

CHAPTER III EXPERIMENTAL

3.1 Materials

3.1.1 Chemicals

- Benzene (90% Purity) obtained from Carlo Erba
- Ethanol (99.8% Purity) obtained from Carlo Erba
- Alumina source ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$)
- Tetrapropylammonium bromide (TPABr)
- Ludox (40%wt SiO_2)
- Sodium hydroxide (NaOH)
- Hydrochloric (HCl)

3.1.2 Gases

- N_2 (99.99 % Purity) will be obtained from Thai Industrial Gas Co., LTD.
- H_2 (99.99 % Purity) will be obtained from Thai Industrial Gas Co., LTD.
- He (99.99 % Purity) will be obtained from Thai Industrial Gas Co., LTD.
- Air Zero (99.99% Purity) will be obtained from Thai Industrial Gas Co., LTD.

3.2 Equipment

The equipment used in this work is listed below.

- Fixed-bed continuous flow reactor system
- Agilent Technologies model 5890N gas chromatograph with a flame ionization detector and HP-5 column for detecting the alkylated aromatic hydrocarbons

3.3 Methodology

3.3.1 Catalyst Preparation

Chemicals used for synthesizing ZSM-5 catalysts were Ludox, aluminium nitrate ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$), tetrapropylammonium bromide (TPABr), sodium hydroxide pellets (NaOH), and de-ionized water. The resultant mixture with molar composition $10\text{Na}_2\text{O}:180\text{SiO}_2:\text{Al}_2\text{O}_3:20\text{TPABr}:16,000\text{H}_2\text{O}$ was prepared by combining the mixture of Ludox and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ with each clear solution of TPABr, H_2O , and NaOH. After being stirred for 30 minutes it was put in a stainless steel autoclave, and heated in an oven at various conditions. After the hydrothermal synthesis, the autoclave was cooled down to room temperature. The powder was washed by de-ionized water to reduce pH from 10.5 to 7. After that it was dried at 120°C overnight and calcined to remove the precursor at 550°C for 4 h. Then, the as-synthesized ZSM-5 was exchanged with 1 M NH_4Cl solution for three times at 80°C , and then washed with de-ionized water to remove the chloride ions. The H^+ form of the zeolites (HZSM-5) was obtained by calcination of the NH_4^+ form at 500°C for 5h.

3.3.2 Catalyst Characterization

3.3.3.1 *X-ray Diffraction (XRD)*

The crystalline phase of catalyst was analyzed by a Rigaku Dmax X-Ray diffractometer, RINT-2200 with Cu tube for generating $\text{CuK}\alpha$ radiation (1.5406 \AA). The system consists of a voltage generator of 40 kV. The 2θ is in the range between 5 and 50 with a scanning rate of $5^\circ/\text{min}$. This analysis is generally performed based on the fact that an x-ray diffraction pattern is unique for each crystalline substance. Thus, if an exact match can be found between the pattern of an unknown and sample, chemical identity can be assumed. It is also possible to make a relatively quantitative analysis by comparing the intensity of the diffraction lines. When comparing the same crystalline substance of different samples, the higher intensity indicates the higher content.

3.3.3.2 Thermogravimetric/Differential Thermal Analyzer (TG/DTA)

TG and DTA profiles were recorded on a Perkin-Elmer instrument. The uncalcined catalyst (0.005 g) was heated from room temperature to 800 °C at a heating rate of 10 °C/min in a nitrogen stream. The flow rate of nitrogen was 30 ml/min.

3.3.3.3 Temperature Programmed Oxidation (TPO)

This technique is employed to analyze the amount of the coke deposited on the catalysts during reaction. 50 mg of catalyst is placed in a quartz reactor and heated (10 °C/min) under N₂ flow (20 ml/min) up to 120 °C for 30 minute in order to clean the catalyst surface. The reactor is cooled down to 30 °C. Then the catalyst particles were heated from room temperature to 950 °C at a heating rate of 10 °C/min in a flow of 4.99 % O₂/He (20 ml/min). The CO₂ was produced by the oxidation of the coke species. The amount of CO₂ is analyzed on-line by a TPDRO/MS 1100 TCD detector as a function of temperature.

3.3.3.4 Temperature Programmed Desorption (TPD) of Isopropylamine

The surface acid properties of ZSM-5 catalysts are characterized with temperature programmed desorption of isopropylamine (TPD-IPA). 50 mg of catalyst is placed in a quartz tube and heated (10 °C/min) under He flow (10 ml/min) up to 300 °C for 1 h in order to clean the catalyst surface. The reactor is cooled down to 100 °C. Then 4.0 µl of isopropylamine was injected over the sample. After purging by He (10 ml/min) for 20 min to eliminate non adsorbed IPA molecules, the sample is heated linearly ramp temperature (10 °C/min) to 550 °C under the same He flow. Mass 44, 41, and 17 were monitored to determine the evolution of isopropylamine, propylene, ammonia, respectively by Cirrus MKS Spectra products.

