

## CHAPTER III

### EXPERIMENTAL SECTION

#### 3.1 Materials

##### 3.1.1 Chemicals

K-LTL zeolite (HSZ-500,  $\text{SiO}_2/\text{Al}_2\text{O}_3 = 6$ , surface area =  $280 \text{ m}^2/\text{g}$ ) was supplied from Tosoh (Tokyo, Japan).

n-Octane ( $\text{C}_8\text{H}_{18}$ ) of min 99% purity was obtained from Merck (Darmstadt, Germany).

n-Hexane ( $\text{C}_6\text{H}_{14}$ ) of min 99% purity was obtained from Merck (Darmstadt, Germany).

Platinum (II) acetylacetonate ( $[\text{CH}_3\text{COCH}(\text{-CO-})\text{CH}_3]_2\text{Pt}$ ) of 97% purity was supplied from Alfa Aesar (Weat Deptford, USA).

Carbontetrachloride ( $\text{CCl}_4$ ) of 99.8% purity was obtained from Carlo Erba Reagenti.

Aluminium hydroxide ( $\text{Al}(\text{OH})_3$ ) of 99.8% purity was purchased from Merck.

Colloidal silica , 40 wt% suspension was obtained from Aldrich.

Potassium hydroxide pellet (KOH) of min 85% purity was obtained from Carlo Erba Reagenti.

Barium hydroxide ( $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ ) of min 98% purity was purchased from Carlo Erba Reagenti.

##### 3.1.2 Gases

High Purity (HP) nitrogen

High purity (HP) hydrogen

Ultra high purity (UHP) hydrogen

High purity (HP) helium

3 vol% carbonmonoxide balance in helium

Air zero grade

All gases were obtained from Thai Industrial Gas Public Co., Ltd.

## 3.2 Instruments and Equipment

### 3.2.1 Instruments

Glovebox  
Dessicator  
Continuous flow reactor  
Magnetic stirrer  
Magnetic bar  
Mechanical stirrer  
Spatula  
Plastic spoon

### 3.2.2 Equipment

X-ray diffraction, XRD (Rigaku, RINT-2200)  
X-ray Fluorescence Photometer, XRF (Bruker Axs, SRS3400)  
Scannig Electron Microscope, SEM (JEOL, JSM-5200)  
Fourier Transform Infared Spectrophotometer, FTIR (Bruker, Equinox 55)  
Gas Chromatograph, GC (Shimadzu, GC-17A)  
Microwave Oven, MW ( CEM corporation, MARS 5)  
Surface Area Analyzer, BET (Quantachrome, Autosorb-1)  
Centrifuge (CWS, ALC 4236)  
Particle Size Analyzer, PSA (Malvern, HPPS 5001)  
Thermogravimetric Analyzer, TGA (Perkin Elmer, TGA 7)  
Hydrogen Chemisorption (Thermo Finnigan, TPD/R/O 1100)

## 3.3 Support Preparation

### 3.3.1 Preparation of the Hydrogels

For the preparation the alumina was dissolved in the KOH solution by boiling. The solution was cooled to room temperature and corrected for weight loss.

The barium source was dissolved in a portion of the water and was added to the colloidal silica with another portion of the water which was used to rinse the beaker containing the barium source. The resulting solution was stirred for 5 minutes. The aluminate solution including the rinse water was then added and the whole was mixed for at a desired time and room temperature. The time used for stirring the mixture at room temperature is called ageing time. In this experiment, the ageing time varied from 0 to 30 hours.

The molar composition of the synthesis mixture was:



### 3.3.2 Hydrothermal Synthesis

20 g of the synthesis mixture was transferred to a microwave vessel. The vessel was placed in microwave machine. This microwave system delivers approximately 600 watts of microwave energy. The temperature of the samples was controlled by a temperature controller via a thermocouple inserted into the vessel. The synthesis mixture was heated up to 170 °C in 2 minutes and was kept at this temperature for a desired time. In each ageing time, the heating time (crystallization time) varied from 17 to 50 hours. The set of experiments was reported in Table 4.1. After microwave heating, the solid and solution phases were separated by centrifugation before characterization.

