

## CHAPTER III

### EXPERIMENTAL SECTION



#### 3.1 Materials

The gases used in this research were:

1. Helium (He 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.
4. Nitrogen gas (99.74%) was obtained from TIG that was used as a purged gas for aerogel preparation.

The chemical reagents used for catalyst preparation were as follows:

5. Cerous (III) nitrate hexahydrate (>99%) was obtained from Fluka Chemie A.G.
6. Zirconyl chloride octahydrate (>99%) was obtained from Fluka Chemie A.G.
7. Urea (>99%) was obtained from Fluka Chemie A.G.
8. Nickel (II) nitrate hexahydrate (>99%) was obtained from Fluka Chemie A.G.
9.  $\alpha$ -Alumina (>96%) was provided by Johnson Matthey.

## 3.2 Catalyst Preparation

In this study, sol-gel method was used for catalyst preparation.  $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$  and  $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  were dissolved in distilled water to the concentration 0.1M. Then, 50 ml. of urea was added to the previous solution as a hydrolysis catalyst. The sample was heated to  $100^\circ\text{C}$  in the oven for a period of time. After that, the sample was cooled to room temperature. In order to remove the excess ions from 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 remove the solvent from gel.

There are many factors that effect to gel formation during the reaction time such as urea concentration, drying condition, reaction time and etc. In this study, molar ratios of Ce/Zr, urea concentration, reaction time and drying method were investigated.

### 3.2.1 Molar Ratios

The molar ratios of Cerium to Zirconium were varied to determine the optimum ratio that gives the maximum yield of product. The following molar ratios were used to investigate this variable:

Molar Ratios of Ce/Zr: 100:0

75:25

50:50

25:75

0:100

### 3.2.2 Reaction Time

In this work, the samples were initially heated at 100°C in an oven for 50 hours. After several results had been collected for these conditions, the time was changed to 120 hours. The urea concentration was 0.4M.

### 3.2.3 Urea Concentration

For this section,  $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$  was preliminary prepared by hydrolyzing with 0.4M urea with reaction time 120 hours. Then, the urea concentration was swapped from 0.4M to 1M and 2M.

### 3.2.4 Drying Method

In this part,  $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$  was formerly prepared by hydrolyzing with 0.4M urea and the reaction time equal to 120 hours. After that the gel of  $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$  was dried at 100°C in an oven for overnight. The resulting sample is called xerogel.

For an aerogel sample,  $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$  was prepared by hydrolyzing with 0.4M urea and the reaction time equal to 120 hours. Then, the gel was dried under supercritical condition of ethanol ( $P_c=70\text{bar}$ ,  $T_c=243^\circ\text{C}$ ) at 100 bar and 280°C for 30 minutes in Parr Reactor. Finally, the aerogel of  $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$  was dried at 100°C to remove the remaining solvent.

### 3.3 Catalyst Characterization

#### 3.3.1 Determination of BET Surface Area

The surface areas of all catalysts prepared were measured by the five-point BET method using a Quantachrome Corporation Autosorb I. Before measurement, a catalyst sample was outgassed by being heated under vacuum to eliminate volatile adsorbents on the surface (523 K, 4 hours). By measuring the quantity of gas adsorbed onto or desorbed from a solid surface at 5 equilibrium vapor pressure ( $P/P_0$ ) value (0.1115, 0.1615, 0.2115, 0.2615 and 0.3115) 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 that is 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.

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

$$\begin{aligned} \text{Where } A_{\text{nitrogen}} &= \text{Cross-sectional area of one molecule} \\ &\text{nitrogen} \\ &= 0.162 \text{ nm}^2 \text{ (at 77K);} \\ M_{w,\text{nitrogen}} &= \text{molecular weight of nitrogen (28)} \end{aligned}$$

### 3.3.2 Determination of Catalyst Structure

A Rigagu X-ray diffractometer (XRD) system equipped with a RINT 2000 wide angle goniometer and a Cu Tube for generating a CuK  $\alpha$  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  $K_{\beta}$  filter. The goniometer parameters were divergence slit =  $1^{\circ}(2\theta)$ ; scattering slit =  $1^{\circ}(2\theta)$ ; and receiving slit = 0.3nm. The catalyst samples were compared on a glass slide. Firmly pressed by another glass slide. A scan speed of  $5^{\circ}(2\theta)/\text{min}$  with a scan step of  $0.02^{\circ}(2\theta)$  was used during a continuous run in the 5 to  $90^{\circ}(2\theta)$  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  $\lambda$  = wave length of the monochromatic X-ray diffraction ( $\text{A}^\circ$ );  
 $K$  = 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);  
 $\theta$  = glancing angle (degree);  
 $d_b$  = mean crystallite diameter ( $\text{A}^\circ$ )

### 3.3.4 Determination of Functional Groups of Catalysts

FT-Raman spectra were performed on a Perkin Elmer 2000 FT-Raman instrument, which 64 scans at a resolution of  $4 \text{ cm}^{-1}$  were taken, with diode pumped YAG laser and a room temperature super InGaAs detector. The laser power was about 460 mW. The frequency of  $4000\text{-}100 \text{ cm}^{-1}$  was observed.