3.3.3.5 Scanning Electron Microscope (SEM) with Energy Dispersive Spectrometer (EDS)

Scanning Electron Microscope (SEM), Hitachi S4800, was utilized to identify the microstructure and capture the micrograph of catalyst

morphology. And Energy Dispersive Spectrometer (EDS), Oxford Model 6111, was utilized to identify the presence of element (from characteristic x-ray) in the catalyst region being examined. The catalyst sample was placed on stub and coated by platinum in sputtering device before place in the sample holder in SEM.

3.3.3.6 Surface Area Analyzer

The surface area of the fresh and spent catalysts was measured by BET surface area analyzer (Quantachrome/Autosorb 1). The sample was first outgassed to remove the humidity and volatile adsorbents adsorbed on surface under vacuum at 300°C for 4 h prior to the analysis. Then, N₂ was purged to adsorb on surface, measuring the quantity of gas adsorbed onto or desorbed from their solid surface at some equilibrium vapor pressure by static volumetric method. The solid sample was maintained at a constant temperature of the sample cell until the equilibrium is established. This volume-pressure data was used to calculate the BET surface area.

3.3.4 Catalytic Activity Testing

The synthesized HZSM-5 zeolite catalysts were tested for the catalytic activity of the ethylation of benzene in different reaction conditions using a fixed-bed continuous down-flow reactor having 12 mm in outside diameter and 37 cm in length. The catalyst was loaded into the middle of the reactor and supported in the both sides with a thin layer of glass wool. Prior to the catalytic measurements, the catalyst was activated at temperature 300 °C for an hour under flowing nitrogen.

The temperature of catalyst bed was monitored and controlled by a PID temperature controller (Shinko) equipped with a K-typed thermocouple. The reaction was carried out at atmospheric pressure. The reactant mixture of benzene and ethanol was fed using a syringe pump and preheated before entering the reactor. The nitrogen as a carrier gas was controlled at a flow rate of 40 ml/min by a mass flow controller (Sierra C100L). The product was allowed to flow through a condenser attached to the end of reactor. The liquid product was attained and collected for sampling every 70 minutes on stream. The on-line gas and liquid products were chromatographically analyzed using a gas chromatograph (HP 5890)

equipped with an FID and an HP-5 column. A schematic diagram of the system is shown in Figure 1.

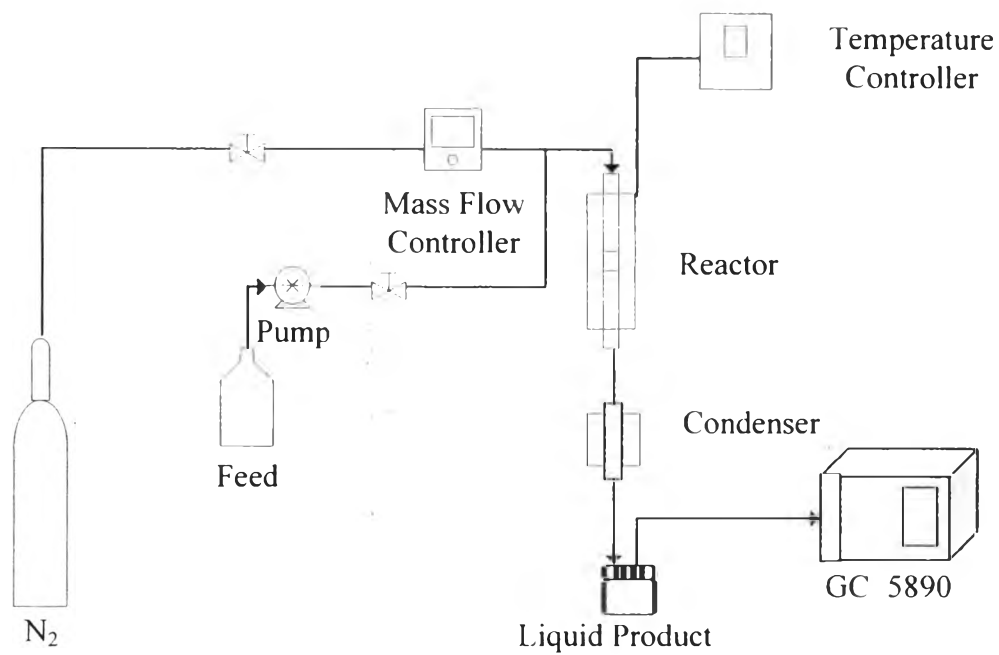


Figure 3.1 Schematic of the experimental system.