

CHAPTER III METHODOLOGY

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 are from Thai Industrial Gases Public Company limited.

3.1.2 Chemicals

- Hydrogen tetrachloroaurate (III) (HAuCl₄.3H₂O) 99.9% purity from ACROS
- Titanium (IV) oxide, nanopowder (Degussa P25) from ALDRICH
- Iron (III) nitrate nonahydrate (Fe(NO₃)₃.9H₂O) 99.999% purity from ALDRICH
- Sodium carbonate anhydrous (Na₂CO₃) from MERCK
- Deionized water

3.2 Equipment

The experiment system for PROX reaction can be divided into 3 main parts, which are gas blending section, catalytic reactor section, and analytical instrumentation section, as shown in Figure 3.1.

3.2.1 Mass Flow Controller and Gas Blending Section

The mass flow controller was used to measure and control the rate of flow of gases to the desired concentration. Before gas streams is sent to the mass flow controllers, the dust particles will be eliminated by a micro filter. The reactant gases used in this research work consisted of 1% CO, 1% O₂, and 40% H₂ balanced in He. After that, all of streams are mixed in a mixer chamber before going into the reactor with a total flow rate of 50 ml/min (GHSV = 30,000 mlg⁻¹h⁻¹) under atmospheric pressure.

3.2.2 Catalytic Reactor

The preferential CO oxidation (PROX) was carried out under atmospheric pressure during the gases mixture enter the micro-catalytic reactor. The reactor was carried out in a pyrex glass U-tube micro-reactor 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

The effluent gas which leaves from the reactor was passed through water trapper to remove the presence of water. After that, it was passed to the analytical instrument, gas chromatography (GC) where the concentration of each product gas will be analyzed qualitatively and quantitatively 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).

