CHAPTER III
EXPERIMENTAL

3.1 Materials

3.1.1 Gases

The gases used in this research were:

a) 5% carbon monoxide in helium from Thai Industrial Gases Public Company Limited.

b) 20% carbon dioxide in helium from Praxair (Thailand) Co., LTD.

c) High purity oxygen (99.7%) from Praxair (Thailand) Co., LTD.

d) 8% oxygen in helium from Thai Industrial Gases Public Company Limited.

e) Ultra high purity hydrogen (99.999%) from Thai Industrial Gases Public Company Limited.

f) High purity helium (99.999%) from Thai Industrial Gases Public Company Limited.

g) Nitrogen gas from Thai Industrial Gases Public Company Limited.

3.1.2 Chemicals

The chemical reagents used for catalyst preparation were as follows:

a) Palladium (II) chloride anhydrous ($PdCl_2$) AR grade of 60 percent purity from Fluka Chemie A.G.

b) Cerium (III) nitrate hexahydrate ($Ce(NO_3)_3.6H_2O$) AR grade of 99.99 percent purity from Aldrich Chemical Company, Inc.

c) Zirconium (IV) oxide chloride octahydrate ($ZrOCl_2.8H_2O$) AR grade of 99.99 percent purity from Aldrich Chemical Company, Inc.

d) Sodium carbonate anhydrous (Na_2CO_3) AR grade from Aldrich Chemical Company, Inc.

e) Urea ($CO(NH_2)_2$) AR grade of 99.99 percent purity from Fluka Chemie A.G.

3.2 Equipment

The experimental setup for selective CO oxidation as 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, H_2, CO_2, and O_2 balance in helium. Each gas was supplied from a compressed gas cylinder at initial pressure approximately of 2000 psig. Each stream was passed through the micron line filter to remove particles and check valve to prevent reverse flow. The individual stream flow rates were controlled by 840 Sierra Instruments model mass flow controllers to achieve the desired composition. Different components of the feed stream were mixed in the mixer and bubbled through water to humidify before going into the reactor.

3.2.2 Catalytic Reactor

The selective CO oxidation was carried out at atmospheric pressure in a Pyrex glass U-tube microreactor with an inside diameter of 4 mm. The catalyst was packed between glass wool plugs in the middle of the reactor. The temperature of catalyst bed was monitored and controlled by PID temperature controller equipped with a chromel-alumel thermocople (Type K).
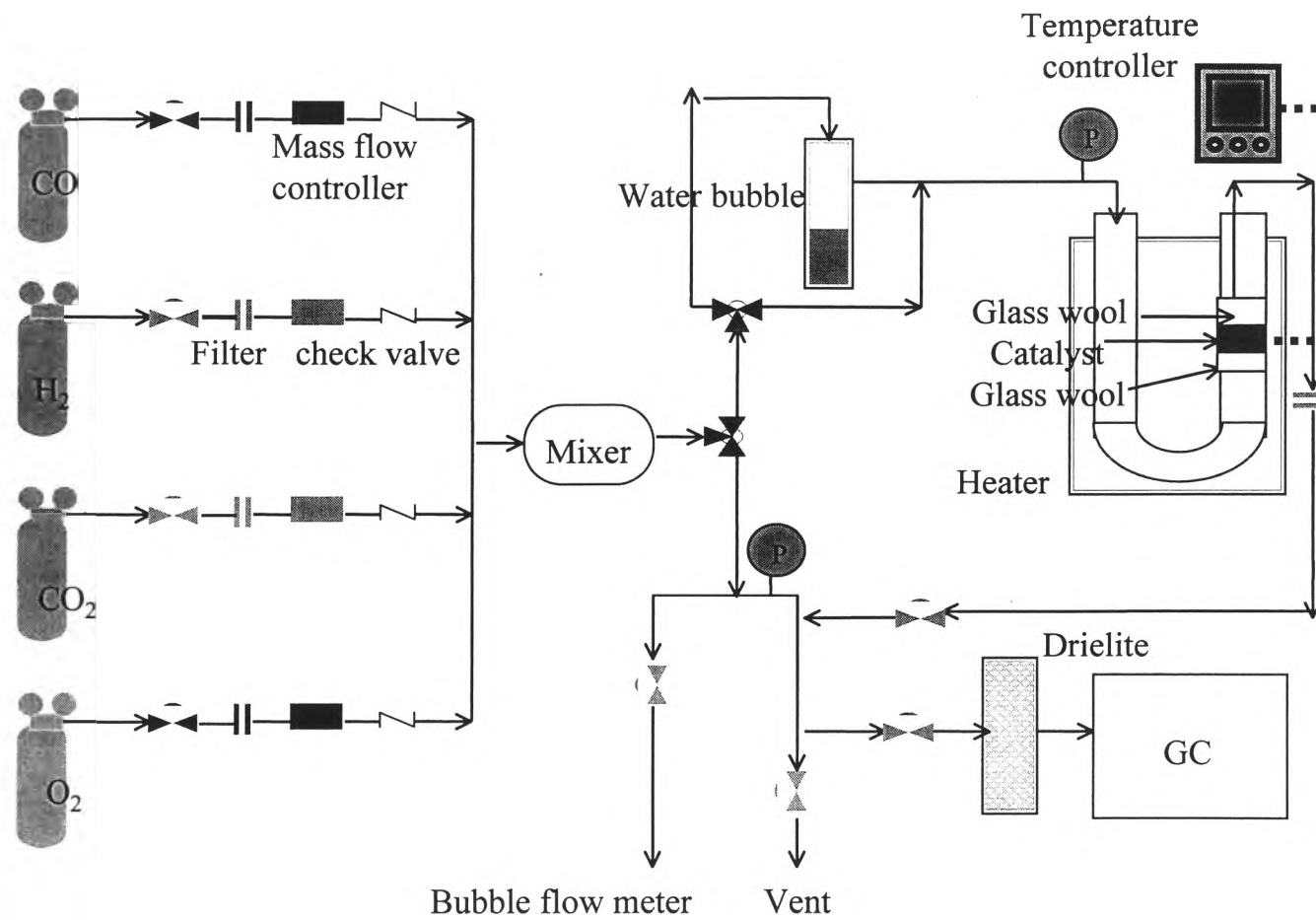
Figure 3.1 The schematic flow diagram of experimental equipment.

