

CHAPTER III

EXPERIMENTAL SECTION

3.1 Materials

The gases used in this research were:

1. Helium (99.999%) was obtained from Thai Industrial Gas Co., Ltd., (TIG), which was used as diluted gas, purged gas, and carrier gas in a gas chromatograph and an elemental analyzer.
2. Oxygen (99.7%) was obtained from Praxair (Thailand) Co., LTD., which was used as a reactant gas.
3. Iso-octane ($C_8H_{18} \geq 99.5\%$) was obtained from Lab-Scan, Analytical Sciences, and used as a reactant.

The chemical reagents used for catalyst preparations were as follows:

1. Cerous (III) nitrate hexahydrate (>99%) was obtained from Fluka Chemie A.G.
2. Zirconyl chloride octahydrate (>99%) was obtained from Fluka Chemie A.G.
3. Urea (>99%) was obtained from Fluka Chemie A.G.
4. Nickel (II) nitrate hexahydrate (>99%) was obtained from Fluka Chemie A.G.
5. α -Alumina (>96%) was provided by Johnson Matthey, Inc..

3.2 Catalyst Preparation

In order to study the effect of Ni amounts and its loading methods, the catalyst was prepared by various Ni (5, 10 and 15% by weight) over $Ce_{0.75}Zr_{0.25}O_2$, and two techniques were employed to prepare the catalysts in this research: sol-gel method and impregnation method. The $Ce_{0.75}Zr_{0.25}O_2$ support catalyst was prepared by urea hydrolysis or sol-gel method.

3.2.1 Preparation of $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$ Support Catalyst

For $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$ catalyst preparation, The salt solutions of zirconium ($\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$) and cerium ($\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$) were dissolved in distilled water to the Ce/Zr concentration with 0.75/0.25 as a molar ratio of Ce/Zr. Then, urea was added to the solution of zirconium and cerium. It should be noticed that $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$ mixed oxide catalyst was prepared by mixing equal volume of each solution of zirconia, ceria and urea together. Urea has to be added for the reaction to take place because during the reaction the zirconia and ceria react with each other and produce H^+ ions, the urea meanwhile decomposes during the reaction and produce OH^- ions which react with the H^+ ions to form water, H_2O . It was important that the amount of urea was always one third of the total volume of the sample, and that it was the last solution to be added to sample, since it was the hydrolysis catalyst.

After the preparation of the solutions, The sample was heated to 100°C in an oven for 120 hours. The sample was cooled to room temperature. In order to remove the all ions from the gel, the catalyst was washed with distilled water for twice and centrifuged at 1600 rpm for 10 minutes. Then, gel was washed with ethanol before drying. Finally, the sample was dried to vaporize the remaining solvent in the gel at 100°C in an oven for over night and heated at 500°C , 4 hours for calcination.

3.2.2 Sol-Gel Technique

This technique was applied to prepare Ni supported on $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$ catalyst. To prepare Ni/ $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$ catalysts, Ni metal was loaded during the gel step. The washed gel was dissolved as just mixed with aqueous solution of nickel (II) nitrate hexahydrate to obtain a desired %Ni loading (5, 10 and 15% by weight on $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$) before the drying and calcination as the same condition as the $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$ preparation step.

3.3.3 Impregnation Technique

When $Ce_{0.75}Zr_{0.25}O_2$ catalyst was passed all above step, Ni metal was loaded on the catalysts. The $Ce_{0.75}Zr_{0.25}O_2$ catalyst was impregnated by aqueous solution of nickel (II) nitrate hexahydrate to obtain a required % Ni loading by weight on $Ce_{0.75}Zr_{0.25}O_2$. Then, the wet catalyst was dried at 100°C for over night and heated at 500°C, 4 hours for calcination again.

3.3 Catalyst Characterization

3.3.1 BET Surface Area

The surface areas of all catalysts were measured by the five-point BET method using a Quantachrome Corporation Autosorb I. Before the measurement, a catalyst sample was outgassed by heating under vacuum to eliminate volatile adsorbents on the surface (523 K, 4 hours). The quantity of gas adsorbed onto or desorbed from a solid surface at 5 equilibrium vapor pressure (P/P_0) values (0.1115, 0.1615, 0.2115, 0.2615 and 0.3115) was measured by the static volumetric method. The data were obtained by admitting or removing a known adsorbate gas, nitrogen, into or out of a sample cell containing the solid adsorbent maintained at a constant temperature below critical temperature of the adsorbate, that is, 77 K for nitrogen.