## 3.4 Characterization of Synthesized KL Zeolites

The solid fractions were washed with deionized water to pH about 7 and dried overnight at 110 °C. The products were calcined in flow of air (100 cc/min/g. of KL zeolite) then used 2 h to ramp temperature to 500 °C and held for 4 h. Then the zeolite was cooled in air, after that it was removed and kept in dessicator.

Synthesized KL zeolites were identify by X-ray diffraction (XRD). Crystal size of KL zeolite was measured by Scanning Electron Microscope (SEM) and Ligth Scattering.

### 3.4.1 Phase Identify and Crystallinity

The samples were examined using X-ray diffractometer (XRD) with Rigaku, RINT-2200 using  $\text{CuK}\alpha$  radiation ( $1.5418 \text{ \AA}$ ) at  $2\theta$  from 3 to 50. The crystallinity of the samples was obtained from X-ray powder diffraction data using equation

$$\% \text{ crystallinity} = \frac{\sum I}{\sum I_{\text{ref}}} \quad (3.1)$$

where  $I$  is the line intensity of the synthesized KL zeolite and  $I_{\text{ref}}$  is that of commercial KL zeolite. The intensities of X-ray lines at  $d$  values of 16.1, 4.57, 3.91, 3.66, 3.47, 3.28, 3.17, 3.07, 2.91, 2.65 were used to avoid the possible interference of the coexisting other phases such as W or T for a given sample.

### 3.4.2 Morphology and Crystal Size

The morphology of the crystalline phase and crystal size were examined by using Scanning Electron Microscope (JEOL JSM-840). Samples were stuck on the stubs and coated with gold by ion sputtering device (JFC-1100E) for 4 minutes to prevent specimen charging. The examinations were taken through this microscope with magnification 7,500.

### 3.4.3 Surface Area and Pore Volume

The specific areas and micropore volumes were determined by a Quantachrome surface area analyzer (Autosorb-1). Nitrogen was used as a probe gas. A sample was dried and outgassed in the sample cell at  $250 \text{ }^\circ\text{C}$  about 10 hr before adsorption. The specific area and micropore volumes were calculated from 22 points adsorption isotherm. The results were analyzed by the Autosorb ANAGAS software version 2.10.

#### 3.4.4 Crystal Size

The Malvern Instruments High Performance Particle Sizer (HPPS) 5001 was used to obtain the size of KL zeolite. The measurements were conducted at room temperature with standard disposable polystyrene cuvettes. Samples were dispersed in deionized water by sonication.

#### 3.4.5 Si/Al Ratio

The Si and Al ratio of the samples was determined by using X-ray Fluorescence Photometer (Bruker Axs, SRS 3400). 0.5 grams of sample and 4.5 grams of boric acid were grinded with a Rocklab machine. Then the specimen was put on the center of the sample cup for being analyzed.

#### 3.4.6 Thermal Stability

Thermogravimetric analysis (TGA) was carried out by utilizing a Perkin Elmer TGA7 at a scanning rate of 10 °C/min from 25 to 800 °C under oxygen atmosphere.

### **3.5 Catalyst Preparation via Vapor Phase Impregnation Method (VPI)**

#### 3.5.1 Calcination of KL Zeolite

KL zeolite was calcined in flow of air (100 cc/min/g. of KL zeolite) then used 2 h to ramp temperature to 400 °C and held for 4 h. Then the zeolite was cooled in air, after that it was removed and quickly transferred to inert atmosphere (used grove box with N<sub>2</sub> flow).

#### 3.5.2 Loading Pt

According to Chanajaranwit *et al.* (2002), it was found that 1 % Pt loading on KL zeolite showed the highest catalytic activity among the other percentage of Pt loading. Therefore, 1 % Pt loading was selected to prepare the catalysts. The procedure was described below.

In the inert atmosphere, platinum acetylacetonate were weighed out to yield 1.0 % loading in KL zeolite and mixed with a spatula to give uniformly. The

solid mixture with well mixed was transferred into the reactor tube (sealed at one end). Flow He (<10 cc/min per gram of catalyst) was performed to make inert atmosphere and then temperature was ramped to 40 °C, held for 3 h. After that temperature was slowly ramped to 60, 80, 90 °C to trace water. Then temperature was ramped to 100 °C and held for 1 h to sublime the Platinum acetylacetonate compound. Next step, temperature were ramped in flow of air (100cc. /min per gram of catalyst) to 350 °C and held for 2 h for make sure that the platinum acetylacetonate had sublimed. The reactor tube was cooled to room temperature, the sample was removed and kept in dessicator.

