CHAPTER III

EXPERIMENTAL

3.1 Materials and Equipment

3.1.1 Materials

3.1.1.1 Gases

1. Argon (Ar, 99.99% purity)
2. Hydrogen (H_2, 99.99% purity)
3. Nitrogen (N_2, 99.99% purity)
4. Carbon monoxide (CO, 1% purity in Helium)
5. Carbon dioxide (CO_2, 99.99% purity)
6. Methane (CH_4, 99.99% purity)
7. Ammonia (NH_4 99.99% purity)

3.1.1.2 Chemicals

1. Nickel (II) nitrate hexahydrate ($\geq$97% purity), Sigma-Aldrich

2. Cerium (III) nitrate hexahydrate ($\geq$99% purity), Fluka, Sigma-Aldrich

3. Zirconium oxychloride octahydrate ($\geq$99% purity), Fluka, Sigma-Aldrich

4. Zirconium (IV) oxynitrate hydrate ($\geq$99.5% purity), Arcos

5. Magnesium nitrate hexahydrate($\geq$99% purity), Sigma-Aldrich

6. Manganese (II) nitrate tretahydrate ($\geq$99% purity), Sigma-Aldrich

7. Urea ($\geq$99% purity), Fluka Chemical A.G.
8. Hydrazine hydrate (37.5% purity), Carlo Erba reagents
9. α-phase Aluminum oxide ($\geq$99% purity), 100-200 mesh, Sigma-Aldrich

3.1.2 Equipment

1. Quantachrome Surface Area Analyzer, Model: Autosorb-1 MP
2. Rigaku X-ray Diffractometer (XRD), Model: D8-Discover
3. Shimadzu Gas Chromatograph (GC), Model: GC-8A
4. PANalytical X-Ray Fluorescence (XRF), Model: AXIOS/PW 4400
5. Brooks Mass Flow Controller, Model: 5850E
6. Brooks Mass Flow Microprocessor Control & Readout, Model: 0154

3.2 Experimental Procedures

3.2.1 Support Preparation

3.2.1.1 $Ce_{0.75}Z_{0.25-x}Mn_xO_2$

$Ce_{0.75}Z_{0.25-x}Mn_xO_2$ mixed oxide supports were prepared via urea hydrolysis. $Ce(NO_3)_3 \cdot 6H_2O$, $ZrOCl_2 \cdot 8H_2O$ and $Mn(NO_3) \cdot 4H_2O$ were used as sources of Ce, Zr and Mn, respectively. The starting metal salts were dissolved in distilled water to the desire concentration (0.1M). The ratio between the metal salts was altered depending on the desired solid solution concentration: $Ce_{0.75}Z_{0.25-x}Mn_xO_2$ in which x = 0, 0.10 and 0.20 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 as-prepared samples were calcined at 500 °C for 4 h (Bampenrat *et al.*, 2010). The samples were labeled as CZO-S, CZN-1 and CZN-2.

3.2.1.2 $Ce_{0.75}Z_{0.25-x}Mg_{2x}O_2$

$Ce_{0.75}Z_{0.25-x}Mg_{2x}O_2$ mixed oxide supports were prepared via co-precipitation. $Ce(NO_3)_3 \cdot 6H_2O$, $ZrO(NO_3)_2 \cdot xH_2O$ and $Mg(NO_3)_2 \cdot 6H_2O$ were used as sources of Ce, Zr and Mg, respectively. The starting metal salts were dissolved in distilled water to the desire concentration: 10 g/l of cerium nitrate solution, 10 g/l of

Zirconyl nitrate solution and 4.16 g/l of Magnesium nitrate solution. The ratio between the metal salts was altered depending on the desired solid solution concentration: $Ce_{0.75}Z_{0.25-x}Mg_{2x}O_2$ in which x = 0, 0.10 and 0.20 then, the mixed metal salt solution was poured dropwise into an aqueous solution of hydrazine (5.0 M). The excess of base solution is about 150 % (v/v). the pH varied from about 12 to 9.8 then, the mixed solution was formed gel. The gel was *digested*, i.e. heated with reflux under agitation during 120 h while the pH was kept higher than 9.0 by addition of the hydrazine solution. Finally, the gel was filtered, washed with ethanol to remove nitrate ions, then the as-prepared samples were dried at 110 °C for 12 h and calcined at 750 °C for 4 h (Ciuparu *et al.*, 2007). The samples were labeled as CZO-C, CZM-1 and CZM-2.

