



## CHAPTER III EXPERIMENTAL

In this chapter the materials used in this research are described. The various experimental techniques utilized in the catalyst preparation, characterization and reaction studies will be explained. Details of the catalyst activity test system are also given.

### 3.1 Materials

#### 3.1.1 Gases

The gases used in this research were:

1. Helium (He 99.99%) was obtained from Praxair (Thailand) Co., LTD.
2. Air Zero was obtained from Thai Industrial Gas Co., LTD.
3. Hydrogen ( $H_2$  99.99%) was obtained from Thai Industrial Gas Co., LTD.
4. Methane ( $CH_4$  99.99%) was obtained from Thai Industrial Gas Co., LTD.

#### 3.1.2 Chemicals

The chemical reagents used in this research were:

1. Nickel (II) nitrate hexahydrate ( $\geq 99\%$ ) was obtained from Fluka Chemie A.G.
2. Cerous (III) nitrate hexahydrate ( $\geq 99\%$ ) was obtained from Fluka Chemie A.G.
3. Zirconium oxychloride ( $\geq 99\%$ ) was obtained from Fluka Chemie A.G.
4. Urea ( $\geq 99\%$ ) was obtained from Fluka Chemie A.G.
5. Sodium hydroxide was obtained from Fluka Chemie A.G.

## 3.2 Equipment

### 3.2.1 Catalyst characterization

#### 3.2.2.1 BET Surface Area

BET surface area was determined by N<sub>2</sub> adsorption at 77 K (a five point Brunauer–Emmett–Teller (BET) method using a Quantachrome Corporation Autosorb-1). Prior to the analysis, the samples were out gassed to eliminate volatile adsorbents on the surface at 250°C for 4 hr. The quantity of gas adsorbed onto or desorbed from a solid surface was measured at 5 equilibrium vapor pressure (P/P<sub>0</sub>) values of 0.1115, 0.1615, 0.2115, 0.2615, and 0.3115 by the static volumetric method. The adsorption data were calculated using 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)  
 $C$  = constant that is related to the energy of adsorption in the first adsorbed layer and magnitude of adsorbate/adsorbent interaction

and then the surface area 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 77 K  
 $Mw_{\text{nitrogen}}$  = molecular weight of nitrogen (g/mol)

### 3.2.2.2 H<sub>2</sub> Chemisorption

The amount of H<sub>2</sub> uptake due to the exposed metal was determined by H<sub>2</sub> pulse chemisorption. This technique was carried on the temperature programmed analyzer using a pulse technique. Prior to pulse chemisorption, 250 mg of sample was reduced in H<sub>2</sub> atmosphere at 500°C for 1 hr. Then the sample was purged with N<sub>2</sub> at 500°C for 30 min and cooled down to 50°C in flowing N<sub>2</sub>. A H<sub>2</sub> pulse (99.99% H<sub>2</sub> with a sample loop volume of 0.4 ml) was injected into the sample at 50°C. The metal dispersion was calculated by assuming the adsorption stoichiometry of one hydrogen atom per nickel surface atom.

### 3.2.2.3 X-ray Diffraction

A Rigaku X-ray diffractometer (XRD) system equipped with a RINT 2000 wide-angle goniometer using CuK<sub>α</sub> radiation (1.5406 Å) and a power of 40 kV×30 mA was used for examination of the crystalline structure. The sample was ground to a 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° ( $2\theta$ ).

### 3.2.2.4 Transmission Electron Microscopy

The size of supported metal crystallites and morphology of carbon deposition on the spent catalysts was observed by transmission electron microscopy (TEM) with a JEOL (JEM-2010) transmission electron microscope operated at 200 kV. The samples were dispersed in absolute ethanol ultrasonically, and the solutions were then dropped on copper grids coated with a lacey carbon film.

### 3.2.2.5 Temperature Programmed Oxidation

Temperature programmed oxidation (TPO) was carried out in a TPO micro-reactor coupled to an FID analyzer. TPO was used to quantify the amount of carbonaceous deposition on the used catalysts. After keeping the catalyst on stream for partial oxidation, the spent catalyst was cooled down to room temperature in He stream. Then, about 30 mg samples was heated in a 2%O<sub>2</sub> in He (40 ml/min) mixture at a heating rate of 10°C/min up to 850°C. The output gas was passed to a methanation reactor containing 15 wt% Ni/Al<sub>2</sub>O<sub>3</sub> as catalyst. In this 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 FID detector. After the TPO system reached 850°C, where all carbon had been 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

