

CHAPTER III

EXPERIMENTAL

3.1 Materials and Equipment

3.1.1 Materials

3.1.1.1 *Gases*

1. Hydrogen (H₂, 99.99% purity)
2. Nitrogen (N₂, 99.99% purity)
3. Oxygen (O₂, 99.7% purity) -
4. Carbon monoxide (CO, 1% purity)
5. Carbon dioxide (CO₂, 99.99% purity)
6. Methane (CH₄, 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 ($\geq 99\%$ purity), Merck.
4. Urea ($\geq 99\%$ purity), Fluka Chemie A.G.
5. Acetic acid (100% AR grade), Labscan.

3.1.2 Equipment

1. Quantachrome Surface Area Analyzer, Model : Autosorb-1 MP
2. ThermoFinnigan TPDRO, Model : 1100
3. Bruker X-ray Diffractometer (XRD), Model : D8-Discover
4. Shimadzu Gas Chromatograph (GC), Model : GC-14B
5. PANalytical X-Ray Fluorescence (XRF), Model : AXIOS/PW 4400
6. Scanning Electron Microscope (SEM), Model : TM300
7. Brooks Mass Flow Controller, Model : 5850E
8. Brooks Mass Flow Microprocessor Control & Readout, Model : 0154

3.2 Experimental Procedures

3.2.1 Catalysts Preparation

3.2.1.1 Synthesis of $Ce_{0.75}Zr_{0.25}O_2$ support

$Ce_{0.75}Zr_{0.25}O_2$ supports was prepared via urea hydrolysis method from salt solution of $ZrOCl_2 \cdot 8H_2O$ (99.0%) and $Ce(NO_3)_3 \cdot 6H_2O$ (99.0%). The support was in the form of mixed oxide solid solution with empirical formula: $Ce_{1-x}Zr_xO_2$, in order to obtain $Ce_{0.75}Zr_{0.25}O_2$, the Ce/Zr ratio in mixed solution had to be 0.75:0.25. The ratio was determined by the volume proportion of each metal salt aqueous solution (0.1 M) added. After mixing, 0.4 M of urea solution was added with a salt to urea volume ratio of 2:1 which made the urea solution be 1/3 of entire solution. Afterward, the mixture was subsequently stirred for 2 hours and kept in an oven at 100 °C for 50 hours in order to form a gel. When finished, it was allowed to cool down to room temperature. After having been filtrated with Buchner funnel in order to separate a gel support from the solution, it was washed with ethanol and dried overnight in an oven at 110 °C, the reason it was washed with ethanol is to prevent agglomeration (Matina Thammachart, *et al.*, 2001). Then, the support will be calcined at 500 °C for 4 hours with heating rate 10 °C/min.

3.2.1.2 Impregnation of nickel on $Ce_{0.75}Zr_{0.25}O_2$ support

The supported catalysts was prepared by the impregnation method using aqueous solutions of $Ni(NO_3)_2 \cdot 6H_2O$ was 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 hours and then calcined at 550 °C for 4 hours with heating rate 10 °C/min. The powder $Ni/Ce_{0.75}Zr_{0.25}O_2$ and $Co/Ce_{0.75}Zr_{0.25}O_2$ catalysts were ground and sieved to a particle size 125-180 μ m (mesh 80-120).

3.2.2 Catalyst Characterization

3.2.2.1 BET Surface Area and Pore Volume

Surface area and pore volume were determined by N_2 adsorption at -196 °C using a Quantachrome Autosorb-1 MP. Both surface and pore volume were obtained from multipoint Brunauer–Emmett–Teller (BET) method. Prior to the analysis, the samples will be out gassed to eliminate volatile adsorbents on the sur-

face at 250°C for 4 hours. 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.

3.2.2.2 *H₂-Temperature Programmed Reduction*

Hydrogen temperature-programmed reduction (H_2 -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% H_2/Ar flow (50 ml/min) from 30 to 900°C at a linearly programmed rate of 10°C/min

3.2.2.3 *X-ray Diffraction*

A Rigaku 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 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).

3.2.2.4 *Scanning Electron Microscopy (SEM)*

Supported metal crystallites, morphologies of sample and carbon deposition on the catalysts were investigated using a TM300 scanning electron microscope operated at 5kV and 10 mA.

3.2.2.5 *X-Ray Fluorescence Spectroscopy (XRF)*

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

3.2.2.6 *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. 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/Al₂O₃ catalysts. In this methanation reactor, CO₂ formed from the carbon will be completely converted with excess H₂ 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 CO₂ 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 Experimental Setup

The reaction was carried out in quartz tube micro-reactor (internal diameter 6 mm) at atmospheric pressure. In quartz tube, 100 mg of catalyst was packed between the layers of quartz wool. In order to ensure eliminating of back filling and channeling in this reactor, a plug flow condition was achieved by providing a catalyst bed length (L) to particle diameter (d_p) ratio at least 50 ($L/d_p > 50$) and a tube diameter (D) to particle diameter (d_p) ratio at least 10 ($D/d_p > 30$).

The temperature of catalyst bed was monitored and controlled using Shinko temperature controllers with electric furnace and K-type thermocouples. Liquid feed was pumped into evaporator by Eldex HPLC pump. Gas feeds were monitored and controlled by Brooks mass flow controllers. Gas products were analyzed by on-line gas chromatograph (GC) using Shimadzu GC-14B with thermal-conductivity detectors (TCD).