### 3.3.5 Examination of Catalyst Morphology

Scanning electron micrographs (SEM) were taken on the JEOL5200, magnification: 35-200,000, scanning electron microscope. The SEM provides unique information about the surfaces of materials, which are the catalysts for the present research. All of the catalysts, which had to be characterized by SEM, were heated at about  $100^\circ\text{C}$  for one hour to removed moisture and stored in dessicator before microscopic examinations. The sample was sticked on the stub and coated with gold by ion sputtering device (JFC-1100E) for 4 minutes to prevent specimen charging. The examinations were taken through this microscope with magnification range from 750 to 2,000.

### 3.3.6 Examination of Coke Formation

A thermogravimetric analysis was used to determine coke formation on a catalyst. The catalyst is loaded in pan and heated. The mass of specimen in a controlled atmosphere is recorded continuously as a function of temperature or time as the temperature of the sample is increased linearly with time. A plot of mass percent as a function of temperature is called a thermogram.

A Simultaneous Thermal Analyzer (STA 409) consists of a sensitive analytical balance, a furnace, a purge gas system for providing nitrogen and oxygen gases and a computer for instrument control and data acquisition and display.

Thermograms were obtained using this instrument under nitrogen and oxygen environments by heating to 900°C at a rate of 10°C/min.

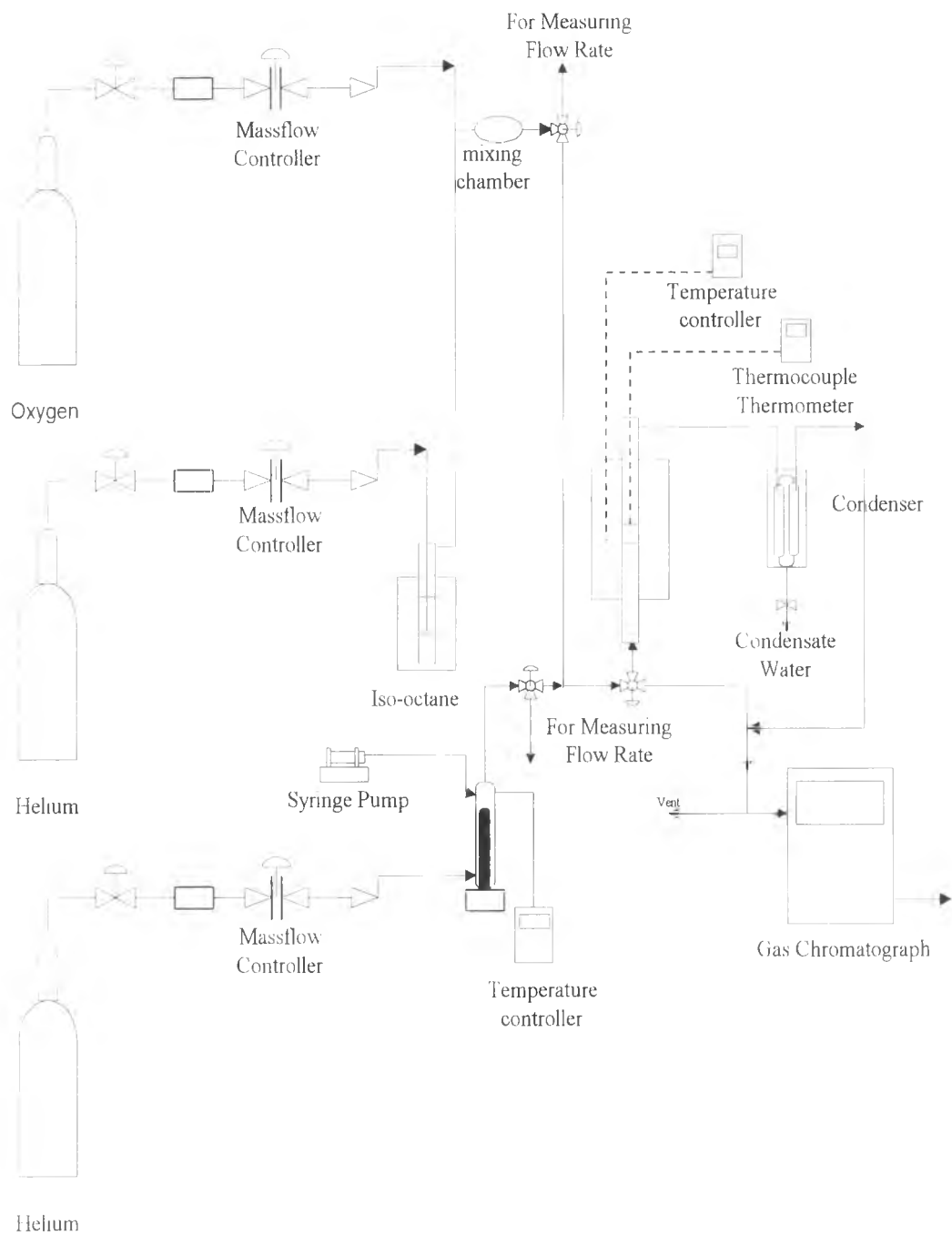
### 3.4 Experimental Apparatus

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. A volumetric flow rate of each gases were controlled by Aalborg mass flow controllers (Model GFC17). Iso-octane was contained in a dresshler bottle in which its temperature was maintained at 7.5°C for controlling the vapor pressure of iso-octane at 20 mmHg. Helium was applied to carry the iso-octane to mix with oxygen at mixing chamber. Water was injected by 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 catalyst reactor, the total flow rate of the mixed gas was 160 ml/min at 25°C, atmosphere pressure. The concentration of iso-octane was controlled to be less than 1% by volume for safety since a concentration was considered to be fallen off a range of explosion limitation.





