

CHAPTER III

METHODOLOGY

3.1 Material

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, Na_2CO_3 , (Riedel-de Haen) (purity 99.99%)
- Zirconium (IV) oxide chloride octahydrate, $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$, (Merck) (purity 99.99%)
- Gold standard solution for AAS (Fluka)

- Copper (II) nitrate trihydrate, $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, (Merck) (purity 99.99%)
- Deionized water

3.2 Equipment

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

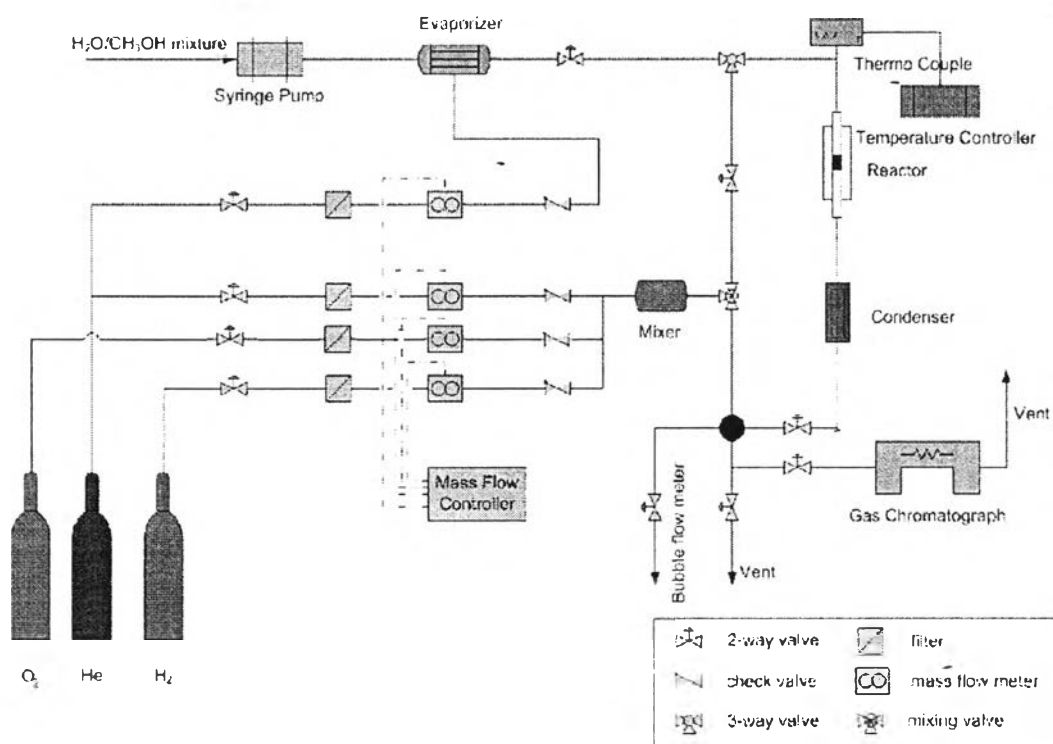


Figure 3.1 Schematic for experimental system of oxidative steam reforming of methanol.

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

3.2.1 Liquid Feed System

Distilled water and methanol were mixed together and filled in a syringe. This mixture was injected by a syringe pump at a rate of 1.5 ml/hour and passed through a vaporizer for making the vapor of methanol and steam. The methanol vapor and steam are carried by helium, mixed with oxygen stream before entering a catalytic reactor and a flow rate of He and oxygen are varied to keep the constant gas hourly space velocity (GHSV) at 30,000 ml/g-cat.hour.

3.2.2 Gas Blending System

The pretreatment gas (H_2 or O_2), the balance gas and purge gas (He) was delivered from the storage cylinder 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 OSRM was carried out in a vertical pyrex glass microreactor with an inside diameter (ID) of 9 mm at atmospheric pressure and in the temperature range of 200 to 400 °C. In the middle part of the reactor, 0.1 g of catalyst was packed between quartz wool plugs for preventing the spread catalyst. 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_2 , CO, CO_2 , and CH_4) from the reactor were 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 (99.995% purity), 30 ml/min

The experimental results were recorded by Agilent Chemstation software. The observed peaks were identified by comparing 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 that obtained from known composition gases.