The adsorption data were calculated using the Brunauer-Emmett-Teller (BET) equation.

$$1/[W((P_0/P)-1)] = 1/[W_m C] + [(C-1)/(W_m C)]*(P/P_0) \quad (3.1)$$

Where W = weight of gas adsorbed at relative pressure P_0 ;

W_m = weight of adsorbate constituting a monolayer of surface coverage;

C = constant related to the energy of adsorption in the first adsorbed layer and magnitude of adsorbate/adsorbent interaction.

The surface area can be obtained from the following equation.

$$\text{Surface area of sample} = W_m A_{\text{nitrogen}} (6.02 \times 10^{23}) / M_{w, \text{nitrogen}} \quad (3.2)$$

Where A_{nitrogen} = Cross-sectional area of one molecule nitrogen
= 0.162 nm² (at 77K);

$M_{w, \text{nitrogen}}$ = molecular weight of nitrogen (28)

3.3.2 X-ray Diffraction Methods

A Rigaku X-ray diffractometer (XRD) system equipped with a RINT 2000 wide angle goniometer and a Cu Tube for generating a CuK α 1 radiation ($\lambda = 1.54 \text{ \AA}$) was used to obtain the X-ray diffraction patterns at a generator voltage of 40 kV and a generator current of 30 mA. Nickel filter was used as the K_{β} filter. The goniometer parameters were divergence slit = 1°(2 θ); scattering slit = 1°(2 θ); and receiving slit = 0.3nm. The catalyst samples were compared on a glass slide; firmly pressed by another glass slide. A scan speed of 5°(2 θ)/min with a scan step of 0.02° (2 θ) was used during a continuous run in the 5 to 90°(2 θ) range.

The Scherrer equation, which relates the mean crystallite diameter and the broadening of the X-ray diffraction lined per the expression, can be written as.

$$d_b = K\lambda / B_d \cos\theta \quad (3.3)$$

where λ = wave length of the monochromatic X-ray diffraction (\AA);

K = Scherrer constant whose value depends on the shape of the particle (assume equal to 1);

B_d = angular width of the peak in the terms of $\Delta(2\theta)$ (radian);

- θ = glancing angle (degree);
 d_b = mean crystallite diameter (\AA°)

3.3.3 Temperature Programmed Reduction (TPR)

Temperature Programmed Reduction (TPR) experiments were carried out with temperature controller (Shinko Model FCD-13A) and mass spectrometer for analyzing gas quantitative (Balzers instrument/thermostar GSD 300T). Firstly, 0.05 g of samples was heated from room temperature to 400 °C in a 5% mixture of carbonmonoxide in helium gas flow at the rate 20ml/min for 1 hour. The samples were cooled down to room temperature. Therefore, TPR profiles were conducted by 50 ml/min of 1% CO/He reduction reaction heated to 900°C at the rate of 10°C/min. The quantity of CO gas was detected and analyzed with MS signal as a function of temperature.

3.3.4 Transmission Electron Microscopy (TEM)

Transmission Electron Microscopy (TEM), JEOL 2010 operating at the accelerating voltage of 200 kV, was used to determine the homogeneity and the coke formation of the various nickel loading on Ce/Zr mixed oxide catalysts. The bright-field images were taken at magnifications between 50K-3000K with an aperture in place. The sample was prepared by sonicating in ethanol for a few minutes followed by deposition a few drops of the resulting suspension on the TEM copper grids and dried in air.

3.4 Experimental Apparatus

The experimental apparatus used in this research is schematically shown in Figure 3.1. It consists of three parts: (i) gas mixing section, (ii) catalytic reactor, and (iii) analytical instrument.

3.4.1 Gas Mixing Section

This section was used for preparing the reactant gases to desired flow rate and concentration before being fed to a reactor. All gases, helium and oxygen, were passed through a 7-micron stainless steel filter to remove the particle in the gases. Aalborg mass flow controllers (Model GFC17) controlled a volumetric flow rate of each gas. Iso-octane was contained in a dressler bottle in which its temperature was maintained at 7.5°C for controlling the vapor pressure of iso-octane at 20 mm Hg. Helium was applied to carry the iso-octane to mix with oxygen in a mixing chamber. Water was injected by a syringe pump to an evaporator for producing steam. The steam, then, was carried by helium to mix with oxygen and iso-octane before entering the catalytic reactor, the total flow rate of the mixed gas was 160 ml/min at 25°C and 1 atm. The concentration of iso-octane was controlled to be less than 1% by volume for safety since this concentration was considered to be fallen off a range of explosion limitation.