### **3.6 Characterization of Pt/KL zeolite**

Fresh and spent samples were characterized by FTIR of adsorbed CO in order to qualify the location of Pt particles and by Temperature Programmed Oxidation (TPO) to analyze the amount of the coke deposits on spent catalysts.

#### **3.6.1 Location of Pt Particles**

The location of Pt particles were determined by DRIFTS using adsorbed CO as a probe in a Bruker Epuinox 55 spectrometer equipped with a MCT detector. Experiments were performed in a diffuse reflectance cell from Harrick Scientific, type HVC-DR2, with ZnSe windows. For each IR spectrum, 128 scans were taken at a resolution of 8 cm<sup>-1</sup>. Prior to taking each spectrum, a background was collected on the sample reduced in situ under a flow of hydrogen at 300 °C for 1 hour and purged in helium for 30 minutes at room temperature. Then, a flow of 5 % CO in helium for 30 minutes was sent over sample, followed by a purge in helium flow for 30 minutes. After this treatment, the spectrum of adsorbed CO was collected.

#### **3.6.2 Pt Dispersion**

H<sub>2</sub> uptake and degree of dispersion were determined by using pulse technique (Thermo Finnigan modeled TPDRO 1100). Prior to pulse chemisorption,

the sample was reduce in H<sub>2</sub> atmosphere at 500°C for 1 h. Then the sample was purged with N<sub>2</sub> at 500°C for 30 min and cooled to 50°C in flowing N<sub>2</sub>. A H<sub>2</sub> pulse (pure H<sub>2</sub>, 0.4 ml) was injected into the sample at 50°C.

### 3.6.3 Amount of Coke Deposit

The spent catalyst was performed in a continuous flow of 5% O<sub>2</sub>/He while the temperature was linearly increased at a heating rate of 12 °C/min. Before conducting the TPO on a sample placed in a ¼” quartz fixed-bed reactor, a 0.05 g spent catalyst was dried at 110°C overnight. The catalyst was then flushed by 5% O<sub>2</sub> in He for 30 min before the temperature ramp was started. The CO<sub>2</sub> produced by the oxidation of coke species was monitored by a mass spectrometer. The amount of coke was calibrated by using 100 µl pulses of pure CO<sub>2</sub>. The evolved CO<sub>2</sub> partial pressure was normalized by the total pressure and the maximum signal in the pulses of CO<sub>2</sub>.

## 3.7 **n-Octane Aromatization Reaction**

Both n-octane and n-hexane were carried out as the same conditions for aromatization reaction. Therefore, the following procedures were described only for n-octane aromatization reaction.

### 3.7.1 Catalyst Reduction

The prepared Pt/KL catalysts were transferred to the reactor that used for *n*-octane aromatization. Then the temperature was slowly ramped in flowing H<sub>2</sub> at 100 cc/min g. for 2 hours up to 500 °C. The catalyst was reduced in situ in the flow of H<sub>2</sub> (100 cc/min/g. of catalyst) for 1 h. at 500 °C.

### 3.7.2 Reaction Testing

Reaction testing was conducted at atmospheric pressure using two fixed-bed, single pass and continuous flow reactors in parallel. Each reactor consisted of a 0.5- inch stainless steel tube with an internal K-type thermocouple and

the oven was monitored with a J-type thermocouple. In each run, the experiments were conducted using 0.2 g. of catalysts. The catalyst bed was supported on a bed of glass wool. The reactor was operated under flowing H<sub>2</sub>, and *n*-octane was added by infusion with a syringe pump through a T-junction prior to the reactor. In all experiments, the molar ratio of H<sub>2</sub> to *n*-octane was kept at 6:1, the reaction was conducted at 500 °C for 1.5 hr. while the space velocity was fixed at 5 h<sup>-1</sup>.