3.2.3 Analytical Instrumentation

The effluent gas from the reactor was analyzed qualitatively and quantitatively by autosampling with a Hewlett Packgard 5890 series II gas chromatograph equipped with a 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 41.2 ml/min. The temperature of the oven, injector, and detector was maintained at 55, 110, and 175°C, respectively. The output of chromatograph was recorded by a Hewlett Packgard 3365 series II chemstation.

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

3.3 Catalyst Preparation Procedure

Two techniques were employed to prepare the catalysts in this research. In the first technique, co-precipitation method, one or more soluble salts, which contain the metal of interest, are neutralized through the addition of base to form a co-precipitate of the corresponding metal oxide. This method was applied when the catalysts with mixed-supports were prepared. The second technique was impregnation on sol-gel synthesized supports. In this research work, Pd/CeO_2, Pd/ZrO_2, and Pd/CeO_2-ZrO_2 were synthesized. The notations for all catalysts were given in Table 3.1 and Table 3.2.

Table 3.1 Notation for the 1% by weight of Pd catalysts.

Catalyst preparation method	wt %Ce	wt %Zr	Notation
Co-precipitation	100	0	1%Pd/CeO$_2$ Co-pre
	75	25	1%Pd/CeO$_2$-ZrO$_2$ (75:25) Co-pre
	50	50	1%Pd/CeO$_2$-ZrO$_2$ (50:50) Co-pre
	25	75	1%Pd/CeO$_2$-ZrO$_2$ (25:75) Co-pre
	0	100	1%Pd/ZrO$_2$ Co-pre
Impregnation on sol-gel	100	0	1%Pd/CeO$_2$ Im-sol
	50	50	1%Pd/CeO$_2$-ZrO$_2$ (50:50) Im-sol
	0	100	1%Pd/ZrO$_2$ Im-sol

Table 3.2 Notation for the Pd supported on CeO$_2$ catalysts.

Catalyst preparation method	wt % Pd	Notation
Co-precipitation	1	1%Pd/CeO$_2$ Co-pre
	3	3%Pd/CeO$_2$ Co-pre
	5	5%Pd/CeO$_2$ Co-pre

3.3.1 Co-precipitation Method

The preparation steps were as the following:

a) The corresponding chemical compounds were dissolved in deionized water at a total concentration of 0.1 M.

b) The aqueous solution of one molar sodium carbonate was prepared.

c) The mixture of precursor from step a) was stirred.

d) The basic solution from step b) was added to the mixture of precursor and pH adjusted to 8. During this step precipitation of the metal and the support oxide occurred.

e) The precipitates were separated by centrifuge at 2000 rpm for five minutes and washed thoroughly by warm deionized water.

