



## CHAPTER III EXPERIMENTAL

### 3.1 Materials

#### 3.1.1 Reactants

- Deionized water
- Methanol (purity  $\geq 99.8\%$ )

#### 3.1.2 Gases

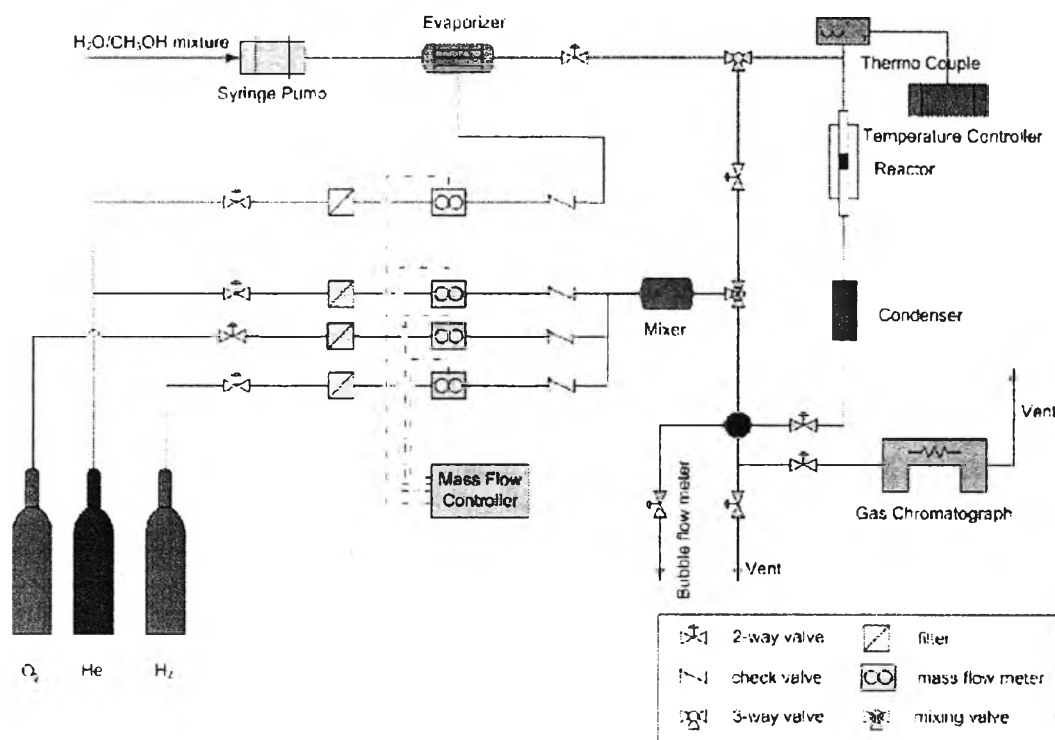
- Hydrogen (Thai Industrial Gases Public Company Limited) of 99.99% purity was used as a reduction gas.
- Oxygen (Thai Industrial Gases Public Company Limited) of 99.97% purity was used as a reduction gas.
- Helium (Thai Industrial Gases Public Company Limited) of 99.995% purity was used as a diluted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

#### 3.1.3 Chemicals

- Hydrogen tetrachloroaurate (III),  $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ , (Alfa AESAR) (purity 99.99%)
- Cerium (III) nitrate hexahydrate,  $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ , (Aldrich) (purity 99.99%)
- Sodium carbonate anhydrous,  $\text{Na}_2\text{CO}_3$ , (Riedel-de Haen) (purity 99.99%)
- Gold standard solution for AAS (Fluka)
- Deionized water
- Acetone, AR, 2.5 L

## 3.2 Equipment

The system of experiment for oxidative steam reforming of methanol (OSRM) is shown in Figure 3.1.



**Figure 3.1** Schematic of oxidative steam reforming of methanol experimental system.

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 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/hour to an evaporator for making the vapor of methanol and steam. The methanol vapor and steam were carried by helium, and mixed with oxygen stream before entering a

catalytic reactor and a flow rate of He and oxygen were varied to keep the constant gas hourly space velocity (GHSV) at 30,000 ml/g-cat. hour.

### 3.2.2 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.

### 3.2.3 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 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)

### 3.2.4 Analytical Instrument

The product gases (e.g. H<sub>2</sub>, CO, CO<sub>2</sub>, and CH<sub>4</sub>) 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.

### 3.3 Methodology

#### 3.3.1 Preparation of Catalyst and Support

In this study, the catalysts were prepared by deposition-precipitation (DP) method and the support ( $\text{CeO}_2$ ) was prepared by precipitation method.

