

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 99% purity was obtained from Fluka Co., Ltd.
- Aluminum isopropoxide ($\text{Al}(\text{OC}_3\text{H}_7)_3$) of 98% purity was obtained from Fluka Co., Ltd.
- 1,3 Butanediol anhydrous ($\text{C}_2\text{H}_4(\text{OH})\text{C}_2\text{H}_4\text{OH}$) of 99% purity was obtained from Aldrich Chemical Co., Ltd.
- Aluminum oxide (Al_2O_3), neutral, was obtained from Merck Chemical Co., Ltd.

3.1.2 Gases

All gases obtained from Thai Industrial Gas Public Co., Ltd. were as follows:

- Methane of 99.99% purity was used as a reactant gas.
- Carbon dioxide of 99.999% purity was used as a reactant gas.
- Helium of 99.99% purity was used as the carrier gas of gas chromatograph.
- Hydrogen of 99.999% purity was used for catalyst reduction.
- Zero-graded air was diluted with He and used for catalyst regeneration.
- Nitrogen of 99.99% purity was used for driving the auto-sampling valve.



3.2 Catalyst Preparation

3.2.1 Sol-Gel Technique

This technique is applied to prepare Ni supported on alumina catalyst and alumina support. To prepare Ni/Al₂O₃ catalyst, aluminum isopropoxide (AIP) powder was dissolved in excess amount of hot water at 85 °C with vigorous stirring. The hydrolysis was assisted by the addition of small amount of nitric acid resulting in the formation of fibrillar aluminum hydroxide sols, which is a clear solution. After that, it was mixed with the solution of Ni(NO₃)₂·6H₂O dissolved in 1,3 butanediol, which was slowly dropped from a burette. The temperature was kept at 85 °C for 1 hour. Then the heater was turned off, but the solution was further stirred vigorously for 24 hours. The gel formed during stirring time and it was then dried at 110 °C for 24 hours to remove the solvent. Finally, it was ground and calcined in air at 500 °C for 5 hours. The alumina support can be prepared in the same way as the catalyst preparation, but the steps involving the dissolution of Ni(NO₃)₂·6H₂O in butanediol are omitted.

3.2.2 Impregnation Technique

The commercial or sol-gel alumina support was impregnated by a specific amount of Ni(NO₃)₂·6H₂O, dissolved in distilled water, to obtain a desired %Ni loading. Then it was dried at 110 °C for 24 hours and calcined in air at 500 °C for 5 hours.

3.3 Catalyst Characterization

3.3.1 Surface Area Measurement

Brunauer-Emmet-Teller (BET) equation was applied to determine the surface area of the catalysts and supports. This measurement is based on

the physical multi-layer adsorption of the inert gas, carried out by Autosorb-1 Gas Sorption System. The liquid Nitrogen (N_2) at 77 K, which has a cross-sectional area of $16.2 \times 10^{-20} \text{ m}^2$ per molecule, was used as the adsorbate. The samples were out-gassed in the flow of He at 150 °C for 2 hours before the analysis was started. The surface area was calculated from the five-point nitrogen adsorption, and the average radius and average pore volume were calculated at P/P_0 ratios close to unity.

3.3.2 Temperature Programmed Reduction (TPR)

TPR is an experiment in which the reduction is monitored while the temperature increases linearly in time. This experiment provides the temperatures needed for the complete reduction of the catalysts. The reactor, charged with the catalyst, is heated at the rate of 0.1 to 20 °C/min. Normally, a mixture of typically 5% H_2 in Ar, which optimizes the thermal conductivity difference between the reactant and carrier gas, is used to reduce the catalysts in TPR experiments. A thermal conductivity detector measures the hydrogen content of gas mixture before and after reaction. The temperature at the maximum consumption rate of hydrogen is the temperature that the catalysts are reduced.

3.3.3 Temperature Programmed Oxidation (TPO) on Thermogravimetric Analyzer (TGA)

TPO is an experiment in which the sample is oxidized by oxygen while the temperature increases linearly in time. In this study, TPO was equipped with a thermogravimetric analyzer (Du Pont, TGA 2950), which recorded the weight of sample that changed continuously as a function of temperature and time.

3.3.4 X-Ray Diffraction (XRD)

X-ray diffraction technique 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. The higher intensity, the higher content it is. In this study the scan speed of 3 degrees/min and scan step of 0.1 degree were applied for all samples.

