

CHAPTER III EXPERIMENTAL

3.1 Materials

3.1.1 Gases

- Helium gas (99.99% of He)
- Hydrogen gas (99.99% of H₂)
- Carbon dioxide in Helium gas (20% of CO₂ in He)
- Carbon monoxide in Helium gas (10.3% CO in He)
- Oxygen in Helium gas (5.46% of O₂ in He)
- Pure nitrogen gas

All the gases used in this research work were obtained from Thai Industrial Gases Public Company limited.

3.1.2 Chemicals

- Hydrogen tetrachloroaurate (III) (HAuCl₄.3H₂O) 99.9% purity from ACROS
- Cerium (III) nitrate hexahydrate (CeN₃O₉.6H₂O) 99.9% purity from ALDRICH
- Zirconium (IV) oxide chloride octahydrate, (ZrOCl₂.8H₂O) 99.999% purity from ALDRICH
- Sodium carbonate anhydrous (Na₂CO₃) from MERCK
- Deionized water

3.2 Equipment

The experiment system for the preferential CO oxidation (PROX) reaction can be divided into 3 main parts, which are gas blending section, catalytic reactor section, and analytical instrumentation section. The schematic of this experiment is shown in Figure 3.1.

3.2.1 Mass Flow Controller and Gas Blending Section

Mass flow controller is the equipment that uses in measuring and controlling the rate of flow of gases to the desired percentage composition. The dust particles in every gas streams will be removed by the means of micro filter before entering to the mass flow controllers to achieve the desired composition. The composition reactant gases that are used in this experiment consisted of 1% CO, 1% O₂, and 40% H₂ balanced in He. Next, all of streams are mixed in a mixer chamber with a total flow rate of 50 ml/min (GHSV = 30,000 mlg⁻¹h⁻¹) under atmospheric pressure before going into the catalytic reactor.

3.2.2 Catalytic Reactor

The gases mixture passed through the micro catalytic reactor for preferential CO oxidation (PROX) under atmospheric pressure. The reactor is a U-shape Pyrex glass tube with an inside diameter of 6 mm. The catalyst was packed between quartz wool plugs in the middle of the reactor. The reaction temperature was monitored and controlled by PID temperature controller equipped with a chromel-alumel thermocouple (Type K).

3.2.3 Analytical Instrumentation

When the effluent gas left from the reactor, it was passed through the water trapper for removal the presence of water. Then the effluent gas entered to the analytical instrument, gas chromatography (GC) for analyzing both qualitatively and quantitatively of the concentration in each gas product by auto-sampling into on-line gas chromatograph equipped with a packed carbosphere column, 80/100 mesh, and 10 ft x 1/8 inch and a thermal conductivity detector (TCD).

The results peaks were recorded by Agilent Chemstation software and compared with the retention time of the standard to identify the peaks which, the concentration of each product will be calculated from the area under the peaks.