3.3 Methodology

3.3.1 Preparation of Catalyst and Support

The supports (CeO_2 , ZrO_2 , and $\text{CeO}_2\text{-ZrO}_2$) were prepared by precipitation, co-precipitation, and sonochemical methods as the first step. After that, the Au metal must be loaded on the prepared supports by deposition-precipitation (DP) method.

3.3.1.1 *Support Preparation*

3.3.1.1.1 Preparation of CeO_2 Support

For precipitation method, the aqueous solution of 0.1 M $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ was dropwised with an aqueous solution of 0.1 M Na_2CO_3 under vigorous stirring condition at 80 °C. The mixture was kept at a pH of 8–9 for 1 hour. Excess ions, CO_3^{2-} and NO_3^- , were eliminated by washing with warm deionized water. The suspension was centrifuged in centrifuge HERMLE Z383 at 10,000 rounds per min. The precipitate was dried at 80 °C overnight and calcined in air at 400 °C for 4 hours. After calcination, the sample was labeled and kept in a desiccator.

For sonochemical method, the aqueous solution of 0.1 M $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ was heated to 80 °C, then, it was sonicated for 5 minutes. After sonication, an aqueous solution of 0.1 M Na_2CO_3 was dropped into the solution of 0.1 M $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ for adjusting the pH of solution (8). After that, this mixture was sonicated for 25 minutes and held at 80 °C during the sonication. Excess ions,

CO_3^{2-} and NO_3^- , were eliminated by washing with warm deionized water. The suspension was centrifuged in centrifuge HERMLE Z383 at 10,000 rounds per min. The precipitate was dried at 80 °C overnight and calcined in air at 400 °C for 4 hours. After calcination, the sample was labeled and kept in a desiccator.

3.3.1.1.2 Preparation of ZrO_2 Support

For precipitation method, the aqueous solution of 0.1 M $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ was dropwised with an aqueous solution of 0.1 M Na_2CO_3 under vigorous stirring condition at 80 °C. The mixture was kept at a pH of 8–9 for 1 hour. Excess ions, CO_3^{2-} and Cl^- , were eliminated by washing with warm deionized water. The suspension was centrifuged in centrifuge HERMLE Z383 at 10,000 rounds per min. The precipitate was dried at 80 °C overnight and calcined in air at 400 °C for 4 hours. After calcination, the sample was labeled and kept in a desiccator.

For sonochemical method, the aqueous solution of 0.1 M $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ was heated to 80 °C, then, it was sonicated for 5 minutes. After sonication, an aqueous solution of 0.1 M Na_2CO_3 was dropped into the solution of 0.1 M $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ for adjusting the pH of solution (~8). After that, this mixture was sonicated for 25 minutes and held the temperature at 80 °C. Excess ions, CO_3^{2-} and NO_3^- , were eliminated by washing with warm deionized water. The suspension was centrifuged in centrifuge HERMLE Z383 at 10,000 rounds per min. The precipitate was dried at 80 °C overnight and calcined in air at 400 °C for 4 hours. After calcination, the sample was labeled and kept in a desiccator.

3.3.1.1.3 Preparation of CeO_2 - ZrO_2 Support

For co-precipitation method, the aqueous solution of 0.1 M Na_2CO_3 was added dropwise in the aqueous mixture of 0.1 M $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and 0.1 M $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ with suitable amounts under vigorous stirring condition at 80 °C. The mixture was kept at a pH of 8–9 for 1 hour. Excess ions, CO_3^{2-} , NO_3^- , and Cl^- , were eliminated by washing with warm deionized water. The suspension was centrifuged in centrifuge HERMLE Z383 at 10,000 rounds per min. The precipitate was dried at 110 °C overnight and calcined in air at 400 °C for 4 hours. After calcination, the sample was labeled and kept in a desiccator.

