

CHAPTER III

EXPERIMENTAL

3.1 Gases

- Hydrogen (H_2 , HP grade, 99.99 % purity) was used for the catalyst activity testing, and FID detector.
- Nitrogen (N_2 , HP grade, 99.99 % purity) was used for the catalyst activity testing.
- Helium (He, HP grade, 99.99 % purity) was used as carrier gas for-gas chromatograph and for temperature programmed desorption (TPD) measurement.
- The zero grade air was used for FID detector.
- 5 vol.% oxygen balanced in helium was used for the temperature programmed oxidation (TPO) measurement.
- 2 vol.% propylene balanced in helium was used for the temperature programmed desorption (TPD) measurement.

All gases mentioned above were supplied from TIG, Thailand.

3.2 Chemicals

- Methanol (CH_4O , reagent grade) was obtained from Fisher Scientific
- 1-Propanol (C_3H_8O , reagent grade) was obtained from Fisher Scientific
- 1-Butanol ($C_4H_{10}O$, reagent grade) was obtained from Fisher Scientific
- Ethanol (C_2H_5OH , 99.99 % purity) was obtained from Merck.
- The commercial ZSM-5 zeolite ($SiO_2/Al_2O_3 = 30$) were obtained from Zeolite, USA.
- Tetraethyl orthosilicate ($SiC_8H_{20}O_4$) was obtained from Aldrich, USA.
- Cyclohexane was obtained from Labscan, Thailand.
- NaOH was obtained from Ajax
- NH_4NO_3 was obtained from Ajax

3.3 Equipment

- High pressure packed-bed continuous flow reactor system consisting of;
 - Mass flow controller (Brooks instrument 5850E)
 - High pressure liquid pump (Water 515 HPLC)
 - Back pressure regulator (SIEMENS)
 - $\frac{3}{4}$ " O.D. stainless steel reactor
 - Tubular furnace with a temperature controller
- Gas chromatograph (Agilent 5890) equipped with a capillary HP-PLOT/ Al_2O_3 "S" deactivated column.
 - Gas chromatograph (Agilent 6890) equipped with a capillary HP-INNOWAX column.
 - X-ray diffractometer (Bruker AXS/D8 advance)
 - X-ray Fluorescence analysis Bruker (SRS3400)
 - Temperature programmed desorption (TPD) apparatus connected to an online MS detector (MKS Cirrus).
 - Temperature programmed oxidation (TPO) apparatus
 - BET surface area analyzer (Quantachrome/Autosorb-1)
 - Atomic absorption spectroscopy (SpectrAA,300)
 - Scanning electron microscope

3.4 Experimental Procedure

3.4.1 Catalyst Preparation

3.4.1.1 *Alkali Treatment*

HZSM-5 (30) samples were calcined in air at 550 °C for 5 h to remove the organic template. In an Alkali treated process, 50 ml NaOH solution with a certain concentration (0.1, 0.3, 0.5, 0.75, and 1.0 M) was heated to 80 °C stirred HZSM-5 zeolite for 2 h the slurry was cooled down immediately and filtered. Dilute HNO_3 was employed to neutralize the left OH that adhered on the zeolite. Finally, all the sodium type ZSM-5 samples, including the alkali-treated, were ion-exchanged with 1 M NH_4NO_3 solution at 80 °C stirred 6 h for twice times to replace Na^+ by

NH_4^+ , and followed by washing and drying. The HZSM-5 zeolites were obtained by subsequent calcinations at 550 °C in air for 5 h. The modified catalyst was noted as AT (alkali treated).

3.4.1.2 Silylation Preparation

In this study, the silylation was performed on HZSM-5 catalysts by chemical liquid deposition (CLD). The modified catalysts were obtained by impregnating 1 mL of tetraethyl orthosilicate (TEOS) per gram catalyst in 20 vol.% of TEOS in cyclohexane at room temperature for 12 h, dried at 110 °C for 2 h and then calcined at 550 °C for 5 h. The silylated catalyst was noted as CLD20/HZSM-5.

3.4.2 Catalytic Activity Testing

The feedstock were fed together with a H_2 carrier at a flow rate giving a molar ratio of N_2/feed of 1:1.4. The reaction was carried out at temperatures of 400 °C, pressure of 1 atm and W/F from 0.02 to 3.3 h (mass of catalyst/mass flow rate of organic). The liquid products, including water, were collected in a cold trap. After accumulating for 3 h, the sample was analyzed by gas chromatography using a Agilent 5890 equipped with a capillary HP-PLOT/ Al_2O_3 "S" deactivated column. Non-condensed products passed through the back-pressure regulator, went to vent, and were not quantified, but some samples were analyzed by gas chromatography using a Agilent 6890 equipped with a capillary HP-INNOWAX column. The schematic of the experiment set up is shown in Figure 3.1.

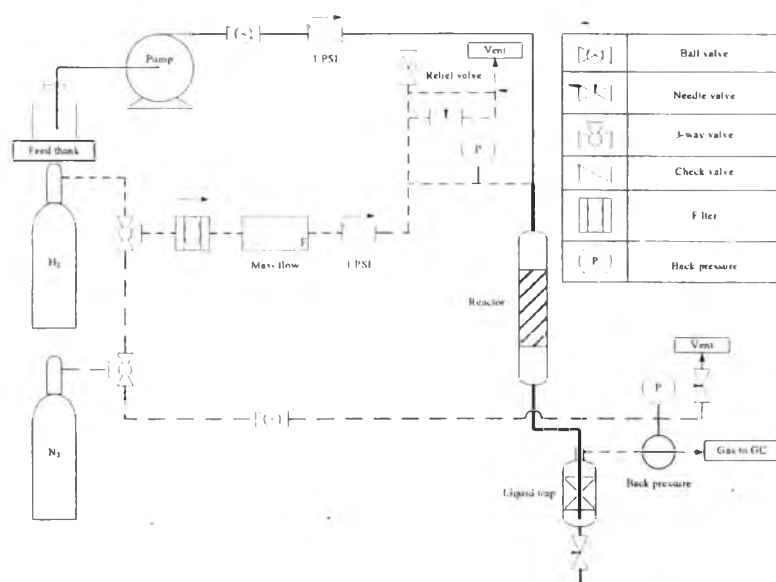


Figure 3.1 A schematic flow diagram of experimental setup.