3.2.2 Supported-Nickel Catalyst Preparation

The nickel catalyst were prepared by the incipient impregnation method. $Ce_{0.75}Z_{0.25-x}Mn_xO_2$ and $Ce_{0.75}Z_{0.25-x}Mg_{2x}O_2$ support prepared as Section 3.2.1. were impregnated with an aqueous solution of $Ni(NO_3)_2 \cdot 6H_2O$. Each of the supports were loaded at 15 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 range of 177-400 μm (40-80 mesh).

3.2.3 Catalyst Characterization

3.2.3.1 BET Surface Area and Pore Volume

Surface area and pore volume were determined by N_2 adsorption at -196 °C using a Quanta chrome Autosorb-1 MP. Both surface are and pore volume were obtained from multi point Brunauer-Emmett-Teller (BET) method. Prior to the analysis, the samples will be out gassed to eliminate volatile adsorbents on the surface at 250 °C for 4 h. The quantity of gas adsorbed onto or desorbed from a solid surface will be measured at 7 equilibrium vapor pressure (P/P_0) values of 0.1115, 0.1615, 0.2115, 0.2615, and 0.3115 by the static volumetric method.

3.2.3.2 H₂-Temperature Programmed Reduction (H₂-TPR)

Hydrogen temperature-programmed reduction (H₂-TPR) experiments were carried out with a Micromeritics TPD/TPR 2900 apparatus equipped with a TCD detector. Prior to the reduction experiments, the sample, about 30 mg, was thermally treated under a helium stream at 100 °C to remove moisture. TPR profiles were attained by heating the samples under a 10 % H₂/Ar flow (50 ml/ min) from 30 to 900 °C at a linearly programmed rate of 10 °C/min.

3.2.3.3 H₂ Chemisorption

The amount of H₂ uptake due to the exposed metal will be determined by H₂ pulse chemisorption. This technique will be carried on the temperature programmed analyzer using a pulse technique. Prior to pulse chemisorption, 50 mg of sample will be reduced in H₂ atmosphere at 500 °C for 1 h. Then the sample will be purged with N₂ at 500 °C for 30 min and cooled down to 50 °C in flowing N₂. A H₂ pulse (99.99 % H₂ with a sample loop volume of 10 μl) will be injected into the sample at 30 °C. The metal dispersion will be calculated by assuming the adsorption stoichiometry of one hydrogen atom per nickel surface atom.

3.2.3.4 X-ray Diffraction

X-ray diffractometer (XRD) system equipped with a RINT 2000 wide-angle goniometer using CuK$_\alpha$ 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 20-80° with a scan speed of 5° (2θ)/min and a scan step of 0.02° (2θ).

Crystallite size (thickness, L) can be estimated using the Scherrer Equation where peak width (B) is inversely proportional to crystallite size (L) and K is 1.

$$L = \frac{K\lambda}{B(2\theta)\cos\theta} \qquad (3.1)$$

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

3.2.3.5 Transmission Electron Microscopy (TEM)

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

3.2.3.6 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.

3.2.3.7 X-Ray Fluorescence (XRF)

The composition of catalyst such as Ce/Zr ratio and wt% of metal was determined by the PAN analytical X-ray fluorescence method (XRF) using the XRF-semi quantitative method with AXIOS&SUPERQ version 4.0 systems. IQ+ program.

3.2.3.8 Temperature Programmed Oxidation (TPO)

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. After keeping the catalyst on stream for partial oxidation, the spent catalyst will be cooled down to room temperature in He stream. Then, about 20 mg samples will be heated in a 2 % O_2 in He (40 ml/min) mixture at a heating rate of 10 °C/min up to 800 °C. The output gas will be passed to a methanation reactor containing 15 wt% Ni/Al_2O_3 catalysts. In this methanation reactor, CO_2 formed from the carbon will be completely converted with excess H_2 into methane, to permit precise quantification in FID detector. After the TPO system reached 800 °C, where all carbon will have been burned off, the FID signal for methane will be 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.

3.2.3.9 Temperature Programmed Desorption (TPD)

Temperature-programmed desorption (TPD) of NH_3 was carried out to estimate the amount of acid in the catalysts. Ammonia-TPD was carried out in the following manner; 30 mg of a powder sample was heated at a rate of 10 °C/min up to 500 °C and kept for 1 h in the He atmosphere to remove adsorbed molecules on the catalyst surface. The sample was cooled down to room temperature in the He atmosphere, then followed by adsorption of NH_3 in pure NH_3 flow for 1 h. Consecutively, ammonia TPD was initiated at a heating rate of 10 °C/min to 800 °C. The rate of NH_3 desorption was determined by using a TCD and recorded on an online personal computer. The amount of desorbed NH_3 was estimated.

