CHAPTER III
METHODOLOGY

3.1 Materials

3.1.1 Chemicals

- Ethylene Glycol (AR grade) obtained from Carlo Erba.
- Sodium hydroxide (NaOH) (AR grade) obtained from Labscan.
- Nickel nitrate hexahydrate ($Ni(NO_3)_2 \cdot 6H_2O$) (AR grade) obtained from Sigma-Aldrich.
- Ammonium heptamolybdate tetrahydrate (($NH_4)_6Mo_7O_{24}.4H_2O$) (AR grade) obtained from Labscan
- Commercially available NH_4ZSM-5 zeolite (SiO_2/Al_2O_3 molar ratio of 50) obtained from Zeolyst, USA.

3.1.2 Gases

- CH_4 (99.99 % Purity) obtained from Labgaz (Thailand) Co., Ltd.
- N_2 (99.99 % Purity) obtained from Praxair (Thailand) Co., Ltd.
- H_2 (99.99 % Purity) obtained from Praxair (Thailand) Co., Ltd.
- He (99.999 % Purity) obtained from Praxair (Thailand) Co., Ltd.
- Air Zero (99.99 % Purity) obtained from Praxair (Thailand) Co., Ltd.

3.2 Equipments

- Fixed-bed continuous flow system
- Temperature controller equipped with a K-type thermocouple
- Gas chromatograp (Perkin Elmer, ARNEL) with a flame ionization detector with HP-5 Innowax and HP-Plot/Al_2O_3 column for detecting the hydrocarbon products
- X-Ray diffractometer (Rigaku Dmax X-ray diffractometer)
- Surface area analyzer (Quantachrome/autosorb 1 MP)

- Scanning electron microscope (Hitachi S4800)
- Thermo Finnigan TPD/R/O 1100 equiped with flame ionization Detector
- Temperature programmed desorption of isopropylamine (IPA-TPD) equipment with an online MS detector (MKS Cirrus)
- X-ray fluorescence spectroscope (XRF, Bruker SRS 3400)

3.3 Methodology

3.3.1 Preparation of Bimetallic Ni-Mo/HZSM-5 Catalysts

Commercially avaiable NH_4ZSM-5 zeolites (SiO_2/Al_2O_3 molar ratio of 50) was calcined at 550 °C at a heating rate of 10 °C/min for 3 h to obtain an HZSM-5 zeolite. For preparation of bimetallic Ni-Mo/HZSM-5 catalysts, The HZSM-5 zeolite was incorporated with Ni and Mo by polyol mediated process. Nickel nitrate hexahydrate ($Ni(NO_3)_2.6H_2O$) and ammonium heptamolybdate tetrahydrate (($NH_4)_6Mo_7O_{24}.4H_2O$) were dissolved in 50 ml ethylene glycol. The pH of the solution was adjusted to pH 10 by adding NaOH. After Ni-Mo 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. Then, a solid was washed several times with excess acetone and distillated water followed by centrifuge at 10,000 rpm for 6 min and filtration to collect the solid particles. After that the as-synthesized catalyst was dried at 160 °C overnight followed by calcination in air at 550 °C for 3 h.

3.3.2 Catalyst Characterization

3.3.2.1 X-ray Fluorescence Spectoscopy (XRF)

The Ni and Mo content (wt%) on HZSM-5 were measured by X-ray fluorescence method (XRF) using the PAN alytical analysis instrument with AXIOS&SUPERQ version 4.0 systems. IQ+ program was used to measure and analyze the samples. In the analysis procedure, the scans were first searched for peaks. The found peaks were identified and analyzed quantitatively using fundamental parameter.

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 5 and 80 with a scanning rate of 2 °C/min. The unique of XRD chromatogram was used to identify or confirm the structure of unknown crystalline materials.

3.3.2.3 Temperature Programmed Desorption of Isopropylamine (IPA-TPD)

Temperature programmed desorption of isopropylamine (IPA-TPD) was used to determine the Brønsted acid sites using a quarter inch quartz tube reactor connected to an online MS detector (MKS Cirrus). A catalyst sample (100 mg) was pretreated for 2 h in flowing He at 500 °C. After pretreatment, the sample was cooled in He to room temperature and then pulses of isopropylamine (IPA) were injected until saturation. The excess IPA was removed by flowing He. The sample was heated to 800 °C at a heating rate of 10 °C/min. The mass peaks used to identify the various desorption products in IPA-TPD are as follows: m/z = 44 for i-propylamine, m/z = 41 for propylene, and m/z = 17 for ammonia.

3.3.2.4 Temperature Programmed Reduction of Hydrogen (H_2-TPR)

The hydrogen chemisorption analysis was used to measure the metal dispersion on catalysts. Before reduction, about 50 mg catalyst sample was pretreated at 600 °C for 1 h in nitrogen and then cooled to room temperature. Then it will be analyzed by using 5 % H_2/N_2 mixture. The metal dispersion was calculated following Equation 1.

$$\text{Metal Dispersion} = V_m \times A_w \times 10^4 / (W\% \times S_f) \qquad (1)$$

V_m is the monolayer volume (moles of gas per gram of sample)

A_w is the metal atomic weight (gram of metal per mole)

$W\%$ is the metal percentage in sample

S_f is a stoichiometric factor (molecule of gas per metal atom)

3.3.2.5 Surface Area Analysis

Surface area analysis was used to measure surface area and pore volume by N_2 physisorption using a Quantachrome, Autosorb-1MP. Catalyst sample was outgassed at 300°C at least 12 h in nitrogen before analysis, then N_2 was purged to adsorb by physical adsorption on the surface of catalyst. The quantity of gas adsorbed or desorbed from solid surface was determined at some equilibrium vapor pressures by static volumetric method.

