

## CHAPTER III EXPERIMENTAL

### 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.

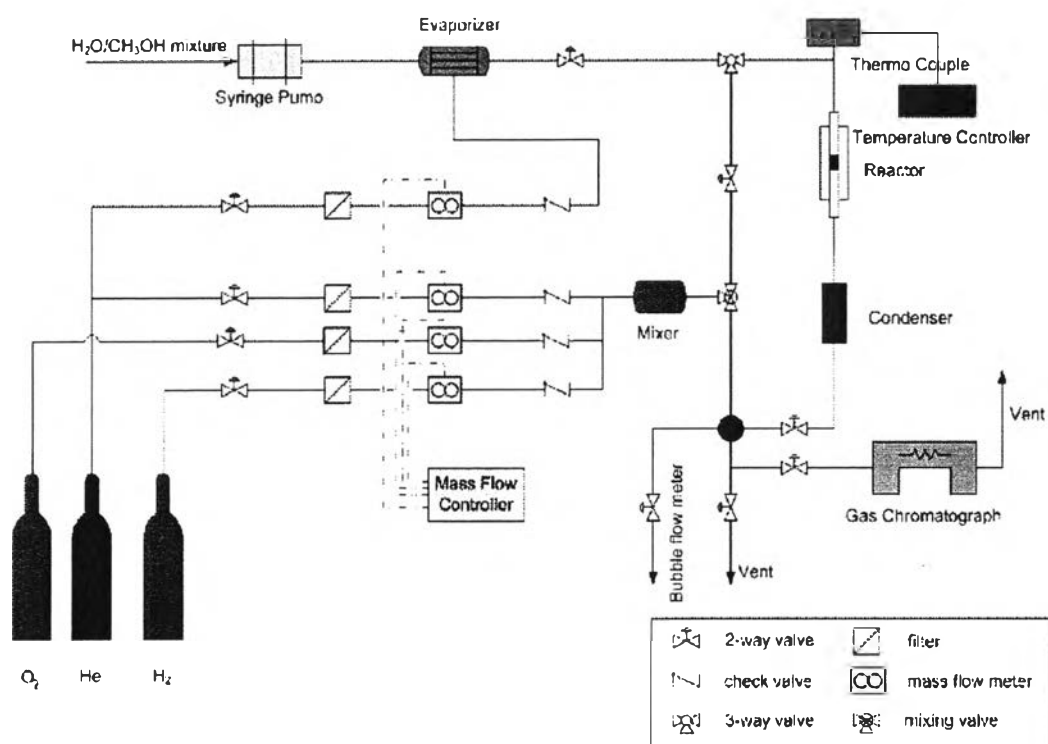
#### 3.1.3 Chemicals

- 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,  $\text{Na}_2\text{CO}_3$ , (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)

- Deionized water

### 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: 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 syringe pump at a rate of 1.5 ml/hour 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 of 9 mm at atmospheric pressure and in the temperature range of 200 to 400 °C. In the middle of the reactor, 0.1 g of 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.  $H_2$ , 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 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

The supports ( $\text{CeO}_2$ ,  $\text{ZrO}_2$ , and  $\text{CeO}_2\text{-ZrO}_2$ ) were prepared by precipitation and co-precipitation 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 $\text{CeO}_2$ Support

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  $\text{Na}_2\text{CO}_3$  under vigorous stirring condition at 80 °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 round 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 $\text{ZrO}_2$ Support

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  $\text{Na}_2\text{CO}_3$  under vigorous stirring condition at 80 °C. The mixture was kept at a pH of 8–9 for 1 hour. Excess ions,  $\text{CO}_3^{2-}$  and  $\text{Cl}^-$ , were eliminated by washing with warm deionized water. 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 $\text{CeO}_2\text{-ZrO}_2$ Support

The aqueous solution of 0.1 M  $\text{Na}_2\text{CO}_3$  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,  $\text{CO}_3^{2-}$ ,  $\text{NO}_3^-$  and  $\text{Cl}^-$ , were eliminated by washing with warm deionized water. 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/CeO<sub>2</sub> Catalysts*