**Figure 3.1** Schematic of the experimental apparatus

### 3.4.2 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  $\alpha$ -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 condenser to remove the unconverted feed, liquid product and steam.

### 3.4.3 Gas Analytical Instrument

The product gases from the condenser were analyzed by gas chromatographs. Shimadzu (GC 14A) with CTRI column were used for analyzing the product gases. The 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 CO<sub>2</sub>, CO, H<sub>2</sub> and O<sub>2</sub>.

## 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 O<sub>2</sub>/C ratio for the autothermal system.

First, the activity of Ce/Zr mixed oxides with reaction time 120 hours, aerogel of Ce<sub>0.75</sub>Zr<sub>0.25</sub>O<sub>2</sub> and 5%Ni/ Ce<sub>0.75</sub>Zr<sub>0.25</sub>O<sub>2</sub> were tested for iso-octane oxidation at O<sub>2</sub>/C of 1/1. The catalytic activity was measured as a function of temperature. The temperature corresponding to 50% conversion of

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 conversion;

$C_{co_2}$  = CO<sub>2</sub> conversion.

### 3.5.2 The Effect of Steam/Carbon Ratio and Temperature

The effect of steam/carbon ratios and temperature on 5%Ni-Ce<sub>0.75</sub>Zr<sub>0.25</sub>O<sub>2</sub> were examined in this part. The experiment was conducted at constant O<sub>2</sub>/C ratio of 1.0. The H<sub>2</sub>O/C ratios were varied from 1.5, 2.0, 2.5, and 3.0. The furnace temperature of 450-590°C was investigated.

The H<sub>2</sub>/CO ratio, the selectivity of CO and conversion of dry product gases 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;

CO<sub>2</sub> = mole of CO<sub>2</sub> product;

H<sub>2</sub> = mole of H<sub>2</sub> product.

### 3.5.3 The Effect of Oxygen/Carbon Ratio and Temperature

The O<sub>2</sub>/C ratios were varied from 0.125, 0.25, 0.50 and 1.0. The effect of temperature was also studied by varying furnace temperature from 500-650°C. In this part, the experiment was carried at constant H<sub>2</sub>O/C = 2/1. The H<sub>2</sub>/CO ratio, the selectivity of CO and conversion of dry product gases were investigated.

### 3.5.4 Coke Formation Study

The coke formation was studied in this work by running the reaction at 650°C, H<sub>2</sub>O/C ratio = 2/1 and O<sub>2</sub>/C ratio = 1/1 for 100 hours. The activity of 5%Ni/Ce<sub>0.75</sub>Zr<sub>0.25</sub>O<sub>2</sub> was investigated every 5 hours. The spent 5%Ni/Ce<sub>0.75</sub>Zr<sub>0.25</sub>O<sub>2</sub> was characterized by Simultaneous Thermal Analyzer (STA) and Scanning Electron Microscope (SEM).

Activity = The iso-octane conversion at specific time

The iso-octane conversion at initial time