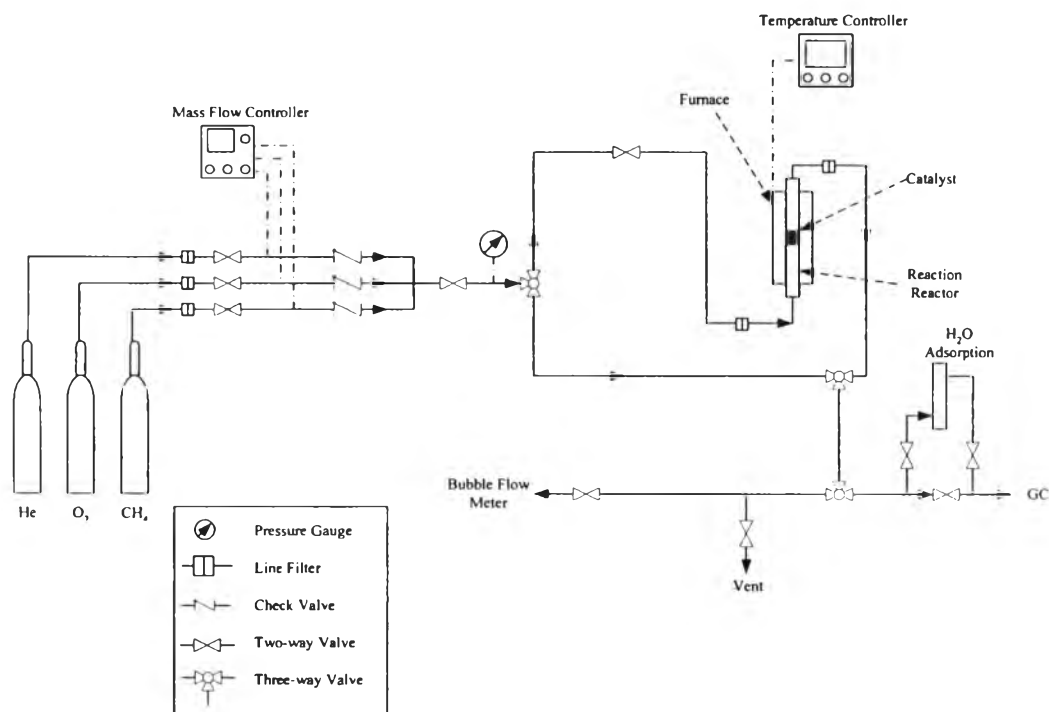
#### 3.3.1 Catalyst Preparation

##### 3.3.1.1 Ce<sub>2.14</sub>Ni<sub>0.86</sub>O<sub>3</sub> and (Ce<sub>0.75</sub>Zr<sub>0.25</sub>)<sub>2.14</sub>Ni<sub>0.86</sub>O<sub>3</sub> mixed oxides

Ce<sub>2.14</sub>Ni<sub>0.86</sub>O<sub>3</sub> and (Ce<sub>0.75</sub>Zr<sub>0.25</sub>)<sub>2.14</sub>Ni<sub>0.86</sub>O<sub>3</sub> mixed oxides were prepared via the co-precipitation method. The starting metal salts consist of 0.1 M aqueous solutions of Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O, ZrOCl<sub>2</sub>·8H<sub>2</sub>O, and Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O. The corresponding nitrates with 0.1 M sodium hydroxide solution were used as precipitant agents. The precipitation was carried out at room temperature, pH 10 with an aging time of 48 hr. The resulting precipitate was filtered off, washed with distilled water to remove excess sodium ions and dried at 110°C overnight in air. Finally, the solids were separately calcined at 500 and 700°C for 6 hr.

#### 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.Ø 6 mm). Typically, a 100 mg catalyst sample was packed between the layers of quartz wool. The reactor was placed in 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% CH<sub>4</sub> and 2% O<sub>2</sub> balanced with He was used with a gas hourly space velocity (GHSV) of 53,000 hr<sup>-1</sup> 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 CH<sub>4</sub> conversion ( $X_{\text{CH}_4}$ ), O<sub>2</sub> consumption ( $X_{\text{O}_2}$ ) and selectivity ( $S$ ) that reported in this work were calculated using the following expressions:

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

(3.3)

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

(3.4)

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

$$\%X_{H_2} = \frac{H_2^{out}}{H_2^{out} + H_2O^{out}} \times 100 \quad (3.6)$$

where

$CH_4^{in}$	=	mole of $CH_4$ in
$CH_4^{out}$	=	mole of $CH_4$ out
$O_2^{in}$	=	mole of $O_2$ in
$O_2^{out}$	=	mole of $O_2$ out
$CO^{out}$	=	mole of $CO$ formed
$CO_2^{out}$	=	mole of $CO_2$ formed
$H_2^{out}$	=	mole of $H_2$ formed
$H_2O^{out}$	=	mole of $H_2O$ formed