3.2.4 Catalytic Activity Testing

The catalytic activity testing will be performed using packed-bed reactor (i.d. 6 mm). Approximately 100 mg of the catalyst will be packed between the layer of quartz wool and placed in an electric furnace. Since the DMR is highly endothermic, the catalyst was mixed with some inert α-phase aluminum oxide (to prevent rapidly occurring coke formation in the catalyst bed) with an inert to catalyst weight ratio of 1:1. Temperature of the catalyst bed was controlled using two K-type thermocouples and a Shinko modeled FCR-13A-S/M temperature controller.

The molar ratio of $CH_4/CO_2/He$ is 1:1:8 will be used as the reactant with total flow rates of 100 ml/min and a gas hourly space velocity (GHSV) of 10,600 h^{-1} controlled by Brooks 5850 E mass flow controllers.

The test will be performed at sequentially various furnace temperature range of 500-900 °C. with interval of 50 °C. A schematic diagram of the experimental set up is shown in Figure 3.1.

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_2O which will be trapped out prior to entering the column. The CH_4 conversion (X_{CH4}), CO_2 conversion (X_{CO2}), CO yield (%) and H_2 yield (%) that reported in this work will be calculated using the following expressions:
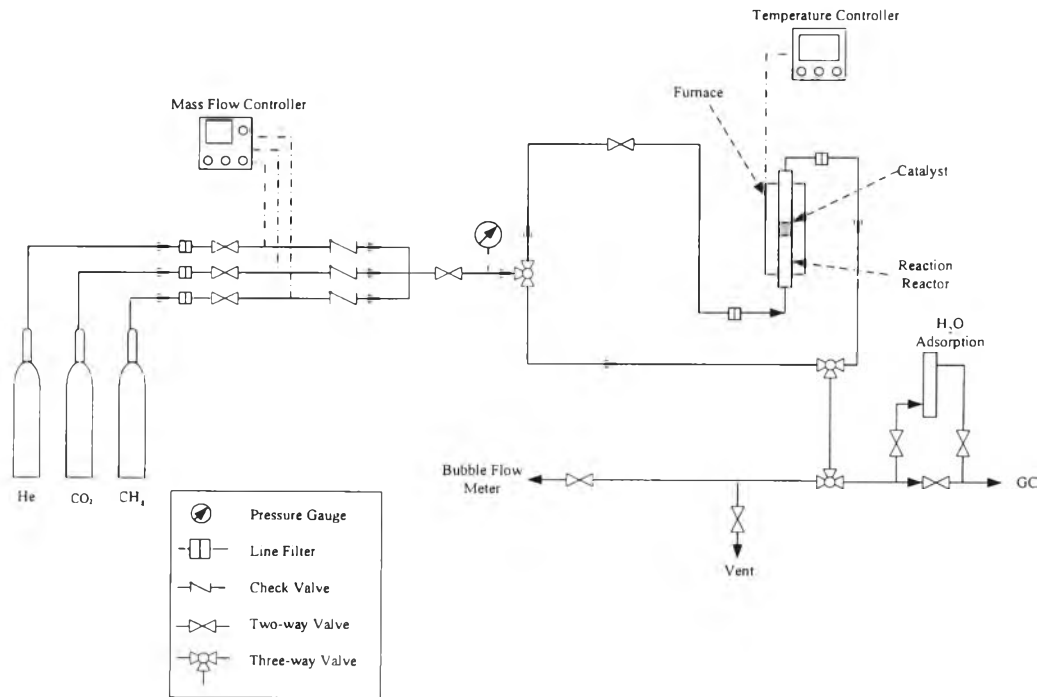
Figure 3.1 Schematic of the experimental setup for methane dry reforming.

$$\%X_{CH_4} = \frac{CH_4^{in} - CH_4^{out}}{CH_4^{in}} \times 100 \tag{3.2}$$

$$\%X_{CO_2} = \frac{CO_2^{in} - CO_2^{out}}{CO_2^{in}} \times 100 \tag{3.3}$$

$$\%S_{CO} = \frac{CO^{out}}{CO^{out} + CO_2^{out}} \times 100 \tag{3.4}$$

$$\%X_{H_2} = \frac{H_2^{out}}{H_2^{out} + H_2O^{out}} \times 100 \tag{3.5}$$

Where CH_4^{in} = mole of CH_4 in

           CH_4^{out} = mole of CH_4 out

           CO_2^{in} = mole of CO_2 in

           CO_2^{out} = mole of CO_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

3.2.5 Stability Test

The catalytic stability tests were performed on Ni-doped catalysts under the following conditions: temperature of 750 °C under the same reaction conditions as for the catalytic activity testing.