

CHAPTER III EXPERIMENTAL

3.1 Materials

3.1.1 Chemicals

- Benzene (99.8% Purity) obtained from Carlo Erba
- Ethanol (99.8% Purity) obtained from Carlo Erba
- Commercial ZSM-5 zeolite catalysts with SiO₂/Al₂O₃ ratio of 23 obtained from Zeolyst and SiO₂/Al₂O₃ ratio of 45 and 195 obtained from Sud-Chemie

3.1.2 Gases

- N₂ (99.99 % Purity)
- H₂ (99.99 % Purity)
- He (99.99 % Purity)
- Air Zero (99.99% Purity)

3.2 Equipment

The equipment used in this work are listed below.

- Fixed-bed continuous flow reactor system
- Temperature controller equipped with a thermocouple (Type K)
- 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 Characterization

3.3.1.1 *X-ray Fluorescence Spectroscopy (XRF)*

X-ray fluorescence spectroscopy was used to determine the actual Cu and Zn content of the catalysts. With a primary X-ray excitation source from an X-ray tube, the X-ray can be absorbed by the atom, and transfer all of its energy is transferred to an innermost electron. During this process, if the primary X-ray has sufficient energy, electrons are ejected from the inner shells, creating vacancies. These vacancies present an unstable condition for the atom. As the atom returns to its stable condition, electrons from the outer shells are transferred to the inner shells, and this process gives off a characteristic X-ray, whose energy is the difference between the two binding energies of the corresponding shells. Because each element has a unique set of energy levels, each element produces X-rays at a unique set of energies, allowing one to non-destructively measure the elemental composition of a sample. The intensities of observed lines for a given atom vary according to the amount of that atom present in the specimen.

3.3.1.2 *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 CuK α radiation (1.5406 Å). 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°/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.

3.1.1.3 Brunauer-Emmett-Teller Method (BET)

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.

3.3.1.4 Temperature Programmed Desorption (TPD) of Ammonia

The surface acid properties of ZSM-5 catalysts are characterized with temperature programmed desorption of ammonia (TPD-NH₃). 200 mg of catalyst is placed in a quartz reactor and heated (10°C/min) under He flow (20 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 the sample was saturated by a flow of 1.5% NH₃/He (20 ml/min) for 2 h. After purging by He (20 ml/min) for 60 min to eliminate non adsorbed NH₃ molecules, the sample is heated linearly ramp temperature (10°C/min) to 700°C under the same He flow. The amount of ammonia eluted is analyzed on-line by a BRI model 110 TCD detector as a function of temperature.

3.3.1.5 Temperature Programmed Oxidation (TPO)

This technique is employed to analyze the amount and characteristics of the coke deposited on the catalysts during reaction. TPO of the spent catalysts is performed in a continuous flow of 2% O₂ in He while the temperature is linearly increased with a heating rate of 12°C/min. The oxidation is conducted in a ¼ in. quartz fixed-bed reactor after the spent catalyst has been dried at 110°C overnight, weighed (20 mg), and placed between two layers of quartz wool. The sample is further purged at room temperature by flowing 2%O₂ in He for 30 min to stabilize the signal before starting a run. The CO₂ produced by the oxidation of the coke species is converted to methane using a methanizer filled with 15% Ni/Al₂O₃

and operated at 400°C in the presence of H₂. The evolution of methane is analyzed using an FID detector.

3.3.1.6 *Thermogravimetric/Differential Thermal Analyzer (TG/DTA)*

TG profiles were recorded on a Perkin-Elmer instrument. The catalyst particles (0.015 g) were heated from room temperature to 800°C at a heating rate of 10°C/min in an air stream. The flow rate of air was 30 ml/min. In the recorded profiles, the weight loss before 120°C was attributed to desorption of water. The decrease of weight from 120 to 700°C was caused by burning-off the coke. Therefore, the amount of coke could be estimated according to the following formula:

$$\text{coke amount (mg/g cat)} = \frac{M_1 - M_2}{M_1} \times 100$$

Here, M₁ represents the weight percent of coked catalyst after desorption of water and M₂ represents the weight percent of coked catalyst after burning-off the coke.

