

## CHAPTER III

### EXPERIMENTAL

#### 3.1 Materials

A Ludox HS-30 (Colloidal silica) and alumina ( $\text{Al}_2\text{O}_3$ ) purchased from Sigma-Aldrich, USA were used as silicon and aluminum sources, respectively, for the zeolite synthesis. Tetrapropylammoniumbromide (TPA-Br) as an organic template was supplied by Fluka, USA. Regent grade Sodium hydroxide pellet (NaOH), Ammonium nitrate ( $\text{NH}_4\text{NO}_3$ ), and Zincnitrate hexahydrate ( $\text{Zn}(\text{NO}_3)_6\text{H}_2\text{O}$ ) were purchased from Ajax Co. Ltd. All of these chemicals were used as received for the preparation of H-ZSM5 and Zn/H-ZSM5 zeolite catalysts. Furthermore, commercial molecular sieve (UOP type 13X, NaX) was obtained from Fluka, USA. Cesium nitrate ( $\text{CsNO}_3$ ; 99.99% trace metals basis) was purchased from Sigma-Aldrich, USA.

Methyl octanoate (99 % min), used as a biodiesel model compound, was purchased from Sigma-Aldrich, USA. n-Octane (99 % min) was also purchased from Sigma-Aldrich, USA. High purity hydrogen and helium were supplied by TIG Co. Ltd.

#### 3.2 Methodology

##### 3.2.1 Catalyst Preparation

###### *3.2.1.1 Synthesis of H-ZSM5 and Zn/H-ZSM5 Zeolite Catalysts*

ZSM5 zeolite was synthesized using the conventional hydrothermal method published in the well-known patent with some modifications (Argauer and Landolt, 1972). Tetrapropylammoniumbromide (TPABr) was used as organic templates for the synthesis. In order to decompose the organic template, the synthesized zeolite was calcined at 873 K for 5 h. The zeolite was ion exchanged with 1 M of  $\text{NH}_4\text{NO}_3$  solution at 353 K for 10 h using 100 ml per gram of zeolite. Then, the zeolite was separated from the solution by filtering and washing. The

exchange procedure was repeated three times to ensure the completion of ion exchange. After that, the catalyst was dried overnight at 383 K and calcined in a flow of dry air (100 ml/min per gram of zeolite) at 773 K for 5 h to produce the acidic form of the zeolite (H-ZSM5). The H-ZSM5 was exchanged with  $\text{Zn}(\text{NO}_3)_2$  solution for 5 h at 353 K using 50 ml per gram of zeolite to attain Zn/H-ZSM5. Then, the exchanged samples were dried overnight at 383 K and calcined at 773 K for 5 h.

### 3.2.1.2 Preparation of CsNaX Zeolite Catalysts

Commercial molecular sieve (UOP type 13X, NaX) was obtained from Fluka. The as-received material was calcined at 723 K. The Cs-containing zeolite (CsNaX) was prepared by ion exchange of molecular sieve 13X with 0.1 M  $\text{CsNO}_3$  solution at 353 K for 24 h. The solid material was filtered and left to dry at 353 K overnight. The sample was then calcined at 723 K for 2 h in a flow of dry air. To investigate the effect of excess Cs in the zeolite, the CsNaX sample was washed repeatedly with deionized water. The samples designated as CsNaX(5) and CsNaX(2) were those that washing with deionized water for 4 and 7 times applied. Then, the samples were calcined in a flow of dry air at 723 K.

### 3.2.2 Characterization of Fresh Catalysts

XRD was employed to identify the phase of zeolite using a Rigaku X-Ray Diffractometer, with  $\text{CuK}_\alpha$  line as incident radiation and a filter at a scanning rate of  $5^\circ/\text{s}$ . Moreover, the crystal morphology and crystal size were investigated by using a JEOL 5200-2AE scanning electron microscope. Nitrogen adsorption was carried out to analyze the surface area of the synthesized ZSM5 zeolite. The adsorption isotherms were collected at 77 K using a Thermo Finnigan Modeled Sorptomatic 1100 series. Elemental analyses were carried out in a Perkin-Elmer Optima 4300 DV inductively coupled plasma – optical emission spectrometer (ICP-OES).