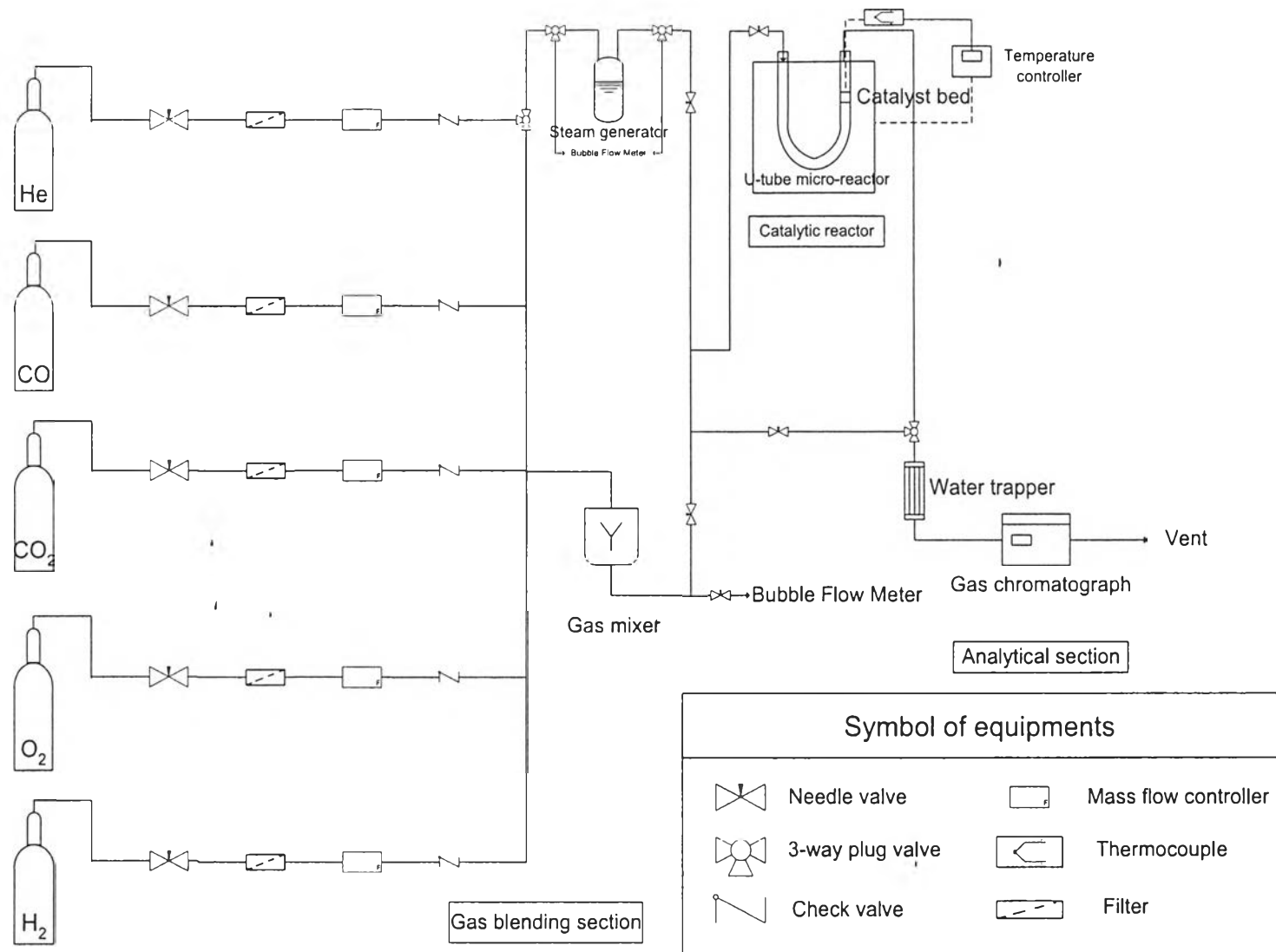


Figure 3.1 Schematic flow of PROX process.

3.3 Preparation of Catalyst and Support

In this study, the supports (CeO_2 , ZrO_2 , and $\text{CeO}_2\text{-ZrO}_2$) were prepared by precipitation and co-precipitation methods. After that, the supported Au catalysts were prepared by deposition-precipitation (DP) method.

3.3.1 Precipitation Method

3.3.1.1 *Preparation of CeO_2 Support*

The aqueous solution of 0.1 M Cerium (III) nitrate hexahydrate, $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, was under vigorously stirring condition $80\text{ }^\circ\text{C}$. When it achieved the desired temperature, the solution was adjusted at a pH of 8–9 by adding an aqueous solution of 0.1 M Na_2CO_3 . Then the mixture was kept at $80\text{ }^\circ\text{C}$ for 1 hour. The suspension was washed with warm deionized water to eliminate the residue ions (CO_3^{2-} and NO_3^-) and it was centrifuged in centrifuge HERMLE Z383 at 10,000 round per min. The precipitate was dried at $110\text{ }^\circ\text{C}$ overnight and calcined in air at $400\text{ }^\circ\text{C}$ for 4 hours. After calcination, the sample was kept in a desiccator.