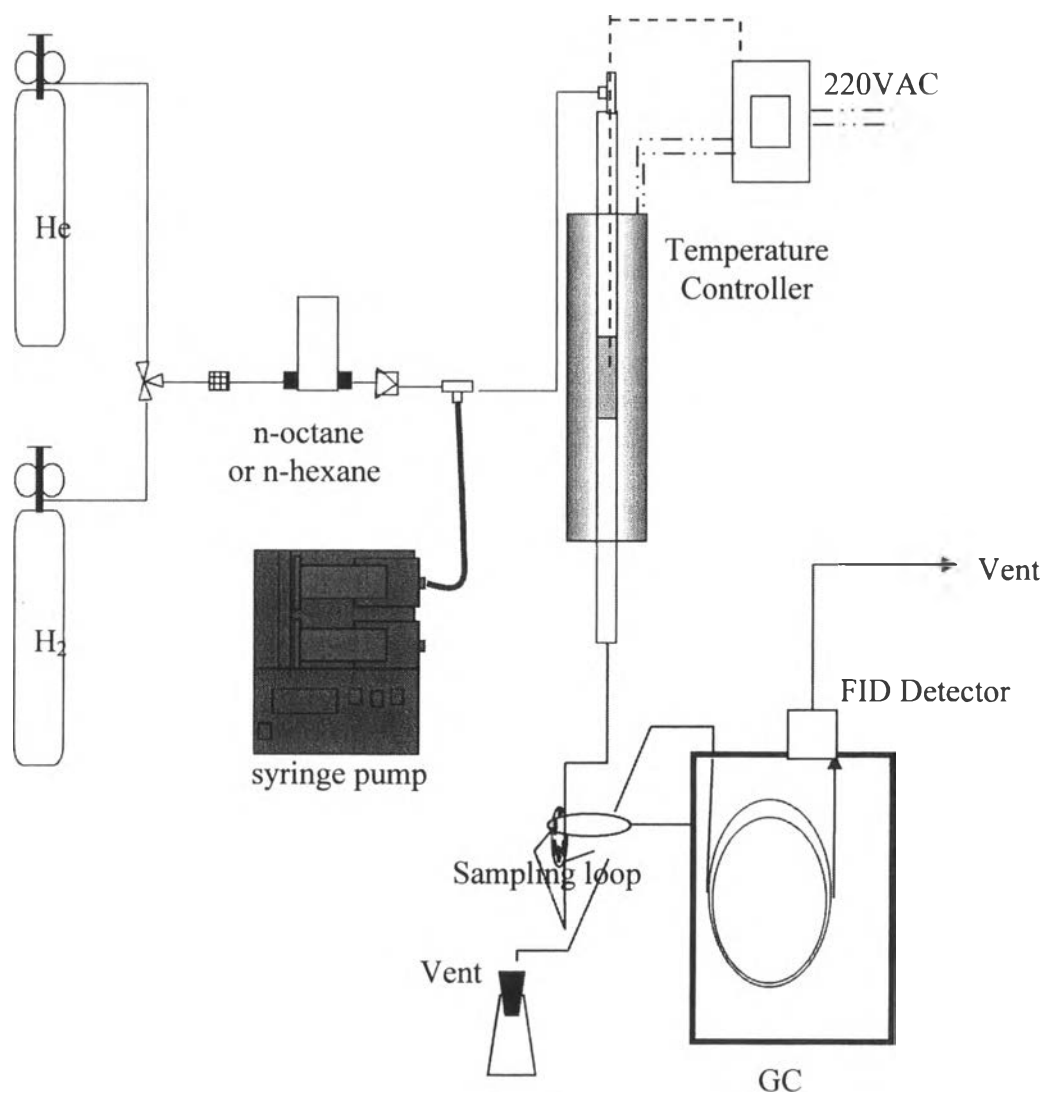
### 3.7.3 The Product of *n*-Octane Aromatization Analysis

The products was analyzed in a Shimadzu GC-17A equipped with a capillary HP-PLOT/Al<sub>2</sub>O<sub>3</sub> "S" deactivated column, using a temperature-programmed mode, to obtain optimal product separation, by starting at 40 °C for 10 min, then the temperature was ramped up to 195 °C with a heating rate of 5 °C/min and held for 30 min. Helium was sent to carry the effluent of each reaction-regeneration cycle through the column to obtain the product separation. The activity data were reported in terms of total *n*-octane conversion and product selectivity defined as weight of each individual product per weight of *n*-octane converted and product yield which is defined as conversion multiplied by selectivity.



### 3.8 Apparatus

The experimental apparatus is schematically shown in Figure 3.1.



**Figure 3.1** Schematic of the experiment setup.