

CHAPTER III

EXPERIMENTAL SECTION

3.1 Materials

3.1.1 Gases

The gases used in this research were:

1. Helium (He 99.999%) was obtained from Praxair (Thailand) Co., LTD., which was used as diluted gas, purged gas, and carrier gas in gas chromatography and elemental analyzer.
2. Oxygen (8 % O₂ in He) was obtained from Praxair (Thailand) Co., LTD., which was used as the reactant gas.
3. Carbonmonoxide (5 % CO in He) was obtained from Praxair (Thailand) Co., LTD., which was used as the reactant gas.
4. Hydrogen (Ultra high purity) was obtained from Praxair (Thailand) Co., LTD., which was used as the reactant gas.

3.1.2 Chemicals

The chemical reagents used for catalyst preparation were as follows:

1. Cerous (III) nitrate hexahydrate ($\geq 99\%$) was AR grade obtained from Aldrich Chemical Company, Inc.
2. Zirconyl chloride octahydrate ($\geq 99\%$) was AR grade obtained from Fluka Chemie A. G.
3. Urea ($\geq 99\%$) was AR grade obtained from Fluka Chemie A. G.

3.2 Experimental Apparatus

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

3.2.1 Gas Mixing Section

The reactant gas mixture consisted of CO and O₂ balanced in oxidizing condition, and in the reducing condition, H₂ was added to the reactant gas mixture. 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 glass wool plugs in the middle of the reactor. The reactor was electrically heated. The temperature of catalyst bed was monitored and controlled by a PID temperature controller equipped with a chromel-alumel thermocouple (Type K).

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

33.75 ml/min in the oxidizing condition and 13.75 ml/min in the reducing condition. The temperature of oven, injector and detector were maintained at 70, 110 and 175°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 times of standard gases. The composition of the effluent gas was Quantitatively determined by comparison of peak area with calibration curve obtained from know composition gases.



