CHAPTER III
EXPERIMENTAL

3.1 Materials

3.1.1 Gases

The gases used in this research supplied by Praxair (Thailand) Co., Ltd. are:

1. Helium (He 99.995 % purity)
2. Hydrogen (H_2 99.99 % purity)
3. Methane (CH_4 99.995 % purity)
4. Air Zero

3.1.2 Chemicals

The chemical reagents used in this research are:

1. Nickel (II) nitrate hexahydrate ($\geq$97 % purity, Sigma-Aldrich)
2. Cerium (III) nitrate hexahydrate ($\geq$99 % purity, Sigma-Aldrich)
3. Zirconium oxide chloride octahydrate ($\geq$99 % purity, Merck)
4. Urea ($\geq$99 % purity, Fluka Chemie A.G)
5. Ethylene glycol (99 % purity, Sigma-Aldrich)
6. Sodium hydroxide (99 % purity, RCI Labscan)
7. Ethanol (AR., RCI Labscan)

3.2 Equipment

3.2.1 Catalyst Characterization

3.2.1.1 BET Surface Area Measurements

BET surface area was determined by N_2 adsorption at -196°C (a five point Brunauer–Emmett–Teller (BET) method using a Quantachrome Autosorb-1 MP). Prior to the analysis, the sample was outgassed to eliminate volatile adsorbates 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/P_0) values of 0.1115, 0.1615, 0.2115, 0.2615, and 0.3115 by the static volumetric method. The adsorption data was calculated using the Brunauer–Emmett–Teller (BET) equation:

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

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

A magnitude of adsorbate/adsorbent interaction and then the surface are of the sample was calculated by

$$\text{Surface area of sample} = \frac{W_m A_{nitrogen}\left(6.02\times10^{23}\right)}{Mw_{nitrogen}} \tag{3.2}$$

where $A_{nitrogen}$ = Crossed-section area of one molecule nitrogen

     = 0.162 nm^2 at -196°C

   $Mw_{nitrogen}$ = molecular weight of nitrogen (g/mol) = 28.0134 g/mol

3.2.1.2 H₂ Chemisorption

H₂ uptake and degree of dispersion were determined by pulse technique using a temperature programmed analyzer (ThermoFinnigan modeled TPDRO 1100). Prior to the pulse chemisorption, 250 mg of sample was reduced in H₂ atmosphere at 500 °C for 1 h. Then the sample was purged with N₂ at 500 °C for 30 min and cooled down to 40 °C. A H₂ pulse (99.99% H₂ with a sample loop volume of 0.4 ml) was injected into the sample at 50 °C.

3.2.1.3 X-ray Diffraction (XRD)

An X-ray diffractometer (XRD) system (Rigaku) equipped with a RINT 2000 wide-angle goniometer using Cu Kα radiation and a power of 40 kV × 30mA was used for examination of the crystalline structure. The intensity data were collected at 25 °C over a 2θ range of 20–80° with a scan speed of 2°/min (2θ) and a scan step of 0.01°(2θ).

Crystallite size (thickness, L) can be estimated using the Scherrer Equation where peak width (B) is the inversely proportional to crystallite size (L) and K is 0.94 and X-ray wavelength (λ) is 0.15418 nm.

$$L = \frac{K\lambda}{B(2\theta)Cos\theta}$$

Full width at half maximum (FWHM) method was used to define the peak width (B) calculated from Origin Pro software.

3.2.1.4 Scanning Electron Microscopy (SEM)

Scanning Electron Microscopy (SEM)with a Tabletop microscope TM 3000 (Hitachi) operated at 5kV and 15 mA was employed to analyze the surface morphologies of catalysts.

3.2.1.5 X-ray Fluorescence Spectrometry (XRF)

The PAN analytical X-ray fluorescence (XRF) using the XRF-semi quantitative method with AXIOS & SUPERQ version 4.0 system was employed to analyze the elemental analysis and chemical analysis such as Ce/Zr ration and weight percent (wt%) of metal.

3.2.1.6 Transmission Electron Microscopy (TEM)

Transmission electron microscopy (TEM) with a JEOL (JEM-2010) transmission electron microscope operated at 200 kV was employed to analyze the morphology of the catalysts. The sampleswere dispersed in absolute ethanol ultrasonically, and the solutions were dropped on copper grids coated with a lacey carbon film.

