

CHAPTER III

EXPERIMENTAL

3.1 Materials

3.1.1 Zirconium Alkoxide Preparation:

Zirconium hydroxide ($Zr(OH)_4$) of 97% purity was obtained from Aldrich Chemical Company and used as received.

Sodium hydroxide (NaOH) of 98% purity was obtained from Asia Pacific Specialty Chemicals Inc. Limited and used as received.

Ethylene glycol (dist. EG) was obtained from J T. Baker and purified by fractional distillation prior to use.

Silicone oil was obtained from Dow Corning Cooperation U.S.A and used as received.

Acetonitrile and methanol (dist. MeOH) of 99.97 % purity were obtained from Labscan Asia Co., Ltd. and F.E.R.O.S.A, respectively. Both were purified using standard purification methods prior to use.

3.1.2 Catalyst Preparation:

Cerium (III) nitrate hexahydrate ($Ce(NO_3)_3 \cdot 6H_2O$) of 99% purity was obtained from Aldrich Chemical Company. Inc.

Lanthanum nitrate hexahydrate (LaN_3O_9) of 99% purity and nickle (II) nitrate hexahydrate ($Ni(NO)_3 \cdot 6H_2O$) of 98% purity were supplied from Fluka Co., Ltd.

Lithium nitrate ($LiNO_3$) of 95% purity was obtained from Riedel-De Haen Ag Seelze-Hannover.

All these materials were used as received.

3.1.3 Reactant Gases:

Carbon monoxide (CO) 1% in air and ultra high purity (UHP) helium (He) were supplied from Thai Industrial Gas (Public) Co., Ltd.

Ultra high purity (UHP) oxygen (O₂) was obtained from Praxair (Thailand) Co., Ltd.

3.2 Catalyst Preparation Procedure

The effect of combination of metal loading on the support for carbon monoxide oxidation was studied in this work.

3.2.1 Catalyst Support

Catalyst libraries were prepared by the sol-gel method using cerium (III) nitrate hexahydrate and sodium tris (glycozirconate) produced from the “OOPS” method, as starting materials. First, sodium tris (glycozirconate) was mixed with the proper amount of water. Oxalic acid was added to promote the gel formation, and the gel was kept at ambient temperature for 1 hour. The obtained gel was washed with deionized water twice and centrifuged at 10,000 rpm for 10 minutes to remove impurities. After that, the gel was mixed with the solution of cerium (III) nitrate hexahydrate and stirred. The ratio between ceria and zirconia precursors was fixed at Ce:Zr of 3:1. Finally, the mixture was dried at 110°C overnight and calcined at 500°C for 4 hours. After calcination the catalysts were stored in a dessicator.

3.2.2 Impregnation Technique

After above step, 0.2 gm of Ce_{0.75} Zr_{0.25} O_y catalyst support was placed in the holes of library plate. The support in the holes was impregnated with aqueous solutions of metal compounds with different desired weight percent loading by micropipet. Finally, all catalysts were dried at 110°C overnight and calcined at 500°C for 4 hours in the plate.

3.3 Catalyst Characterizations

3.3.1 Surface Area Measurement

Autosorb-1 Gas sorbtion system (Quantachrome Cooperation) was utilized for evaluation of surface area, total pore volume and average pore diameter of

catalysts. Brunauer-Emmett-Teller (BET) based on physical adsorption was applied in the calculation. Before measurement, each catalyst was out-gassed by being heated under vacuum to eliminate volatile adsorbents on surface at 250°C for 4 hours.

3.3.2 X-ray Diffraction (XRD)

Powder x-ray diffraction (XRD) patterns were collected on Rigagu X-ray diffractometer system equipped with a Rint 2000 wide-angle goniometer using $\text{CuK}\alpha$ radiation with a generator voltage and generator current of 40 kV and 30 mA, respectively. 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 packed on a glass holder. 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 10° to $90^\circ(2\theta)$ range. The digital output of proportional X-ray diffractor and the goniometer angle measurements were transferred to an online microcomputer to record data and subsequent analysis.

3.3.3 Scanning Electron Microscopy

Scanning electron microscopy (SEM) experiments were performed on the JEOL 5200, with the magnification of 35-200,000. The SEM provides unique information about the surface morphology of materials, which are the catalysts for the present research. Samples were stuck on the stubs and coated with gold by ion sputtering device (JFC-1100E) for 5 minutes to prevent specimen charging. The examinations were taken through this microscope with a magnification ranges from 3,500 to 10,000.