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

g) The deionized precipitate was dried at $110^{\circ}C$ overnight.

h) Dried precipitate was ground to powder and then calcined in air at temperature of 200, 300 and $400^{\circ}C$ for 2 hours.

i) Calcined powder was sieved to 70/120 mesh size and kept in a dessicator before being used.

3.3.2 Impregnation on Sol-gel Method

The preparation steps were as the following:

a) The solutions used for this method were salts of zirconium, cerium, and urea. They were prepared by dissolution in deionized water. Table 3.3 shows the concentration of these three solutions prepared.

Table 3.3 Molecular weight and concentration of the components.

Salt	Molecular weight	Molar concentration
$CO(NH_2)_2$ or (Urea)	60.06	0.4
$ZrOCl_2.8H_2O$	322.25	0.1
$Ce(NO_3)_3.6H_2O$	434.23	0.1

b) The samples were made by mixing equal volume of each solution of ceria, zirconia, and urea together. 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 for the hydrolysis purpose.

c) The solution was measured into the Glass schott bottle; the bottles were sealed and put in the oven at 100°C for 50 hours.

d) After the desired reaction time was passed, the sample was taken outside the oven, and allowed to cool down before lid was removed because if the lid were removed immediately, the sample would boil as it was in the oven at a high temperature.

e) The sample was separated by centrifuge at 2000 rpm for five minutes.

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

g) The sample was washed in the same way with ethanol to prevent the hydroxides from forming agglomerates after the sample had dried.

h) The samples were put in the oven at 110°C overnight to let it dried.

i) The samples were calcined in air at temperature of 300°C for 2 hours.

j) Palladium chloride ($PdCl_2$) was weighed and dissolved in deionized water.

k) The calcined catalyst was impregnated with a solution of $PdCl_2$ by adding a few droplets to support.

l) The sample was dried again in oven at 110°C for 24 hours and calcined in air at temperature of 300°C for 2 hours.

m) Calcined powder was sieved to 70/120 mesh size and kept in a descicator before being used.

3.4 Catalyst Characterization

The catalysts were characterized by 3 techniques described below in order to understand the relation between the catalyst properties and its activity.

3.4.1 BET Surface Area Measurements

The Brunauer-Emmett-Teller method (BET) was used to determine the surface area and pore size. This method is 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 16.2×10^{-20} m^2/molecule was used as the adsobate at liquid nitrogen temperature (77K). All samples were outgassed by heating under vacuum to eliminate volatile absorbents in the surface at $150^{o}C$ for 2 hours before measurement. The surface area of each catalyst was obtained from five point adsorption isotherm at P/P_0 ratio less than 1. The results were analyzed by Autosorb ANAGAS Software Version 2.10, which were calculated using the Brunauer-Emmett-Teller method (BET) equation as shown in equation 3.1.

$$1/ [W ((P_o/P)-1)] = 1/[W_m C] + [(C-1)/ W_m C] \times (P/ P_o) \qquad (3.1)$$

where:

W = weight of gas adsobed at relative pressure P_o

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 equation 3.2.

$$\text{Surface area of sample} = W_m A_{nitrogen}(6.02 \times 1023)/M_{w,nitrogen} \qquad (3.2)$$

Where:

$A_{nitrogen}$ = Cross-sectional area of one molecule nitrogen

= 0.162 nm^2 (at 77K)

$M_{w,nitrogen}$ = molecular weight of nitrogen (28).

