



## CHAPTER III EXPERIMENTAL

### 3.1 Materials

#### 3.1.1 Gases

The gases used in this research were as follows:

- Helium (He 99.99% purity) obtained from Praxair (Thailand) Co., Ltd
- Air Zero obtained from Praxair (Thailand) Co., Ltd.
- Hydrogen (H<sub>2</sub> 99.99% purity) obtained from Praxair (Thailand) Co., Ltd.
- Methane (CH<sub>4</sub> 99.99% purity) obtained from Praxair (Thailand) Co., Ltd.

#### 3.1.2 Chemicals

The chemical reagents used in this research were as follows:

- Nickel (II) nitrate hexahydrate ( $\geq 98.5\%$  purity) obtained from Fluka Chemie A.G.
- Cerium (III) nitrate hexahydrate ( $\geq 99\%$  purity) obtained from Fluka Chemie A.G.
- Zirconium oxychloride ( $\geq 99\%$  purity) obtained from Sigma Aldrich.
- Magnesium nitrate hexahydrate ( $\geq 99\%$  purity) obtained from Fluka Chemie A.G.
- Urea ( $\geq 99\%$  purity) was obtained from Fluka Chemie A.G.

## 3.2 Equipment

### 3.2.1 Catalyst Characterization

#### 3.2.1.1 BET Surface Area Measurements

BET surface area was determined by N<sub>2</sub> adsorption at -196 °C (a five point Brunauer–Emmett–Teller (BET) method using a Quantachrome Autosorb-1 MP). Prior to the analysis, the samples were outgassed to eliminate volatile adsorbents on the surface at 250 °C. The quantity of gas adsorbed onto or desorbed from a solid surface was measured at five equilibrium vapor pressure (P/P<sub>0</sub>) values of 0.1000, 0.1500, 0.2000, 0.2500, and 0.3000 by the static volumetric method. The adsorption data were calculated using the Brunauer–Emmett–Teller (BET) equation:

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

where  $W$  = weight of gas adsorbed at relative pressure  $P_0$  (g);  
 $W_m$  = weight of adsorbate constituting a monolayer of surface coverage (g); and  
 $C$  = constant that is related to the energy of adsorption in the first adsorbed layer and magnitude of adsorbate/adsorbent interaction,

and then the surface of the sample was calculated by

$$\text{Surface area of sample} = \frac{W_m A_{\text{nitrogen}} (6.02 \times 10^{23})}{Mw_{\text{nitrogen}}} \quad (3.2)$$

where  $A_{\text{nitrogen}}$  = Crossed-section area of one molecule nitrogen  
 = 0.162 nm<sup>2</sup> at -196 °C; and

$Mw_{\text{nitrogen}}$  = molecular weight of nitrogen (g/mol).

### 3.2.1.2 $H_2$ Chemisorption

The amount of  $H_2$  uptake due to the exposed metal was determined by  $H_2$  pulse chemisorption. This technique was carried out using a temperature programmed analyzer with a pulse technique. Prior to the pulse chemisorption, 100 mg of sample was reduced in  $H_2$  atmosphere at 500 °C for 1 hr. Then, the sample was purged with  $N_2$  at 500 °C for 30 min and cooled down to 50 °C in flowing  $N_2$ . A  $H_2$  pulse (99.99%  $H_2$  with a sample loop volume 74.79  $\mu$ l) was injected into the sample at 50 °C. The metallic dispersion was calculated by assuming the adsorption stoichiometry of one hydrogen atom per nickel surface atom.

### 3.2.1.3 $H_2$ -Temperature Programmed Reduction ( $H_2$ -TPR)

$H_2$ -TPR experiments were carried out using a TPR analyzer. The sample was pretreated in  $N_2$  atmosphere at 120 °C for 30 min prior to running the TPR experiments, and then cooled down to room temperature in flowing  $N_2$ . A 5%  $H_2/N_2$  gas was used as a reducing gas. The sample temperature was raised at a constant rate of 10 °C/min from room temperature to 800 °C. The amount of  $H_2$  consumption as a function of temperature was determined from a TCD signal.

### 3.2.1.4 X-ray Diffraction (XRD)

An X-ray diffractometer system (Rigaku) equipped with a RINT 2000 wide-angle goniometer using  $CuK_{\alpha}$  radiation (1.5406 Å) and a power of 40 kV $\times$ 30 mA was used for the examination of the crystalline structure. The sample was ground to fine homogeneous powder and was held on thin-walled glass plate against the X-ray beam. The intensity data were collected at 25 °C over a  $2\theta$  range of 20–90° with a scan speed of 5° ( $2\theta$ )/min and a scan step of 0.02° ( $2\theta$ ).

