CHAPTER II

EXPERIMENTAL SECTION

2.1 Catalyst Preparations

In this work, we synthesized transition metal oxide catalysts; Ag, Mn, Co, and Mn-Co (1:1) catalysts and transition metal oxide supported silver catalysts; Ag-Mn (1:1 and 1:9), Ag-Co (1:1 and 1:9), and Ag-Mn-Co (2:1:1) catalysts by coprecipitation method. $AgNO_3$ (Merck, 99.8%), $Mn(NO_3)_2.4$ H_2O (Riedel, 97.0%), and $Co(NO_3)_2.6H_2O$ (Fluka, 99.0%) at known molar ratios were dissolved in distilled water. The total concentration of combined aqueous solution was 0.1 M. This solution was added to sodium carbonate solution (1 M) with stirring at a rate of 2-3 mL/min. The precipitate was kept at its pH of 8 about 3 hours and then centrifuged and washed with distilled water several times for eliminating excess ions. The precipitate was dried in air at 100°C overnight. After drying, catalysts were pretreated with various pretreatment methods.

2.2 Catalyst Pretreatment Procedures

The conditions employed for activating the catalyst have an enormous effect on its subsequent performance, because this variation may be related to the oxidation state of the metal oxide surface (Tanielyan and Augustine, 1992).

In this research, the non-calcined catalysts were subjected to the pretreatment procedures described below:

(1) Samples were placed in the reactor without any pretreatments.

(2) Samples were pretreated with saturated humidified nitrogen at 100 mL/min flow for 1 hour.

(3) Samples were calcined in air at 200°C for 3 hours before samples were placed in the reactor.

(4) Samples were calcined in air at 500°C for 3 hours before samples were placed in the reactor.

(5) Samples were placed in the reactor and purged with hydrogen at 50 mL/min for 1 hour at 200°C.

2.3 Characterization

2.3.1 X-ray Diffraction Methods

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) is used to obtain the XRD patterns. The sample is ground to a fine homogeneous powder and is held in the beam in thin-walled glass. Constructive interference may be achieved with monochromatic irradiation by varying the angle of incidence (5 to 80 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.

Scherrer equation (Baiker, 1985) relates the mean crystallite diameter and the broadening of the X-ray diffraction lines per the expression

$$d_b = K\lambda /B_d \cos \theta$$

where λ is wave length of the monochromatic X-ray radiation ($^\circ$A)

K is the Scherrer constant whose value depends on the shape of the particle (assume equal to 1)

B_d is the angular width of the peak in the terms of $\Delta(2\theta)$ (radian)

θ is the glancing angle (degree)

d_b is the mean crystallite diameter ($^\circ$A)

2.3.2 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).

Netzch (TG 209) consists of: (1) a sensitive analytical balance, (2) a furnace, (3) a purge gas system for providing nitrogen and oxygen gases, and (4) a microcomputer for instrument control and data acquisition and display.

Thermograms are obtained in this instrument under nitrogen and oxygen environments by heating to 900°C at a rate of 10°C/min.

2.3.3 BET Surface Area and Average Pore Radius 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) and average pore radius. Autosorb ANYGAS Software Version 2.10 is used to analyze the results.

2.4 Activity Studies

The catalytic activity was carried out in a fixed bed quartz U-tube reactor using 50 mg of catalyst. The desired concentration of the reactant gases were obtained by blending CO (balanced in N_2), pure N_2, and O_2. The reactant gases containing 1% CO and 20% O_2 balanced in N_2 were passed through bed at total flow rate of 100 mL/min (SV=120,000 mL/g.h) as shown in Figure 2.1. Carbon monoxide was determined using a HP 5890 gas chromatograph equipped with a thermal conductivity detector (TCD). The column packing was carbosphere, and the column temperature was maintained at 95°C throughout the analysis.

For hydrogen reduction, 50 mL/min of pure hydrogen was passed through a bed maintained at 200°C for 1 hour before activity test.

Humidification treatment was operated by passing pure nitrogen at a rate of 100 mL/min through a thermostated water bubber and then through reactor which maintained temperature at 100°C for 1 hour as shown in Figure 2.1.
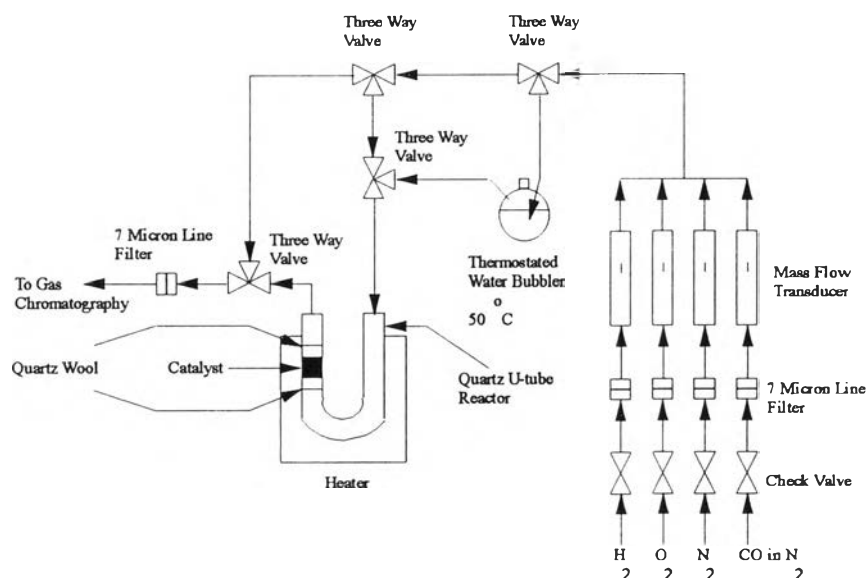
Figure 2.1   Schematic flow diagram of CO oxidation reactor.

2.4.1   Temperature for 50% Conversion Tests

The temperature of catalyst bed was continuously increased at a rate of 1.5°C/min from 50 to 200°C. Catalytic activities were evaluated by determining the temperature at which 50% of the carbon monoxide was oxidized under these conditions ($T_{1/2}$). Consequently, lower temperature of $T_{1/2}$ showed relatively higher catalytic activity (Tanielyan and Augustine, 1992).

2.4.2   Deactivation Tests

To determine the stability of catalysts (Sze, 1995), the tests were carried out at a temperature of 60°C. The conversion was plotted with time to obtain the deactivation curve.