

CHAPTER III EXPERIMENTAL

3.1 Materials

3.1.1 Chemicals

Chemicals used in this research are covered the followings:

- Hydrogen tetrachloroaurate (III), $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$, (Alfa AESAR) (purity 99.99%)
- Cerium (III) nitratehexahydrate, $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, (Aldrich) (purity 99.99%)
- Iron (III) nitrate nonahydrate, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, (Aldrich)
- Zirconium (IV) oxide chloride octahydrate, $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$, (Merck)
- Sodium carbonate anhydrous, Na_2CO_3 , (Riedel-de Haen) (purity 99.99%)
- Urea, $(\text{NH}_2)_2\text{CO}$, (Carlo Erba)
- Deionized water
- Methanol (purity $\geq 99.8\%$)
- Acetone, AR grade

3.1.2 Gases

Gases used in this research are:

- Hydrogen (Thai Industrial Gases Public Company Limited) of 99.99% purity was used as a reduction gas.
- Oxygen (Thai Industrial Gases Public Company Limited) of 99.97% purity was used as a pretreatment gas.
- Helium (Thai Industrial Gases Public Company Limited) of 99.995% purity was used as a diluted gas, purged gas and carrier gas in a gas chromatograph.

- Air zero (Thai Industrial Gases Public Company Limited) of 99.99% purity was used as a diluted gas, purged gas and carrier gas in a gas chromatograph.
- Nitrogen (Thai Industrial Gases Public Company Limited) of 99.99% purity was used as a diluted gas, purged gas and carrier gas in a gas chromatograph.

3.2 Methodology

The main purpose of this research is to produce the high purity of the hydrogen with very low CO concentration under the low-temperature MFP by using Au based catalysts. In order to achieve this goal, the SRM operation must be optimized at the first step to obtain the suitable reformat before continually sending to the PROX for reducing CO gas, which contaminated in the reformat, to be lower than 10 ppm. For the CO reduction unit, the comparison between the uses of single- and double-stage PROX reactors was investigated for the optimum condition to minimize CO concentration in the H₂-product stream. The details of the experiments are described below:

3.2.1 Steam Reforming of Methanol (SRM) over monometallic Au- and bimetallic Au-Cu catalysts

Firstly, the catalytic activities of the monometallic Au catalysts supported over mixed oxides—Au/CeO₂, Au/Fe₂O₃, Au/ZrO₂, Au/CeO₂-Fe₂O₃, Au/CeO₂-ZrO₂—were investigated under the SRM reaction. All catalysts were prepared by deposition-precipitation (DP) technique. The effective parameters involve the support composition, Au loading, calcination temperature, gas pretreatment, and H₂O/CH₃OH molar ratio. Moreover, all of optimum conditions of the Au catalyst were chosen for further studying the stability test for 12 hours. For the bimetallic catalysts, the Au-Cu catalysts were prepared by deposition-precipitation technique, and the effective parameters considered were the Au/Cu atomic ratio, pH condition for deposition, gas pretreatment, total metal loading, and

calcination temperature. All entire samples were summarized in Table 3.1. The details of the catalyst preparation, catalytic activity testing, and catalyst characterization are shown below.

3.2.1.1 Monometallic Au Catalyst Preparation (Au/CeO₂, Au/ZrO₂, Au/Fe₂O₃, Au/CeO₂-Fe₂O₃, and Au/CeO₂-ZrO₂) and Bimetallic Au-Cu Catalyst Preparation

3.2.1.1.1 Precipitation Method (CeO₂, ZrO₂, Fe₂O₃, CeO₂-Fe₂O₃, and CeO₂-ZrO₂)

Various ratios of CeO₂-Fe₂O₃ and CeO₂-ZrO₂ mixed oxides supports were prepared by a co-precipitation (CP) method, while the pure CeO₂, Fe₂O₃, and ZrO₂ supports were prepared by a precipitation method. For the CeO₂-Fe₂O₃ supports, the appropriate amounts of 0.1 M aqueous solutions—cerium (III) nitrate hexahydrate [Ce(NO₃)₃.6H₂O; Aldrich], iron (III) nitrate nonahydrate [Fe(NO₃)₃.9H₂O; Aldrich], and Na₂CO₃ (Riedel-de Haen)—were mixed under vigorous stirring condition at 80 °C and pH 8. Afterward, the precipitate was washed with warm deionized water to eliminate the excess ions, CO₃²⁻ and NO₃⁻. The suspension was centrifuged in centrifuge HERMLE Z383 at 500 round per min. The precipitate was dried at 110 °C overnight and calcined in air at 400 °C for 4 h in order to obtain the support. After calcination, the powder of catalysts were labeled and kept in a desiccator.

