

## 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.
- Helium (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

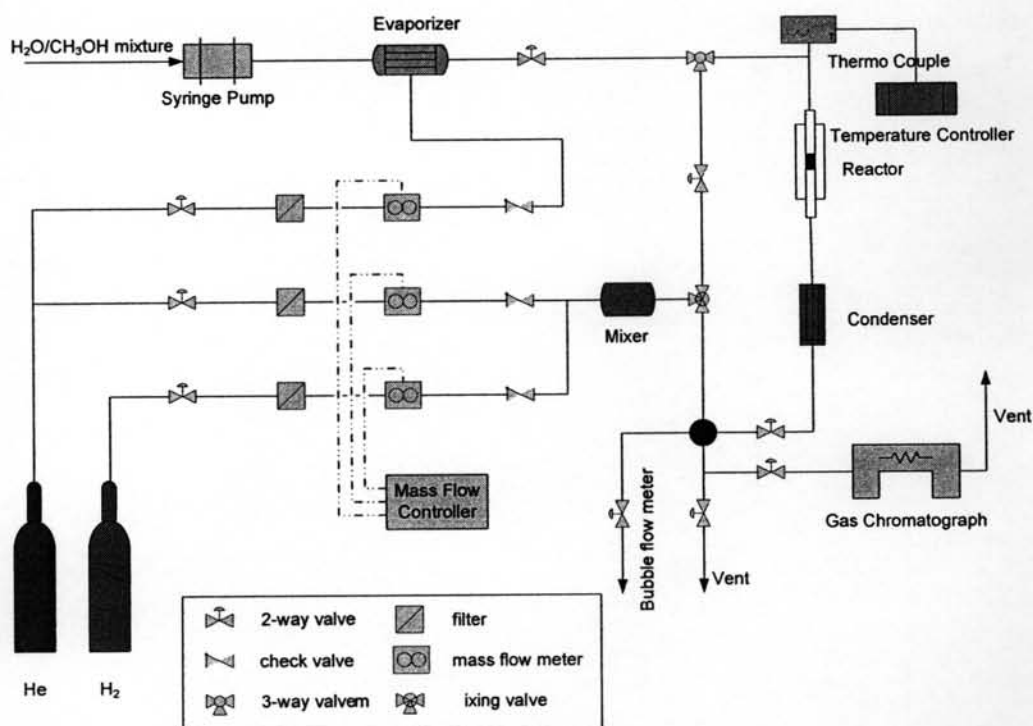
- Commercial cerium (IV) oxide,  $\text{CeO}_2$ , (Aldrich)
- Commercial zinc (II) oxide,  $\text{ZnO}$ , (Fluka)
- Hydrogen tetrachloroaurate (III),  $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ , (Alfa AESAR)
- Sodium carbonate anhydrous,  $\text{Na}_2\text{CO}_3$ , (Riedel-de Haen)
- Sodium hydroxide,  $\text{NaOH}$ , (Fluka)
- Ammonium hydroxide,  $\text{NH}_4\text{OH}$ , (Fluka)
- Silver Nitrate,  $\text{AgNO}_3$ , (Fluka)
- Cerium (III) nitrate hexahydrate,  $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ , (Fluka)
- Zinc (II) nitrate hexahydrate,  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , (Sigma-Aldrich)
- Gold standard solution for AAS (Fluka)
- Deionized water

#### 3.1.4 Solvents

- Acetone, AR, 2.5 L

### 3.2 Equipment

The system of experiment for steam reforming of methanol (SRM) is shown below.



**Figure 3.1** The steam reforming of methanol experimental system.

There are 4 main parts in this system such as liquid feed system, gas blending system, catalytic reactor and analytical instrument.

#### 3.2.1 Liquid Feed System

The mixture of distilled water and methanol is filled in the syringe and this mixture is injected by syringe pump at a rate of 1.5 mL/h to evaporizer for making the vapor of methanol and steam. The methanol vapor and steam, are carried by helium before entering the catalytic reactor and flowrate of carrier gas is adjusted about 34 mL/min.

### 3.2.2 Gas Blending System

The reduction gas ( $H_2$ ), the balance gas and purge gas (He) are delivered from the storage tank, and then pass through a micron filter in order to remove particles and pass the check valve to prevent reverse flow. The flow rates are controlled by 840 Sierra Instrument model mass flow controller in order to achieve the desired flowrate. All streams are mixed in the mixer before passing through the catalytic reactor.