### 3.2.1.5 Scanning Electron Microscopy (SEM)

Supported metal crystallites, morphologies of sample and carbon deposition on the catalysts were investigated using a Hitachi (S-4800) scanning electron microscope operated at 5kV and 10 mA.

### 3.2.1.6 Temperature Programmed Oxidation (TPO)

TPO was carried out in a TPO micro-reactor coupled with an FID analyzer. TPO technique was used to quantify the amount of carbon deposition on the spent catalysts. After keeping the catalyst on stream for partial oxidation, the spent catalyst was cooled down to room temperature in He stream. Then, about 50 mg sample was heated in a flowing 2%O<sub>2</sub> in He (40 ml/min) mixture at a heating rate of 10 °C/min up to 900 °C. The output gas was passed into a methanation reactor containing Ni/Al<sub>2</sub>O<sub>3</sub> catalysts. In the methanation reactor, CO<sub>2</sub> formed from the carbon was completely converted with excess H<sub>2</sub> into methane, to permit precise quantification in an FID detector. After the TPO system had reached 900 °C at which the carbon was burned off, the FID signal for methane was calibrated by injecting 100 µl of CO<sub>2</sub> pulse into the methanation reactor, and sending the methane produced into the FID. By integrating the methane signal during the entire TPO run, it is possible to calculate the amount of coke removed from the catalyst.

## 3.3 Methodology

### 3.3.1 Catalyst Preparation

Ce<sub>0.75</sub>Zr<sub>0.25</sub>O<sub>2</sub> (CZO) mixed oxide support was prepared via urea hydrolysis. The Ce-Zr mixed oxide sample was prepared from Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O and ZrOCl<sub>2</sub>·8H<sub>2</sub>O. The ratio between the metal salts was used depending on the desired solid solution concentration: Ce<sub>1-x</sub>Zr<sub>x</sub>O<sub>2</sub> in which x = 0.25. The starting metal salts were dissolved in distilled water to the desired concentration (0.1 M). Then, the mixed metal salt solution was added with a 0.4 M of urea solution with the salt to urea solution ratio of 2:1 (v/v), and the mixture was kept at 100 °C for 50 hrs. The sample was then allowed to cool to room temperature prior to being centrifuged to separate a gel product from the solution. The gel product was washed with ethanol, and dried overnight in an oven at 110 °C. The product was then calcined at 500 °C for 4 hrs (Pengpanich *et al.*, 2002).

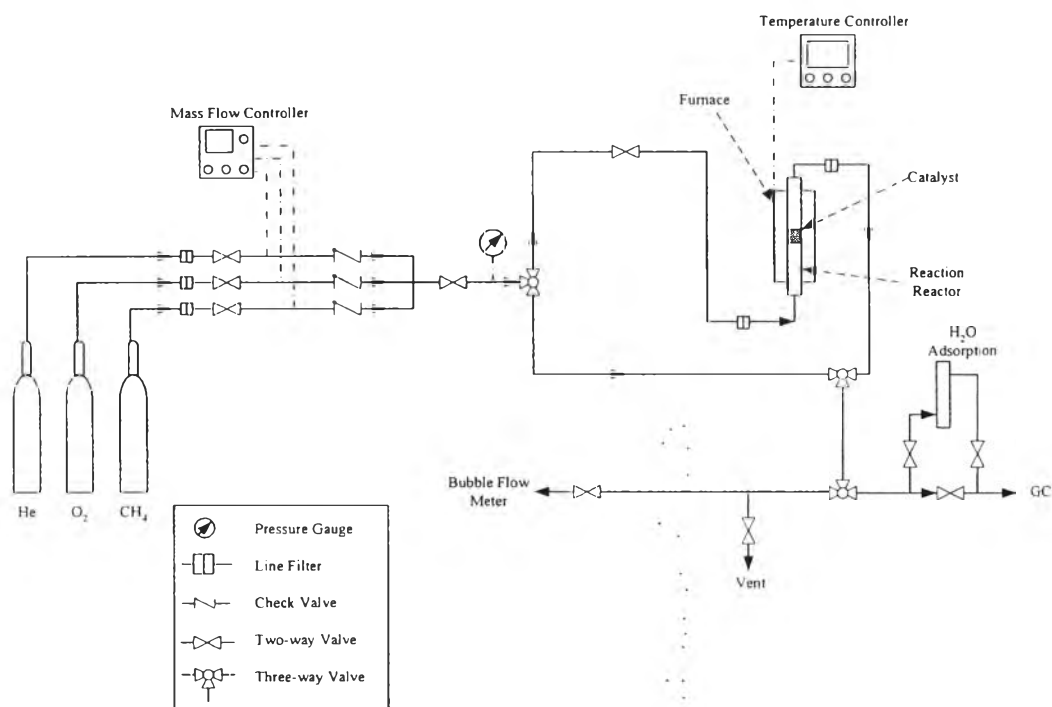
The catalysts were prepared by sequential incipient wetness impregnation and co-impregnation methods. For the sequential incipient wetness impregnation method, the catalysts were prepared by using the aqueous solutions of