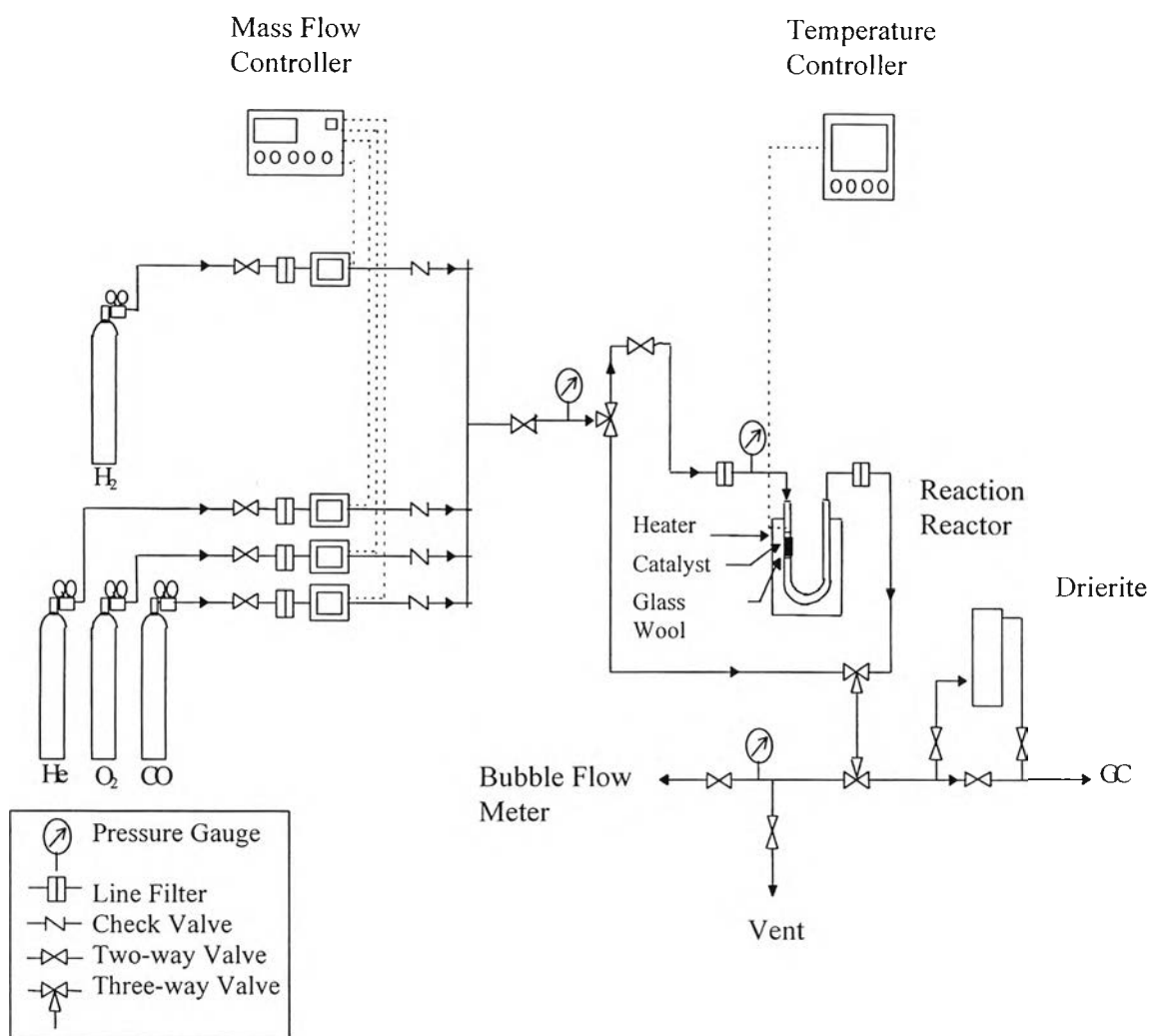


Figure 3.1 Schematic of the experimental apparatus

3.3 Catalyst Preparation Procedure

The catalyst was prepared by sol-gel method. The solutions used for this experiment were salts of zirconium, cerium and urea, and were prepared by dissolution in distilled water. Table 3.1 shows the concentrations of these three solutions prepared.

Table 3.1 Molecular weight and concentration of the components

Salt	Molecular Weight (g/g mole)	Molar Concentration
CO(NH ₂) ₂ (Urea)	60.06	0.4
ZrOCl ₂ .8H ₂ O	322.25	0.1
Ce(NO ₃) ₃ .6H ₂ O	434.23	0.1

The samples were made by mixing together the zirconia, ceria and urea solutions. For example, Ce_{0.50}Zr_{0.50}O₂ mixed oxide catalyst was prepared by mixing equal volume of each solution of ceria, zirconia and urea together. Urea was required for the reaction to take place because during the reaction the zirconia and ceria react with one another and produce H⁺ ions, the urea meanwhile decomposes during the reaction and produces OH⁻ ions which react with the H⁺ ions to form water, H₂O. It was important that the amount of urea was always one third of the total volume of the sample and that it was the last solution to be added to the sample, since it was the hydrolysis catalyst.

After the solutions had been prepared, they were accurately measured into the Glass Schott Bottles, using a pipette to ensure the volume were accurate.

The next step, the solutions had been measured into the Glass Schott bottles; the bottles were sealed and then put in the oven at 100°C. After the desired reaction time was passed, the sample was taken outside the oven, and

allowed to cool down before the lid was removed because if the lid were removed immediately, the sample would boil as it was in the oven at a high temperature.

The sample was then put into the centrifuge tubes, which were then centrifuged at 1600 rpm for 10 minutes. The liquid was poured out and the tubes were filled with distilled water up to the 10 ml mark. This step was to wash the solids. The samples were then centrifuged again for 10 minutes, and then the liquid was poured out. A second washing was repeated as the same procedure. After the second washing with the distilled water, the sample was washed in the same way with ethanol and then centrifuged. The sample was washed with the distilled water to remove ions from the sample, and the ethanol was used to prevent the hydroxides from forming agglomerates after the sample had dried.

After washing and centrifuging had been completed, the samples were then put in the oven at 110°C, for at least 12 hours overnight to let it dried. The samples were then put into the vials and kept in the dessicator until they were ready to be analyzed.

Several parameters were varied during the progression through this experiment; the parameters, which were chose to be changed, were the molar ratios of zirconium and cerium and the reaction times of the samples in the oven.

3.3.1 Molar Ratios

To investigate the optimum yield, the molar ratios were varied several times to determine which ratio of zirconium to cerium resulted in the maximum yield of product. The following molar ratios were used to investigate this variable:

Molar Ratios of Ce : Zr - 100:0

75:25

50:50

25:75

0:100

The total molar concentration of the solutions were equal to 0.1 molar.

3.3.2 Aging Times

The samples were put initially aged in the oven for 50 hours. However, after several results had been collected for these conditions, the time was changed to 120 hours.

3.4 Catalyst Characterization

3.4.1 Determination of BET Surface Area

The surface areas of all catalysts prepared were measured by the five-point BET method using a Quantachrome Corporation Autosorb I. Before measurement, a catalyst sample was outgassed by being heated under vacuum to eliminate volatile adsorbents on the surface (523 K, 4 h). By measuring the quantity of gas adsorbed onto or desorbed from a solid surface at 5 equilibrium vapor pressure (P/P_0) value (0.1115, 0.1615, 0.2115, 0.2615 and 0.3115) by the static volumetric method, the data were obtained by admitting or removing a known adsorbate gas, nitrogen, into or out of a sample cell containing the solid adsorbent maintained at a constant temperature below critical temperature of the adsorbate, that is 77 K for nitrogen.