### 3.2.3 Catalytic Reactor

The steam reforming of methanol is carried out in a vertical pyrex glass micro-reactor with an inside diameter of 6 mm at atmospheric pressure and at temperatures range of 200 – 450°C. In the middle of the reactor is packed with the catalyst between quartz wool plugs. The reactor is installed and electronically heated in the furnace. The temperature of the catalyst bed is 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  $H_2$ , CO,  $CO_2$  and  $CH_4$ ) from the reactor are analyzed both qualitatively and quantitative 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 unreacted reactants (water and methanol) and a byproduct are condensed from the gas stream after passing through the reactor. The gas is delivered to an online HP 5890 GC as discussed above and the condensate is analyzed qualitatively and quantitative by another HP 5890 GC gas chromatograph equipped with a thermal conductivity detector (TCD). The column utilized in the

chromatograph is Hayesep D, 80/120 mesh, 3'x1/8" SS packed column. The gas chromatograph conditions used in this research are summarized as follows:

Injection Temperature:	130°C
Oven Temperature:	100°C
Detector Temperature:	130°C
Carrier gas:	He (99.99% purity), 60 mL/min

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

### 3.3 Catalyst Preparation

In this study, the catalysts are prepared by the various techniques such as Incipient wetness impregnation (IWI), Co-precipitation (CP) and Deposition-precipitation (DP).

#### 3.3.1 Incipient Wetness Impregnation (IWI) Method

Before adding the metals, the support ( $\text{CeO}_2$  or  $\text{ZnO}$ ) is dried in an oven at 100°C for 12 hours. Hydrogen tetrachloroaurate (III),  $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ , is weighted for a desired amount, and then dissolved in deionized water. After that, the support is impregnated by slowly dropping the gold solution. Next, the wet catalyst is dried at room temperature for 2 hours before drying in an oven at 110°C for 24 hours and calcined in air at 400°C for 4 hours. The resulting catalyst is labeled and stored in a desiccator.

#### 3.3.2 Co-precipitation (CP) Method

An aqueous solution of 1M  $\text{Na}_2\text{CO}_3$  is added dropwise in the aqueous mixture of 0.1 M  $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  or 0.1M  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and 0.1 M  $\text{HAuCl}_4$  under vigorous stirring condition at 80°C. The mixture is kept at a pH of 8-9 for 1 hour. Excess ions,  $\text{Cl}^-$  and  $\text{NO}_3^-$ , are eliminated by washing with warm

deionized water. The precipitate is dried at 110°C overnight and calcined in air at 400°C for 4 hours. After calcinations, the powder is ground and sieved to 120 mesh size, labeled and kept in a desiccator.

### 3.3.3 Deposition-precipitation (DP) Method

Before adding the metals, the support ( $\text{CeO}_2$  or  $\text{ZnO}$ ) is dried in an oven at 110°C for 12 hours. Hydrogen tetrachloroaurate (III),  $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ , is weighted for a desired amount, and then dissolved in deionized water under continuous stirring and heating at 80°C, the pH of solution (~ 8) is adjusted by adding  $\text{Na}_2\text{CO}_3$ . The dried support is added to a solution and aged for 1 hour. The suspension is washed by warm deionized water. Deionized precipitate is dried at 110°C overnight and calcined in air at 400°C for 4 hours. After calcinations the powder is ground and sieved to 120 mesh size, labeled and kept in a desiccator.

## 3.4 Catalyst Characterization

The properties and the characteristics of the prepared catalysts are crucial properties due to the difference of the preparation method. The different properties may affect the activities of the catalyst; therefore, it is necessary to conduct some characterizations. In this work, several characterizations are utilized.

### 3.4.1 X-Ray Diffraction (XRD)

The crystalline structure of oxide support and the mean particle diameter of gold are 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° (2 $\theta$ ); scattering slit = 1° (2 $\theta$ ); and receiving slit = 0.3 mm. The scan speed of 5°

( $2\theta$ )/min with scan step of 0.02 ( $2\theta$ ) is used for the continuous run in 5 to 90°C ( $2\theta$ ) 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 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 ( $\theta$ ) 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. Correction factors are given in Table 3.1 for some common geometry.

**Table 3.1** Values of the geometric factor ( $g$ ), such as  $d = gD_b$

Geometry of the crystallite	$g$	Definition of $d$
Sphere	4/3	Diameter
Hemisphere	8/3	Diameter

XRD can also give some information on the dispersion of a supported catalyst only if it is in the form of a separate crystallite phase.

#### 3.4.2 Inductively Coupled Plasma (ICP) Spectroscopy

The content of Au (atomic percentage) in the prepared catalyst is known from the preparation procedure. However, it is necessary to determine the actual one since Au might be lost during the preparation steps leading to the smaller amount of Au compare to the calculated amount. The Inductively Coupled Plasma – Optical Emission Spectroscopy (ICP-OES), Perkin-Elmer Optima 4300 DV is utilized to determine the actual percent Au loading on the supports. A known weight amount of catalyst was dissolved in aqua regia solution composed of hydrochloric acid and nitric acid with a ratio of 3:1 by volume and then heated to 50°C overnight. Several standard solutions were made from stock solution of 1,000 ppm to establish a calibration curve. The amount of gold of the sample solution was measured by mean of radiation intensity. The radiation emitted to the spectrometer optic where it is dispersed into its spectral compound and the particular wavelengths of radiation is emitted for each element. The radiation intensity is proportional to the concentration of that element.

#### 3.4.3 Scanning Electron Microscope (SEM)

The morphology of the catalysts are observed by using a JEOL 5200-2AE scanning electron microscope (SEM) with 1500 to 10000 magnifications and operated at 15 kV. The powder sample is placed on the stub and coated with gold in sputtering device before taking the micrograph.