The acidity of all samples was determined by the amine temperature programmed desorption technique (Parrillo *et al.*, 1990). The sample (30 mg) was initially pretreated in a flow of He for 1 h at 773 K. Then, the sample was cooled in a

flow of He to room temperature. After that, propylamine (10  $\mu$ l) was injected over the sample each time until the sample was saturated. The saturation of propylamine adsorption was confirmed by mass spectrometer. After the removal of the excess propylamine by flowing He for 3 h, the sample was linearly heated to 973 K at a ramping rate of 10 K/min. Masses 30, 41, and 17 were monitored to determine the evolution of propylamine, propylene, and ammonia, respectively. The amount of desorbed propylene was calibrated with 5 ml pulse of 2% propylene in He.

The density and strength of acidic sites of the catalysts were also characterized by FTIR using pyridine as probe molecule. Infrared spectroscopic measurements of adsorbed pyridine (Py-IR) were recorded on a Bruker Equinox 55 spectrometer. The samples (90 mg) were pressed into self-supported wafers with a diameter of 2.5 cm. Then, the wafers were located in a cell with  $\text{CaF}_2$  windows. Prior to pyridine adsorption, the sample was pretreated in a flow of He at 773 K for 2 h. After the pretreatment, the sample was cooled down to 423 K and a blank spectrum was taken. Consequently, the pyridine vapor was introduced into the sample cell for 2 h in order to saturate all the acid sites. Then, the excess pyridine was purged out from the cell by the flow of He for 12 h. Four spectra were obtained for each sample at 423 K, first of the saturated sample, and then after outgassing at 573, 673, and 773 K. The absorption band appearing at  $1545\text{ cm}^{-1}$  was assigned to the pyridinium ion formed on Brønsted acid sites, while the band at  $1455\text{ cm}^{-1}$  was assigned to pyridine coordinated to Lewis acid sites. The density of both Brønsted and Lewis acid sites was quantified by integrating the corresponding absorption bands and using the molar extinction coefficients (Emeis, 1993).

In addition, the FTIR technique was carried out to determine the basic strength of the Cs containing NaX zeolite catalysts using acetonitrile as a probe molecule. The samples were prepared and pretreated in a flow of 2%  $\text{O}_2/\text{He}$  at 723 K for 2 h. After the pretreatment, it was cooled down to room temperature and a blank spectrum was taken. After that, the acetonitrile (10  $\mu$ l) was injected to the sample cell in a flow of He. The helium gas was kept flowing for 1 h to purge the excess acetonitrile. Then, the spectrum was taken again.

### 3.2.3 Temperature Programmed (TP) Techniques

#### 3.2.3.1 *Temperature Programmed Reduction (TPR)*

Temperature programmed reduction was carried out in a ¼ in. quartz reactor. The sample (50 mg) was packed in the reactor. The TPR profile was obtained by flowing 5% H<sub>2</sub> in Ar through the sample and wait until the signal was stable for 20 min before ramping the temperature. Then the temperature was linearly ramped at the rate of 10 K/min to 1173 K. The effluent gas was passed through a moisture trap and detected online by an SRI thermal conductivity detector.

#### 3.2.3.2 *Temperature Programmed Desorption of Methyl Octanoate*

The adsorbed methyl octanoate over CsNaX catalysts was determined by temperature programmed desorption equipped with a mass spectrometer. 50 mg of the sample was initially pretreated in a flow of 2% O<sub>2</sub>/He for 2 h at 723 K. Then, the sample was cooled in He flow to 423 K. Then, methyl octanoate (100 µl) was injected to the sample, and a He flow was introduced for 3 h at 423 K in order to remove the excess methyl octanoate. The sample was then linearly heated to 1173 K at a rate of 10 K/min and masses (m/z) of 2, 28, 29, 56, and 74 were monitored to determine the evolution of hydrogen, carbonmonoxide, formaldehyde, hydrocarbons, and methyl octanoate, respectively.

#### 3.2.3.3 *Temperature Programmed Desorption & Reaction of Methanol*

Desorption characteristics and decomposition of methanol over CsNaX and NaX catalysts were determined by temperature programmed desorption and temperature programmed reaction techniques, respectively. The effluent flow from the temperature programmed unit was sampled into a mass spectrometer. 50 mg of the sample was initially pretreated in a flow of 2% O<sub>2</sub>/He for 2 hours at 723 K. Then, the sample was cooled in He flow to room temperature. In the desorption experiment, 10 µl of methanol was repeatedly injected to the sample until the sample was saturated, as seen by a steady MS signal. After the removal of the excess

