

CHAPTER III

EXPERIMENTAL

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 obtained from Thai Industrial Gas Public Company Limited.
3. Hydrogen (H₂ 99.99% purity) obtained from Thai Industrial Gas Public Company Limited.
4. Methane (CH₄ 99.99% purity) obtained from Thai Industrial Gas Public Company Limited.

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 Equipment

3.2.1 Catalyst Characterization

3.2.1.1 BET Surface Area Measurements

BET surface area was determined by N₂ 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 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 was measured at 5 equilibrium vapor pressure (P/P₀) values of 0.1115, 0.1615, 0.2115, 0.2615, and 0.3115 by the static volumetric method. The adsorption data was 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 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_{nitrogen} = Crossed-section area of one molecule nitrogen
 = 0.162 nm² at -196°C
 Mw_{nitrogen} = molecular weight of nitrogen (g/mol)

3.2.1.2 *H₂-Temperature Programmed Reduction*

H₂ temperature programmed reduction (H₂-TPR) experiments were carried out using a TPR analyzer (ThermoFinnigan modeled TPDRO 1100). The sample was pretreated in N₂ atmosphere at 120°C for 30 min prior to running the TPR experiment, and then cooled down to room temperature in N₂. A 5% H₂/ N₂ gas will be used as a reducing gas. The sample temperature was raised at a constant rate of 10°C/min from room temperature to 850°C. The amount of H₂ consumption as a function of temperature was determined from a TCD signal.

3.2.1.3 *X-ray Diffraction*

A Rigagu X-ray diffractometer (XRD) system equipped with a RINT 2000 wide-angle goniometer using CuK_α 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 was 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).

3.2.1.4 *Scanning Electron Microscopy*

Supported metal crystallites, morphologies of sample and carbon deposition on the catalysts were investigated using a Hitachi (S-4800) scanning electron microscope operated at 2kV and 10 mA.

3.2.1.5 *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 20 mg samples was heated in a 2% O₂ in He (40 ml/min) mixture at a heating rate of 10°C/min up to 800°C. The output gas was passed to a methanation reactor containing 15 wt% Ni/Al₂O₃ catalysts. In this methanation reactor, CO₂ formed from the carbon was completely converted with excess H₂ into methane, to permit precise quantification in FID detector. After the TPO system reached 800°C, where all carbon had been burned off, the FID signal for

methane was calibrated by injecting 100 μl of CO_2 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.

3.2.1.6 *Transmission Electron Microscopy*

The 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 ultrasonically dispersed in absolute ethanol, and small droplets of the solution were then dropped on copper grids coated with a lacey carbon film. After evaporation of the solvent, small amounts of catalyst powder remained on the microscope grids.

3.2.1.7 *X-ray Fluorescence Spectroscopy*

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

3.3 Methodology

3.3.1 Catalyst Preparation

The $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{Mg}_{2x}\text{O}_2$ ternary oxide supports were synthesized by sol-gel method via urea hydrolysis. The $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{Mg}_{2x}\text{O}_2$ solution was prepared at desired concentration, 0.1 M using $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ and $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. The atomic mole fraction of Mg was varied in the range of 0.07-0.19 resulting in altering zirconium atomic mole fraction.

Then $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{Mg}_{2x}\text{O}_2$ solution was mixed with 0.4 M urea solution with the volume ratio of mixed metal salt to urea equals to 2:1. The resulting solution was aging at 100 $^\circ\text{C}$ for 50 hours and then cooled down to the room temperature. The

gel product was separated and washed with ethanol. After being dried at 110 °C for 12 hours and calcined at 500 °C for 4 hours the CZMO was obtained as a support.

The nickel loading was performed on the obtained support $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{Mg}_{2x}\text{O}_2$ by the incipient wetness impregnation method using the $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ solution. The nickel loading was fixed at 15 wt%.

The prepared catalysts were dried at 110 °C for 4 hours and then calcined at 550 °C for 4 hours. Then, the catalysts were crushed, sieved through the 60-80 mesh sieve, and used for this study without reduction pretreatment.