3.3.1.2 *Preparation of ZrO_2 Support*

The aqueous solution of 0.1 M Zirconium (IV) oxide chloride octahydrate, $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$, was mixed under vigorous stirring condition at $80\text{ }^\circ\text{C}$. The solution was adjusted at a pH of 8–9 by adding an aqueous solution of 0.1 M Na_2CO_3 . Then the mixture was kept at $80\text{ }^\circ\text{C}$ for 1 hour. The suspension was washed with warm deionized water to eliminate the residue ions (CO_3^{2-} and Cl^-) and it was centrifuged in centrifuge HERMLE Z383 at 10,000 round per min. The precipitate was dried at $110\text{ }^\circ\text{C}$ overnight and calcined in air at $400\text{ }^\circ\text{C}$ for 4 hours. After calcination, the sample was kept in a desiccator.

3.3.2 Co-precipitation Method

3.3.2.1 *Preparation of $\text{CeO}_2\text{-ZrO}_2$ Catalysts*

The aqueous mixture of 0.1 M $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and 0.1 M $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ was under vigorously stirring condition $80\text{ }^\circ\text{C}$. When it achieved the temperature, the solution was adjusted at a pH of 8–9 by adding an aqueous solution of 0.1 M Na_2CO_3 . Then the mixture was kept at $80\text{ }^\circ\text{C}$ for 1 hour. The suspension

was washed with warm deionized water to eliminate the residue ions (CO_3^{2-} , Cl^- and NO_3^-) and it was centrifuged in centrifuge HERMLE Z383 at 10,000 round per min. The precipitate was dried at 110 °C overnight and calcined in air at 400 °C for 4 hours. After calcination, the sample was kept in a desiccator.

3.3.4 Deposition-precipitation (DP) Method

3.3.4.1 *Preparation of Au/CeO₂ Catalyst*

The amount of hydrogen tetrachloroaurate (III), $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$, was weighted and dissolved in deionized water under continuous stirring at 80 °C. The dried support (CeO_2) was added to the solution and the solution was adjusted the pH of 8–9 by adding an aqueous solution of 0.1 M Na_2CO_3 . Then the mixture was kept at 80 °C for 1 hour. The suspension was washed with warm deionized water to eliminate the residue ions (CO_3^{2-} and NO_3^-) and it was centrifuged in centrifuge HERMLE Z383 at 10,000 round per min. The precipitate was dried at 110 °C overnight and calcined in air at 400 °C for 4 hours. After calcination, the sample was kept in a desiccator.

3.3.4.2 *Preparation of Au/ZrO₂ Catalysts*

The amount of hydrogen tetrachloroaurate (III), $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$, was weighted and dissolved in deionized water under continuous stirring at 80 °C. The dried support (ZrO_2) was added to the solution and the solution was adjusted the pH of 8-9 by adding an aqueous solution of 0.1 M Na_2CO_3 . Then the mixture was kept at 80 °C for 1 hour. The suspension was washed with warm deionized water to eliminate the residue ions (CO_3^{2-} and Cl^-) and it was centrifuged in centrifuge HERMLE Z383 at 10,000 round per min. The precipitate was dried at 110 °C overnight and calcined in air at 400 °C for 4 hours. After calcination, the sample was kept in a desiccator.

