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 99.99% 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.

- 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), $HAuCl_4.3H_2O$, (Alfa AESAR)
- Zinc (II) nitrate hexahydrate, $Zn(NO_3)_2.6H_2O$, (Sigma-Aldrich)
- Ferric (III) nitrate nonahydrate, $Fe(NO_3)_3.9H_2O$, (Fluka)
- Sodium carbonate anhydrous, Na_2CO_3, (Riedel-de Haen)
- Silver Nitrate, $AgNO_3$, (Fluka)
- 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 in Figure 3.1.
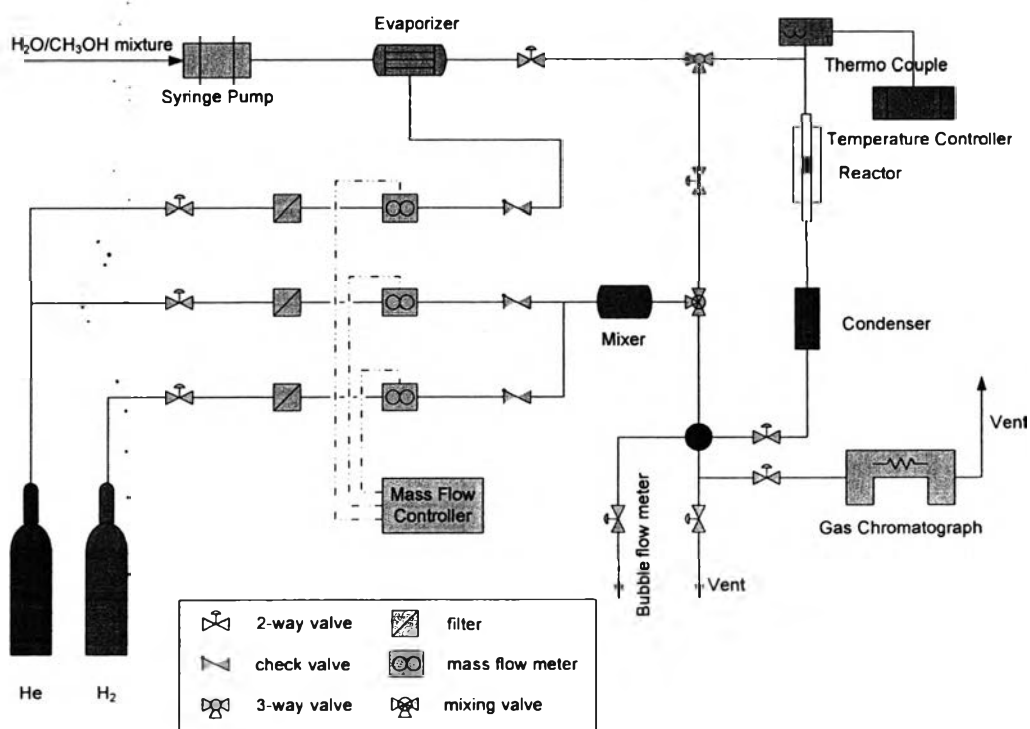

Figure 3.1 Schematic diagram of steam reforming of methanol experimental system.

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 a syringe and this mixture is injected by syringe pump at a rate of 1.5 ml/hour to a vaporizer for making the vapor of methanol and steam. The methanol vapor and steam, are carried

by helium before entering a catalytic reactor and a flow rate of He is maintained about 34 ml/min.

3.2.2 Gas Blending System

The pretreatment gas (H_2 or O_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 flow rate. All streams are mixed in a mixing chamber before passing through the catalytic reactor.

3.2.3 Catalytic Reactor

The steam reforming of methanol is carried out in a vertical pyrex glass microreactor with an inside diameter of 9 mm at atmospheric pressure and in the temperature range of 250 – 450°C. In the middle of the reactor, the catalyst is packed 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 was analyzed qualitatively and quantitatively by another HP 5890 GC, 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:	$130^{\circ}C$
Oven Temperature:	$110^{\circ}C$
Detector Temperature:	$160^{\circ}C$
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 Preparation of Catalyst and Support

In this study, the catalysts are prepared by Deposition-precipitation (DP) method. And the supports (ZnO, Fe_2O_3-ZnO) are prepared by Co-precipitation (CP) method.

3.3.1 Deposition-precipitation (DP) Method

Before adding the metals, the support (ZnO, Fe_2O_3-ZnO) is dried in an oven at $110^{\circ}C$ for 12 hours. Hydrogen tetrachloroaurate (III), $HAuCl_4.3H_2O$, is weighed for a desired amount, and then dissolved in deionized water under continuous stirring and heating at $80^{\circ}C$. The dried support is added to a solution and the pH of solution (~8) is adjusted by adding 0.1 M Na_2CO_3 then the mixture is aged for 1 hour. The suspension is washed by warm deionized water to eliminate the residue ion. Deionized precipitate is dried at $110^{\circ}C$ overnight and calcined in air at various temperatures for 4 hours. After calcinations, the sample was ground and sieved to 80-120 mesh size, and kept in a desiccator.