3.3.2 Catalytic Activity Testing

The catalytic activity testing was performed using a packed-bed reactor (i.d. 6 mm). Approximately 0.1 g of the catalyst was packed between the layer of quartz wool and placed in an electric furnace. Temperature of the catalyst bed was detected with K-typed thermocouple and controlled with Shinko FCR-13A-S/M temperature controllers.

The gaseous mixture of 4% CH_4 , 2% O_2 , 7.5% N_2 balanced with He was used as a reactant with a total flow rate of 123 ml/min and a gas hourly space velocity (GHSV) of 53,000 hour^{-1} controlled by Brooks 5850 E mass flow controllers.

The tests were performed at sequentially varied furnace temperatures in the range of 400-800 °C with an interval of 50 °C. A schematic diagram of the experimental set up is shown in Figure 3.1.

The stability testing was performed at a temperature of 750°C for 50 hours under the same reaction condition as for the catalytic activity testing. After that the spent catalysts were regenerated at 750°C using 10% O_2 in He and performed the stability testing again for 10 hours.

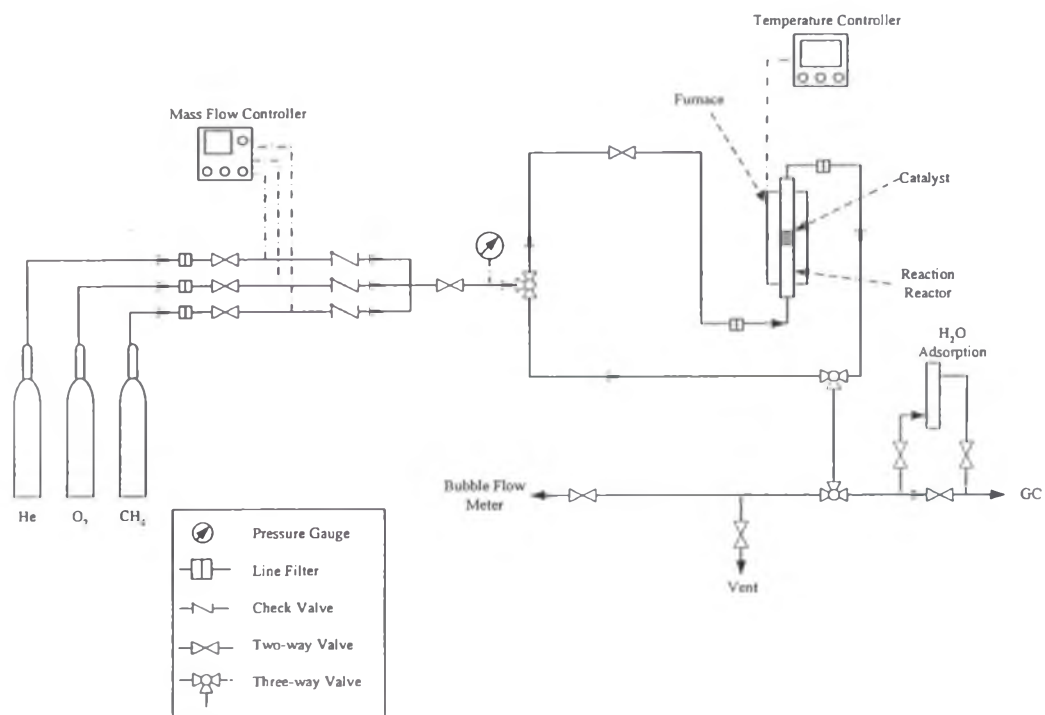


Figure 3.1 Schematic of the experimental setup for methane partial oxidation.

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 H₂O which was trapped out prior to entering the column. The CH₄ conversion (X_{CH_4}), O₂ consumption (X_{O_2}) and selectivity (S) that reported in this work was calculated using the following expressions:

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

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

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

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

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

$$\%Y_{H_2} = \frac{H_2^{out}}{2(CH_4^{in})} \times 100 \quad (3.8)$$

$$\%Y_{CO} = \frac{CO^{out}}{(CH_4^{in})} \times 100 \quad (3.9)$$

$$\%Y_{CO_2} = \frac{CO_2^{out}}{(CH_4^{in})} \times 100 \quad (3.10)$$

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