For sonochemical method, the aqueous solution of 0.1 M $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and 0.1 M $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ 0.1 M were mixed with suitable amounts and heated to 80 °C. This mixture was sonicated for 5 min. and then, Na_2CO_3 was added dropwise in the aqueous mixture of 0.1 M $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and 0.1 M $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ 0.1 M for adjusting the pH of solution (~8) with. This mixture was sonicated continuously for 25 minutes. During the sonication, the temperature of the mixture was kept at 80°C, pH of 8–9. Excess ions, CO_3^{2-} , NO_3^- , and Cl^- , were eliminated by washing with warm deionized water. The suspension was centrifuged in centrifuge HERMLE Z383 at 10,000 rounds per min. The precipitate was dried at 110 °C overnight and calcined in air at 400 °C for 4 hours. After calcination, the sample was labeled and kept in a desiccator.

3.3.1.2 Catalyst Preparation

3.3.1.2.1 Preparation of Au/CeO₂ Catalysts

Before adding the metals, the support (CeO_2) was dried in an oven at 110 °C for 12 hours. Hydrogen tetrachloroaurate (III), HAuCl_4 , was weighed for a desired amount, and then dissolved in deionized water under continuous stirring and heating at 80 °C. After that, the dried support was added to a solution and the pH of solution (~8) was adjusted by adding 0.1 M Na_2CO_3 , then the mixture was held for 1 hour. The suspension was washed by warm deionized water to eliminate the residue ions (CO_3^{2-} , Cl^- , and NO_3^-). Afterwards, the suspension was centrifuged in centrifuge HERMLE Z383 at 10,000 rounds per min. Deionized precipitate was dried at 110 °C overnight and calcined in air at 400 °C for 4 hours. After calcination, the sample was ground and sieved to 80-120 mesh size, and kept in a desiccator.

3.3.1.2.2 Preparation of Au/ZrO₂ Catalysts

Before adding the metals, the support (ZrO_2) was dried in an oven at 110 °C for 12 hours. Hydrogen tetrachloroaurate (III), HAuCl_4 , was weighed for a desired amount, and then dissolved in deionized water under continuous stirring and heating at 80 °C. After that, the dried support was added to a solution and the pH of solution (~8) was adjusted by adding 0.1 M Na_2CO_3 , then the

mixture was held for 1 hour. The suspension was washed by warm deionized water to eliminate the residue ion (CO_3^{2-} , Cl^- , and NO_3^-) and centrifuged in centrifuge HERMLE Z383 at 10,000 rounds per min. Deionized precipitate was dried at 110 °C overnight and calcined in air at 400 °C for 4 hours. After calcination, the sample was ground and sieved to 80-120 mesh size, and kept in a desiccator.

3.3.1.2.3 Preparation of Au/CeO₂-ZrO₂ Catalysts

Before adding the metals, the support (CeO₂-ZrO₂) was dried in an oven at 110 °C for 12 hours. Hydrogen tetrachloroaurate (III), H₂AuCl₄·3H₂O, was weighed for a desired amount, and then dissolved in deionized water under continuous stirring and heating at 80 °C. After that, the dried support was added to the solution and the pH of solution (~8) was adjusted by adding 0.1 M Na₂CO₃, then the mixture was aged for 1 hour. The residue ions (CO_3^{2-} , Cl^- , and NO_3^-) were eliminated by washing with warm deionized water and centrifuged in centrifuge HERMLE Z383 at 10,000 rounds per min. Deionized precipitate was dried at 110 °C overnight and calcined in air at 400 °C for 4 hours. After calcination, the sample was ground and sieved to 80-120 mesh size, and kept in a desiccator.

3.3.1.2.4 Preparation of Cu/CeO₂-ZrO₂ Catalysts

Before adding the metals, the support (CeO₂-ZrO₂) was dried in an oven at 110 °C for 12 hours. Copper (II) nitrate trihydrate, Cu(NO₃)₂·3H₂O, was weighed for a desired amount, and then dissolved in deionized water under continuous stirring and heating at 80 °C. Afterwards, the dried support was added to the solution and the pH of solution (~8) was adjusted by adding 0.1 M Na₂CO₃, then the mixture was aged for 1 hour. The residue ions (CO_3^{2-} , Cl^- , and NO_3^-) were eliminated by washing with warm deionized water and centrifuged in centrifuge HERMLE Z383 at 10,000 rounds per min. Deionized precipitate was dried at 110 °C overnight and calcined in air at 400 °C for 4 hours. After calcination, the sample was ground and sieved to 80-120 mesh size, and kept in a desiccator.