The conversion of feed and selectivity is defined as follows;

$$\text{Conversion (\%)} = \frac{n_{\text{Feed},i} - n_{\text{Feed},o}}{n_{\text{Feed},i}} \times 100$$

$$\text{Molar carbon yield(\%)} = \frac{n_{\text{Product},o}}{n_{\text{Feed},i}} \times 100$$

$$p\text{-Xylene selectivity in xylenes (\%)} = \frac{\text{moles of carbon in } p\text{-xylene}}{\text{moles of carbon in xylenes}} \times 100$$

3.5 Catalyst Characterization

3.5.1 Temperature Programmed Oxidation (TPO)

This technique is employed to quantify the amount and the characteristics of coke deposited on the spent catalysts during reaction and obtain information about how the coke distributes over the catalyst. TPO of the spent catalysts was performed in a continuous flow of 2 % O₂ in He while the temperature was linearly increased with a heating rate of 10 °C/min. The oxidation was conducted in a ¼" quartz fixed-bed reactor after the spent catalyst had been dried at 110 °C overnight, weighted (10 mg), and placed between two layers of quartz wool inside the quartz tube. The sample was further purged at room temperature by flowing 2 % O₂ in He for 30 min before the TPO was started. The CO₂ produced by the oxidation of the coke species was converted to methane using a methanator filled with 15 % Ni/Al₂O₃ and operated at 415 °C. The evolution of methane was analyzed using an FID detector. A 100 µl pulse of methane was used as the internal standard for calculating coke contents.

3.5.2 Temperature Programmed Desorption (TPD) of Isopropylamine

The acidity of parent alkali treated and silylated HZSM-5 was quantified by temperature-program desorption (TPD) of isopropylamine (IPA) in a quarter inch quartz tube reactor with 50 mg of catalyst connected to an online MS detector (MKS Cirrus). First, catalyst was initially pretreated at 300 °C in a flow of He for 0.5 h. After the pretreatment, the sample was cooled in He to 30 °C and then 5 µl pulses of isopropylamine were injected over the sample, until the sample was saturated. The saturation of isopropylamine adsorption was confirmed by mass

spectrometry (MKS Cirrus). After removal of the excess isopropylamine by flowing He for 30 min, the sample was linearly heated to 800 °C at a heating rate of 20 °C/min. The MS signal of m/e 44, 41, and 17 were monitored to determine the evolution of isopropylamine (IPA), propylene, and ammonia, respectively. The amount of desorbed propylene was calibrated with a 2 mL pulse of 2 % propylene in He.

3.5.3 Temperature Programmed Desorption (TPD) of Ammonia

The NH₃ desorption of HZSM-5 was quantified by temperature-program desorption (TPD) of Ammonia (NH₃) in a quarter inch quartz tube reactor with 80 mg of catalyst connected to an online MS detector (MKS Cirrus). First, catalyst was initially pretreated at 600 °C in a flow of He for 30 min. After the pretreatment, the sample was cooled in He to 150 °C and then saturated with NH₃ gas. The sample was flushed in He flow for 30 min to remove the gas phase NH₃. The temperature was then raised from 150 to 700 °C at a heating rate of 18 °C/min and maintained at 700 °C for 10 min. The concentration of ammonia in the exit gas was determined continuously by mass spectrometry (MKS Cirrus), using the fragments with m/e of 17 as the representative of ammonia.

3.5.4. X-ray Fluorescence (XRF)

The quantitative and qualitative elemental analysis of the HZSM-5 zeolite before and after alkali treatment and silylation were analyzed by XRF technique, Philips model PW 2400. 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 to an innermost electron. During the process, if the primary X-ray has sufficient energy, electrons are ejected from the inner shell, 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 the 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.

3.5.5 Brunauer-Emmett-Teller Method (BET)

Surface area and micropore volume of the samples were measured using BET method on a Quantachrom/Autosorb1-MP instrument. The sample was first outgassed to remove the humidity and volatile adsorbents adsorbed on surface under vacuum at 300 °C for 12 h prior to the analysis. Then, N₂ was purged to adsorb on the surface. The quantity of gas adsorbed onto or desorbed from their solid surface at some equilibrium vapor pressure by static volumetric method was measured. The solid sample was maintained at a constant temperature of the sample cell until the equilibrium was established. This volume-pressure data was used to calculate the BET surface area and pore volume.

3.5.6 X-ray Diffraction (XRD)

The relative crystallinities of the HZSM-5 zeolite before and after alkali treatment and silylation were analyzed by a Rigaku X-ray diffractometer with Cu tube for generating CuK α radiation ($\lambda = 1.5418 \text{ \AA}$) at room temperature. The 2θ is in the range between 10 and 55 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, chemical identity can be assumed. It is also possible to make a relatively quantitative analysis by comparing substance of different samples, the higher intensity indicates the higher content.

3.5.7 Scanning Electron Microscopes (SEM)

The morphology of the samples was observed by Hitachi/S-4800 scanning electron microscopy (SEM). The zeolite samples were dried overnight and then coated with gold prior to the SEM observation to avoid charge effect of the samples.