

CHAPTER III METHODOLOGY

3.1 Materials

The gases used in this research were:

1. Helium (He 99.999%) was obtained from Praxair (Thailand) Co.,LTD.
2. Oxygen (O₂ 99.7 %) was obtained from Praxair (Thailand) Co.,LTD.
3. Iso-octane (C₈H₁₈) was obtained from Lab-Scan, Analytical Sciences (≥99.5%).

The chemical reagents used for catalyst preparation were as follows:

1. Nickel (II) nitrate hexahydrate (≥99%) was obtained from Fluka Chemie A.G.
2. Chromium (III) nitrate nonahydrate (99%) was from Aldrich Chemical Company,Inc.
3. Cerous (III) nitrate hexahydrate (≥99%) was from Fluka Chemie A.G.
4. γ -Alumina was from EM Science
5. α -Alumina (>96%) was from Johnson Matthey

3.2 Catalyst Preparation

The catalyst was prepared by co-impregnation method. The support was γ -alumina (125 m²g⁻¹) which was impregnated with aqueous solution of nickel nitrate associated with aqueous solutions of cerium nitrate or chromium nitrate to obtain a 15%Ni5%Ce/Al₂O₃ and 15%Ni5%Cr/Al₂O₃ after

calcination. The mixture was dried at 110°C overnight and subsequently calcined under stagnant air at 750°C for 6 hrs.

3.3 Characterization

3.3.1 BET Surface Area

The surface area of catalyst was measured by the five-point BET method using a Quantachrome Corporation autosorb I. Before measurement, the sample was outgased by being heated under vacuum to eliminate volatile adsorbents on the surface (393 K, 12 hrs). By measuring 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) 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.

$$1/[W((P_0/P)-1)] = 1/[W_m C] + [(C-1)/(W_m C)] * P/P_0 \quad (10)$$

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.

$$\text{Surface area of sample} = W_m A_{\text{nitrogen}} (6.02 \times 10^{23}) / M_{w, \text{nitrogen}} \quad (11)$$

where A_{nitrogen} = Crossed-section area of one molecule nitrogen
 = 0.162 nm² (at 77 K);
 $M_{w, \text{nitrogen}}$ = molecule weight of nitrogen (28).

3.3.2 X-ray Diffraction Methods

X-ray diffraction is based upon the fact that an X-ray diffraction pattern is unique for each crystalline substance. Thus, if an exact match can be found between the patterns of an unknown and an authentic sample. Chemical identity can be assumed. It is also possible to make a relatively quantitative analysis by comparing the intensity of the diffraction lines. Comparing the same crystalline substance of two different samples, the higher intensity shows the higher content.

A Philips X-ray diffractometer system (PW 3020) equipped with a graphite monochromator and a CU tube for generating a CuK radiation (1.5406 Å) was used to obtain the XRD patterns. The sample was ground to a fine homogeneous powder and was held on a thin-walled glass plate against the X-ray beam. Constructive interference can be achieved with monochromatic irradiation by varying the angle of incidence (5 to 8 degrees). The digital outputs of the proportional X-ray detector and the goniometer angle measurements are acquired by an online microcomputer for the storage and subsequent data analysis by PC-APD version 3.5B.

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

$$d_b = K\lambda / B_d \cos \theta \quad (12)$$

where λ is the wave length of the monochromatic X-ray radiation (\AA):

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

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

θ is the glancing angle (degree);

d_b is the mean crystallite diameter (\AA).

3.3.3 Thermogravimetric Analysis

In a thermogravimetric analysis, the mass of a 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 Netzch thermogravimetric analyzer used in this study (TG 209) consists of: (1) a sensitive analytical balance, (2) a furnace, (3) a purge gas system for providing nitrogen and oxygen gases, and (4) a microcomputer 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 $10^\circ\text{C}/\text{min}$.

3.3.4 Temperature-Programmed Reduction

A Micromeritics TPD/TPR 2900 was employed as an analyzer for Temperature-Programmed Reduction. The temperatures of thermal conductivity detector (TCD), valve and loop were maintained at 100°C , 100°C and 75°C , respectively. Hydrogen 5% was selected as a carrier gas with a flow rate of $50 \text{ ml}/\text{min}$. The detector current was set at 55 mA . The furnace

controller was set to increase the furnace temperature up to 900°C at the linear ramp rate of 10°C/min. As the temperature increases, a surface species begins to be reduced and the signal from the thermal conductivity detector is displayed as a function of temperature.