3.3.2 Co-precipitation (CP) Method

3.3.2.1 Preparation of ZnO support

An aqueous solution of 1M Na_2CO_3 is added dropwise in an aqueous solution of 0.1 M $Zn(NO_3)_3.6H_2O$ under vigorous stirring condition at 80°C. The mixture is kept at a pH of 8-9 for 1 hour. Excess ions, Cl^- and 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 calcination, the powder is labeled and kept in a desiccator.

3.3.2.2 Preparation of Fe₂O₃-ZnO support

An aqueous solution of 1M Na_2CO_3 is added dropwise in the aqueous mixture of 0.1 M $Zn(NO_3)_3.6H_2O$ and 0.1 M $Fe(NO_3)_3.9H_2O$ under vigorous stirring condition at 60°C. The mixture is kept at a pH of 8-9 for 1 hour. Excess ions, Cl^- and NO_3^-, are eliminated by washing with warm deionized water. The precipitate is dried at 80°C overnight and calcined in air at 400°C for 2 hours. After calcination, the powder labeled and kept in a desiccator.

3.4 Catalyst Characterization

The properties and characteristics of the prepared catalysts (Au/ZnO, Au/Fe₂O₃-ZnO) are different due to the effect of Au content, calcination temperature and gas pretreatment. 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.

3.4.1 BET Surface Area Measurement.

Autosorb-1 Gas Sorption System (Quantachrome Corparation) 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 1.62×10^{-19} m^2/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_0 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.

$$\frac{1}{W.(\frac{P_o}{P} - 1)} = \frac{1}{W_m.C} + \frac{(C-1)}{(W_m.C)}\left(\frac{P_0}{P}\right) \qquad (3.1)$$

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

C   = constant that is related to the energy of adsorption in the first adsorbed layer and magnitude of the adsorbent/adsorpbate interaction

The surface area is calculated by Equation 3.2.

$$S = \frac{W_m.A_{N_2}.(6.02 \times 10^{23})}{M_{W.N_2}} \qquad (3.2)$$

Where:

S   = specific surface area (m^2/g)

A_{N2} = cross-sectional area of one molecule N_2 (0.162 nm^2 at -196°C)

$M_{W.N2}$ = molecule weight of nitrogen (28 g/g-mol)

3.4.2 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 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°C (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 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).

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

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.

3.4.3 Transmission Electron Microscopy (TEM)

The transmission electron micrographs will be employed for investigating the average particle size and identifying the microstructure of prepared catalysts. The catalyst samples will be grounded into fine powder and ultrasonically dispersed in ethanol. A small droplet of the suspension will be deposited on a copper grid, and the solvent will be evaporated prior to loading the sample into the micro-

scope. TEM will be carried out using in 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.

3.4.4 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 10% H_2 in Ar for 30 ml/min. The reduction temperature is raised from 30 to 850°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.

3.4.5 Temperature Programmed Oxidation (TPO)

Temperature Programmed Oxidation (TPO) is used to evaluate 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_2 in He for 30 ml/min before the temperature is linearly increase at a ramp rate of 12°C/min. Carbon formation 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 result from measurement can be used to determine amount of deposited carbon.

3.5 Activity Measurement

Steam reforming of methanol reaction is carried out in a fixed bed rector under atmospheric pressure. After the catalyst is packed in the reactor, it is pretreated with H_2 or O_2 at the flow rate 34 ml/min. Then, it is flushed with He for 60 min at the desired reaction temperature.

Many parameters affecting the activity and selectivity of the Au/ZnO and Au/ZnO-Fe$_2$O$_3$catalysts are studied in this research such as the effects of ZnO-Fe$_2$O$_3$ molar ratio, Au content, calcination temperature, catalyst pretreatment, and reaction temperature. Moreover, the suitable condition of Au/ZnO and Au/ZnO-Fe$_2$O$_3$ catalysts are chosen for further study in the presence of decomposition of methanol (DM) and water gas shift reaction (WGS) reactions. Finally, the deactivation tests of both catalysts are also performed for 24 hours. All of these parameters are summarized in Table 3.1.