3.4.1 Catalyst Reactor

A 10-mm O.D. quartz tube was used as a catalytic reactor. The reactor was loaded with a mixture of 0.0653 g of catalyst and 0.1625g of α -alumina sieved to 180-245 mesh. The reactant gases were fed at the bottom of the reactor. The reactor was heated and controlled by a Shinko temperature controller (Model FCR-13A) using thermocouple type K. The leaving gases from reactor were fed through a condenser to remove the unconverted feed, liquid product and the remaining steam.

3.4.2 Gas Analytical Instrument

The product gases from the condenser were analyzed by a gas chromatograph. Shimadzu (GC 14A) with CTRI column was used for analyzing the product gases. Th sampling gases were injected at 120°C, and the oven temperature

was 70°C. A thermal conductivity detector (TCD) was set at 120°C. The calibration standard gases were CO₂, CO, H₂ and O₂.

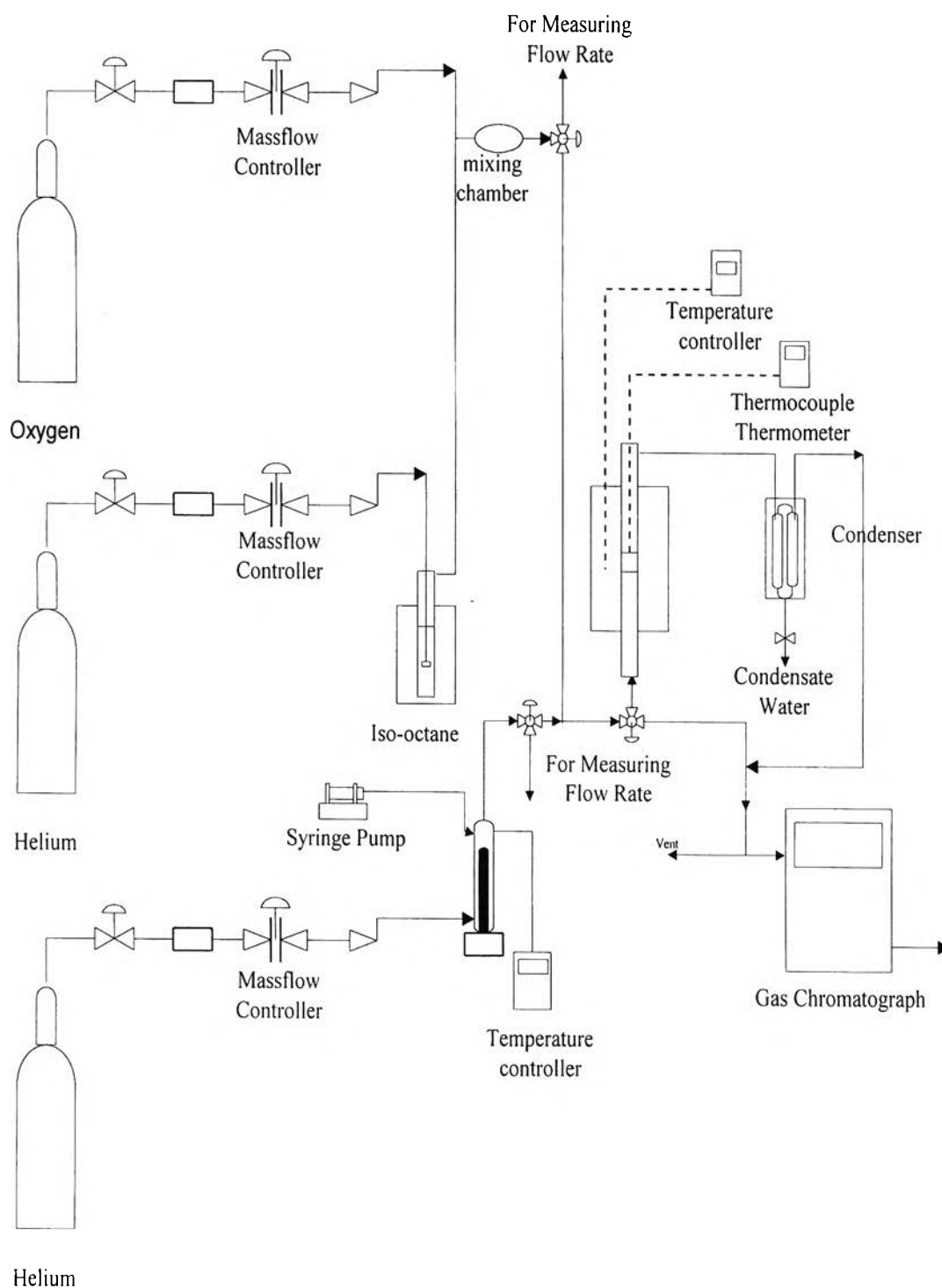


Figure 3.1 Schematic of the experimental apparatus

3.5 Experimental Section

3.5.1 Catalyst Testing

In this work, hydrogen was produced from iso-octane by autothermal system. Therefore, the iso-octane oxidation was investigated in this part to test the catalytic activity of catalyst and find the optimum O₂/C ratio for the autothermal system.

First, the activity of all different Ni loading samples was tested for iso-octane oxidation at O₂/C of 1/1. The catalytic activity was measured as a function of temperature. The temperature corresponding to 50% conversion of iso-octane (T₅₀) or light-off temperature was used as the index to determine the catalytic activity. The furnace temperature was varied from 200-600°C.

The conversion of iso-octane was determined by using the following expression:

$$x = 1/8 [C_{co} + C_{co_2}] \quad (3.4)$$

where x = iso-octane conversion;

C_{co} = CO yield;

C_{co_2} = CO₂ yield.

3.5.2 The Effect of Steam/Carbon Ratio and Temperature

The effect of steam/carbon ratios and temperature on 15%Ni-Ce_{0.75}Zr_{0.25}O₂ of both sol-gel and impregnation methods were examined in this part. The experiment was conducted at constant O₂/C ratio of 1.0. The H₂O/C ratios were varied from 1.5, 2.0, 2.5, and 3.0. The furnace temperature of 450-590°C was investigated. The H₂/CO ratio, the selectivity of CO and conversion of reactant gas were discussed. The selectivity of CO was determined by using the following expression:

