

CHAPTER III

EXPERIMENTAL SECTION

3.1 Materials

3.1.1 Catalyst Preparation Materials

Nickel (II) nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) of 98% purity was obtained from Fluka Co., Ltd.

Cerium (III) nitrate hexahydrate ($\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$) of 99% purity was obtained from Aldrich Chemical Co., Ltd.

K-LTL zeolite (HSZ-500, $\text{SiO}_2/\text{Al}_2\text{O}_3 = 6$, surface area = $280 \text{ m}^2/\text{g}$) was obtained from Tosoh (Tokyo, Japan).

Aluminum oxide (Al_2O_3) was obtained from Merck Chemical Co., Ltd.

3.1.2 Gases

Methane of 99.99% purity was used as a reactant gas.

Helium of 99.99% purity was used as diluted gas, purged gas, and carrier gas in a gas chromatograph.

Hydrogen of 99.99% purity was used as reduction gas.

3.2 Catalyst Preparation Procedure

In this study, the catalysts were prepared by incipient wetness impregnation method (IWI). Before adding the metals, the zeolite was dried in an oven at 110°C for 12 hours. Nickel (II) nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) was weighted for a desired amount, then dissolved in deionized water. After that, the support was impregnated by slowly dropping the metal solution. For ceria promoted Ni/KL zeolite catalyst was impregnated by Cerium (III) nitrate hexahydrate ($\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$) and dried before impregnated by Nickel (II) nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$). Next, the wet catalyst was dried at room temperature for 2 hours

before drying in an oven at 110°C for 24 hours and calcined in air at 700°C for 4 hours. The resulting catalyst was labelled and stored in a desiccator.

3.3 Catalyst Characterization

3.3.1 Surface Area Measurement

Autosorb-1 Gas Sorption System was used to measure the BET surface area, total pore volume and average pore diameter of the catalysts. The measurement was based on Brunauer-Emmet-Teller (BET) equation. This technique was done by calculating the physical multi-layer adsorption of N₂. A sample was outgassed by heating under vacuum to eliminate volatile adsorbents in the surface at 250°C for at least 4 hours prior to the analysis. N₂ gas with cross-sectional area of $16.2 \times 10^{-20} \text{ m}^2$ per molecule was adsorbed on to the catalyst surface at liquid N₂ temperature (-196°C). The surface area was calculated from the 22 points nitrogen adsorption. The average pore diameter and pore volume were obtained at P/P₀ ratios close to unity.

3.3.2 X-Ray Diffraction (XRD)

X-Ray Diffraction patterns were determined by Rigaku X-Ray diffractometer system (RINT-2200) equipped with graphite monochromator and a Cu tube for generation a CuK_α radiation (1.5406 Å) was used to obtain the XRD patterns at a generator voltage of 40 kV and generator current of 30 mA. X-Ray Diffraction is a qualitative and quantitative analysis of crystallographic phase form of the catalysts. The qualitative analysis is based on the fact that the X-Ray Diffraction pattern is unique for each crystallite phase. If the observed diffraction pattern of the samples can be matched to that of the reference substance, they are the same crystallite phase. For the individual substance which has the same diffraction pattern, the intensity of crystallite indicates its content. For the same crystalline substance, the higher intensity shows higher content of that phase.

3.3.3 Temperature Programmed Reduction (TPR)

Temperature Programmed Reduction (TPR) was conducted using a Thermo Finigan TPDRO 1100. A measurement was carried out by placing a sample in a quartz reactor. The sample was subjected to TPR analysis using 5% H₂ in N₂, 30 ml/min. The reduction temperature was raised from 40 to 900°C at a ramp rate of 10°C/min. A thermal conductivity detector was used to monitor the difference of hydrogen content before and after the reduction. The temperature, at which the reduction was completed, could be determined from TPR pattern.

3.3.4 Temperature Programmed Oxidation (TPO)

Temperature Programmed Oxidation (TPO) was used to evaluate amount of carbon formation on spent catalysts. The 30 mg of spent catalyst was placed in quartz tube reactor. The spent catalyst was conducted to TPO analysis using 2%O₂ in He for 30 min before the temperature was linearly increased at a ramp rate of 12°C/min. Carbon formation was oxidized into carbon dioxide then convert to methane in the methanator. FID SRI model 110 was used to detect the effluent gas from methanator. The result from measurement can be used to determine amount of deposited carbon.

3.4 **Experimental Apparatus**

The experimental apparatus used in this research is schematically shown in Figure 3.1. It consists of three parts: (1) gas mixing section, (2) catalytic reactor, and (3) analytical instrument.