3.3.2 Catalytic Activity Testing

The HZSM-5 catalysts are tested the catalytic activity for the ethylation of benzene in the different reaction condition to demonstrate the effects of reaction temperature, weight hourly space velocity (WHSV), benzene to ethanol ratio (B/E).

The ethylation reaction is carried out in a fixed-bed continuous down-flow reactor, with 12 mm outside diameter and 37 cm length. About 0.2 g of the catalyst as pellets of 20-40 mesh was loaded into the middle of the reactor and support in the either side with a thin layer of glass wool. Before carrying out the catalytic measurements, the catalyst samples was activated at reaction temperature for 1 hour under flowing nitrogen.

The temperature of catalyst bed is monitored and controlled by a PID temperature controller equipped with a thermocouple (Type K). The reaction is carried out at atmospheric pressure. The reactant mixture of benzene and ethanol was fed by a piston pump and preheated before entering the reactor. The nitrogen flowing at a rate of about 40 ml/min that employed as the carrier gas was controlled by a

mass flow controller (Sierra C100L). The products are passed through a condenser attached to the end of reactor and collected for every 60 minutes of time on stream. The on-line gas analyses of the reaction products and the collected liquid products were done using a Gas chromatograph (HP 5890) equipped with a flame ionization detector (FID) and HP-5 column. The schematic diagram of the system is shown in Figure 3.1.

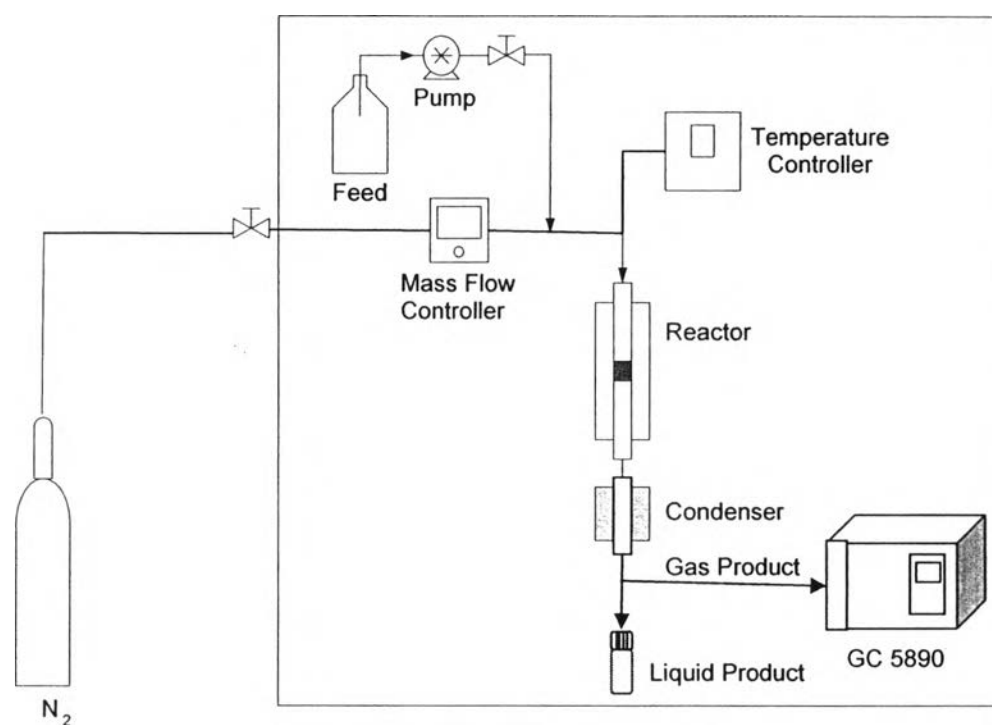


Figure 3.1 Schematic of the experimental apparatus.