For the CeO₂-ZrO₂ supports, the appropriate amounts of 0.1 M aqueous solutions—Ce(NO₃)₃.6H₂O, zirconium (IV) oxide chloride octahydrate [ZrOCl₂.8H₂O; Merck], and Na₂CO₃—were mixed under vigorous stirring conditions at 80 °C and pH 8. Afterward, the precipitate was washed with warm deionized water to eliminate the excess ions; CO₃²⁻, Cl⁻, and NO₃⁻. The suspension was centrifuged at 500 round per min. The precipitate was dried at 110 °C overnight and calcined in air at 400 °C for 4 h in order to obtain the support. After calcination, the powder of catalysts were labeled and kept in a desiccator.

3.2.1.1.2 Deposition Method (Au, Cu, and Au-Cu)

For the Au deposition, the prepared supports were then deposited by an aqueous solution of $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ (Alfa AESAR) under vigorous stirring conditions at $80\text{ }^\circ\text{C}$ and pH 8, adjusted by the addition of Na_2CO_3 . Afterward, the precipitate was washed with warm deionized water to eliminate the excess ions. The suspension was centrifuged, dried, and calcined in air at various temperatures for 4 h. After calcination, the powder of catalysts were labeled and kept in a desiccator.

For the Cu deposition, the preparation was similar to gold deposition, but the metal solution was used as copper (II) nitrate trihydrate [$\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$; MERCK], and the solution was adjusted to pH 8.

For the bimetallic Au–Cu catalysts, two metal aqueous solutions— $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ and $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ —were used as co-depositing agents, and then heated to $80\text{ }^\circ\text{C}$ with various pH values (6–9) adjusted by the addition of Na_2CO_3 . The appropriate amounts of mixing solutions followed the Au/Cu ratio of 3/1, 1/1, and 1/3. The total loading was varied in the range of 3–7 wt% under the suitable Au/Cu ratio. After the resulting solution was stirred for 1 h, the suspension was washed and dried as same as the deposition step. Finally, the catalyst was calcined in air at various temperatures ($200\text{--}400\text{ }^\circ\text{C}$) for 4 h. The optimum Au/Cu ratio was chosen for further pretreating with H_2 and O_2 gases at $200\text{ }^\circ\text{C}$ for 2 h before testing the SRM.

Table 3.1 All studied catalysts for the SRM*

Catalysts	Studied parameters	Details
Au/CeO ₂ -Fe ₂ O ₃	Support composition	Ce:Fe = 1:0, 8:1, 1:1, 1:8, and 0:1
	Au content	1, 3, and 5 wt%
	Calcination temperature	200, 300, and 400 °C
	Gas pretreatment	O ₂ pretreatment
	H ₂ O/CH ₃ OH molar ratio	1:1, 2:1, 3:1, and 4:1
	Reaction temperature	200–400 °C
	Stability observation	12 hours
	Regeneration of the spent catalyst	O ₂ pretreatment over spent catalyst
Au/CeO ₂ -ZrO ₂	Support preparation and support composition	Sol-gel and co-precipitation
		Zr/(Ce + Zr) = 0, 0.25, 0.50, 0.75, and 1.0

Table 3.1 All studied catalysts for the SRM* (cont'd)

Catalysts	Studied parameters	Details
Au/CeO ₂ -ZrO ₂	Reaction temperature	200–500 °C
Au-Cu/CeO ₂ -ZrO ₂	pH condition for deposition	6, 7, 8, and 9
	Au/Cu atomic ratio	0/1, 1/3, 1/1, 3/1, and 1/0
	Gas pretreatment	H ₂ and O ₂ pretreatments
	Total metal loading	3, 5, and 7 wt%
	Calcination temperature	200, 300, and 400 °C
	Reaction temperature	200–500 °C
	Stability observation	
		Au-Cu/CeO ₂ -ZrO ₂ and Cu/CeO ₂ -ZrO ₂

*All supports were calcined at 400 °C.

