



## CHAPTER III EXPERIMENTAL

### 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).

NaHBeta zeolite ( $\text{SiO}_2/\text{Al}_2\text{O}_3 = 25$ ) was supplied from Zeolyst International (Kansas City, USA).

HOmega zeolite was supplied from Zeolyst International (Conshohocken, USA).

NaY zeolite (Type Y-54) was supplied from UOP (New York, USA).

$\text{SiO}_2$  (Type 233) was supplied from Altech Associates, Inc. (Deerfield, USA).

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

Tetraammineplatinum(II) nitrate ( $\text{Pt}(\text{NH}_3)_4(\text{NO}_3)_2$ ) was supplied from Aldrich (Milwaukee, USA).

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

#### 3.1.2 Gases

High purity (HP) nitrogen

Ultra high purity (UHP) hydrogen

High purity (HP) helium

3 vol% carbonmonoxide balanced in helium

Air zero grade

Gases used were obtained from Thai Industrial Gas Public Co., Ltd. and Praxair Co., Ltd.

## 3.2 Catalyst Preparation

### 3.2.1 Ion Exchange Procedure (for only Beta-, Omega-, and Y zeolites)

Acid zeolite (Beta, Omega and Y) was ion-exchanged with Potassium Nitrate ( $\text{KNO}_3$ ) solution at 70 cc. per gram of zeolite. Exchange step was operated at 80 °C for 3 hours, for 3 times. The exchanged zeolite was then dried overnight (The exchange level was calculated from the total alumina content determined by Atomic Absorption Spectrometer).

### 3.2.2 Vapor Phase Impregnation method (VPI)

#### 3.2.2.1 *Calcination of support*

A support was calcined in the flow of air (100 cc/min per gram of support), then, the temperature was ramped to 500 °C in 2 hours and held for 4 hours. The support was cooled in air, and after that it was removed and quickly transferred to an inert atmosphere (using glove box with nitrogen flow).

#### 3.2.2.2 *Pt loading*

In the inert atmosphere, platinum acetylacetonate was weighed to yield 1.0 (0.5,1.5)% loading in the support and mixed uniformly using a spatula. The solid mixture was transferred into the reactor tube (sealed at one end). Helium was employed (<10 cc/min per gram of catalyst) to make inert atmosphere and temperature was ramped up to 40 °C and held for 3 hours. Temperature was slowly ramped to 60, 80, 90 °C to trace water. After that temperature was ramped to 100 °C and held for 1 hour to sublime the platinum acetylacetonate compound. Temperature was ramped again at 1 °C/min to 130 °C and held for 15 minutes to make sure that all the platinum acetylacetonate had sublimed. The reactor tube was cooled to room temperature, the sample was removed and loaded back into calcination reactor.

#### 3.2.2.3 *Pretreatment*

The catalyst was ramped in flow of air (100 cc/min per gram of catalyst) to 350 °C and held for 2 hours. Then the catalyst was removed and kept in a dessicator (Catalyst should be stored in vial with paraffin covering).

### 3.3 Reaction Testing

#### 3.3.1 Reduction the Catalyst

The prepared catalyst was transferred to the reactor used for n-octane aromatization. Then, the catalyst was ramped in the flow of H<sub>2</sub> (100 cc/min per gram of catalyst) to 500 °C for 2 hours. Catalyst was reduced in situ in the flow of H<sub>2</sub> (100 cc/min per gram of catalyst) at 500 °C for 1 hour.

#### 3.3.2 Reaction Testing

Reaction testing was conducted at atmospheric pressure using fixed-bed, single pass continuous flow reactor. The reactor consisted of a 0.5-inch stainless steel tube with an internal K-type thermocouple, and its oven was controlled with a J-type thermocouple. In each run, the experiment was conducted using the amount of catalyst of 0.1 – 0.2 gram. The catalyst bed was supported by a bed of glass wool. The reactor was operated under the flow of H<sub>2</sub>, and n-octane was added by infusion with a syringe pump through a T-junction to the reactor. In all experiments, the molar ratio of H<sub>2</sub> and n-octane was kept at 6.0, and reaction was conducted at 500 °C while the space velocity was fixed at 5 h<sup>-1</sup>.