3.5.1 Effect of ZnO-Fe$_2$O$_3$ Molar Ratio

In the case of Au/ZnO-Fe$_2$O$_3$ catalysts, the effect of ZnO-Fe$_2$O$_3$ ratios is studied on the activity and selectivity in methanol steam reforming reaction. The ZnO-Fe$_2$O$_3$ ratios are varied with a 9:1, 3:1, 1:1, 1:3, and 1:9 molar ratio of ZnO to Fe$_2$O$_3$. The suitable ZnO-Fe$_2$O$_3$ ratio is chosen for the next study.

3.5.2 Effect of Au Content

The effect of gold content with the suitable ZnO-Fe$_2$O$_3$ ratio on Au/ZnO and Au/ZnO-Fe$_2$O$_3$ catalysts are studied on the activity and selectivity in methanol steam reforming reaction. The gold contents are varied with 1% atom, 3% atom and 5% atom. The suitable gold content is chosen for the next study.

3.5.3 Effect of Calcination Temperature

The effect of calcination temperature with the suitable ZnO-Fe$_2$O$_3$ ratio and gold content on Au/ZnO and Au/ZnO- Fe$_2$O$_3$ catalysts are studied on the activity and selectivity in methanol steam reforming reaction. The calcination temperatures of 300, 400 and 500°C are studied for Au/ZnO catalysts and 200, 300 and

400°C are studied for Au/Fe_2O_3-ZnO catalysts. The suitable calcination temperature is chosen for the next study.

3.5.4 Effect of Catalyst Pretreatment

The effect of catalyst pretreatment with the suitable ZnO-Fe_2O_3 ratio, gold content and calcination temperature on Au/ZnO and Au/ZnO-Fe_2O_3 catalysts is studied on the activity and selectivity in methanol steam reforming reaction. H_2 pretreatment at 400 °C for 1 hour and O_2 pretreatment at 200 °C for 1 hour are studied. The suitable catalyst pretreatment is chosen for the next study.

3.5.5 Effect of Reaction Temperature

The effect of reaction temperature with the suitable ZnO-Fe_2O_3 ratio, gold content, calcinations temperature and catalysts pretreatment on Au/ZnO and Au/ZnO-Fe_2O_3 catalysts is studied on the activity and selectivity in methanol steam reforming reaction. Reaction temperatures are varied in the range of 200-450°C. The suitable reaction temperature is chosen for study the deactivation test.

3.5.6 Effect of DM and WGS Reactions

The effect of DM and WGS reaction with the suitable ZnO-Fe_2O_3 ratio, gold content, calcination temperature, and catalyst pretreatment on Au/ZnO and Au/ZnO-Fe_2O_3 catalysts is studied. The reaction temperature of DM and WGS reaction are varied in the range of 250-450 °C and the molar ratio of CO to H_2O is 1:2 for water gas shift reaction.

3.5.7 Deactivation Test

The deactivation test of the catalyst is studied on methanol steam forming for 24 hours. This study is conducted with the optimum ZnO-Fe_2O_3 ratio, gold content, calcination temperature, catalyst pretreatment and reaction temperature.

Table 3.1 Summary of the work plan

Studies	Catalysts	Parameter	Run No.
1. Effect of ZnO-Fe_2O_3 molar ratio	Au/Fe_2O_3-ZnO	9:1 (ZnO:Fe_2O_3)	1
		3:1	2
		1:1	3
		1:3	4
		1:9	5
2. Effect of Au Content	Au/ZnO	1% atom	6
		3% atom	7
		5% atom	8
	Au/Fe_2O_3-ZnO	1% atom	9
		3% atom	10
		5% atom	11
3. Effect of calcination temperature	Au/ZnO	300 °C	12
		400 °C	13
		500 °C	14
	Au/Fe_2O_3-ZnO	200 °C	15
		300 °C	16
		400 °C	17
4. Effect of catalyst pretreatment	Au/ZnO	O_2 pretreatment (200°C)	18
		H_2 pretreatment (400 °C)	19
	Au/Fe_2O_3-ZnO	O_2 pretreatment (200 °C)	20
		H_2 pretreatment (400 °C)	21
5. Effect of reaction temperature	Au/ZnO	200-450 °C	22
	Au/Fe_2O_3-ZnO	200-450 °C	23

Studies	Catalysts	Parameter	Run No.
6. Effect of DM and WGS reaction	Au/ZnO	DM	24
		WGS	25
	Au/Fe₂O₃-ZnO	DM	26
		WGS	27
7. Deactivation test	Au/ZnO	24 hours	28
	Au/Fe₂O₃-ZnO	24 hours	29

3.6 Calculations

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

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

where

X = methanol conversion (%)

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

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

where

$$S_{H_2} = \frac{H_2}{H_2 + CH_4 + CO + CO_2} \cdot 100\% \qquad (3.6)$$

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

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

where

Y_{H_2} = H₂ 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