3.3.4.3 *Preparation of Au/CeO₂-ZrO₂ Catalysts*

The amount of hydrogen tetrachloroaurate (III), $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$, was weighted and dissolved in deionized water under continuous stirring at 80 °C. The dried support ($\text{CeO}_2\text{-ZrO}_2$) was added to the solution and the solution was adjusted the pH of 8–9 by adding an aqueous solution of 0.1 M Na_2CO_3 . Then the mixture was kept at 80 °C for 1 hour. The suspension was washed with

warm deionized water to eliminate the residue ions (CO_3^{2-} , Cl^- , and NO_3^-) and it was centrifuged in centrifuge HERMLE Z383 at 10,000 round per min. The precipitate was dried at 110 °C overnight and calcined in air at 400 °C for 4 hours. After calcination, the sample was kept in a desiccator.

3.4 Catalyst Characterization

In this research work, the effects of atomic ratio of Ce and Zr, the feed stream composition, side reaction (water-gas shift and CO oxidation), and deactivation test were investigated on the catalytic activity of Au/CeO₂-ZrO₂ catalysts. There are several characterizations used in this work in order to explain the relationship between the properties and characteristics of the catalysts.

3.4.1 BET Surface Area Measurement

The total surface area, total pore volume, and average pore diameter of the prepared catalysts (the values are expressed in m²/g) are evaluated by Autosorb-1 Gas Sorption system (Quantachrome Corporation). The equipment measurement is based on Brunauer-Emmet-Teller (BET) equation. This technique is determined by calculating the physical multi-layer adsorption of N₂ gas with the cross-sectional area of 16.2x10⁻²⁰ m²/molecule. N₂ gas is adsorbed on the catalyst surface at liquid nitrogen temperature (- 196 °C).

Prior to analysis, all of samples are degassed by heating under vacuum at 150 °C for 2 hours. to eliminate adsorbed species at surface. The surface area is calculated from the 22 points nitrogen adsorption. The average pore diameter and pore volume are obtained at P/P₀ ratios close to unity. The result is analyzed by Autosorb Anygas Software version 2.1, which are calculated using the BET equation, as shown in Equation 3.1.

$$\frac{1}{W \cdot \left(\frac{P_0}{P} - 1\right)} = \frac{1}{W_m \cdot C} + \frac{(C-1)}{(W_m \cdot C)} \left(\frac{P_0}{P}\right) \quad (3.1)$$

where:

- P = pressure of gas,
 P_0 = saturated vapor pressure of the liquid at the operating temperature,
 W = weight of gas adsorbed at a relative pressure, P_0 ,
 W_m = weight of adsorbate constituting a monolayer of surface coverage and
 C = constant that is related to the energy of adsorption in the first adsorbed layer and magnitude of the adsorbent/adsorbate interaction.

The surface area is calculated by Equation 3.2.

$$S = \frac{W_m \cdot A_{N_2} \cdot (6.02 \times 10^{23})}{M_{w,N_2}} \quad (3.2)$$

where:

- S = specific surface area (m^2/g),
 A_{N_2} = cross-sectional area of one molecule N_2
= 0.162 nm^2 ($-196 \text{ }^\circ\text{C}$) and
 M_{w,N_2} = molecule weight of nitrogen (28 g/g-mol).

3.4.2 X-ray Diffractometry (XRD)

X-ray diffraction (XRD) is used to identify the crystalline structure of oxide support and the mean particle diameter of gold by using a Rigaku X-Ray Diffractometer system (DMAX 2200 HV) with copper tube for generating CuK_α radiation (1.5406 \AA) and nickel filter. XRD is capable of analyzing the intensity of the peak. For the same crystalline substance the higher of the peak indicates the higher content of that phase. DMAX 2200 HV was used to obtain XRD pattern at a generator voltage of 40 kV and a generator current of 30 mA. The goniometer parameters are divergence slit is $1^\circ (2\theta)$; scattering slit is $1^\circ (2\theta)$; with receiving slit

equals 0.3 mm. The scan speed of $5^\circ (2\theta)/\text{min}$ with scan step of 0.02 (2θ) is used for the continuous run in 5 to $90^\circ (2\theta)$ range. Generally, the sample should be ground to the fine homogeneous powder and held in a beam in a thin-walled glass container. The signal is sent to the on-line computer to record and analyze. The average dimension of crystallites can be determined by Scherrer equation. Equation 3.3 shows the relationship between the crystalline thickness (D_b) and the broadening (B_d) of the diffraction line corresponding to the Bragg angle (θ) using wavelength (λ).