3.2.1.2 Catalytic Activity Testing

The system of experiment for steam reforming of methanol (SRM) is shown in Figure 3.1. There are 4 main parts in this system such as liquid feed section, gas blending section, catalytic reactor section, and analytical instrument section.

3.2.1.2.1 Liquid Feed System

The mixture of distilled water and methanol was filled in a syringe and this mixture was injected by a syringe pump at a rate of 1.5 mL/h to an evaporator for making the vapor of methanol and steam. The methanol vapor and steam were carried by helium and entered a catalytic reactor and a flow rate of He was varied to keep the constant gas hourly space velocity (GHSV) at 21,000 ml/g-cat. h or 35 mL/min.

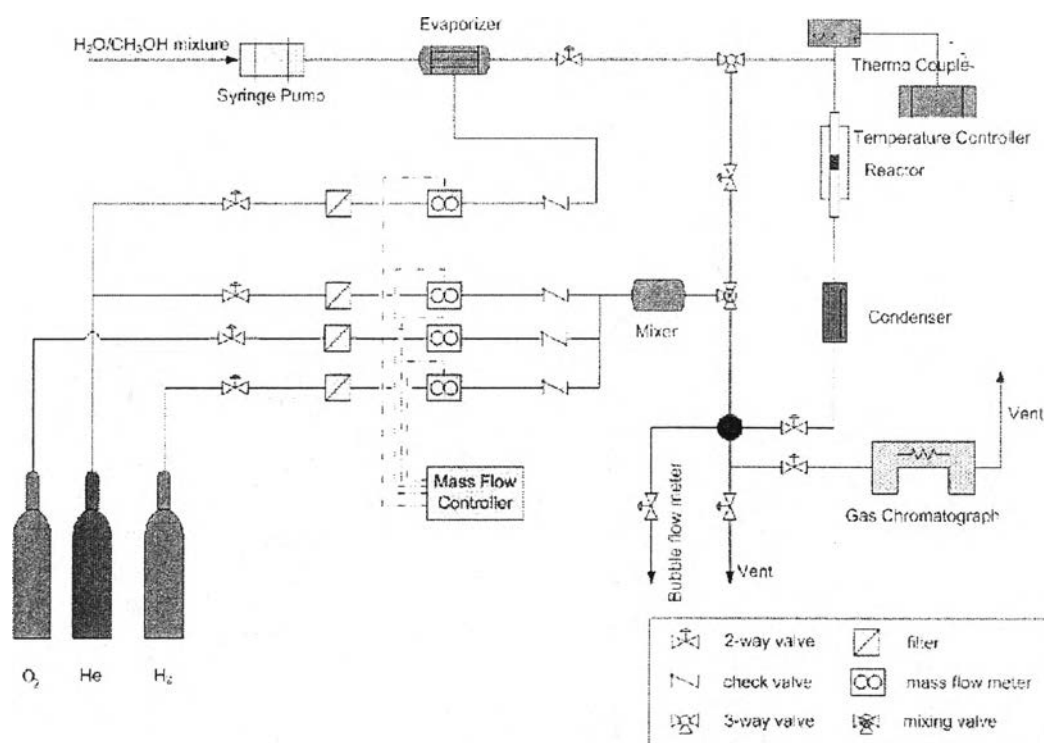


Figure 3.1 Schematic of steam reforming of methanol experimental system.

3.2.1.2.2 Gas Blending System

The purge gas (He) was delivered from the storage tank, and then passed through a micron filter in order to remove particles and passes the check valve to prevent reverse flow. The flow rate was controlled by 840 Sierra Instrument model mass flow controller in order to achieve the desired flow rate. All streams were mixed in a mixing chamber before passing through the catalytic reactor.

3.2.1.2.3 Catalytic Reactor

The steam reforming of methanol was carried out in a vertical pyrex glass microreactor with an inside diameter of 9 mm at atmospheric pressure and in the temperature range of 200–500 °C. In the middle of the reactor, the 100 mg of the catalyst was packed between quartz wool plugs. The reactor was installed and electronically heated in the furnace. The temperature of the catalyst bed was controlled and monitored by PID temperature controller equipped with a chromel-alumel thermocouple (Type K)

3.2.1.2.4 Analytical Instrument

The product gases (e.g. H₂, CO, CO₂, and CH₄) from the reactor are analyzed both qualitatively and quantitatively by a Hewlett Packard 5890 series II gas chromatograph equipped with a thermal conductivity detector (TCD). The column utilized in a gas chromatograph is Carbosphere®, 80/100 mesh, 10 ft x 1/8 inch stainless steel packed column. The gas chromatograph conditions used in this study are summarized as follows:

Injection Temperature:	95 °C
Oven Temperature:	95 °C
Detector Temperature:	145 °C
Carrier gas:	He (99.99% purity), 30 mL/min

The results were recorded by Agilent Chemstation software. The observed peaks were identified by comparison with the retention time of the standard gas. For quantitative analysis, the peaks area was used to determine the concentration of each component based on the calibration curves obtained from known composition gases.