3.3.1.2.5 Preparation of Au-Cu/CeO₂-ZrO₂ Catalysts

Before adding the metals, the support (CeO₂-ZrO₂) was dried in an oven at 110 °C for 12 hours. Hydrogen tetrachloroaurate (III), H₂AuCl₄·3H₂O, and Copper (II) nitrate trihydrate, Cu(NO₃)₂·3H₂O, were weighed for

a desired amount at total metal loading 3wt%, and then dissolved in deionized water under continuous stirring and heating at 80 °C. The dried support was added to the solution and the pH of solution (~7) was adjusted by adding 0.1 M Na₂CO₃, then the mixture was aged for 1 hour. The residue ions (CO₃²⁻, Cl⁻, and NO₃⁻) were eliminated by washing with warm deionized water and centrifuged in centrifuge HERMLE Z383 at 10,000 rounds per min. Deionized precipitate was dried at 110 °C overnight and calcined in air at 400 °C for 4 hours. After calcination, the sample was ground and sieved to 80-120 mesh size, and kept in a desiccator.

3.3.2 Catalyst Characterization

The properties and characteristics of the prepared catalysts (Au–Cu/CeO₂–ZrO₂) are different due to the effect of bimetallic (Au/Cu atomic ratio), calcination temperature, and gas pretreatment. The different properties may affect the activity and selectivity of the catalyst; hence, 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) was used to measure total pore volume, and average pore diameter of the catalysts. The equipment measurement is based on Brunauer-Emmet-Teller (BET) equation. This technique of calculation is the physical multi-layer adsorption of Nitrogen. A sample is outgassed by heating under vacuum to eliminate volatile adsorbents in the surface at 250 °C for at least 4 hours prior to the analysis. Nitrogen gas with the cross-sectional area of 1.62x10⁻¹⁹ m²/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/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.

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

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,
 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^2/g),
 A_{N_2} = cross-sectional area of one molecule N_2 (0.162 nm^2 at $-196 \text{ }^\circ\text{C}$),
 M_{W, N_2} = molecule weight of nitrogen (28 g/g-mol).

3.3.2.2 X-Ray Diffraction (XRD)

Analysis the crystalline structure of oxide support and the mean particle diameter of gold by means of a Rigaku X-Ray Diffractometer system (RINT-2200) with copper tube for generating CuK_α radiation (1.5406 \AA), 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 20 to 80° (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_h) 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:

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).

The results from the Scherrer's 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 will be carried out using 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 is carried out by placing a sample in a quartz reactor. Range 10 to 50 mg of the sample was subjected to TPR analysis using 10% H₂ in Ar for 30 ml/min. The reduction temperature was raised from 30 to

850 °C at 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 is completed, could be determined from TPR pattern.

3.3.2.5 Temperature-programmed Oxidation (TPO)

Temperature-programmed Oxidation (TPO) was used to evaluate amount of carbon formation of spent catalysts. About 10 to 50 mg of spent catalyst is placed in quartz tube reactor. The spent catalyst was conducted to TPO analysis using 2% O₂ in He for 30 ml/min before the temperature was linearly increased at a ramp rate of 12 °C/min. Carbon formation was oxidized into carbon dioxide then convert to methane in the methanator. FID SRI model 110 was used to detect the effluent gas from methanator. The result from measurement can be used to determine amount of deposited carbon.

3.3.2.6 UV-vis Spectrophotometer

UV-vis Spectrophotometer was performed on air-exposed samples at an ambient temperature of between 200 and 800 nm. for measuring. The absorption intensity was expressed by using Kubelka-Munk function.

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

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

3.3.2.7 Atomic Absorption Spectroscopy (AAS)

Elemental analysis were performed by using Varian, SpectrAA 300 instrument. The actual content of gold and copper loading on support were determined. The catalyst was dissolved in a mixture of HF and aqua regia solution (HCl: HNO₃ = 82:18). Then, the dissolved catalyst was heated to 70 °C and diluted to 50 ml with deionized water. Several standard solutions were prepared from stock solution of 1000 ppm to perform the calibration curve. The actual concentration of sample was measured based on the absorption intensity. The specific wavelength can generate in each element by using the cathode lamp that absorbed by specific elements. The absorbed intensity was calculated internally from calibration curves and showed directly as percent or measured concentrations.