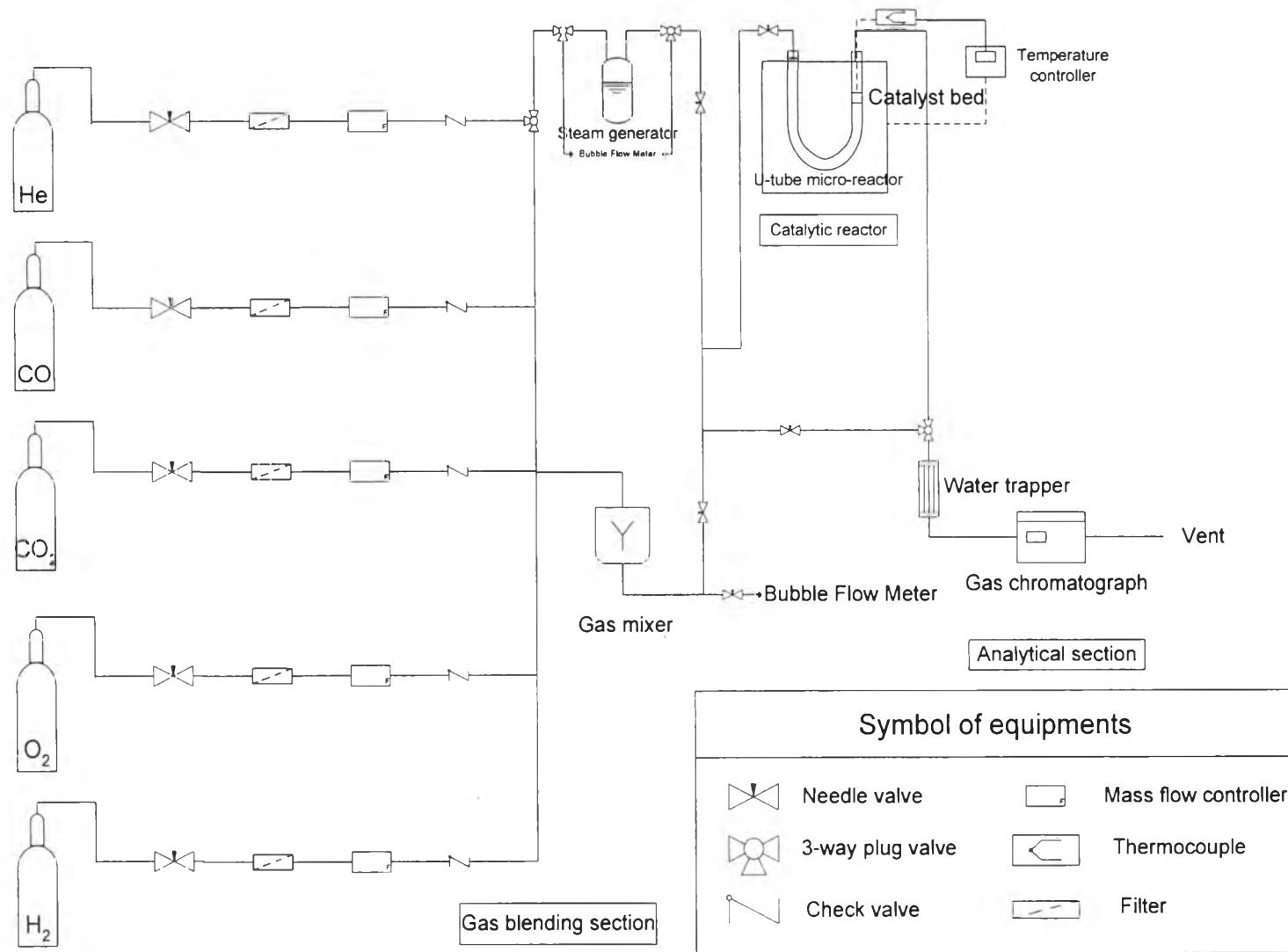


Figure 3.1 Schematic flow of PROX process.

3.3 Preparation of Catalyst and Support

In this study, the supports ($\text{Fe}_2\text{O}_3\text{-TiO}_2$) were prepared by incipient-wetness impregnation method. Then, the supported Au catalysts were prepared by deposition-precipitation (DP) method.

3.3.1 Precipitation Method

3.3.1.1 *Preparation of Fe_2O_3 Support*

The aqueous solution of 0.1 M iron (III) nitrate nonahydrate, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, was under vigorously stirring condition at 80 °C. The pH of solution was adjusted by adding 0.1 M Na_2CO_3 to 8–9, then the mixture was kept for 1 h. The suspension was washed by warm deionized water to get rid of the residue ions, CO_3^{2-} and NO_3^- . Deionized precipitate was dried at 110 °C overnight and calcined in air at 400 °C for 4 h.

3.3.2 Incipient-wetness Impregnation

3.3.2.1 *Preparation of $\text{Fe}_2\text{O}_3\text{-TiO}_2$ Support*

The mixed support, $\text{Fe}_2\text{O}_3\text{-TiO}_2$, was prepared by incipient-wetness impregnation method. The atomic ratios of metals (Fe:Ti) were chosen as follows: 0:1, 4:1, 1:1, 1:4, and 1:0. The desired amount of iron (III) nitrate nonahydrate, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ solution was dropped into titanium (IV) oxide powder (Degussa P25) under grinding. The support slurry was dried at 110 °C overnight and calcined in air at 400 °C for 4 h.

3.3.3 Deposition-precipitation (DP) Method

3.3.3.1 *Preparation of $\text{Au/Fe}_2\text{O}_3$ Catalyst*

The desired weight amount of hydrogen tetrachloroaurate (III), $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$, was dissolved in deionized water under continuous stirring at 80 °C. The dried support (Fe_2O_3) was added to the solution and the solution was adjusted by adding 0.1 M Na_2CO_3 to 8–9. Then, the mixture was aged for 1 h. The suspension was washed by warm deionized water to eliminate the residue ions, CO_3^{2-} , Cl^- , and

NO_3^- . Deionized precipitate was dried at 110 °C overnight and calcined in air at various temperatures for 4 h.

