



## CHARTER III EXPERIMENT

### 3.1 Materials

#### 3.1.1 Gases

The gases used in this research are:

1. Helium (He 99.99% purity) was obtained from Praxair (Thailand) Co., LTD.
2. Air Zero was obtained from Thai Industrial Gas Co., LTD.
3. Hydrogen (H<sub>2</sub> 99.99% purity) was obtained from Thai Industrial Gas Co., LTD.
4. Methane (CH<sub>4</sub> 99.99% purity) will be obtained from Thai Industrial Gas Co., LTD.

#### 3.1.2 Chemicals

The chemical reagents used in this research are:

1. Nickel (II) nitrate hexahydrate ( $\geq 97\%$  purity) was obtained from Ajax Finechem.
2. Cerous (III) nitrate hexahydrate ( $\geq 99\%$  purity) was obtained from Fluka Chemie A.G.
3. Zirconium oxychloride ( $\geq 99\%$  purity) was obtained from Fluka Chemie A.G.
4. Magnesium nitrate hexahydrate ( $\geq 99\%$  purity) was obtained from Sigma-Aldrich.
5. Urea ( $\geq 99\%$  purity) was obtained from Fluka Chemie A.G.

## 3.2 Equipments

### 3.2.1 Catalyst Characterization

#### 3.2.1.1 BET Surface Area

BET surface area measurements were 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 will be out gassed to eliminate volatile adsorbents on the surface at 250°C for 4 hours. The quantity of gas adsorbed onto or desorbed from a solid surface will be 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 will be calculated using Brunauer–Emmett–Teller (BET) equation:

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

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 are of the sample will be 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  
 $Mw_{\text{nitrogen}}$  = molecular weight of nitrogen (g/mol)

### 3.2.1.2 *H<sub>2</sub>-Temperature-programmed Reduction*

H<sub>2</sub>-TPR experiments were carried out using a TPR analyzer. A 5% H<sub>2</sub>/Ar 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<sub>2</sub> consumption as a function of temperature was determined from a TCD signal.

### 3.2.1.3 *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 out using a temperature programmed analyzer with a pulse technique. Prior to the pulse chemisorption, 100 mg of sample was reduced in H<sub>2</sub> atmosphere at 500 °C for 1 hr. Then, the sample was purged with Ar at 500 °C for 30 min and cooled down to 50 °C in flowing Ar. A H<sub>2</sub> pulse (5% H<sub>2</sub> in Ar with a sample loop volume 74.79 µl) 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.

### 3.2.1.4 *X-ray Diffraction Analysis*

A Rigagu 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 will be used for examination of the crystalline structure. The sample will be ground to a fine homogeneous powder and will be held on thin-walled glass plate against the X-ray beam. The intensity data will be collected at 25°C over a 2θ range of 20–90° with a scan speed of 5° (2θ)/min and a scan step of 0.02° (2θ).

### 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

Temperature programmed oxidation (TPO) will be carried out in a TPO micro-reactor coupled to an FID analyzer. TPO will be used to quantify the amount of carbonaceous deposition on the used catalysts. The samples about 20 mg will be heated in a 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 will be passed to a methanation reactor containing 15 wt% Ni/Al<sub>2</sub>O<sub>3</sub> catalysts. In this methanation reactor, CO<sub>2</sub> formed from the carbon will be completely converted with excess H<sub>2</sub> into methane, to permit precise quantification in FID detector. After the TPO system reached 900°C, where all carbon will have been burned off, the FID signal for methane will be 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.

### 3.2.1.7 X-ray Fluorescence (XRF)

The composition of materials is determined by the X-ray fluorescence method (XRF) using PANalytical analysis instruments with AXIOS & SUPERQ version 4.0 systems. IQ+ program is used to measure and analyze the samples. In the analysis procedure, the scans are first searched for peaks. The found peaks are identified and analyze quantitatively using fundamental parameter.