3.4.2 X-ray Diffraction

Powder diffractometry both qualitatively and quantitatively was used to investigate crystallographic phase of the catalysts. X-ray diffraction (XRD) is based upon the fact that an X-ray diffraction is unique for each crystalline substance. Thus, if the observed diffraction pattern is 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 Rigaku X-ray diffractometer system (RINT-2200) equipped with graphite monochromator and a Cu tube for generating a Cuk$_\alpha$ radiation (1.5406 Å) was used to obtain the XRD patterns at a generator voltage of 40 KV and a generator current of 30 mA. Nickel filter was used as the K$_\alpha$ filter. The goniometer parameters were divergence slit = 1° (2θ); scattering slit = 1° (2θ); and receiving slit = 0.3 mm. The sample was ground to a fine homogeneous powder and held in a beam in a thin-walled glass container. A scan speed of 5° (2θ)/minute with a scan step of 0.02 (2θ) was used during a continuous run in the 5 to 90° (2θ) range. The digital output of the proportional X-ray detector and the goniometer angle measurements were sent to a on-line microcomputer to record and subsequent data analysis. The XRD

patterns were used for crystallite size estimation by line broadening measurements and use of Scherrer equation in the form

$$D_b = K\lambda \ / \ B_d \cos \theta \qquad (3.3)$$

Where:

λ = the X-ray wavelength (Å)

K = the Scherrer constant which is equal to 1

B_d= the angular width of the peak in the terms of $\Delta(2\theta)$(Radian)

θ = the Bragg angle of the reflection (degree)

D_b= the mean crystallite diameter (Å)

3.4.3 Atomic Absorption Spectroscopy

The AAS, VARIAN model 300/400 was employed to determine the content of Pd on CeO_2, ZrO_2 and CeO_2-ZrO_2 mixed oxide supports. One hundred milligrams of the prepared catalyst was dissolved in Aqua regia solution with the hydrochloric acid to nitric acid of 82 to 18 ratios and then heated to 100°C for one hour. A standard solution of 1000 ppm from Merck was used to establish a calibration curve. The amount of Pd loaded on the CeO_2, ZrO_2 and CeO_2-ZrO_2 mixed oxide supports was obtained by measuring the absorbance of the solution prepared.

3.5 Activity Measurement

The selective CO oxidation reaction was carried out in the fixed bed reactor as described previously using 100 mg of catalyst of 70-120 mesh size. The reactant gas containing 1%CO, 2%CO_2, 1%O_2, 2.6%H_2O, and 40%H_2 balance in helium was passed through the catalyst bed at a total flow rate of 50 ml/min (SV=30,000 ml g^{-1} h^{-1}) and at atmospheric pressure.

3.5.1 Effect of Catalyst Pretreatment

The calcined catalysts were subjected to the pretreatment procedure described below:

a) Samples were placed in the reactor without any pretreatment.

b) Samples were pretreated with

- 50 ml/min of 10%H_2 at 300°C for 3 hours

- 50 ml/min of pure H_2 at 300°C for 2 hours

- 50 ml/min of pure O_2 at 300°C for 2 hours

c) Sample were placed in the reactor and purged with helium at 50 ml/min for one hour.

3.5.2 Effect of Palladium Loading

The activity testing were conducted using 100 mg of catalyst with different Pd loadings (1%, 3%, and 5% by weight) and 70-120 mesh size. The reactant feed contained 1%CO, 2%CO_2, 1%O_2, 2.6%H_2O, and 40%H_2 balance in helium flowing at 50 ml/min and under atmospheric pressure.

3.5.3 Effect of Calcination Temperature

The effect of calcination temperature on catalyst activity was examined using 100 mg of each catalyst calcined at different temperatures (200, 300, and 400°C) for 2 hours. The reactant feed contained 1%CO, 2%CO_2, 1%O_2, 2.6%H_2O, and 40%H_2 balance in helium flowing at 50 ml/min and under atmospheric pressure

3.5.4 Effect of Support

The Palladium catalysts with different supports (CeO_2 and ZrO_2) were tested under reaction temperature 50-190°C. The reactant feed contained 1%CO, 2%CO_2, 1%O_2, 2.6%H_2O, and 40%H_2 balance in helium flowing at 50 ml/min and under atmospheric pressure.

3.5.5 Effect of Ratio of Ce and Zr Support

The effect of ratio of Ce and Zr support on catalyst activity was tested using $1\%Pd/CeO_2$-ZrO_2 at different ratio of Ce to Zr. The catalysts were prepared at a ratio of Ce to Zr; 25:75, 50:50, and 75:25.

3.5.6 Effect of Catalyst Preparation

The effect of catalyst preparation method on catalyst activity was examined using 100 mg of each catalyst prepared by different methods. The catalysts were prepared by 2 techniques; co-precipitation and impregnation on sol-gel method.