##### 3.3.1.1 *Precipitation Method*

###### 3.3.1.1.1 Preparation of $\text{CeO}_2$ support

An aqueous solution of 0.1M  $\text{Na}_2\text{CO}_3$  was added dropwise in an aqueous solution of 0.1 M  $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  under vigorously stirring condition at  $80^\circ\text{C}$ . The mixture was kept at a pH of 8-9 for 1 hour. Excess ions,  $\text{CO}_3^{2-}$  and  $\text{NO}_3^-$ , were eliminated by washing with warm deionized water. The suspension was centrifuged in centrifuge HERMLE Z383 at 500 rpm. The precipitate was dried at  $80^\circ\text{C}$  overnight and calcined in air at  $400^\circ\text{C}$  for 4 hours. After calcination, the powder of catalysts were labeled and kept in a desiccator.

##### 3.3.1.2 *Deposition-precipitation (DP) Method*

Before adding the metals, the support ( $\text{CeO}_2$ ) was dried in an oven at  $110^\circ\text{C}$  for 12 hours. Hydrogen tetrachloroaurate (III),  $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ , was weighed for a desired amount, and then dissolved in deionized water under continuous stirring and heating at  $80^\circ\text{C}$ . The dried support was added to a solution and the pH of solution ( $\sim 8$ ) was adjusted by adding 0.1 M  $\text{Na}_2\text{CO}_3$  then the mixture was aged for 1 hour. The suspension was washed by warm deionized water to eliminate the residue ions. The suspension was centrifuged in centrifuge HERMLE Z383 at 500 rpm. Deionized precipitate was dried at  $110^\circ\text{C}$  overnight and calcined in air at various temperatures for 4 hours. After calcination, the sample was ground and sieved by 80–120 mesh size, and was kept in a desiccator.

### 3.3.2 Catalyst Characterization

The properties and characteristics of the prepared catalysts (Au/CeO<sub>2</sub>) are different due to the effect of the Au contents and calcination temperatures. The different properties may affect the activities and selectivity of the catalyst; therefore, it is necessary to conduct some characterizations. In this work, several characterizations are utilized.

#### 3.3.2.1 *BET Surface Area Measurement*

Autosorb-1 Gas Sorption System (Quantachrome Corporation) are used to measure the BET surface area, total pore volume, and average pore diameter of the catalysts. The equipment measurement is based on Brunauer-Emmet-Teller (BET) equation. This technique is done by calculating the physical multi-layer adsorption of Nitrogen. A sample is outgassed by heating under vacuum to eliminate volatile absorbents in the surface at 250°C for at least 4 hours prior to the analysis. Nitrogen gas with the cross-sectional area of  $1.62 \times 10^{-19}$  m<sup>2</sup>/molecule is adsorbed on the catalyst surface at liquid Nitrogen temperature (-196°C). The surface area is calculated from the 22 points nitrogen adsorption. The average pore diameter and pore volume are obtained at P/P<sub>0</sub> 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<sub>0</sub> = saturated vapor pressure of the liquid at the operating temperature

W = weight of gas adsorbed at a relative pressure, P<sub>0</sub>

W<sub>m</sub> = 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 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<sup>2</sup>/g)

A<sub>N2</sub> = cross-sectional area of one molecule N<sub>2</sub> (0.162 nm<sup>2</sup> at -196°C)

M<sub>w, N2</sub> = molecule weight of nitrogen (28 g/g-mol)

### 3.3.2.2 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 CuK<sub>α</sub> 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. 3.3 shows the relationship between the crystalline thickness ( $D_b$ ) and the broadening ( $B_d$ ) of the diffraction line corresponding to the Bragg angle ( $\theta$ ) using wavelength ( $\lambda$ ).

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

where:

$D_b$  = mean crystalline diameter (Å)

K = Scherrer constant, 0.9

$\lambda$  = X-Ray wavelength (Å)

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

$\theta$  = 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.

### 3.3.2.3 *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.

### 3.3.2.4 *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% H<sub>2</sub> 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.

### 3.3.2.5 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% O<sub>2</sub> 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.

### 3.3.2.6 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.

$$F(R_{\infty}) = \frac{(1 - R_{\infty})^2}{2R_{\infty}} \quad (3.4)$$

where  $R_{\infty}$  is the diffuse reflectance from a semi-infinite layer.

### 3.3.2.7 Atomic Absorption Spectrometer (AAS)

Atomic Absorption Spectrometer (Varian/SpectraAA 300) was used to determine the actual Au metal content.