#### 3.4.4 Transmission Electron Microscopy (TEM)

A TECNAI G<sup>2</sup> transmission electron microscope was used with an accelerating voltage of 200 kV to study the gold catalysts (Au/CeO<sub>2</sub> and Au/ZnO) interface structure. The prepared catalyst was suspended in ethanol with ultrasonic for 15 min, then a few drop of the suspended solution were deposited on a copper grid and subsequently dried and evacuated before taking the micrograph.

#### 3.4.5 Temperature Programmed Reduction (TPR)

Temperature Programmed Reduction (TPR) is conducted using a in-house TPR system. A measurement is carried out by placing a sample in a quartz

reactor. The sample is subjected to TPR analysis using 5% H<sub>2</sub> in Ar, 30 ml/min. The reduction temperature is raised from 40 to 800°C at a ramp rate of 10°C/min. A thermal conductivity detector is 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.

### 3.5 Activity Measurement

Steam reforming of methanol reaction is carried out in a fixed bed reactor under atmospheric pressure. After the catalyst is packed in the reactor, it is reduced in pure H<sub>2</sub> flow 30 mL/min at 400°C for one hour. Then, it is flushed with He for 30 min at the reaction temperature. The concentrations of reactants are measured by pass line to the condenser, then to the manual mode gas chromatograph to meet the desired concentration before feeding the reactants to the reactor.

Many parameters affecting the activity of the prepared catalysts are studied in this research such as the reaction temperature, the steam/methanol molar ratio, the preparation method, and the effect of support.

#### 3.5.1 Effect of Catalyst Preparation and Reaction Temperature

The various techniques such as the conventional Incipient wetness impregnation, Co-precipitation (CP), and Deposition-precipitation (DP) are simultaneously studied versus reaction temperatures from 200 to 450 °C. The reaction is carried out at atmospheric pressure, steam/methanol molar ratio = 4/3, and the catalyst weight of 0.1 grams.

The effect of catalyst preparation on the gold particle size is also studied. The gold particle size with less than 5 nm (Haruta, 2005) is recommended for the catalytic reaction (e.g. oxidation of CO); therefore, the proper catalyst preparation is selected for the next study.

#### 3.5.2 Effect of Steam/Methanol Molar Ratio

The effect of steam/methanol molar ratio on the selectivity of CO and hydrogen are studied. The steam/methanol molar ratios at 0, 1.3, and 2 are studied.



The suitable steam/methanol molar ratio is chosen for the next study. For steam/methanol molar ratio at 0, this condition is known as decomposition of methanol (DM).

### 3.5.3 Effect of Support

The support also play an important role on the catalytic performance; therefore, CeO<sub>2</sub> and ZnO were chosen as a support for Au catalyst. The effect of support on the steam reforming of methanol activity and selectivity for CO and hydrogen are investigated.

### 3.5.4 Deactivation Test

The deactivation test of the catalyst is studied for methanol steam forming for more than 15 hours. This study is conducted with the optimum steam/methanol molar ratio, reaction temperature, and catalyst preparation.

**Table 3.2** Summary of the work plan

Studies	Catalysts	Techniques	Run no.
Effect of reaction temperature (200°C -450°C)	Au/CeO <sub>2</sub>	IWI	1
		1%CP	2
		5%CP	3
		DPC	4
		DPS	5
	Au/ZnO	CP	6
Effect of preparation techniques (selected temperature)	Au/CeO <sub>2</sub>	IM	7
		5%CP	8
		DPC	9
		DPS	10
Effect of steam/methanol molar ratio (selected temperature and selected catalyst preparation techniques)	Au/CeO <sub>2</sub> (s/m = 0)	IWI	11
		5%CP	12
		1%CP	13
		DPC	14
		DPS	15
	Au/ZnO (s/m=0)	CP	16
	Au/CeO <sub>2</sub> (s/m = 1.3)	IWI	17
		5%CP	18
		1%CP	19
		DPC	20
		DPS	21
	Au/ZnO (s/m=1.3)	CP	22
	Au/CeO <sub>2</sub> (s/m = 2.0)	5%CP	23
		1%CP	24
DPS		25	
Au/ZnO (s/m=2.0)	CP	26	
Deactivation test	Au/CeO <sub>2</sub>	5%CP	27
	Au/ZnO	CP	28

### 3.6 Calculations

The methanol conversion, hydrogen yield, hydrogen selectivity, carbon monoxide selectivity and carbon dioxide selectivity are calculated by Equations 3.4 to 3.8.

$$X = \frac{CO + CO_2 + CH_4}{MeOH_{(in)}} \cdot 100\% \quad (3.4)$$

where

$X$  = methanol conversion (%)

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

$$Y_{H_2} = X * S_{H_2} \quad (3.5)$$

where

$$S_{H_2} = \frac{2H_2}{2H_2 + CH_4} \cdot 100\% \quad (3.6)$$

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

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

where

$Y_{H_2}$  = H<sub>2</sub> 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