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 utilized for preparing the reactant gases to a desired concentration and flow rate before being flowed to the catalyst reactor. All gases were passed through a 7-micron stainless steel filter for removing the particle in the gas. Sierra mass flow controllers (Model 904C-PE-I1-PM) were used to control a volumetric flow rate of each gas. Helium was used to carry iso-octane from a dresshler bottle in which its temperature was maintained at 7.5°C for controlling the iso-octane vapor pressure of 20 mmHg. Water was pumped by syringe pump to an evaporator for producing steam. The steam was carried by helium to mix with iso-octane and oxygen. The total flow rate of the mixed gas was 260 mL/min at 25 °C , atmospheric pressure. The concentration of iso-octane was controlled to less than 1% by volume for safety since a concentration was considered to be fallen off a range of explosion limitation.

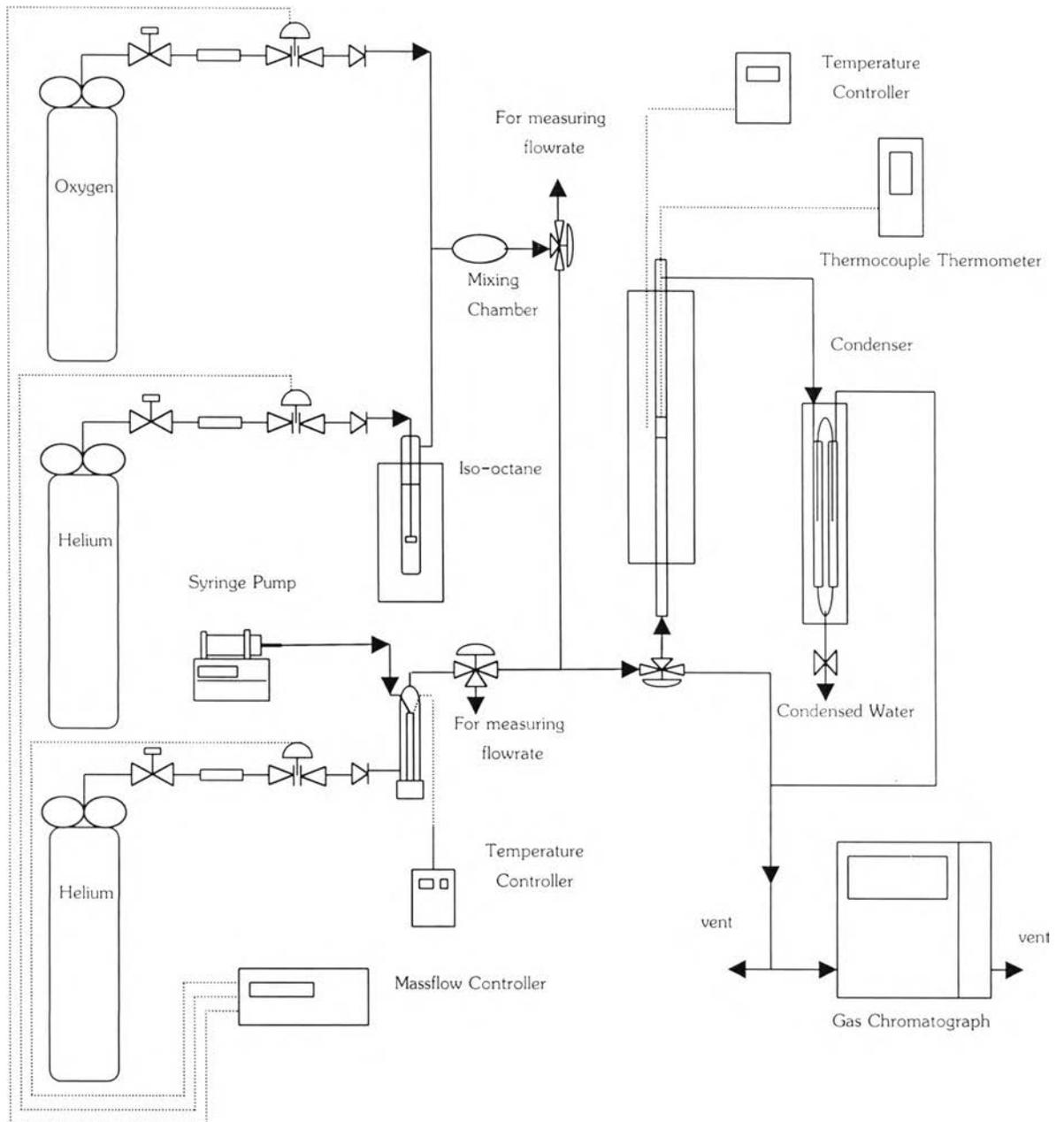


Figure 3.1 Schematic of the Experimental Apparatus

3.4.2 Catalyst Reactor

An 10-mm O.D quartz reactor used as a catalytic reactor was typically loaded with a mixture of 0.285 g catalyst and 0.1715 g α -alumina at which the reactant gases were fed at the bottom. The reactor was electrically heated and controlled by a Yokogawa temperature controller (Model UT 37) using a type-K thermocouple. The gas leaving was fed through condenser. Most of unconverted feed, liquid products, and steam were revered in the condenser.

3.4.3 Gas Analytical Instrument

The product gases from the condenser were analyzed by gas chromatographs. H_2 , CO, and O_2 were analyzed by a Fison (GC 8000) gas chromatograph using a molecular sieve 13 X column. The sampling gases were injected at 160°C , the oven temperature was 31°C . A thermal conductivity detector (TCD) was set at 140°C . For CO_2 , it was analyzed by a Hewlett Packard (HP 5890 series II) gas chromatograph using a Porapak Q column. The injection temperature, oven temperature and detector temperature were operated at 180°C , 55°C and 120°C , respectively.

The calibration standard gases were CO_2 , CO, O_2 and H_2 .

3.5 Experimental Section

This experiment was investigated by using 0.1285 g fresh catalyst diluted with 0.1715 g α -alumina sieved to 180-245 μm for preventing any mass transfer effect. Before the experimental run, the catalyst was pretreated by a helium flow of 250 mL/min at 200°C for 2 hours.