### 3.3.2.8 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 cmK1. Spectra of frequency range of 4000–400cm<sup>-1</sup> were measured using a deuterated triglycerinesulfate detector (DTGS) with specific detectivity of  $1 \times 10^9$  cm Hz<sup>1/2</sup> w<sup>-1</sup>.



### 3.4 Optimum Condition and Activity Measurement

Oxidative steam reforming of methanol reaction was carried out in a fixed-bed reactor under atmospheric pressure. Many parameters affecting the activity and selectivity of the Au/CeO<sub>2</sub> catalysts, will be studied in this research such as the effects of Au content, calcination temperature, and reaction temperature. Moreover, the suitable condition of Au/CeO<sub>2</sub> catalysts was chosen for further study in the presence of decomposition of methanol (DM), partial oxidation of methanol (POM), and water gas shift (WGS) reactions. Finally, the deactivation tests of both catalysts were also performed for 24 hours. All of these parameters were summarized in Table 3.1.

#### 3.4.1 Effect of Steam/Methanol (S/M or H<sub>2</sub>O/CH<sub>3</sub>OH) Molar Ratio

The effect of steam/methanol molar ratio was studied on the methanol conversion and hydrogen selectivity in the OSRM reaction over the reaction temperatures varied in the range of 200–400°C. The S/M molar ratios were varied from 0 to 4. The suitable S/M molar ratio will be chosen.

#### 3.4.2 Effect of O<sub>2</sub>/CH<sub>3</sub>OH Molar Ratio

The effect of O<sub>2</sub>/CH<sub>3</sub>OH molar ratio was studied on the methanol conversion and hydrogen selectivity in the OSRM reaction over the reaction temperatures varied in the range of 200–400°C. The O<sub>2</sub>/CH<sub>3</sub>OH molar ratios were varied from 0 to 2.5. The suitable O<sub>2</sub>/CH<sub>3</sub>OH molar ratio will be chosen.

#### 3.4.3 Effect of Au Content

The effect of gold content was studied on the activity and selectivity in OSRM reaction. The gold contents were varied from 1 to 5% wt. The suitable gold content will be chosen.

#### 3.4.4 Effect of Calcination Temperature

The effect of calcination temperature with the suitable gold content on Au/CeO<sub>2</sub> catalysts was studied on the activity and selectivity in the OSRM

reaction. The calcination temperatures of 300, 400, 500, and 600°C were studied for Au/CeO<sub>2</sub> catalysts. The suitable calcination temperature will be chosen.

#### 3.4.5 Effect of Reaction Temperature

The effect of reaction temperature with the suitable gold content and calcination temperature on Au/CeO<sub>2</sub> catalysts was studied on the activity and selectivity in the OSRM reaction. Reaction temperatures were varied in the range of 200–400°C. The suitable reaction temperature will be chosen.

#### 3.4.6 Effect of DM, POM, and WGS Reactions

The effects of DM, POM, and WGS reactions with the suitable gold content and calcination temperature on Au/CeO<sub>2</sub> catalysts was studied. The reaction temperature of DM, POM, and WGS reactions were varied in the range of 200–400°C.

#### 3.4.7 Deactivation Test

The deactivation test of the catalyst was studied on the OSRM for 1 week or 168 hours. This study was conducted with the optimum gold content, calcination temperature, and reaction temperature.

### 3.5 Calculations

The methanol conversion, hydrogen yield, hydrogen selectivity, carbon monoxide selectivity, and carbon dioxide selectivity are calculated by Eqs. 3.5 – 3.9.

$$X = \frac{CO + CO_2 + CH_4}{MeOH_{(in)}} \times 100(\%) \quad (3.5)$$

where

$X$  = methanol conversion (%)

$MeOH_{(in)}$  = mole of methanol inlet

$$Y_{H_2} = X \times S_{H_2} \quad (3.6)$$

where

$$S_{H_2} = \frac{H_2}{H_2 + CH_4 + CO + CO_2} \times 100(\%) \quad (3.7)$$

$$S_{CO} = \frac{CO}{H_2 + CH_4 + CO + CO_2} \times 100(\%) \quad (3.8)$$

$$S_{CO_2} = \frac{CO_2}{H_2 + CH_4 + CO + CO_2} \times 100(\%) \quad (3.9)$$

where

$Y_{H_2}$  = hydrogen yield (%)

$S_{H_2}$  = hydrogen selectivity (%)

$S_{CO}$  = carbon monoxide selectivity (%)

$S_{CO_2}$  = carbon dioxide selectivity (%)

$H_2$  = mole of hydrogen in the product stream

$CO$  = mole of carbon monoxide in the product stream

$CO_2$  = mole of carbon dioxide in the product stream

$CH_4$  = mole of carbon methane in the product stream