3.2.1.7 H_2-Temperature Programmed Reduction (H_2-TPR)

H_2-Temperature programmed reduction was employed for evaluating the number and quantity of the reducible species present in the prepared catalyst and the temperature, at which the reduction itself takes place as a function of temperature. In each test, 50 mg of catalyst was placed in a quartz reactor, and heated (10 °C/min) under a He flow up to 550 °C, and held at the temperature for 1 h in order to remove moisture from the catalyst surface. The sample was then cooled down to 30 °C. Then, the sample was exposed to a stream of 5%H_2/Ar with a flow rate of 20 ml/min. After that, the sample was heated to 900 °C with a ramping rate of 10°C/min. The amount of hydrogen consumed was monitored on-line by an SRI model 110 TCD detector as a function of temperature.

3.2.1.8 Temperature Programmed Oxidation (TPO)

TPO technique was employed to analyze the amount and characteristics of the coke formation on the catalysts during reaction. TPO of the spent catalysts were performed in a continuous flow of 2% O_2 in He while the temperature will be linearly increased with a heating rate of 10 °C/min. The oxidation was conducted in a 1/4" quartz fixed-bed reactor. The spent catalyst was placed between two layers of quartz wool. The CO_2 produced by the oxidation of the coke species were converted to methane using a methanizer filled with 15% Ni/Al_2O_3 and operated at 400 °C in the presence of H_2. The evolution of methane was analyzed using an FID detector.

3.3 Methodology

3.3.1 Catalyst Preparation

3.3.1.1 $Ce_{0.75}Zr_{0.25}O_2$ Support

$Ce_{0.75}Zr_{0.25}O_2$ (CZO) mixed oxide support was prepared via urea hydrolysis. The Ce-Zr mixed oxide supports were prepared from $Ce(NO_3)_3.6H_2O$ and $ZrOCl_2.8H_2O$. The ratio between the metal salts was used depending on the desired solid solution concentration: $Ce_{1-x}Zr_xO_2$ in which $x = 0.25$. The starting metal salt was 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 h. 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 calcined at 500 °C for 4 h (Pengpanich *et al.*, 2002).

3.3.3.2 Supported – Nickel Catalyst Preparation

The catalyst was prepared by incipient impregnation and polyol method. For the incipient impregnation method, the $Ce_{0.75}Zr_{0.25}O_2$ supports prepared as Section 3.3.1.1 were impregnated with an aqueous solution of $Ni(NO_3)_3.6H_2O$. The supports were loaded at 5, 10, 15 and 25 wt%. The support was heated at 50 – 60 °C on the hotplate while impregnating in order to prevent the support from forming slurry. The supported catalysts were dried at 110 °C for 4-12 h and then calcined at 500 °C for 4 h with heating rate 10 °C /min. The powder catalysts were ground and sieved to a particle size 180 – 250 μm (60 – 80 mesh)

For the polyol process, 5, 10, 15 and 25 wt%Ni/$Ce_{0.75}Zr_{0.25}O_2$ $Ni(NO_3)_2.6H_2O$ and $Ce_{0.75}Zr_{0.25}O_2$ is dissolved in 50 ml of ethylene glycol with 0.4 g (1M) of NaOH. The solution is stirred for 24 h and then heated up to boiling point of EG~197.3 °C for 3 h under reflux condition to reduce the Ni ions and formation of nano Ni particles on support. After reduction, the homogeneous colloidal suspension is rapidly cooled down to room temperature in an ice bath and is separated by filtration and subsequently washed several times with excess of acetone and distilled water in order to remove organic phase. Afterwards,

the supported Ni catalyst is dried overnight and then is calcined at 500 °C for 4 h with heating rate 10 °C /min (Sarkar *et al.*, 2012).

3.3.2 Catalytic Activity Testing

Catalytic activity tests for methane partial oxidation were carried out in a packed-bed quartz microreactor (i.d. 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 thermocuples. The catalyst bed temperature was monitored and controlled by Shinko FCR-13A-S/M temperature controllers.

The feed gas mixture containing 4% CH_4, 2% O_2 and balanced with He was used with a total flow rate of 100 ml/min and a gas hourly space velocity (GHSV) of 53,000 h^{-1} was introduced into the rector using Brookes 5850E mass flow controllers (Sukkaeo *et al.*, 2013).