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

$$1/[W((P/P_0)-1)] = 1/[W_m C] + [(C-1)/(W_m C)] * (P/P_0) \quad (3.1)$$

where W = weight of gas adsorbed at relative pressure P_0 ;
 W_m = weight of adsorbate constituting a monolayer of surface coverage;
 C = constant that is related to the energy of adsorption in the first adsorbed layer and magnitude of adsorbate/adsorbent interaction.

The surface area can be obtained from the following equation.

$$\text{Surface area of sample} = W_m A_{\text{nitrogen}} (6.02 \times 10^{23}) / M_{w, \text{nitrogen}} \quad (3.2)$$

where A_{nitrogen} = Cross-sectional area of one molecule nitrogen
= 0.162 nm² (at 77K);
 $M_{w, \text{nitrogen}}$ = molecular weight of nitrogen (28).

3.4.2 Determination of Catalyst Structure

A Rigagu X-ray diffractometer (XRD) system equipped with a RINT 2000 wide angle goniometer and a Cu tube for generating a CuK α 1 radiation ($\lambda = 1.54 \text{ \AA}$) was used to obtain the X-ray diffraction patterns at a generator voltage of 40 kV and a generator current of 30 mA. Nickel filter was used as the K_{β} filter. The goniometer parameters were divergence slit = 1°(2 θ); scattering slit = 1°(2 θ); and receiving slit = 0.3 mm. The catalyst samples were compared on a glass slide, firmly pressed by another glass slide. A scan speed of 5°(2 θ)/min with a scan step of 0.02°(2 θ) was used during a continuous run in the 5 to 90°(2 θ) range.

The Scherrer equation, which relates the mean crystallite diameter and the broadening of the X-ray diffraction lined per the expression, can be written as,

$$d_b = K\lambda / B_d \cos \theta \quad (3.3)$$

where λ = wave length of the monochromatic X-ray diffraction (\AA);
 K = Scherrer constant whose value depends on the shape of the particle (assume equal to 1);
 B_d = angular width of the peak in the terms of $\Delta(2\theta)$ (radian);
 θ = glancing angle (degree);
 d_b = mean crystallite diameter (\AA).

3.4.3 Determination of Desorption Property of Catalysts

A Micromeritics TPD/TPR 2900 was employed as an analyzer for temperature programmed reduction (TPR). The temperatures of thermal conductivity detector (TCD), valve and loop were maintained at 100°C, 100°C and 25°C, respectively. 5 % hydrogen was selected as a carrier gas with a flow rate of 50 ml/min. The detector current was set at 55 mA. The furnace controller was set to increase the furnace temperature up to 900°C at the linear ramp rate of 10°C/min. As the temperature increases, a surface species begins to be reduced and the signal from the thermal conductivity detector is displayed as a function of temperature.

3.4.4 Determination of Functional Groups of Catalysts

FT-Raman spectra were performed on a Perkin Elmer 2000 FT-Raman instrument, which 64 scans at a resolution of 4 cm^{-1} were taken, with

diode pumped YAG laser and a room temperature super InGaAs detector. The laser power was about 460 mW. A frequency of 4000-100 cm^{-1} was observed.

3.4.5 Examination of Catalyst Morphology

Scanning electron micrographs (SEM) were taken on the JEOL 5200, magnification: 35-200,000) scanning electron microscope. The SEM provides unique information about the surfaces of materials, which are the catalysts for the present research. All of the catalysts, which had to be characterized by SEM, were heated at about 100°C for one hour to removed moisture and stored in dessicator before microscopic examinations. The pure CeO_2 , ZrO_2 and the CeO_2 - ZrO_2 mixed oxide catalysts, which were calcined at 500 and 900°C and aged at 50 and 120 hours were examined. The catalysts were stick on the stubs and coated with gold by ion sputtering device (JFC-1100E) for 4 minutes to prevent specimen charging. The examinations were taken through this microscope with magnification range from 750 to 2,000.

3.5 Reaction Experiment

CO oxidation experiment was carried out at atmospheric pressure in the fixed bed reactor as described previously. 100 mg of catalyst was used in this study. The reactant gas mixture consisted of 1 % CO and 1 % O_2 balanced in helium in the oxidation condition, and 1 % CO, 1 % O_2 and 40 % H_2 balanced in helium in the reducing condition. The total flow rate was 50 ml/min.

The $\text{Ce}_{1-x}\text{Zr}_x\text{O}_2$ mixed oxide catalysts ($x = 0, 0.25, 0.50, 0.75, 1.0$) were screened by continuously increasing the temperature from 200 to 400°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_{50}) or light off temperature was use as the index to determine the catalytic

activity. The lower T_{50} showed relatively higher catalytic activity of the $\text{Ce}_{1-x}\text{Zr}_x\text{O}_2$ mixed oxide catalysts (Tanielyan and Augustine, 1992).