

CHAPTER III EXPERIMENTAL

3.1 Materials

3.1.1 Chemicals:

- Nickel nitrate hexahydrate, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ of 98% purity obtained from Fulka Co., Ltd.
- KL zeolite (HSZ-500 series) was obtained from TSHO Company as the catalyst support.
- Calcium nitrate penta-hydrate, $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ 99.5% purity obtained from Ajax as the catalyst promoter.
- Magnesium nitrate hexa-hydrate, $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ 99.4% purity obtained from BDH as the catalyst promoter.
- Potassium hydroxide pellet, KOH, 85% purity obtained from Lab scan Co., Ltd. as the hydrolytic agent for KH zeolite synthesis.
- Ludox HS-40 colloidal silica, 40 wt% suspension in water obtained from Sigma-Aldrich as the precursor for KH zeolite synthesis.
- Aluminium Isopropoxide, 98% purity obtained from Acros organics as precursor for KH zeolite synthesis.

3.1.2 Gases:

- Methane of 99.99% purity supplied from Thai Industrial Gas Public Co., Ltd. was used as a reactant gas.
- Carbon dioxide 20% purity in Helium supplied from Praxair (Thailand) Co., Ltd. was used as a reactant gas.
- Helium of 99.99% purity supplied from Thai Industrial Gas Public Co., Ltd. was used as a balance gas and carrier gas in a gas chromatograph.
- Hydrogen of 99.99% purity supplied from Thai Industrial Gas Public Co., Ltd. was used as a reduction gas.
- Nitrogen of 99.99% purity supplied from Thai Industrial Gas Public Co., Ltd. was used as driving the auto-sampling valve.

3.2 Experiment

3.2.1 Catalyst Preparation

In this work, the catalysts were prepared by using incipient wetness impregnation technique. Supported Ni catalysts with various Ni loadings were prepared by impregnating the appropriate amount of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ onto supports followed by dried overnight at 110°C and calcined at 500°C for 5 hours in air. For the catalysts modified with Ca and Mg, the aqueous solution of $\text{Mg}(\text{NO}_3)_2 \cdot 8\text{H}_2\text{O}$ or $\text{Ca}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were added to zeolite first followed by dried at 110°C overnight and calcined at 500°C for 5 hours. After that the modified support were impregnated by aqueous solution of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. The impregnated catalysts were dried at 110°C overnight and then calcined in air at 500°C for 5 hours.

3.2.2 Synthesis of KH Zeolite

KH-zeolite was prepared by the sol-gel process using colloidal silica (Ludox HS-40) and Aluminium Isopropoxide as a precursors and KOH as the hydrolytic agent. The colloidal silica was mixed with KOH solution at room temperature after that the Aluminium Isopropoxide was added. Gel formation was studied at a ratio of $\text{SiO}_2 : 0.1\text{Al}_2\text{O}_3 : 4\text{K}_2\text{O} : 410\text{H}_2\text{O}$. This mixture was dissolved while being stirred and aged for 50 hours. After homogenization, the gel was transferred into a Teflon lined vessel sealed with a Teflon cap contained in a microwave oven. Temperature measurement was conducted by inserting a fiber optic temperature probe inside the vessel. The mixture was heated at 150°C for 5 hours. The obtained white precipitate was washed with distilled water about 4 times until its pH equals 7 and finally dried overnight at 110°C . The dried solid product was analyzed by X-ray diffraction.

3.3 Activity Measurement and Characterization

3.3.1 Activity Measurement

Catalytic reaction experiments were conducted in a stainless steel reactor (10 mm. i.d.). 0.2 g catalyst was placed between quartz wool layer. A

thermocouple was placed in the tube with one end touching on the catalyst in order to measure the temperature. A ceramic ball was used to support the catalyst for prevent the catalyst fall from gas flow. Figure 3.1 shows the layout of catalyst packing in the reactor. The stream of reactions of CH_4 and CO_2 at a molar ratio of 1:1 and using He as the diluent gas were fed into the reactor at the total flow rate of 100 ml/min. The analysis of gases was carried out using an on-line Hewlett Packard 5890 series II gas chromatograph with a thermal conductivity detector. Prior to each reaction run the catalyst was reduced at 600°C in 30 ml/min of H_2 flow for 1 hour. The activity tests were carried out at 700°C for 5 hours.