3.3.4 Atomic Absorption Spectroscopy (AAS)

The amount of sodium content in support catalyst was determined by VARIAN Model 300/400. A known weight of catalyst was digested in *aqua regia* solution (nitric acid and hydrochloric acid with the ratio of 3:2). The metal solution was diluted to the measuring range. The concentration of sodium was obtained by comparing the absorbance with the calibration curve of standard solution.

3.4 Experimental Apparatus

3.4.1 High-throughput IR Reactor System

The experimental apparatus used in this research is schematically shown in Figure 3.1. It consists of three parts, which are: (i) gas mixing section, (ii) catalytic reactor, and (iii) analytical instrumentation.

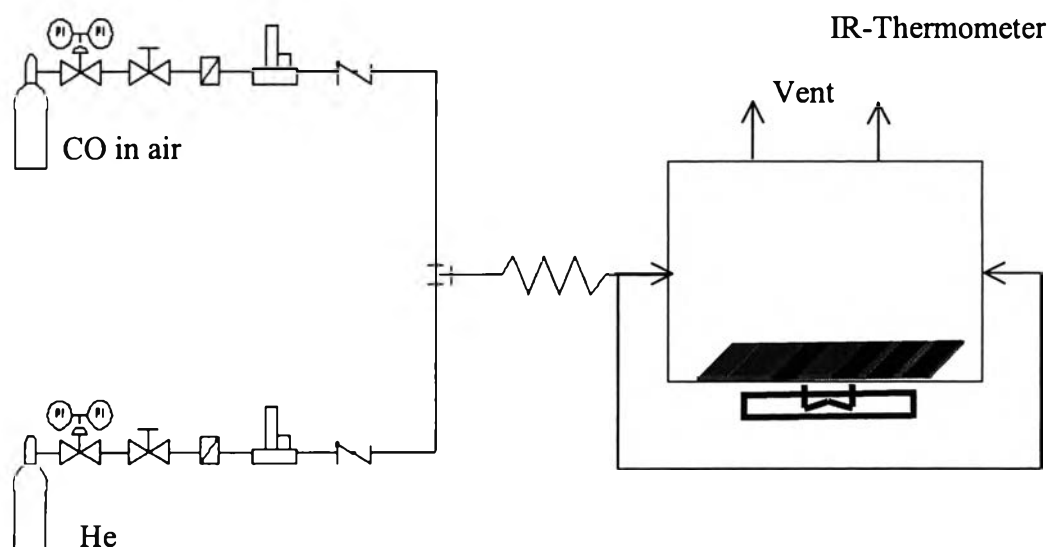


Figure 3.1 Schematic flow diagram of High-throughput IR reactor system.

3.4.1.1 Gas Mixing Section

The reactant gas mixtures consisted of carbon monoxide, oxygen, nitrogen, and helium. Each gas was passed through a micro filter to remove small particles and through a check valve to prevent reverse flow. The individual stream flow rate was controlled using a mass flow controller to achieve the desired flow rate. Then, the gas streams were adjusted to desired direction by three way valves, and passed to the reactor. The total flow rate of feed gas was kept at 50 and 100 ml/min, with the composition of 1% CO and 20% O₂.

3.4.1.2 Catalytic Reactor

Firstly, catalytic activity tests for carbon monoxide oxidation were carried out in the IR-reactor. Catalyst samples were packed on a ceramic library plate containing up to 18 samples in one batch, as illustrated in Figure 3.2.

Then, the library plate was placed into the reactor. IR thermometer was used to detect surface temperature of each catalyst on library plate with time-on-stream. The temperature of library plate was monitored and controlled by Omron temperature controller model E5CK equipped with J-type thermocouples.

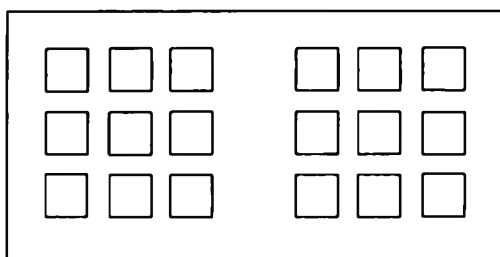


Figure 3.2 Library plate.

3.4.1.3 *Analytical Instrument*

The increased temperature of all catalyst samples on the library plate can be monitored using an infrared thermometer. The infrared thermometer used in this work was obtained from Mitchell Instrument Co. model Mitrpm50. The resolution of this thermometer was 0.1°C.