$$D_b = \frac{K \cdot \lambda}{B_d \cdot \cos\theta} \quad (3.3)$$

where:

- D_b = mean crystalline diameter (\AA),
- K = Scherrer constant, 0.9,
- λ = X-Ray wavelength (\AA),
- B_d = angle width of peak in term of $\Delta(2\theta)$ (radian) and
- θ = Bragg angle of the reflection (degree).

3.4.3 Atomic Absorption Spectroscopy (AAS)

The Atomic Absorption Spectrophotometer is utilized to determine the actual concentration of gold loading on the supports. Due to the gold content might be loss during catalyst preparation steps. A known weight amount of catalyst was dissolved in aqua regia solution, which is composed of hydrochloric acid and nitric acid with a ratio of 82:18 and then heated the solutions to 60°C for one hour. Normally, several standard solutions were made from stock solution of 1,000 ppm to create a calibration curve. By measuring the absorbance of the prepared solution, the amount of gold loaded on the supports was obtained.

3.4.4 Temperature-programmed Reduction (TPR)

Temperature-programmed reduction (TPR) is a widely used tool for the characterization of metal oxides, mixed metal oxides, metal oxides dispersed on a support including metal-metal and metal-support interaction.

In this experiment, TPR will be carried out by placing a sample in a quartz reactor and subjected to TPR analysis using 10 % H₂ in Ar at a total flow of 30 ml/min. The reduction temperature was raised from 30 to 850 °C with a ramp rate of 10 °C/min. A thermal conductivity detector was used to monitor the difference of hydrogen content before and after the reduction. The temperature, at which the reduction was completed, could be determined from TPR pattern.

3.4.5 UV-vis Spectrophotometry

UV visible spectrophotometer is typically used for the quantitative determination of a colorless substance in solution, measuring transition metal ions and highly conjugated organic compounds. UV-vis spectrophotometers function within the spectral range of 200 to 750 nm. These units measure the intensity of light that passes through the sample and compares it with the intensity of light before it passed through the sample, providing a ratio known as transmittance. UV Visible models are available with a variety of features including scanning, multiple cells, integral printers, and user interfaces.

Diffuse reflectance spectra were recorded by UV-vis spectrophotometer-2550 by using light in the visible and adjacent near ultraviolet (UV) and near infrared (NIR) ranges, used in the quantitative determination the transition metal ions. The samples were packed in the sample holder and analyzed by limiting wavelength in the range of 800–200 nm. And the data would be converted using Kubelka-Munk formula.

3.4.7 The Fourier Transform Raman Spectra (FT-Raman)

Fourier transform Raman spectra (FT-Raman) was used to examine the formation of oxygen vacancies at the surface and in the solid. The FT-Raman spectra were recorded using a Perkin Elmer (Spectrum GX) FT-Raman spectrometer using a Nd-YAG laser (1064 nm) in absorbance mode at 2000 scans with a

resolution of 16 cm^{-1} . The frequency range of $3500\text{--}200\text{ cm}^{-1}$ was obtained. The sample powders were pressed into small disc and then mounted on the analytic chamber.

3.5 Activity Measurement

The catalysts were tested for the preferential CO oxidation (PROX) in the presence of H_2 . Catalytic activity measurement was carried out in a packed-bed quartz U-tube reactor with a 0.6 mm inner diameter. A 100 mg of sample was packed between two layers of quartz wool. The feed stream consisted of 1% CO, 1% O_2 , and 40% H_2 balanced in He passing through the catalyst bed at the total flow rate of 50 ml/min (GHSV = $30,000\text{ mlg}^{-1}\text{h}^{-1}$). The activity was observed at various temperatures over the range of 50 to 190 °C. The reactant and the product gases were analyzed by auto-sampling in an on-line gas chromatograph equipped with a packed column, 80/100 mesh, 10 ft \times 1/8 in. and a thermal conductivity detector (TCD).