Before adding the metals, the support (CeO<sub>2</sub>) was dried in an oven at 110 °C for 12 hours. Hydrogen tetrachloroaurate (III), HAuCl<sub>4</sub>, was weighed for a desired amount, and then dissolved in deionized water under continuous stirring and heating at 80 °C. The dried support was added to a solution and the pH of solution (~8) was adjusted by adding 0.1 M Na<sub>2</sub>CO<sub>3</sub> then the mixture was aged for 1 hour. The suspension was washed by warm deionized water to eliminate the residue ions ( $\text{CO}_3^{2-}$ ,  $\text{Cl}^-$  and  $\text{NO}_3^-$ ). The suspension was centrifuged in centrifuge HERMLE Z383 at 500 round 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/ZrO<sub>2</sub> Catalysts*

Before adding the metals, the support (ZrO<sub>2</sub>) was dried in an oven at 110 °C for 12 hours. Hydrogen tetrachloroaurate (III), HAuCl<sub>4</sub>, was weighed for a desired amount, and then dissolved in deionized water under continuous stirring and heating at 80 °C. The dried support was added to a solution and the pH of solution (~8) was adjusted by adding 0.1 M Na<sub>2</sub>CO<sub>3</sub>, then the mixture was aged for 1 hour. The suspension was washed by warm deionized water to eliminate the residue ion ( $\text{CO}_3^{2-}$ ,  $\text{Cl}^-$  and  $\text{NO}_3^-$ ). 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/CeO<sub>2</sub>-ZrO<sub>2</sub> Catalysts*

Before adding the metals, the support (CeO<sub>2</sub>-ZrO<sub>2</sub>) was dried in an oven at 110 °C for 12 hours. Hydrogen tetrachloroaurate (III), HAuCl<sub>4</sub>.3H<sub>2</sub>O, was weighed for a desired amount, 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 (~8) was adjusted by adding 0.1 M Na<sub>2</sub>CO<sub>3</sub>, then the mixture was aged for 1 hour. The suspension was washed by warm deionized water to eliminate the residue ions (CO<sub>3</sub><sup>2-</sup>, Cl<sup>-</sup> and NO<sub>3</sub><sup>-</sup>). Deionized precipitate was dried at 110 °C overnight and calcined in air at various temperatures 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/CeO<sub>2</sub>-ZrO<sub>2</sub>) are different due to the effect of Au content, calcination temperature, and gas pretreatment. The different properties may affect the activity 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*

The BET surface area used Autosorb-1 Gas Sorption System (Quantachrome Corporation) 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 absorbents in the surface at 250 °C for at least 4 hours prior to the analysis. Nitrogen gas with the cross-sectional area of 1.62x10<sup>-19</sup> 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.

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

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,  $P/P_0$ ,

$W_m$  = 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  $N_2$  ( $0.162 \text{ nm}^2$  at  $-196 \text{ }^\circ\text{C}$ ),

$M_{W, N_2}$  = molecule weight of nitrogen ( $28 \text{ g/g-mol}$ ).

### 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  $\text{CuK}_\alpha$  radiation ( $1.5406 \text{ \AA}$ ), 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 =  $1^\circ$  ( $2\theta$ ); scattering slit =  $1^\circ$  ( $2\theta$ ); and receiving slit = 0.3 mm. The scan speed of  $5^\circ$  ( $2\theta$ )/min with scan step of 0.02 ( $2\theta$ ) is used for the continuous run in  $5$  to  $90^\circ$  ( $2\theta$ ) 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).

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% H<sub>2</sub> 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% O<sub>2</sub> 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  $R_{\infty}$  is the diffuse reflectance from a semi-infinite layer.