3.4 Experimental Apparatus

The experimental apparatus used in this study is schematically shown in Figure 3.1. It consists of 3 parts: (i) gas mixing section, (ii) catalytic reactor, and (iii) gas analytical instrument.

3.4.1 Gas Mixing Section

This section was used for blending gases to a desired concentration and flow rate before it was fed into the catalytic reactor. Methane, carbon dioxide and helium were used as the reactant gases in the experiments. All gases were passed through 7 micron stainless steel filters to remove the small particles which may be containing in the gases. Sierra mass flow controllers (Model 904C-PE-I1-PM) were used to control the flow rates of each gas to attain the exact value of desired concentration.

3.4.2 Catalytic Reactor

Reactant gases were fed in a vertical 8-mm-inside-diameter quartz reactor. The 0.1 g catalyst was packed between quartz wool at the

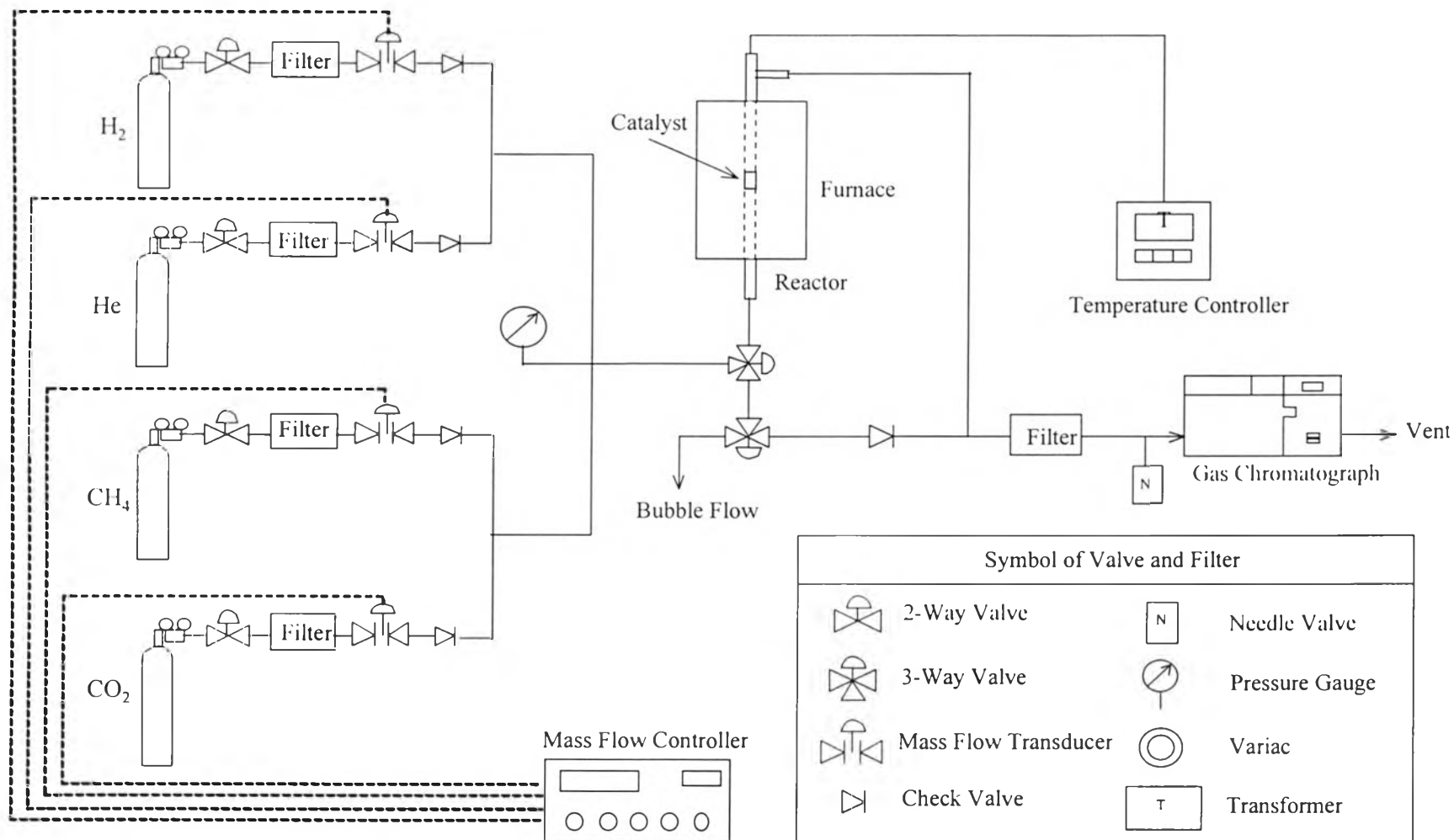


Figure 3.1 Schematic of experimental apparatus.