3.4.1 Gas Mixing Section

The gas mixing section was utilized to prepare reactant gases to a desired concentration and flow rate before being introduced into the catalytic reactor. Methane and steam were used as reactant gases. Helium was used as the diluent gas for the reaction and used as the purge gas for the catalyst reduction, in which hydrogen was used as the reduction gas. At first, each gas was passed through a

7-micron stainless steel filter to remove small contaminants from the gases. Water was injected by syringe pump to a steam generator for producing steam. The steam, then, was carried by helium to mix with methane before entering the catalytic reactor. In order to control a volumetric flow rate, mass flow controller (840 Sierra Instruments Model) was used for each gas. Check valves were installed to prevent deterioration of the mass flow controller from back pressure. A gas mixing chamber was used to promote the complete blending of the reactant gases before proceeding through the reactor. The total flow rate of the mixed gas was 120 ml/min at 25°C and 1 atm.

3.4.2 Catalytic Reactor

The steam reforming of methane was employed in a vertical quartz tube reactor with an outside diameter of 10 mm. The catalyst (0.2 g) was packed between quartz wool plugs in the reactor. The reactor was installed and electrically heated in the furnace. The temperature of catalyst bed was monitored and controlled by PID temperature controller equipped with a chromel-alumel thermocouple (Type K).

3.4.3 Analytical Instrument

The product gases from the reactor were analyzed qualitatively and quantitatively by a Hewlett Packard 5890 series II gas chromatograph equipped with a thermal conductivity detector (TCD). The column utilized in the chromatograph was carbosphere, 80/100 mesh, 10 ft x 1/8 inch stainless steel packed column. The GC conditions used in this research were summarized as follows:

Injection Temperature:	110°C
Oven Temperature:	110°C
Detector Temperature:	175°C
Carrier Gas:	He (99.99% purity)