#### 3.3.2.7 *X-ray Fluorescence Spectroscopy (XRF)*

The quantitative and qualitative elemental analysis of the catalysts were analyzed by XRF technique, Philips model PW 2400. With a primary

X-ray excitation source from an X-ray tube, the X-ray can be absorbed by the atom, and transfer all of its energy to an innermost electron. During the process, if the primary X-ray has sufficient energy, electrons are ejected from the inner shell, creating vacancies. These vacancies present an unstable condition for the atom. As the atom returns to its stable condition, electrons from the outer shells are transferred to the inner shells, and the process gives off a characteristic X-ray, whose energy is the difference between the two binding energies of the corresponding shells. Because each element has a unique set of energy levels, each element produces X-rays at a unique set of energies, allowing one to non-destructively measure the elemental composition of a sample. The intensities of observed lines for a given atom vary according to the amount of that atom present in the specimen.

#### 3.3.2.8 *Fourier Transform Infrared Spectroscopy (FT-IR)*

The FTIR spectra were used to record the samples by Thermo Nicolet Nexus 670 FTIR spectrometer in the absorbance mode at 32 scans with a resolution of  $4\text{ cm}^{-1}$ . Spectra of frequency range of  $4000\text{ to }400\text{ cm}^{-1}$  were measured by using a deuterated triglycerinesulfate detector (DTGS) with specific detectivity of  $1 \times 10^9\text{ cm Hz}^{1/2}\text{ w}^{-1}$ .

### 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 affecting the activity and selectivity of the Au/CeO<sub>2</sub>-ZrO<sub>2</sub> catalysts are studied in this research such as the effects of support composition (atomic ratio) of Ce/(Ce+Zr), Au content, 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) 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 Calcination Temperature

The effect of calcination temperature with the suitable atomic ratio of Ce/(Ce+Zr) and gold content on Au/CeO<sub>2</sub>-ZrO<sub>2</sub> catalysts was studied on the activity and selectivity in OSRM reaction. The calcination temperatures of 400, 500, and 600 °C were studied for CeO<sub>2</sub>-ZrO<sub>2</sub> supports. The suitable calcination temperature is chosen for the next study.

#### 3.4.3 Effect of Au Content

The effect of gold content with the suitable atomic ratio of Ce/(Ce+Zr) was studied on the activity and selectivity in OSRM reaction. The gold contents were varied with 1%, 3%, and 5% wt. The suitable gold content will be chosen for the next study.

#### 3.4.4 Effect of O<sub>2</sub> Pretreatment

The effect of O<sub>2</sub> pretreatment on the catalytic performance at 200 °C for 2 hour was studied, the suitable Ce/(Ce+Zr) atomic ratio, gold content, and calcination temperature on the Au/CeO<sub>2</sub>-ZrO<sub>2</sub> catalysts was studied on the activity and selectivity in OSRM reaction. The suitable catalyst pretreatment will be chosen for the next study.

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

The effect of S/M molar ratios was studied on the methanol conversion and hydrogen selectivity in OSRM reaction over the reaction temperature range of 200 to 400 °C. The S/M molar ratios were varied with 0, 1, 2, 3, and 4. The suitable S/M molar ratio will be chosen for the next study.

#### 3.4.6 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 ratios was studied on the methanol conversion and hydrogen selectivity in the OSRM reaction over the reaction

temperatures varied in the range from 200 to 400 °C. The O<sub>2</sub>/CH<sub>3</sub>OH molar ratios were varied with 0, 0.09, 0.17, and 0.25. The suitable O<sub>2</sub>/CH<sub>3</sub>OH molar ratio will be chosen for the next study.

#### 3.4.7 Deactivation Test

The deactivation test of the catalyst was studied on the OSRM for 12 hours. This study was conducted with the optimum conditions of Ce/(Ce+Zr) atomic ratio, gold content, calcination temperature, and reaction temperature.

### 3.5 Calculations

The hydrogen selectivity, carbon monoxide selectivity, carbon dioxide selectivity, and methane selectivity are calculated by Equation 3.5–3.8.

where:

$$S_{H_2} = \frac{H_2}{H_2 + CH_4 + CO + CO_2} \times 100(\%) \quad (3.5)$$

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

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

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

where:

$S_{H_2}$  = 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