center of reactor and placed in a tubular furnace equipped with a temperature controller. The temperature controller which connected to a K-type thermocouple was placed into the reactor with one end touching on the catalyst in order to measure the catalyst bed temperature. The variation of temperature was ± 5 °C.

3.4.3 Analytical Instrument

Product gases leaving the reactor were analyzed by a Perkin-Elmer “Autosystem” gas chromatograph (GC). Two packed columns were used for the separation of sample: HayeSep DB for analysis of H₂, CO, CH₄, CO₂, and C₂H₆ with a thermal conductivity detector (TCD), HayeSep T for analysis of CH₃OH with a flame ionization detector (FID). A 10-port valve was used for injection of the sample into the packed columns simultaneously.

Each cycle of GC analysis required about 15 minutes to complete before the next injection can start. The GC conditions used in this research were summarized as follows:

| | |
|------------------------|-------------|
| Injector Temperature: | 110 °C |
| Oven Temperature: | 120 °C |
| Detector Temperature: | 160 °C |
| Carrier Gas: | He (99.99%) |
| Carrier Gas Flow Rate: | 28 ml/min |

3.5 Experimental Procedures

At first, the TPR experiment must be carried out to find the reduction temperature for the catalysts. After packed in the reactor, the catalyst was pretreated in He at 500 °C for 1 hour and reduced in pure H₂ at the suitable temperature for 4 hours. Then flushed with He for 1 hour at the reaction temperature. The 30% of methane and carbon dioxide balanced in He with a

total flow rate of 200 ml/min was used as feed in all of the experiments. The concentrations of reactant gases were checked by using a by-pass line to a GC to meet the desired concentration before feeding the reactant gases to the reactor.

3.5.1 The Effect of Calcination Temperature

The 5% Ni on alumina, prepared by sol-gel technique, calcined in air at 500 and 600 °C and reduced at 785 and 810 °C respectively for 4 hours were tested at 700 °C. The methane and carbon dioxide conversions of each catalyst were compared.

3.5.2 The Effect of Reduction Time

The 5% Ni on alumina, prepared by sol-gel technique, calcined at 500 °C in air, and reduced at 785 °C for 3, 4, 5 hours were tested at 700 °C. The methane and carbon dioxide conversions of each catalyst were compared.

3.5.3 The Effect of Reaction Temperature

The 5% Ni on alumina, prepared by sol-gel technique, calcined at 500 °C in air, and reduced at 785 °C for 4 hours were tested at 600, 650, 700 and 750 °C. The methane and carbon dioxide conversions of each catalyst were compared.

3.5.4 Activation Energy

Three of 5% Ni supported on Al₂O₃ catalysts, prepared by sol-gel technique and by impregnation technique on commercial alumina and on sol-gel alumina, were tested at 600, 650, 700 and 750 °C. The activation energy is calculated by the slope obtained from the plot of logarithm of reaction rate versus the reciprocal of temperature (1/T). The activation energy is equal to the slope multiply by -R, where R is gas constant.

3.5.5 Carbon Deposition Studies

Temperature programmed oxidation (TPO) of carbon species formed on the catalyst were conducted on a thermogravimetric analyzer (Du Pont TGA 2950) in 5% oxygen with a total flow rate of 100 ml/min. The temperature was first raised to 150 °C and kept for 30 minutes and then raised to 800 °C with a heating rate of 10 °C per minute. At high enough temperature, carbon will be oxidized resulting in the decrease of catalyst weight. The decreased catalyst weight was recorded continuously as a function of temperature and time by TGA. The amount of carbon is total catalyst weight loss and the temperature that carbon was oxidized is the temperature at the maximum catalyst-weight loss rate.