3.3.2.6 Field Emission Scanning Electron Microscopy (FE-SEM)

The morphology and crystal size were characterized by using scanning electron microscope, Hitachi S4800 .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 FE-SEM.

3.3.2.7 Temperature Programmed Oxidation (TPO)

Temperature programmed oxidation (TPO) was used to analyze the amount of coke deposited on the catalyst. A sample of approximately 0.05 g was packed into a 4 mm quartz tube reactor. The 5 % O_2 in He as oxidizing agent was introduced into the reactor with a flow rate of 40 ml/min. The outgoing gas was passed through the methanator unit before being sent to the detector. The reactor was heated from 30 to 900 °C with a heating rate 10 °C/min. The received area was then converted into the carbon amount by the calibration factor obtained from the CO_2 calibration.

3.3.3 Catalytic Activity Testing

Catalytic activity testing was performed using a fixed-bed quartz tube reactor at temperatures of 750 and 800 °C, GHSV of 1,500 ml/g/h, and methane concentrations of 20 % and 40 %. The catalyst sample (0.2 g) having particle size of 60-80 mesh was placed into the reactor between the thin layers of quartz wool. Before the reaction, the catalyst was activated at 500 °C for 2 h in flowing hydrogen of 60 ml/min. The reaction was carried out for 3 h on stream and the product gas was analyzed using a gas chromatograph (HP 6890) equipped with an FID detector connected to a capillary HP Innowax and HP-Plot/Al_2O_3 columns. A schematic diagram of the experimental system is shown in Figure 3.1.

In this work, methane conversion, selectivity and yield of product are defined as follows Equations 2-8.

$$\text{Methane conversion (mol\%)} = \frac{\text{(Moles of methane fed - moles of methane out)}}{\text{Moles of methane fed}} \times 100 \quad (2)$$

$$\text{Ethylene selectivity (mol\%)} = \frac{\text{moles of ethylene produced}}{\text{moles of all gaseous products produced}} \times 100 \quad (3)$$

$$\text{Benzene selectivity (mol\%)} = \frac{\text{moles of benzene produced}}{\text{moles of all gaseous products produced}} \times 100 \quad (4)$$

$$\text{Toluene selectivity (mol\%)} = \frac{\text{moles of toluene produced}}{\text{moles of all gaseous products produced}} \times 100 \quad (5)$$

$$\text{Ethylene yield (mol\%)} = \frac{2 \times \text{moles of ethylene produced}}{\text{moles of methane fed}} \times 100 \quad (6)$$

$$\text{Benzene yield (mol\%)} = \frac{6 \times \text{moles of benzene produced}}{\text{moles of methane fed}} \times 100 \quad (7)$$

$$\text{Toluene yield (mol\%)} = \frac{7 \times \text{moles of toluene produced}}{\text{moles of methane fed}} \times 100 \quad (8)$$
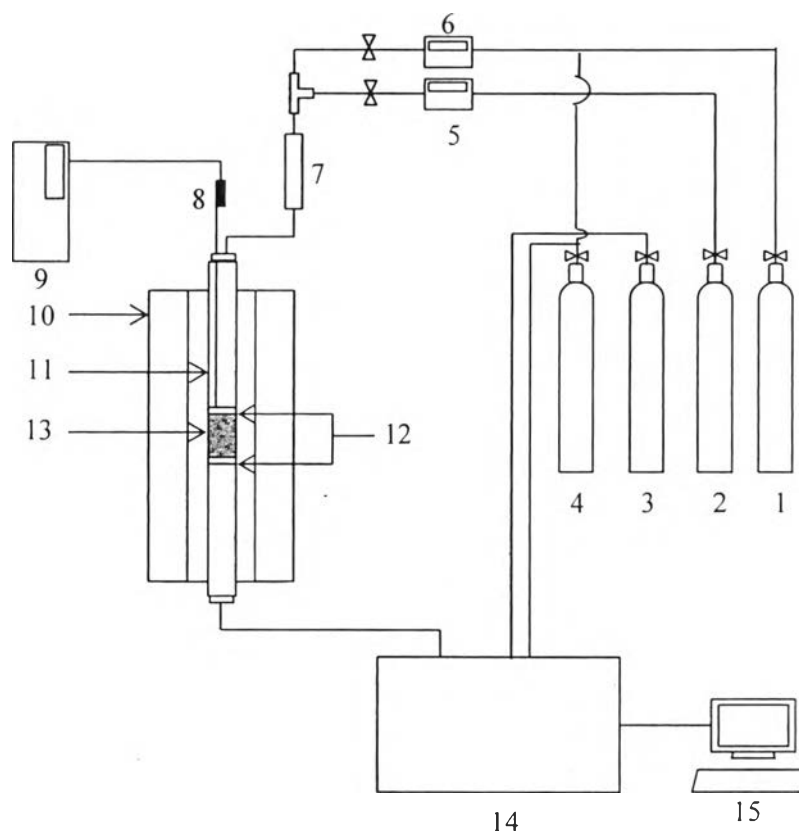
Figure 3.1 Schematic of the experimental system: (1) N_2, (2) CH_4, (3) Air zero, (4) H_2, (5) Mass flow rate controller for CH_4, (6) Mass flow rate controller for N_2 or H_2, (7) Gas mixer, (8) K-Type thermocouple, (9) Temperature controller, (10) Furnace, (11) Quartz tube reactor, (12) Quartz wool, (13) Catalyst bed, (14) Gas Chromatograph, (15) Computer.