3.5.1 Light Off Temperature

The light off temperature of Ni commercial catalyst, Ni-Cr catalyst, and Ni-Ce catalyst were investigated in this part. The feed composition of iso-octane was 1 %. The temperature was varied from 200-700 °C.

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

$$x = 1/8 [C_{CO} + C_{CO_2}] \quad (13)$$

where x = iso-octane conversion

C_{CO} = CO conversion

C_{CO_2} = CO₂ conversion

The effect of O₂/C ratios on the light off temperature was also investigated by which the plots of conversion and temperature at various O₂/C ratios were accomplished.

3.5.2 The Effect of Steam /Carbon Ratio and Temperature

The effects of steam / carbon ratio and temperature on the Ni-Ce and Ni-Cr catalyst were investigated in this experiment. The experiment was carried at a constant O₂/C ratio of 0.5. The H₂O/C ratios were varied from 1.5, 2.0, 2.5, and 3. The furnace temperature was varied from 450°C –650°C. The steam reforming in the absence of oxygen was also investigated in this part.

The H₂/CO ratio, the selectivity of CO and conversion of dry product gases were considered in this study.

3.5.3 The Effect of Oxygen/Carbon Ratio and Temperature

In this test, the ratios of O_2/C were varied from 0.125, 0.25, 0.5, and 1. The experiment is carried on constant H_2O/C at 2.0 and the temperature was varied from 450 °C-650 °C. The H_2/CO ratio, the selectivity of CO and conversion of dry product gases were investigated.

3.5.4 The Effect of Promoter

The experiments were investigated at constant steam/carbon and oxygen/carbon ratio; 2.0 and 0.5, respectively. The activity of Ni-Ce and Ni-Cr catalysts were studied and compared with the activity of Ni catalyst.

3.5.5 The Effect of Ceria Loading

The effect of ceria loading was investigated with constant metal loading. The test was carried at the constant steam/carbon ratio and oxygen/carbon ratio, which are 2.0 and 0.5, respectively. The temperature was varied from 450°C-650°C. The H_2/CO ratio, the selectivity of CO and conversion of dry product gases were considered in experimental part.

3.5.6 Coke Formation

The coke formation was studied in this study by using TGA and SEM analysis. The reaction carried at 650°C, H_2O/C ratio: 2 and O_2/C ratio: 0.5 for 20 hrs.