$$\text{CO selectivity (\%)} = \text{CO}/(\text{CO}_2 + \text{CO} + \text{H}_2) * 100 \quad (3.5)$$

where CO = mole of CO product;
 CO₂ = mole of CO₂ product;
 H₂ = mole of H₂ product.

3.5.3 The Effect of Oxygen/Carbon Ratio and Temperature

The O₂/C ratios were varied from 0.125, 0.25, 0.50 and 1.0. The effect of temperature was also studied by varying furnace temperatures from 500-650°C. In this part, the experiments were carried at constant H₂O/C = 2/1. The H₂/CO ratio, the selectivity of CO and conversion of reactant gas were investigated.

3.5.4 Coke Formation Study

The coke formation was studied in this work by running the reaction at 600°C, H₂O/C ratio = 2/1 and O₂/C ratio = 1/1 for 10 hours. The activity of 15%Ni/Ce_{0.75}Zr_{0.25}O₂ from both sol-gel and impregnation method was investigated every 1 hours. The spent 15%Ni/Ce_{0.75}Zr_{0.25}O₂ was characterized by Simultaneous Thermal Analyzer (STA), Temperature Programmed Oxidation (TPO) and Transmission Electron Microscopy (TEM). For Temperature Programmed Oxidation (TPO), the experiments were carried out at the same condition from the characterization of Temperature Programmed Reduction (TPR) but it used 5% mixture of oxygen in helium gas flow instead.

$$\text{Activity} = \frac{\text{The iso-octane conversion at specific time}}{\text{The iso-octane conversion at initial time}}$$

3.5.5 Catalyst Bed Temperature Profile

The temperature profiles inside the reactor bed were investigated by measuring the temperature difference, which was defined as the temperature difference between catalyst bed and furnace, at 0, 2, 4 and 6 cm. from the bottom of catalyst bed:

$$\text{Temperature difference} = \text{Bed temperature} - \text{Furnace temperature}$$

The experiments were carried out individually with three concerned reactions: steam reforming, partial oxidation and autothermal system reactions. The temperature profile was studied by running the reaction at 600°C, H₂O/C ratio = 2/1 and O₂/C ratio = 1/1 depend on which reactants were used.