3.2.2 Preferential CO Oxidation over monometallic Au catalysts

The reformat from the SRM unit was injected into the PROX reactor, and the oxygen gas was fed into the PROX reactor with different O₂/CO ratios under 100 mg of 1 wt% Au/CeO₂ catalyst calcined at 300 and 400 °C, which was packed in the single-stage PROX as the fixed-bed reactor. Afterwards, the amount of use catalyst was varied from 100 to 600 mg during the operating temperature range of 90–150 °C. Based on the optimum conditions from the first-stage PROX, the O₂ and weight split ratios, and reaction temperature must be optimized in the double-stage PROX, where the reaction temperature was varied in the range of 90–150 °C as well. Again, the outlet products from the PROX were directly analyzed by the same on-line gas chromatograph. To better understand the PROX unit, the process flow diagram is shown in Figure 3.2.

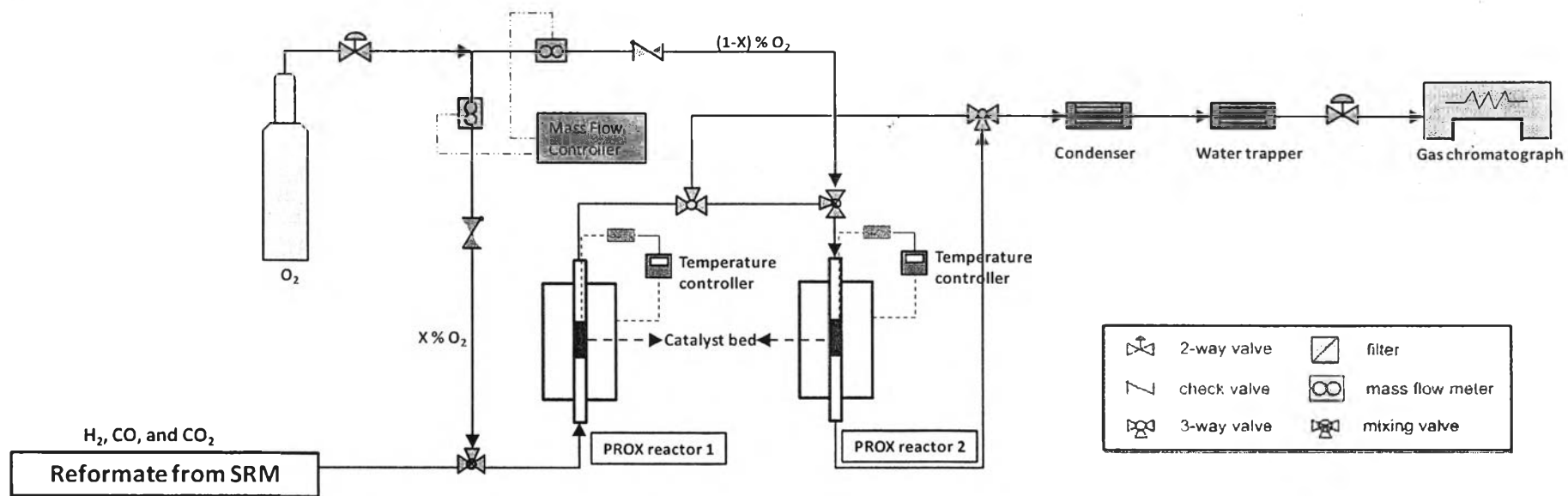


Figure 3.2 Process flow diagram of the single- and double-stage PROX.

3.2.3 Catalyst Characterization

The properties and characteristics of the prepared catalysts significantly affect the activities and selectivity of the catalyst; therefore, it is necessary to conduct some characterizations.

