CHAPTER III
METHODOLOGY

3.1 Materials

3.1.1 Chemicals

- Ethylene Glycol (Analytical grade) obtained from (Carlo Erba)
- Sodium hydroxide (NaOH) (Analytical grade) (Labscan)
- Nickel nitrate hexahydrate (Ni(NO$_3$)$_2$ 6H$_2$O) (Sigma-Aldrich)
- Commercial NH$_4$ZSM-5 zeolite (SiO$_2$/Al$_2$O$_3$ molar ratio of 50) obtained from Zeolyst, USA.

3.1.2 Gases

- CH$_4$ (99.99% Purity) obtained from BOC Scientific Gas Company Limited.
- N$_2$ (99.99% Purity) obtained from Praxair (Thailand) Company Limited.
- H$_2$ (99.99% Purity) obtained from Praxair (Thailand) Company Limited.
- He (99.999% Purity) obtained from Praxair (Thailand) Company Limited.
- Air Zero (99.99% Purity) obtained from Praxair (Thailand) Company Limited.

3.2 Equipment

- Fixed-bed continuous flow system
- Temperature controller equipped with a K-type thermocouple
- Gas chromatograph (Agilent Technologies model 6890) with a flame ionization detector with HP-5 Innowax and HP-Plot/Al$_2$O$_3$ column for detecting the hydrocarbon products
- X-Ray Diffractometer (Rigaku model DMAX 2200 HV)

- Surface Area Analyzer (Quantachrome/autosorb 1 MP)
- Scanning Electron Microscope (Hitachi model teeletop microscope TM3000)
- Thermo Finnigan TPD/R/O 1100 equiped with flame ionization detector
- X-ray fluorescence spectroscope (XRF, Bruker SRS 3400)

3.3 Methodology

3.3.1 Preparation of Ni/HZSM-5 Catalysts

Commercial NH_4ZSM-5 zeolites (SiO_2/Al_2O_3 molar ratio of 50) were calcined at 550 °C at a heating rate of 10 °C/min for 3 h to obtain the HZSM-5 catalysts. Part of HZSM-5 was treated with 2 wt% hydrofluoric acid (HF). Then treated HZSM-5 catalyst was dried at 110°C overnight and calcined in air at 500°C for 3 h to obtain HZSM-5 (HF). For preparation of Ni/HZSM-5 or Ni/HZSM-5 (HF) catalysts, HZSM-5 and HZSM-5 (HF) zeolite were incorporated with Ni by polyol mediate process. Ni nanoparticles were prepared by the dissolvation of $Ni(NO_3)_2 \cdot 6H_2O$ into ethylene glycol by varying the percentage of Ni loading at 1, and 3wt % then 1 M NaOH was added and stirred at room temperature for 30 minutes. Following Ni nanoparticle preparation, about 2 g of HZSM-5 zeolite was added in the resultant solution and further stirred overnight. The mixture was placed to reflux at 160 °C for 3 h and a solid was washed several times with excess distillated water and acetone followed by centrifuging at 10,000 rpm for 6 min to collect the solid particles. After that the catalyst was dried at 160 °C overnight followed by calcination in air at 550 °C for 3 h at a heating rate of 10 °C/min. (Sarkar *et al.*, 2012 and Aboul-Gheit *et al.*, 2014)

3.3.2 Catalyst Characterization

3.3.2.1 X-ray Fluorescence Spectoscopy (XRF)

The Ni content (wt%) on HZSM-5 was determined by X-ray fluorescence method (XRF) using a PANalytical analysis instrument with AXIOS&SUPERQ version 4.0 systems. IQ+ program was used to measure and

analyze the samples. In the analysis procedure, course scans were initially searched for peaks. The found peaks were identified and analyzed quantitatively using fundamental parameters.

3.3.2.2 X-ray Powder Diffraction (XRD)

X-ray powder diffraction (XRD) technique was use to characterize the structure of the catalyst was characterized using a Rigaku Dmax X-ray diffractometer, RINT-2200 with Cu tube for generating CuKα radiation (1.5418 Å). The system consists of a voltage generator of Z0 kV. The 2θ is in the range between 10 and 70 with a scanning rate of 5°C/min. The unique of XRD chromatogram was used to identify or confirm the structure of unknown crystalline materials.

3.3.2.4 Temperature Programmed Desorption of Isopropylamine (IPA-TPD)

The acid properties of catalysts were characterized by temperature program desorption of isopropylamine (TPD-IPA). To clean the surface of catalyst, 100 mg of catalyst was placed in a quartz tube and heated with rate of 10 °C/min under H_2 flow with the flow rate of 10 ml/min up to 500°C for 1 h. After reduction, the reactor was cooled to 30 °C, then isopropylamine was injected over the sample, after that He was purged with the flow rate of 10 ml/min for 20 min to eliminate non adsorbed isopropylamine, the sample was heated with the flow rate of 10 °C/min to 800 °C under the He atmosphere, m/e 44, 41, and 17 were monitored to determine the evolution of isopropylamine, propylene, ammonia.

3.3.2.5 Temperature Programmed Reduction of Hydrogen (H_2-TPR)

Before reduction, about 50 mg catalyst sample was pretreated at 700 °C for 1 h in nitrogen and then cooled to room temperature. Then it will be analyzed by using 5% H_2/Ar mixture at a flow rate of 30 ml/min and by heating the sample from room temperature to 800 °C at a heating rate of 10 °C/min.