3.3.3.2 Preparation of Au/TiO₂ Catalyst

The desired weight amount of hydrogen tetrachloroaurate (III), $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$, was dissolved in deionized water under continuous stirring at 80 °C. The dried support (TiO_2) was added to the solution and the solution was adjusted by adding 0.1 M Na_2CO_3 to 8–9. Then, the mixture was aged for 1 h. The suspension was washed by warm deionized water to eliminate the residue ions, CO_3^{2-} , Cl^- , and NO_3^- . Deionized precipitate was dried at 110 °C overnight and calcined in air at various temperatures for 4 h.

3.3.3.3 Preparation of Au/Fe₂O₃-TiO₂ Catalysts

The desired weight amount of hydrogen tetrachloroaurate (III), $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$, was dissolved in deionized water under continuous stirring at 80 °C. The dried support ($\text{Fe}_2\text{O}_3\text{-TiO}_2$) was added to the solution and the solution was adjusted by adding 0.1 M Na_2CO_3 to 8–9. Then, the mixture was aged for 1 h. The suspension was washed by warm deionized water to eliminate the residue ions, CO_3^{2-} , Cl^- , and NO_3^- . Deionized precipitate was dried at 110 °C overnight and calcined in air at various temperatures for 4 h.

3.4 Catalyst Characterization

In this research work, the effect of supported atomic ratio (Fe:Ti), calcination temperature, and gas pretreatment of Au/Fe₂O₃-TiO₂ catalysts on the activity and selectivity were investigated. Because of the difference in properties and characteristics of the prepared catalysts, it is necessary to conduct some catalyst characterizations.

3.4.1 BET Surface Area Measurement

The determination of the total surface area, total pore volume, and average pore diameter of the prepared catalysts (the values are expressed in m^2/g) was done by Autosorb-1 Gas Sorption system (Quantachrome Corporation). The equipment measurement is based on Brunauer-Emmet-Teller (BET) equation. This

technique is done 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 were degassed by heating under vacuum at 150 °C for 2 h 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.

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

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:

$$\begin{aligned}
 S &= \text{specific surface area (m}^2\text{/g),} \\
 A_{N_2} &= \text{cross-sectional area of one molecule N}_2 \\
 &= 0.162 \text{ nm}^2 \text{ (-196 }^\circ\text{C) and} \\
 M_{w, N_2} &= \text{molecule weight of nitrogen (28 g/g-mol).}
 \end{aligned}$$

3.4.2 X-ray Diffractometry (XRD)

X-ray diffraction (XRD) will be used to identify the crystalline structure of oxide support and the mean particle diameter of gold by using a Rigaku X-Ray Diffractometer system (RINT-2200) with copper tube for generating $\text{CuK}\alpha$ radiation (1.5406 Å) 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. RINT-2200 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° (2θ); scattering slit is 1° (2θ); with receiving slit equals 0.3 mm. The scan speed of 5° (2θ)/min with scan step of 0.02 (2θ) is used for the continuous run in 5 to 90° (2θ) 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 in the form of 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:

$$\begin{aligned}
 D_b &= \text{mean crystalline diameter (\AA),} \\
 K &= \text{Scherrer constant, 0.9,}
 \end{aligned}$$

λ = X-Ray wavelength (Å),

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)

Atomic Absorption Spectrophotometer was 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 100 °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 were obtained.

3.4.4 Transmission Electron Microscopy (TEM)

Transmission Electron Microscopy (TEM) is the technique that use an electron beam to image a sample. High energy electrons, incident on an ultra-thin samples allow for a high resolution image of the microstructure. Not only can obtain outstanding image resolution, it is also possible to characterize the morphology, crystal structure, and defects crystal phases and composition, magnetic microstructure can be obtained by a combination of electron-optical imaging (2.5Å point resolution), electron diffraction, and small probe capabilities. In this work, this technique is used to determine the average crystalline size of gold particle. The TEM was carried out by using a JEM 2010 operating at 200 kV in bright and dark field modes. More or less parallel electron beam uniformly irradiated the part of studied specimen. The transmitted beam was focused by the objective lens and then propagated through several subsequent lenses. Diffraction pattern and the image of the specimen were observed from selected area. The way to prepare catalysts in a thin form suitable for TEM is to crush and grind the samples (catalyst) in a mortar. Then the sample in the form of fine powder will be dispersed in ethanol by use of an ultrasonic bath, and drop of the suspension was deposited on a thin carbon film

supported on a standard electron microscope grid. The average Au size diameter (d_{TEM}) was calculated from the following formula: $d_{\text{TEM}} = \Sigma(n_i d_i) / n_i$ where n_i is the number of Au particles of diameter d_i .