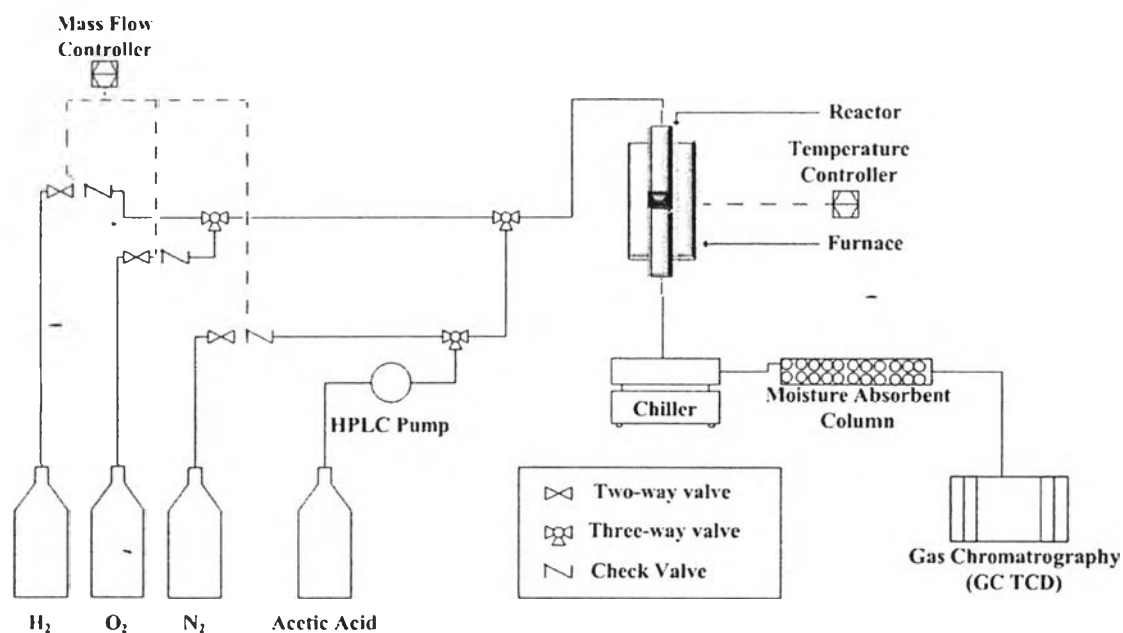


Figure 3.1 Schematic of the experimental setup for steam reforming of acetic acid.

3.2.4 Catalyst Testing

Prior to running the reaction, the catalyst was reduced in situ with a flow of 50% H₂ in N₂ gas at 600°C for 2 h. After reduction, Acetic acid aqueous solution with a known composition was pumped by using HPLC pump into line and vaporized at 140 °C by using heating tape at 200°C. Nitrogen was applied to carry acetic acid. Oxygen was fed into line for autothermal condition. Prior to entering the reactor set at a desired temperature. The gaseous products leaving the reactor will be condensed and separated gases from liquids; non-condensable gases will be pass through a moisture trap column (packed with silica gel desiccant) and analyzed by GC connected to separating flask. The liquid products will be collected and analyzed by GC as well.

3.2.5 Catalytic Activity Testing

The C–C bond breakage conversion of acetic acid will be calculated from a ratio of the gaseous single carbon compounds (CH₄, CO and CO₂) in the product steam to the acetic acid reactant. The product yield will also be calculated from a ratio of the actual product to the theoretical amount of product produced from

steam reforming of acetic acid. Conversion and yields used in this work are shown as follows.

3.2.5.1 Conversion

C-C breakage conversion (%)

$$= \frac{\text{mol CH}_4, \text{ out} + \text{mol CO, out} + \text{mol CO}_2, \text{ out}}{2 \times \text{mol AcOH, in}} \times 100$$

3.2.5.2 Yields

$$\% \text{ H}_2 \text{ yield} = \frac{\text{mol H}_2, \text{ out}}{3 \times \text{mol AcOH, in}} \times 100$$

$$\% \text{ CO yield} = \frac{\text{mol CO, out}}{2 \times \text{mol AcOH, in}} \times 100$$

$$\% \text{ CO}_2 \text{ yield} = \frac{\text{mol CO}_2, \text{ out}}{2 \times \text{mol AcOH, in}} \times 100$$

$$\% \text{ CH}_4 \text{ yield} = \frac{\text{mol CH}_4, \text{ out}}{2 \times \text{mol AcOH, in}} \times 100$$

3.2.6 Steam Reforming Activity Measurement

3.2.6.1 *Effects of Temperature*

The effects of temperature for autothermal steam reforming reaction was carried out at temperature range from 550-700 °C, S/C ratio = 6 and O₂/AcOH ratio = 0.25-0.35 depend on temperature for reach neutral condition; the total flow rate of 170 cm³/min and the contact (W/F) equal to 0.22 gh/mol.

3.2.6.2 *Effects of Oxygen*

The effects of oxygen for steam reforming reaction was carried out at various oxygen to acetic acid ratio (O₂/AcOH ratio = 0, 0.1, 0.2, 0.3 and 0.4) and S/C ratio = 6; the total flow rate of 170 cm³/min and the contact (W/F) equal to 0.22 gh/mol.

3.2.6.3 *Effects of Steam*

The autothermal steam reforming reaction was carried out at various oxygen to steam molar ratio (O₂/S ratio = 0.017, 0.027 and 0.055) at 650 °C, The total flow rate of

each S/C ratios were fixed at 170 cm³/min making the contact (W/F) equal to 0.22 gh/mol.

3.2.7 Coke Formation Studies

The coke formation will study by running the reaction. The spent 15%Ni/Ce_{0.75}Zr_{0.25}O₂ catalyst will characterize by Temperature Programmed Oxidation (TPO). For Temperature Programmed Oxidation (TPO), the experimental will carry out at the same condition from characterization of Temperature Programmed Reduction (TPR) but it using 5% mixture of oxygen in helium gas flow instead.