3.3.2.6 Surface Area Analysis

This analyze is used to measure surface area and pore volume of Ni/HZSM-5 and Ni/HZSM-5 (HF) catalysts by N_2 physisorption using a Quantachrome, Autosorb-1MP. Catalyst samples were outgassed at 300 °C at least 12 h in nitrogen before analysis.

3.3.2.7 *Scanning Electron Microscopy (SEM)*

The morphology and crystal size were characterized by using a scanning electron microscope (TM3000). The catalyst sample was placed on stub and coated by platinum in sputtering device, after that the sample was placed in the sample holder in SEM.

3.3.3 Catalytic Activity Testing

Catalytic activity testing was investigated at temperatures ranging from 700 °C to 800 °C, GHSV of 1500 ml/g/h, and methane concentration of 20% methane balanced in nitrogen or pure methane, using a continuous down flow fixed-bed reactor. The reactor is made of quartz with I.D. 6 mm. About 0.2 g catalyst sample having particle size of 60-80 mesh was placed into the reactor and supported with thin layers of quartz wool. Before the reaction, the catalyst was activated at 500 °C for 2 h under flowing hydrogen of 60 ml/min. The reaction was carried out for 3 h on stream. The product was analyzed using a gas chromatograph (GC 6890) equipped with an FID connected to a capillary HP Innowax and a HP-Plot/Al$_2$O$_3$ columns. A schematic diagram of the experimental system is shown in Figure 3.1.

The methane conversion, ethylene and propylene selectivities, and ethylene and propylene yield are defined as follows:

$$\text{Methane conversion (\%)} = \frac{\text{(Moles of methane fed - moles of methane out)}}{\text{Moles of methane fed}} \times 100 \quad (3.1)$$

$$\text{Ethylene selectivity (mol\%)} = \frac{\text{moles of ethylene produced}}{\text{moles of all gasnouse products produced}} \times 100 \quad (3.2)$$

$$\text{Propylene selectivity (mol\%)} = \frac{\text{moles of propylene produced}}{\text{moles of all gasnouse products produced}} \times 100 \quad (3.3)$$

$$\text{Ethylene yield (mol\%)} = (\text{CH}_4 \text{ conversion} \times \text{ethylene selectivity})/100 \quad (3.4)$$

$$\text{Propylene yield (mol\%)} = (\text{CH}_4 \text{ conversion} \times \text{propylene selectivity})/100 \quad (3.5)$$
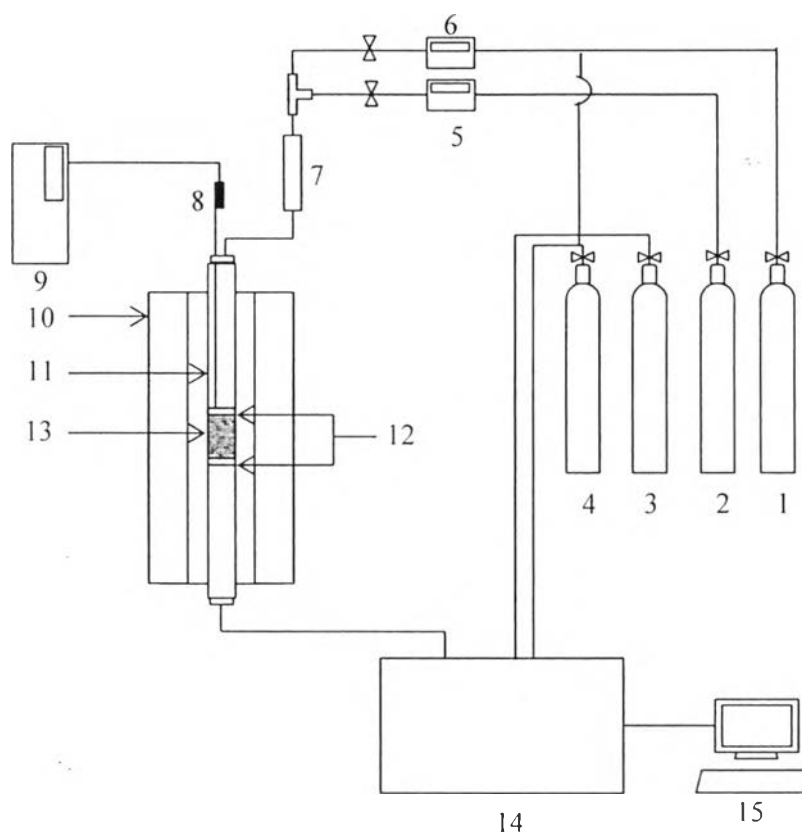
Figure 3.1 Schematic of the experimental system: (1) N_2 (2) CH_4, (3) Air zero, (4) H_2 (5) Mass flow controller for CH_4 (6) Mass flow controller for N_2 or H_2 (7) Gas mixer, (8) K-type Thermocouple, (9) Temperature controller. (10) Furnace, (11) Quartz tube reactor, (12) Quartz wool, (13) Catalyst bed, (14) Gas Chromatograph. (15) Data acquisition system.