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

In order to investigate the concentration of oxygen vacancy on the surface, the FT-Raman spectra was recorded by 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 $3500\text{--}200\text{ cm}^{-1}$ was obtained.

3.4 Activity Measurement

The OSRM reaction was carried out in a fixed-bed reactor under atmospheric pressure and reaction temperatures were varied from 200 to 400 °C. Many parameters that affects the activity and selectivity of the Au-Cu/CeO₂-ZrO₂ catalysts are studied in this research such as the effects of support composition (atomic ratio) of Ce/(Ce+Zr), bimetallic (atomic ratio) of Au/Cu, calcination temperature, catalyst pretreatment, and reaction temperature. Finally, the deactivation test of the both catalysts was also performed for 24 hours.

3.4.1 Effect of Support Composition (Atomic Ratio) of Ce/(Ce+Zr)

The effect of Ce/(Ce+Zr) atomic ratios was studied on the activity and selectivity in OSRM reaction. The Ce/(Ce+Zr) atomic ratios were varied with 0, 0.25, 0.5, 0.75, and 1 by loading Au content 3% wt. The suitable atomic ratio will be chosen for the next study.

3.4.2 Effect of Support Preparation Technique

The suitable atomic ratio of Ce/(Ce+Zr) were used to prepare by using the various techniques; co-precipitation, and sonochemical. For metal loading, Au content was fixed at 3% wt. for each supports. The catalyst that gave the best activity will be chosen in the next study.

3.4.3 Effect of Bimetallic (Au/Cu Atomic Ratio)

The effect of bimetallic with the suitable atomic ratio of Ce/(Ce+Zr) and preparation method was studied on the activity and selectivity in OSRM

reaction. The atomic ratios of Au/Cu were varied with 1/0, 3/1, 1/1, 1/3, and 0/1. The suitable condition will be chosen for the next study.

3.4.4 Effect of Total Metal Loading

The effect of total metal loading with the suitable atomic ratios of Ce/(Ce+Zr) and Au/Cu on Au–Cu/CeO₂–ZrO₂ catalysts was studied on the activity and selectivity in OSRM reaction. The total metal loading of 3%, 5%, and 7% were studied. The suitable total metal loading will be chosen for the next study.

3.4.5 Effect of Calcination Temperature

The effect of calcination temperature with the suitable atomic ratio of Ce/(Ce+Zr), Au/Cu, and total metal loading on Au–Cu/CeO₂–ZrO₂ catalysts was studied on the activity and selectivity in OSRM reaction. The calcination temperatures of 200, 300, and 400 °C were studied for Au–Cu/CeO₂–ZrO₂ catalysts. The suitable calcination temperature is chosen for the next study.

3.4.6 Effect of DM and SRM Reactions

The effect of DM and SRM reactions with the suitable conditions (Ce/(Ce+Zr) atomic ratio, support preparation method, Au/Cu atomic ratio, total metal loading, and calcination temperature) on Au–Cu/CeO₂–ZrO₂ catalyst are studied. The reaction temperature of DM and SRM reactions are varied from 200 to 400 °C.

3.4.7 Deactivation Test

The deactivation test of the catalyst was studied on the OSRM for 21 hours. This study was conducted with the optimum conditions of Ce/(Ce+Zr) atomic ratio, support preparation method, Au/Cu atomic ratio, total metal loading, calcination temperature of catalyst, and reaction temperature.

3.5 Calculations

The methanol conversion, hydrogen yield, hydrogen selectivity, carbon monoxide selectivity, carbon dioxide selectivity, and methane selectivity are calculated by Equation 3.5–3.10.

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

where

X = methanol conversion (%)

MeOH_(in) = mole of methanol inlet

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

where

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

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

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

$$S_{CH_4} = \frac{CH_4}{H_2 + CH_4 + CO + CO_2} \times 100(\%) \quad (3.10)$$

where

Y_{H_2} = hydrogen yield (%)

S_{H_2} = hydrogen selectivity (%)

S_{CO} = carbon monoxide selectivity (%)

S_{CO_2} = carbon dioxide selectivity (%)

S_{CH_4} = methane 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