3.5.1 Effect of Support Atomic Ratio

In order to study the activity and selectivity for the preferential CO oxidation (PROX) on Au/CeO₂-ZrO₂ catalysts, various atomic ratio of Ce:Zr-0:1, 1:3, 1:1, 3:1, and 1:0 were investigated by loading 1%wt of Au. The supports were prepared by deposition-precipitation technique.

3.5.2 Effect of Feed Stream on Temperature

The effect of feed stream on temperature on the catalytic activity was studied and reaction was performed at the temperature of 50 °C to 110 °C in the presence of 10% H_2O and 10% CO_2 .

3.5.3 Effect of Feed Stream Composition

Laguna *et al.* (2010) studied the influence of the presence of 10% CO_2 and 10% H_2O in the gas stream. The results were compared between in the presence and absence of H_2O and CO_2 . They found that the presence of these species reduced the activity because there are competitive adsorptions between CO and block

the active sites. The effect of the presence of CO₂ and H₂O in feed stream should be considered in the work.

3.5.4 Catalytic Activity for Water-Gas Shift and CO Oxidation Reaction

The catalytic activity of the catalysts in preferential CO oxidation was compared with low temperature water-gas shift (WGS) and CO oxidation reaction. The activity was performed with a reactant mixture composition of 1–4% CO, 10% H₂O and He balanced in the low temperature range of 150–350 °C for water-gas shift reaction and 2% CO, 1% O₂ and He balanced in the temperature of 50–190 °C for CO oxidation.

3.5.5 Effect of Deactivation Test

The deactivation test of the prepared catalyst was studied in dry and wet condition for 33 hours on the preferential CO oxidation reaction. The reaction was tested in feed stream composition of 1% CO, 1% O₂, 40% H₂, and He balanced for dry condition and 1% CO, 1% O₂, 40% H₂, 10% H₂O, 10% CO₂ and He balanced for wet condition.

3.6 Calculation

- The effluent gas was pass through the reactor, it was analyzed by auto-sampling in an on-line gas chromatograph equipped with a thermal conductivity detector (TCD) using He as a carrier gas. The CO and O₂ conversions were calculated based on the consumption of reactant gases along the preferential CO oxidation reaction by Equations (3.4–3.5). The CO selectivity was defined by the O₂ consumption for the desired CO oxidation reaction over the total O₂ consumption by Equation (3.6).

$$\text{CO conversion (\%)} = \frac{[\text{CO}]_{in} - [\text{CO}]_{out}}{[\text{CO}]_{in}} \times 100 \quad (3.4)$$

$$\text{O}_2 \text{ conversion (\%)} = \frac{[\text{O}_2]_{in} - [\text{O}_2]_{out}}{[\text{O}_2]_{in}} \times 100 \quad (3.5)$$

$$\text{Selectivity (\%)} = \frac{[\text{O}_2]_{\text{CO}}}{[\text{O}_2]_{\text{CO}} + [\text{O}_2]_{\text{H}_2}} \times 100 \quad (3.6)$$

where:

$[\text{CO}]_{in}$ = concentration of CO in the reactant gas,

$[\text{CO}]_{out}$ = concentration of CO in the effluent gas,

$[\text{O}_2]_{in}$ = concentration of O₂ in the reactant gas,

$[\text{O}_2]_{out}$ = concentration of O₂ in the effluent gas,

$[\text{O}_2]_{\text{CO}}$ = amount of O₂ for CO oxidation, and

$[\text{O}_2]_{\text{H}_2}$ = amount of O₂ for H₂ oxidation.