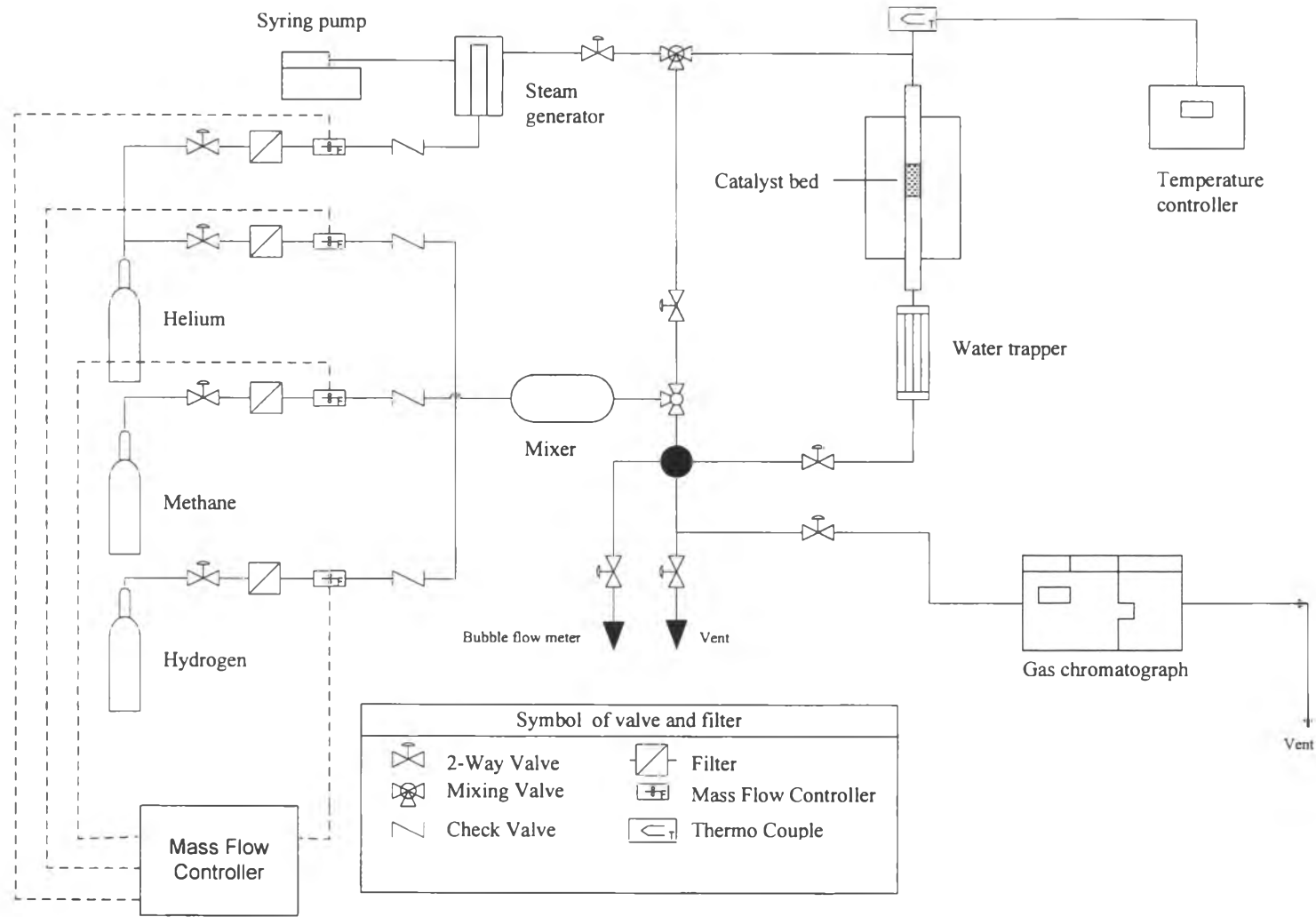


Figure 3.1 Schematic of experimental apparatus.

3.5 Experimental Procedure

Steam reforming of methane reaction was carried out in the fixed bed reactor under atmospheric pressure. After the catalyst was packed in the reactor, it was reduced in pure H₂ flow of 30 ml/min at 700°C for one hour. Then, it was flushed with He for 30 min at the reaction temperature. The concentration of reactant gases were measured by using a by-pass line to a gas chromatograph to meet the desired concentration before feeding the reactant gases to the reactor.

3.5.1 Effect of Nickel Loading

The effects of nickel loading (3, 5, 7, 10 and 10wt%Ni on the KL zeolite catalysts) were investigated. The experiment was conducted at constant H₂O/CH₄ ratio of 3. The temperature of 700°C was investigated. The CH₄ conversion H₂ yield, H₂ selectivity and CO selectivity were calculated to determine the optimum loading for studying in next part.

3.5.2 Effect of Ceria Content

The 7%Ni/KL zeolite promoted with various ceria contents (1, 3, 5 and 7wt%) were tested on steam reforming of methane. The experiment was conducted at constant H₂O/CH₄ ratio of 3 and the reaction temperature of 700°C. The effect of ceria content on catalytic activity was investigated in this part.

3.5.3 Effect of Steam to Methane Ratio

The effect of steam to methane ratio was investigated on 7%Ni/KL zeolite catalyst. The experiment was conducted at reaction temperature of 700°C and steam to methane ratios of 1, 2 and 3. The catalytic activity of each condition was compared.

3.5.4 Comparison between KL Zeolite Catalyst and Commercial Catalyst

In this part, α -alumina is defined as commercial catalyst support (Lee, 1997), the catalytic activity of nickel supported on KL zeolite catalyst and nickel supported on α -alumina were compared. The experiment was conducted at reaction temperature of 700°C and steam to methane ratios of 1 and 3.

3.5.5 Stability Test

7%Ni/KL zeolite, 7%Ni-3%Ce/KL zeolite and 7%Ni/ α -alumina were tested on steam reforming of methane. The experiment was conducted at constant H₂O/CH₄ ratio of 3 and the reaction temperature of 700°C within 48 hours of reaction time.

3.6 Calculations

The methane conversion, hydrogen yield, hydrogen selectivity and carbon monoxide selectivity were calculated by Equations 3.1 - 3.4, respectively.

$$X = \frac{CH_4(\text{in}) - CH_4(\text{out})}{CH_4(\text{in})} \times 100\% \quad (3.1)$$

where X = CH₄ conversion (%)
 CH₄(in) = mole of initial CH₄
 CH₄(out) = mole of residual CH₄

$$Y_{H_2} = X * S_{H_2} \quad (3.2)$$

where Y_{H₂} = H₂ yield (%)
 X = CH₄ conversion (%)
 S_{H₂} = H₂ selectivity (%)

$$S_{H_2} = \frac{H_2}{H_2 + CO + CO_2} \times 100\% \quad (3.3)$$

where S_{H_2} = H_2 selectivity (%)
 H_2 = mole of H_2 product
 CO = mole of CO product
 CO_2 = mole of CO_2 product

$$S_{CO} = \frac{CO}{H_2 + CO + CO_2} \times 100\% \quad (3.4)$$

where S_{CO} = CO selectivity (%)
 CO = mole of CO product
 H_2 = mole of H_2 product
 CO_2 = mole of CO_2 product