3.5.7 Comparison of Activity with Conventional Catalyst

After selecting the active catalyst in part 3.5.1-3.5.6, the best catalyst was compared with conventional catalyst. The conventional catalyst was Pd/Al_2O_3 prepared by sol-gel method, which is the catalyst used for fuel cell applications.

3.6 Experimental Plan

Condition: 100 mg of catalyst (70-120 mesh size)

Reactant gas: 1%CO, 2%CO_2, 1%O_2, 2.6%H_2O, and 40%H_2 balance in helium

Flow rate: 50 ml/min

Space velocity: 30,000 ml $g^{-1} h^{-1}$

Reaction temperature: 50-190°C

Pressure: atmospheric pressure

3.6.1 Effect of Catalyst Pretreatment

Catalyst preparation method: co-precipitation method

Calcination condition: 300°C for 2 hours

Table 3.4 Experimental plan for effect of catalyst pretreatment.

Run No.	Type of catalyst	10%H_2	Pure H_2	Pure O_2
1-3	1%Pd/CeO_2	*	*	*
4-5	1%Pd/CeO_2-ZrO_2(25:75)	*	*	
6-7	1%Pd/CeO_2-ZrO_2(50:50)	*	*	
8-9	1%Pd/CeO_2-ZrO_2(75:25)	*	*	
10-12	1%Pd/ZrO_2	*	*	*

3.6.2 Effect of Palladium Loading

Catalyst preparation method: co-precipitation method

Calcination condition: 300°C for 2 hours

Pretreatment condition: 10%H_2 at 300°C for 2 hours

Table 3.5 Experimental plan for effect of palladium loading.

Run No.	Type of catalyst	1%Pd	3%Pd	5%Pd
13-15	Pd/CeO$_2$	*	*	*

3.6.3 Effect of Calcination Temperature

Catalyst preparation method: co-precipitation method

Pretreatment condition: 10%H$_2$ at 300°C for 2 hours

Table 3.6 Experimental plan for effect of calcination temperature.

Run No.	Type of catalyst	200°C	300°C	400°C
16-18	1%Pd/CeO$_2$	*	*	*

3.6.4 Effect of Support

Pretreatment condition: 10%H$_2$ at 300°C for 2 hours

1 by weight of Pd loading

Table 3.7 Experimental plan for effect of support.

Run No.	Catalyst preparation method	CeO$_2$	ZrO$_2$
19-20	Co-precipitation	*	*
21-22	Impregnation on sol-gel	*	*

3.6.5 Effect of Ratio of Ce and Zr Support

Catalyst preparation method: co-precipitation method

Calcination condition: 300°C for 2 hours

Pretreatment condition: 10%H_2 at 300°C for 2 hours

1 by weight of Pd loading

Table 3.8 Experimental plan for effect of ratio of Ce and Zr support (co-precipitation method).

Run No.	100:0	75:25	50:50	25:75	0:100
23-27	*	*	*	*	*

Catalyst preparation method: Impregnation on sol-gel method

Calcination condition: 300°C for 2 hours

Pretreatment condition: 10%H_2 at 300°C for 2 hours

1 by weight of Pd loading

Table 3.9 Experimental plan for effect of ratio of Ce and Zr support (impregnation on sol-gel method).

Run No.	100:0	50:50	0:100
28-30	*	*	*

3.6.6 Effect of Catalyst Preparation

Calcination condition: 300°C for 2 hours

Pretreatment condition: 10%H_2 at 300°C for 2 hours

Catalyst: 1%Pd/CeO_2-ZrO_2 (100:0, 50:50, and 0:100)

Table 3.10 Experimental plan for effect of catalyst preparation.

Run No.	Type of catalyst	Co-precipitation	Impregnation on sol-gel
31-32	$1\%Pd/CeO_2$	*	*
33-34	$1\%Pd/CeO_2-ZrO_2(50:50)$	*	*
35-36	$1\%Pd/ZrO_2$	*	*

3.6.7 <u>Comparison of Activity with Conventional Catalyst</u>

Calcination condition: $300^{\circ}C$ for 2 hours

Pretreatment condition: $10\%H_2$ at $300^{\circ}C$ for 2 hours

Table 3.11 Experimental plan for comparison of activity with conventional catalyst.

Run No.	$1\%Pd/CeO_2$ co-precipitation	$1\%Pd/Al_2O_3$ sol-gel
37-38	*	*