Measurements were performed at various furnace temperatures adjusted sequentially from 400 to 800 °C with an interval of 50 °C. The effect of feed ratio was studied at CH_4/O_2 ratio of 2:1 and 4:1. The coke formations on the catalysts were further studied in the same system as for CPOM at 750 °C with different conditions (CH_4/O_2 ratio of 2:1 and 4:1). A schematic diagram of the experimental setup was shown in Figure 3.1.
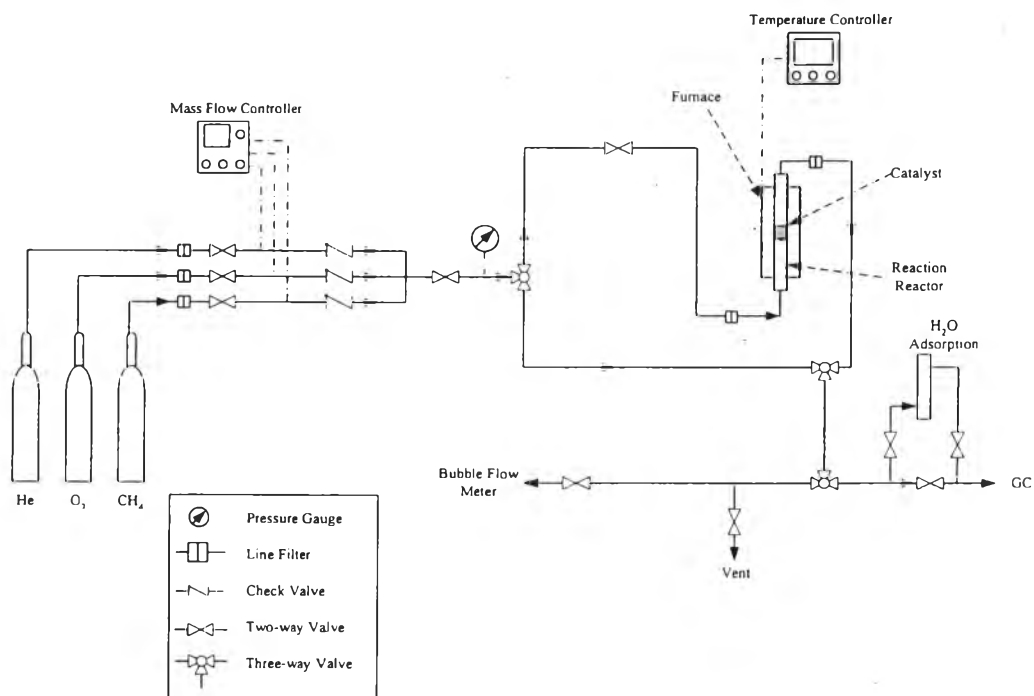
Figure 3.1 Schematic of the experimental setup for methane partial oxidation.

The product gases were chromatographically analyzed using a Shimadzu GC 8A installed with a 5890 SERIES 2 (P/W HAYESEP DB) column for TCD detector. A CTR was used to separate all products at 50 °C except for H_2O which is trapped out prior to entering the column. The CH_4 conversion (X_{CH4}), selectivity (S), and yield (Y) that reported in this work would be calculated using the following expressions:

$$\%X_{CH_4} = \frac{CH_4^{in} - CH_4^{out}}{CH_4^{in}} \times 100 \tag{3.1}$$

$$\%S_{CO} = \frac{CO^{out}}{CO^{out} + CO_2^{out}} \times 100 \tag{3.2}$$

$$\%S_{CO_2} = \frac{CO_2^{out}}{CO^{out} + CO_2^{out}} \times 100 \tag{3.3}$$

$$\%S_{H_2} = \frac{H_2^{out}}{H_2^{out} + H_2O^{out}} \times 100 \tag{3.4}$$

$$\%Y_{H_2} = \frac{H_2^{out}}{2CH_4^{in}} \times 100 \qquad (3.5)$$

$$\%Y_{CO} = \frac{CO^{out}}{CH_4^{in}} \times 100 \qquad (3.6)$$

$$\%Y_{CO_2} = \frac{CO_2^{out}}{CH_4^{in}} \times 100 \qquad (3.7)$$

where CH_4^{in} =   mole of CH_4 in;

                CH_4^{out} =   mole of CH_4 out;

                CO^{out} =   mole of CO formed;

                CO_2^{out} =   mole of CO_2 formed;

                H_2^{out} =   mole of H_2 formed; and

                H_2O^{out} =   mole of H_2O formed.