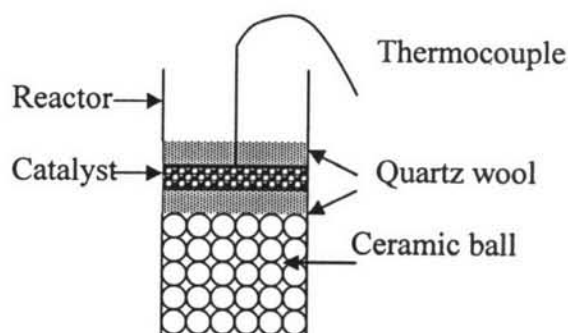


Figure 3.1 The catalyst packing in the reactor.

3.3.2 Characterizations

3.3.2.1 *Inductively Coupled Plasma (ICP)*

Elemental analyses were performed by a Perkin-Elmer Optima 4300 DV inductively coupled plasma – optical emission spectrometer (ICP-OES) that used to measure the actual amount of metal in the prepared catalyst. The concentrations of standard solutions were 2, 5, and 10 ppm. The actual concentrations of the sample were determined base on the radiation intensity. The radiation emitted can be passed to the spectrometer optic, where it is dispersed into its spectral components. The specific wavelengths are emitted by each element. The radiation intensity, which is proportional to the concentration of the element in the sample, is recalculated internally from a stored set of calibration curves and can be shown directly as percent or measured concentration.

3.3.2.2 *H₂ Pulse Chemisorption*

H₂ pulse chemisorption was carried out by using Temperature Program Desorption Reduction Oxidation (TPDRO/MS 1100). About 200 mg. of catalyst was placed in a quartz reactor. Prior H₂ pulse chemisorption, the catalyst was reduced in 5%H₂/N₂ at 600°C for one hour. Then, the system was purged and cooled to 50°C in flowing N₂. H₂ pulse chemisorption was performed at 50°C using H₂ 99.99% purity and repeated at 5 min intervals for 10 times. The Ni dispersion was calculated by assuming the adsorption stoichiometry of one hydrogen atom per nickel surface atom (H/Ni = 1).

3.3.2.3 *X-ray Diffraction (XRD)*

X-ray power diffraction (XRD) patterns were used to identify the crystalline phases of supported Ni catalysts before and after reaction. The X-ray diffraction patterns of the catalysts were obtained by using a Rigaku CuK_α radiation at 40 kV and 25 mA with the wavelength of 1.5406 angstrom. The CuK_α radiation was employed covering 2θ between 5° and 90° with a scan speed of 5°/min and a scan step of 0.02°. The samples were finely ground and then placed on the glass slide. The signal was sent to an on-line computer to record and analyze. The mean metal crystallite diameter was estimated by XRD line broadening using the Scherrer equation.

3.3.2.4 *Thermogravimetric Analysis (TGA)*

The amount of coke formation on the catalysts after deactivation tests at 700°C for 5 hours were examined by a Du Pont TGA 2950 Thermogravimetric Analyzer. The samples were placed in the Pt pan. The weight loss from the combustion of the deposited carbon was examined with heating rate of 10°C/min from room temperature to 800°C under air flow. The purge gas was used to prevent back diffusion of the evolved gases from the operation. Heating rate and sample temperature are measured by the thermocouple located above the sample.

3.3.2.5 *Temperature Programmed Oxidation (TPO)*

Temperature programmed oxidation (TPO) of carbon deposits was carried out in quartz reactor. The TPO experiments were used to determine the amounts and locations of carbon that were deposited under reaction

condition. In other word, carbons with different morphology or different locations are burnt at different temperatures. About 30 mg of catalysts were loaded into the reactor and thermocouple was placed near the catalyst layer. The samples were heated up to 800°C at rate of 12°C/min in 2%O₂/He mixiure (26.3 ml/min). Carbon formation was oxidized into CO₂ then convert to CH₄ in the methanator. FID SRI model 110 was used to detect the effluent gas from methanator.