$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ . The amount of MgO loading was varied with 5, 10, and 15 wt%. The CZO was impregnated with  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  aqueous solution prior to drying at 110 °C for 4 hrs, and calcination at 500 °C for 4 hrs in air. All the MgO/CZO supported catalysts were impregnated with  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  aqueous solution (15 wt%) prior to drying at 110 °C for 4 hrs, and calcination at 500 °C for 4 hrs in air. These catalysts are denoted as 15Ni $x$ Mg/CZO (S) where  $x$  represents the amount of MgO loading.

For the co-impregnation method, the catalysts were prepared by using the aqueous solutions of  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ . The amount of Ni loading was fixed at 15 wt% whereas the amount of MgO loading was varied with 5, 10, and 15 wt%. All the catalysts were dried at 110 °C for 4 hrs, and calcined at 500 °C for 4 hrs in air. These catalysts are denoted as 15Ni $x$ Mg/CZO (C), where  $x$  represents the amount of MgO loading.

### 3.3.2 Catalytic Activity Testing

Catalytic activity tests for methane partial oxidation were carried out in a packed-bed quartz micro reactor (i.d.6 mm). Typically, a 100 mg catalyst sample was packed between the layers of quartz wool. The reactor was placed into an electric furnace equipped with K-type thermocouples. The catalyst bed temperature was monitored and controlled by Shinko FCR-13A-S/M temperature controllers. The feed gas mixture containing 4%  $\text{CH}_4$  and 2%  $\text{O}_2$  balance with He at a gas hourly space velocity (GHSV) of 53,000  $\text{h}^{-1}$  was introduced into the reactor using Brooks 5850E mass flow controllers. Measurements were performed at various furnace temperatures adjusted sequentially from 400 to 800 °C with an interval of 50 °C. A schematic diagram of the experimental setup is shown in Figure 3.1.



**Figure 3.1** Schematic of the experimental setup for methane partial oxidation.

The gaseous products were chromatographically analyzed using a Shimadzu GC 8A fitted with a TCD. A CTR I (Alltech) packed column was used to separate all products at 50 °C except for H<sub>2</sub>O which was trapped out prior to entering the column. The percentages of CH<sub>4</sub> conversion ( $X_{\text{CH}_4}$ ), O<sub>2</sub> consumption ( $X_{\text{O}_2}$ ) and selectivity ( $S$ ) reported in this work were calculated using the following expressions:

$$\%X_{\text{CH}_4} = \frac{\text{CH}_4^{\text{in}} - \text{CH}_4^{\text{out}}}{\text{CH}_4^{\text{in}}} \times 100 \quad (3.3)$$

$$\%X_{\text{O}_2} = \frac{\text{O}_2^{\text{in}} - \text{O}_2^{\text{out}}}{\text{O}_2^{\text{in}}} \times 100 \quad (3.4)$$

$$\%S_{\text{CO}} = \frac{\text{CO}^{\text{out}}}{\text{CO}^{\text{out}} + \text{CO}_2^{\text{out}}} \times 100 \quad (3.5)$$

$$\%S_{\text{H}_2} = \frac{\text{H}_2^{\text{out}}}{\text{H}_2^{\text{out}} + \text{H}_2\text{O}^{\text{out}}} \times 100 \quad (3.6)$$

where	$\text{CH}_4^{\text{in}}$	=	mole of $\text{CH}_4$ in
	$\text{CH}_4^{\text{out}}$	=	mole of $\text{CH}_4$ out
	$\text{O}_2^{\text{in}}$	=	mole of $\text{O}_2$ in
	$\text{O}_2^{\text{out}}$	=	mole of $\text{O}_2$ out
	$\text{CO}^{\text{out}}$	=	mole of $\text{CO}$ formed
	$\text{CO}_2^{\text{out}}$	=	mole of $\text{CO}_2$ formed
	$\text{H}_2^{\text{out}}$	=	mole of $\text{H}_2$ formed
	$\text{H}_2\text{O}^{\text{out}}$	=	mole of $\text{H}_2\text{O}$ formed