3.4.5 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 was 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.

3.4.6 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.

3.5 Activity Measurement

The catalysts were tested for the preferential CO oxidation (PROX) in the presence of hydrogen. These tests were carried out in a fixed-bed catalytic micro-reactor at atmospheric pressure. A sample of 100 mg of dried catalyst was loaded into the quartz reactor, fixed by quartz wool plug, located in a ceramic furnace. The reactant mixture (1% CO, 1% O₂, 40% H₂ and balanced in He) was introduced through the catalyst bed with a total flow rate of 50 ml/min (GHSV=30000 mlg⁻¹h⁻¹) and the reactivity was observed at various temperatures over the range of 40 to 180 °C. The gas mixture leaving the reactor tube was analyzed by auto-sampling in an on-line gas chromatograph equipped with a packed carbon sphere column, 80/100 mesh, 10 ft × 1/8 inch. 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/Fe₂O₃-TiO₂ catalysts, the various atomic ratios of Fe:Ti—0:1, 4:1, 1:1, 1:4, and 1:0—was investigated.

3.5.2 Effect of Au Loading

The gold content on the support could lead to improve the catalytic activity of the catalysts in PROX reaction. In this work, the effect of gold loadings on the catalytic activity was investigated. The gold loading percentages were varied with 1, 3, and 5 wt%.

3.5.3 Effect of Calcination Temperature

In this research work, the effect of calcination temperature (200, 300, and 400 °C) of Au/Fe₂O₃-TiO₂ catalysts on the catalytic activity was studied for 4 h.

3.5.4 Effect of Catalyst Pretreatment

To understand the effect of pretreatment with oxygen on the activity and selectivity of the catalyst CO oxidation (PROX). So, in this work, the catalyst

was treated in situ with oxygen (30 ml/min) at 200 °C for 2 h, then the temperature was cooled down to the reaction temperature.

3.5.5 Deactivation Test

In order to observe the activity of the catalyst in the long period, the influence of CO₂ and H₂O on the PROX of CO activity in simulated reformat must be investigated.

3.5.5.1 *Effect of H₂O Concentration in the Feed Gas*

Avgourropoulos *et al.* (2002) studied the influence of H₂O on the PROX activities of the prepared catalysts. They reported that the presence of H₂O in feedstream reduced the CO conversion as a result of the blocking active site of this catalyst. Therefore, the effect of water content on the catalytic activity of the prepared catalyst was conducted by adding 10% of H₂O in the feed gas.

3.5.5.2 *Effect of CO₂ Concentration in the Feed Gas*

Schumacher *et al.* (2004) found that CO₂ in the reactant gas mixture made the amount of CO adsorbed in steady state decreases considerably during the reaction, which provides a plausible explanation for the decay in activity caused by the growth of carbonate and formate species, which increasingly cover the surface of the catalyst and act as poison resulting in preventing O₂ adsorption and splitting on support. Thus, the effect of CO₂ (10% CO₂) in the feed gas on the catalytic activity was investigated.

3.6 Calculation

The effluent was passed through the condenser before entering a gas chromatograph. The effluent gas from the reactor was analyzed by auto-sampling in an on-line gas chromatography equipped with a thermal conductivity detector (TCD) using He as the carrier gas. The CO and O₂ conversions are calculated based on the consumption of reactant gases along the preferential CO oxidation reaction. The CO selectivity was defined by the O₂ consumption for the desired CO oxidation reaction over the total O₂ consumption.

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

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

$$\text{Selectivity (\%)} = \frac{[\text{O}_2]_{CO}}{[\text{O}_2]_{CO} + [\text{O}_2]_{H_2}} \times 100 \quad (3.6)$$

where:

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

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

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

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

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

$[\text{O}_2]_{H_2}$ = amount of O₂ for H₂ oxidation.