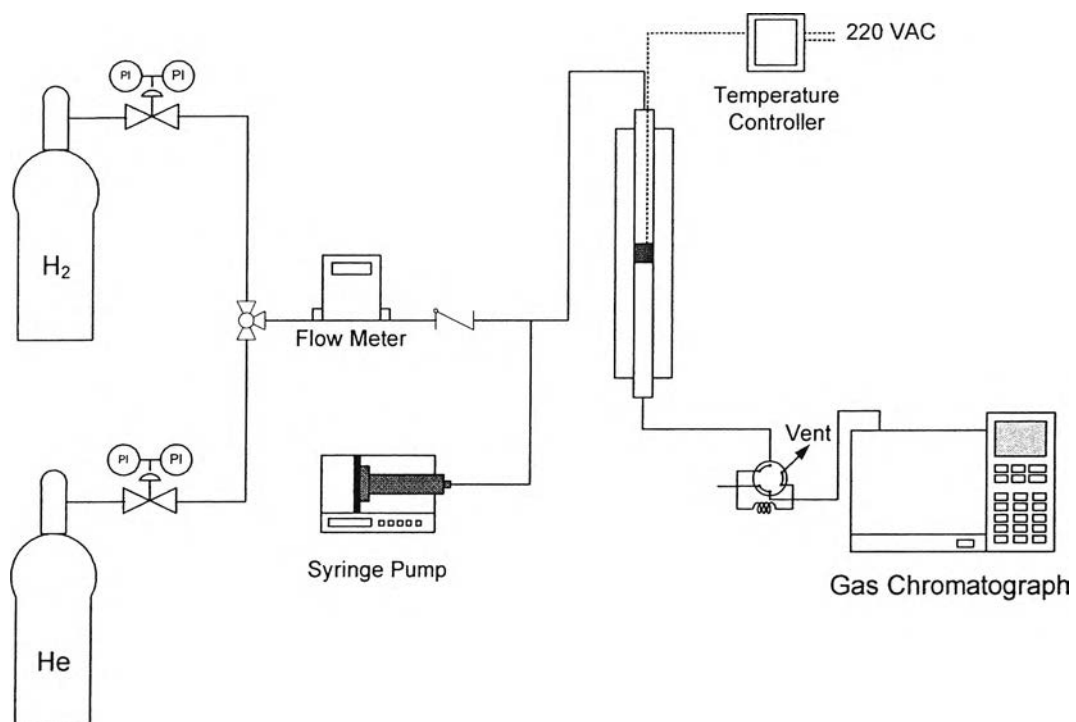
methanol by flowing He for 3 h at room temperature, the sample was then heated to 1173 K at a rate of 10 K/min. For the decomposition experiment, methanol was continuously fed through the sample bed at a flow rate of 1 ml/h. The sample was linearly heated to 973 K with a ramping rate of 10 K/min. Masses ( $m/z$ ) of 2, 28, 29, 31, and 45 were monitored to determine the evolution of hydrogen, carbonmonoxide, formaldehyde, methanol, and dimethylether, respectively.

### 3.2.4 Characterization of Spent Catalysts

Temperature programmed oxidation (TPO) was carried out to determine the amount and characteristics of coke formed on the spent catalysts. TPO profiles of the spent catalysts were performed in a continuous flow of 2% O<sub>2</sub>/He while the temperature was linearly ramped to 1073 K with a heating rate of 12 K/min. The sample (30 mg) was placed in a 1/4" quartz fixed bed reactor. The CO<sub>2</sub> produced by the oxidation of coke was further converted to methane over 15% Ni/Al<sub>2</sub>O<sub>3</sub> catalyst in the presence of hydrogen at 673 K. The methane obtained was analyzed online by a FID detector. The amount of oxidized coke was calibrated using 100  $\mu$ l pulses of pure CO<sub>2</sub>.

### 3.3 Catalytic Activity Testing Apparatus

The catalytic activity tests were performed in a 0.5 in. pyrex glass reactor at 773 K under atmospheric pressure with a variety of contact time (W/F). The reactor was a single-pass continuous flow type packed with a catalyst bed. Prior to the reaction, the catalysts were *in situ* reduced at 773 K for 1 h. Methyl octanoate was injected using a syringe pump. The molar ratio of hydrogen to feed was kept at 6:1 in all experiments. The products were detected using an online gas chromatograph (Shimadzu GC-17A) equipped with either a capillary HP-5 or a capillary HP-Plot/Al<sub>2</sub>O<sub>3</sub> "S" deactivated column, and a temperature program to obtain optimal product separation. The liquid products were identified using GC/MS (Shimadzu Q-5000). A schematic of the activity testing apparatus is shown in Figure 3.1.



**Figure 3.1** Schematic of the catalytic activity testing apparatus.