200 °C for 8 hours.

3.6 Catalyst Characterization

The active and deactivated composite silver oxide catalysts were investigated with regard to their physical and chemical properties using powder X-ray diffraction (XRD), BET surface area analyser, Transmission electron microscopy (TEM), and Thermogravimetry analyser (TG).

3.6.1 X-ray Diffraction

X-ray diffraction is based upon 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 (Baiker, 1985). It is also possible to make a relatively quantitative analysis by comparing the intensity of the diffraction lines. Comparing the same crystalline substance of two different samples, the higher intensity shows the higher content.

A Philips X-ray diffractometer system (PW 3020) equipped with a graphite monochromator and a Cu tube for generating a CuK radiation (1.5406 °A) was used to obtain the XRD patterns. The sample is ground to a fine homogeneous powder and is held in the beam in a thin-walled glass container. Constructive interference may be achieved with monochromatic irradiation by varying the angle of incidence (15 to 75 degrees). The digital output of the proportional X-ray detector and the goniometer angle measurements are sent to an on-line microcomputer for storage and subsequent data analysis by PC-APD version 3.5B.

3.6.2 BET Surface Area Measurements

All samples are outgassed at 120 °C for 6 hours and then a Autosorb-1 Gas Sorption System (Quantachrome Corporation) at liquid nitrogen temperature (77 K) is used to obtain the BET surface area (Baiker, 1985). Autosorb ANYGAS Software Version 2.10 is used to analyze the results.

3.6.3 Transmission Electron Microscopy

The catalysts were ultrasonically dispersed in water for 30 minutes. The suspended composites were dropped onto copper grid coated with

polyvinyl formvar desiccate. These samples were coated with carbon in order to enhance the conductivity.

The available instrument was a JEOL 2000 CX atomic resolution transmission electron microscope.

3.6.4 Thermogravimetric Analysis

In a thermogravimetric analysis, the mass of a specimen in a controlled atmosphere is recorded continuously as a function of temperature or time as the temperature of the sample is increased linearly with time. A plot of mass percent as a function of temperature is called a thermogram (Baiker, 1985).

Netch (TG 209) consists of (i) a sensitive analytical balance, (ii) a furnace, (iii) a purge gas system for providing nitrogen and oxygen gases, and (iv) a microcomputer for instrument control and data acquisition and display.

Thermograms are obtained in this instrument under nitrogen heating to 600 °C at a rate of five °C /minute.