3.2.3.1 X-Ray Diffraction (XRD)

The crystalline structure of oxide support and the mean particle diameter of gold were analyzed by means of a Rigaku X-Ray Diffractometer system (RINT-2200) with copper tube for generating $\text{CuK}\alpha$ radiation (1.5406 Å), and nickel filter. It is also possible to achieve a relative analysis by the intensity of the peak. For the same crystalline substance the higher of the peak indicates the higher content of that phase.

RINT-2200 is 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 = 1° (2θ); scattering slit = 1° (2θ); and receiving slit = 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. 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. Scherrer equation in the form of Eq. 3.1 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).

$$D_b = \frac{K \cdot \lambda}{B_d \cdot \cos \theta} \quad (3.1)$$

where:

D_b = mean crystalline diameter (Å)

K = Scherrer constant, 0.9

λ = X-Ray wavelength (Å)

B_d = angle width of peak in term of $\Delta(2\theta)$ (radian)

θ = Bragg angle of the reflection (degree)

It is important to note here that the results from the Scherrer equation are a crystalline thickness that is perpendicular to the diffraction planes rather than an actual particle size. It is necessary to apply a correction factor that

depends on the actual shape of the crystallinities and on the Millers indices of the diffraction planes in order to obtain the actual crystallite size from the thickness.

3.2.3.2 Transmission Electron Microscopy (TEM)

The transmission electron micrographs were employed for investigating the average particle size and identifying the microstructure of prepared catalysts. The catalyst samples were grounded into fine powder and ultrasonically dispersed in ethanol. A small droplet of the suspension was deposited on a copper grid, and the solvent will be evaporated prior to load the sample into the microscope. TEM analysis was performed on a JEOL 2000CX operated at an accelerating voltage of 120 kV in bright field modes. A beam will be passed through a series of lenses to form a magnified image of a sample that is inserted in the area of the objective lens. The image from selected area will be viewed through projection onto a view of screen. However, electron beams can be easily scattered by air molecules, and TEM columns must be kept under high vacuum. Additionally, the electromagnetic lenses will be used for focusing the electron beam.

3.2.3.3 Temperature-Programmed Reduction (TPR)

Temperature-programmed reduction (TPR) was conducted using an in-house TPR system. A measurement was carried out by placing a sample in a quartz reactor. About 50 mg of the catalyst was subjected to TPR analysis using 10% H₂ in Ar at a flow rate of 30 mL/min. The reduction temperature was raised from 30 to 850 °C at a heating ramp 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 is completed, could be determined from TPR pattern.

3.2.3.4 Temperature-Programmed Oxidation (TPO)

Temperature-programmed oxidation (TPO) is used to evaluate the amount of carbon formation of spent catalysts. The 50 mg of spent catalyst is placed in quartz tube reactor. The spent catalyst is conducted to TPO analysis using 2% O₂ in He for 30 mL/min before the temperature is linearly

increased at a ramp rate of 12 °C/min. Carbon is oxidized into carbon dioxide then convert to methane in the methanator. FID SRI model 110 is used to detect the effluent gas from methanator. The obtained results can be used to determine the amount of deposited carbon.

3.2.3.5 *UV-vis Spectrophotometer*

The measurements were performed on air-exposed samples at an ambient temperature of between 200 and 800 nm. The absorption intensity was expressed using the Kubelka-Munk function.

$$F(R_{\infty}) = \frac{(1 - R_{\infty})^2}{2R_{\infty}} \quad (3.2)$$

where R_{∞} is the diffuse reflectance from a semi-infinite layer.

3.2.3.6 *X-Ray Fluorescence Spectrometry (XRF)*

An X-Ray Fluorescence Spectrometry, XRF (AXIOS PW4400) was used to determine the actual surface (Au, Ce, and Fe) composition.

3.2.3.7 *Fourier Transform Infrared Spectroscopy (FT-IR)*

The FTIR spectra of the samples were recorded using a Thermo Nicolet Nexus 670 FTIR spectrometer in the absorbance mode at 32 scans with a resolution of 4 cm⁻¹. Spectra of frequency range of 4000–400 cm⁻¹ were measured using a deuterated triglycerinesulfate detector (DTGS) with specific detectivity of 1×10^9 cm Hz^{1/2} w⁻¹.

3.2.3.8 *Fourier Transform Raman Spectroscopy (FT-Raman)*

The FT-Raman of the samples 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 to 200 cm⁻¹ was obtained.