## 3.3 Methodology

### 3.3.1 Catalyst Preparation

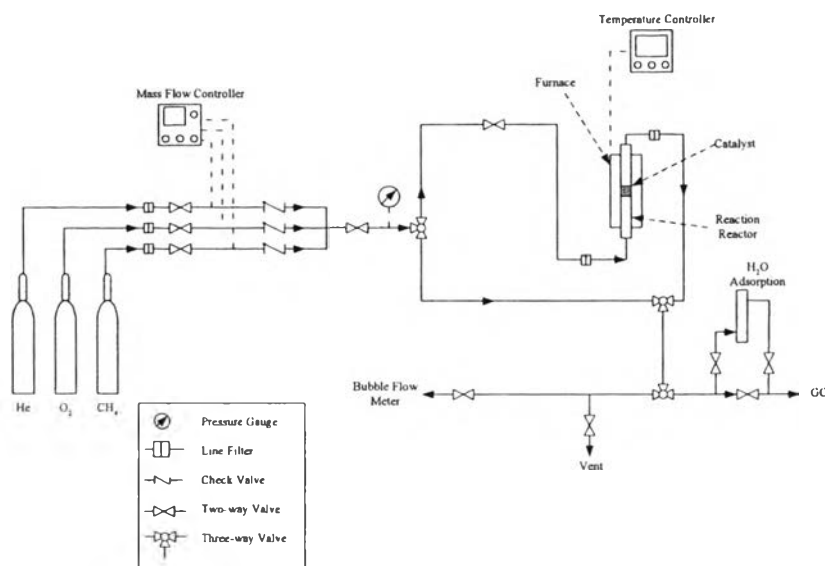
Mixed oxide solid solutions of Ce<sub>0.75</sub>Zr<sub>0.25</sub>O<sub>2</sub> support will be prepared via urea hydrolysis. The Ce-Zr mixed oxide sample will be prepared from Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O and ZrOCl<sub>2</sub>·8H<sub>2</sub>O. The ratio between the metal salts will be 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 will be dissolved in distilled water to the desired concentration (0.1 M). Then, the mixed metal salt solution will be added with a 0.4 M of urea solution with the salt to urea solution ratio of 2:1 (v/v), and the mixture will be kept at 100°C for 50 hours. The sample will be then allowed to cool to room temperature prior

to being centrifuged to separate a gel product from the solution. The gel product will be washed with ethanol and dried overnight in an oven at 110°C. The product will be then calcined at either 500°C for 4 hours (Pengpanich *et al.*, 2002).

The catalysts will be prepared by the sequential incipient wetness impregnation method using aqueous solutions of  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and  $\text{Mg}(\text{NO}_3)_2$ . The loading amount of MgO will be varied in the range of 1-5 wt% on the supported catalysts. During impregnation step, sample is continuously heated on the water bath at temperature ca. 60°C. After drying at 110°C for 4 hours and calcined at 550°C for 4 hours in air, the  $\text{MgO-Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$  support will be obtained. The  $\text{MgO-Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$  support will be impregnated with  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  solution (15 wt%) on the water bath, then drying at 110°C for 4 hours and calcined at 550°C for 4 hours. On the other hand, the other order will be prepared by adding Ni prior to Mg.

### 3.3.2 Catalytic Activity Testing

Catalytic activity tests for methane partial oxidation will be carried out in a packed-bed quartz micro reactor (i.d.Ø 6 mm). Typically, a 100 mg catalyst sample will be packed between the layers of quartz wool. The reactor will be placed in an electric furnace equipped with K-typed thermocouples. The catalyst bed temperature will be monitored and controlled by Shinko FCR-13A-S/M temperature controllers. The feed gas mixture containing 4%  $\text{CH}_4$ , 2%  $\text{O}_2$  and 7.5%  $\text{N}_2$  balances with He will be used with the total flow rates of 100 ml/min and a gas hourly space velocity (GHSV) of 53,000  $\text{hour}^{-1}$  using Brooks 5850E mass flow controllers. Measurements will be 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 will be chromatographically analyzed using a Shimadzu GC 8A fitted with a TCD. A CTR I (Alltech) packed column will be used to separate all products at 50°C except for H<sub>2</sub>O which will be trapped out prior to entering the column. After duration of catalytic test, admission of CH<sub>4</sub>, O<sub>2</sub> and N<sub>2</sub> was stopped, and the reactor was cooled to room temperature under a constant flow of helium. The CH<sub>4</sub> conversion ( $X_{CH_4}$ ), O<sub>2</sub> consumption ( $X_{O_2}$ ) and selectivity (S) that reported in this work will be calculated using the following expressions:

$$\%X_{CH_4} = \frac{CH_4^{in} - CH_4^{out}}{CH_4^{in}} \times 100 \quad (3.3)$$

$$\%X_{O_2} = \frac{O_2^{in} - O_2^{out}}{O_2^{in}} \times 100 \quad (3.4)$$

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

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

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