3.4.2 Conventional Packed-bed Reactor System

From IR-reactor primary screening, the lead catalyst formulations were selected for further testings. The gas mixing section was set the same as in high-throughput case. These formulations were tested for carbon monoxide oxidation reaction in a 1 cm outside diameter of borosilicate glass tube at atmospheric pressure. Each catalyst was packed in the middle of reactor and held in place with glass wool. The temperature catalyst bed was examined and controlled by PID temperature controller equipped with K-type thermocouple (Yokohama, Model UP27). The effluent gases from reactor were passed to analytical section.

For fixed bed reactor, the effluent gas was analyzed both quantitatively and qualitatively by Hewlett Packard 3365 series II chemstation to analyze the concentration of carbon monoxide remaining using a molecular sieve 13X column. The helium carrier flow rate was about 28 ml/min. The temperature of

oven, injector, and detector were maintained at 40°C, 110°C, and 175°C, respectively. The conventional packed-bed reactor system is illustrated in Figure 3.3.

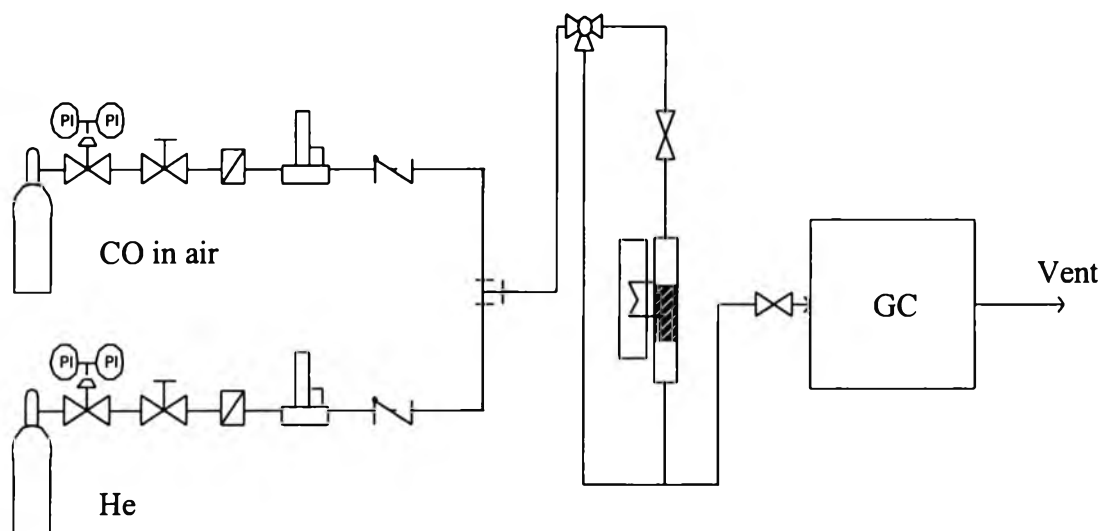


Figure 3.3 Schematic flow diagram of conventional packed-bed reactor system.

3.5 Catalytic Activity Measurement

For IR thermography experiments, catalytic oxidation of carbon monoxide (CO) on mixed oxide catalysts was carried out in the IR-reactor heated by electricity. Catalysts of 0.2 gm each packed in a square hole of the library plate, at which a small diameter thermocouple was located, were placed in the reactor. Then the reactor was heated to 350°C in the stream of helium at 50 ml/min. After that, reactant gas composition containing 1% CO and 20% O₂ balanced in N₂ and He was passed through the reactor atmospheric pressure with 50 ml/min of total flow rate. The temperature of each square hole was measured with time-on-stream using the IR thermometer. The activity of each catalyst sample was exhibited in terms of average temperature recorded over stability time. Two criteria were applied and assisted in the selection of lead catalytic formulations from the IR primary screening (Appendix A).

For conventional testing, 0.15 g of catalyst sample was packed into the reactor. The reactor was, then, heated to 350°C under helium flow at 25 ml/min.

The reactant gas mixture consisting of 0.5% CO, 10% O₂, 39% N₂ balanced in helium was passed through the reactor when the desired temperature was reached. The total gas flow rate was maintained at 50 ml/min. The activity of catalyst was reported in percent conversion of carbon monoxide as presented in Appendix B.