#### 3.3.3 The Product of n-Octane Aromatization Analysis

A purge valve was used to send the product to Shimadzu GC-17 A for analysis. Helium was sent to purged the effluent of reaction through the column to achieve product separation. The column was operated in a temperature-programmed mode by starting at 40 °C for 10 minutes, then the temperature was ramped up to 195 °C with a heating rate of 5 °C/min and held. The catalytic activities were defined in terms of conversion, selectivity and aromatics yield as follows:

$$\text{Conversion} = ([\text{n-Octane}]_{\text{in}} - [\text{n-Octane}]_{\text{out}}) / [\text{n-Octane}]_{\text{in}}$$

$$\text{Aromatics Selectivity} = [\text{Aromatics}] / ([\text{n-Octane}]_{\text{in}} - [\text{n-Octane}]_{\text{out}})$$

$$\text{Aromatics Yield} = \text{Conversion} \times \text{Aromatics Selectivity}$$

where

$$[\text{n-Octane}]_{\text{in}} = \text{Total normalized product signals}$$

$$[\text{n-Octane}]_{\text{out}} = \text{Normalized n-octane product signal}$$

$$[\text{Aromatics}] = \text{Normalized aromatics product signal}$$

### 3.4 Characterization of Catalyst

Fresh and spent samples were characterized by FTIR of adsorbed CO and Temperature Programmed Oxidation (TPO).

#### 3.4.1 Fourier Transform Infrared Spectroscopy of CO Adsorbed

The platinum clusters loaded in the catalyst were characterized by Fourier transform-infrared spectroscopy Nicolet AVATAR 360 FT-IR E.S.P., equipped with a DTGS detector using CO as a probe. Experiments were conducted in a diffuse reflectance cell that allowed performing in-situ thermal pretreatment. For each IR spectrum, taken at a resolution of  $8 \text{ cm}^{-1}$ , 128 scans were added. Samples were in-situ reduced in a flow of  $\text{H}_2$  at  $500 \text{ }^\circ\text{C}$  for 1 hour, cooled under Helium flow, and purged by Helium at room temperature for 30 minutes.  $\text{N}_2$  was flowed in a chamber to remove moisture and  $\text{CO}_2$  to make background collection. The background was recorded. Then catalyst was exposed to a flow of 3 vol% CO in Helium for 30 minutes and then Helium was purge for 30 minutes to remove weakly adsorbed CO.  $\text{N}_2$  was flowed in chamber to collect IR spectra.

#### 3.4.2 Temperature Programmed Oxidation (TPO)

Reactions were conducted in quartz fixed bed reactor, and 25 mg of spent catalyst was placed on a bed of the quartz wool. The catalyst was flushed by Helium at least for 30 minutes before performing the TPO. The amount of  $\text{CH}_4$  produced by methanater was monitored by Gas Chromatograph.

Surface area and stability of fresh catalyst were characterized by BET and XRD techniques.

### 3.4.3 Surface Area Measurement (BET)

The Brunauer-Emmett-Teller (BET) method was utilized for determining the surface area of the catalyst. The characterization was based on the physical adsorption of an inert gas by using Autosorb-1 Gas sorption system (Quantachrome Corporation). It operated by measuring the quantity of gases adsorbed on a solid surface at some equilibrium vapor pressures. Nitrogen gas with cross sectional area of  $16.2 \times 10^{-2} \text{ m}^2/\text{molecule}$  was employed as an adsorbate at a liquefied nitrogen temperature. The sample amount of 0.1 - 0.2 gram was dried and outgassed in the sample cell at 300 °C for 3 hours before adsorption. The specific surface area of each catalyst was evaluated from five points adsorption isotherm.

### 3.4.4 X-ray Diffraction (XRD)

The XRD was utilized to identify the stability of catalyst structure. The XRD pattern was obtained by a Phillips X-ray diffractometer system (PW 3020) equipped with a graphite monochromator and a Cu tube for generating a CuK radiation (1.5406 °A). The catalyst sample was ground to a fine homogeneous powder and held in the beam of thin-walled glass container. Constructive interference could be achieved with monochromatic irradiation by varying the angle of incidence (5 to 90 degrees). The digital output of the proportional X-ray detector and the goniometer angle measurement were sent to an online computer to record and subsequently analyzed by PC-APD version 3.5B.

### 3.5 Apparatus

The experimental apparatus is schematically shown in Figure 3.1.

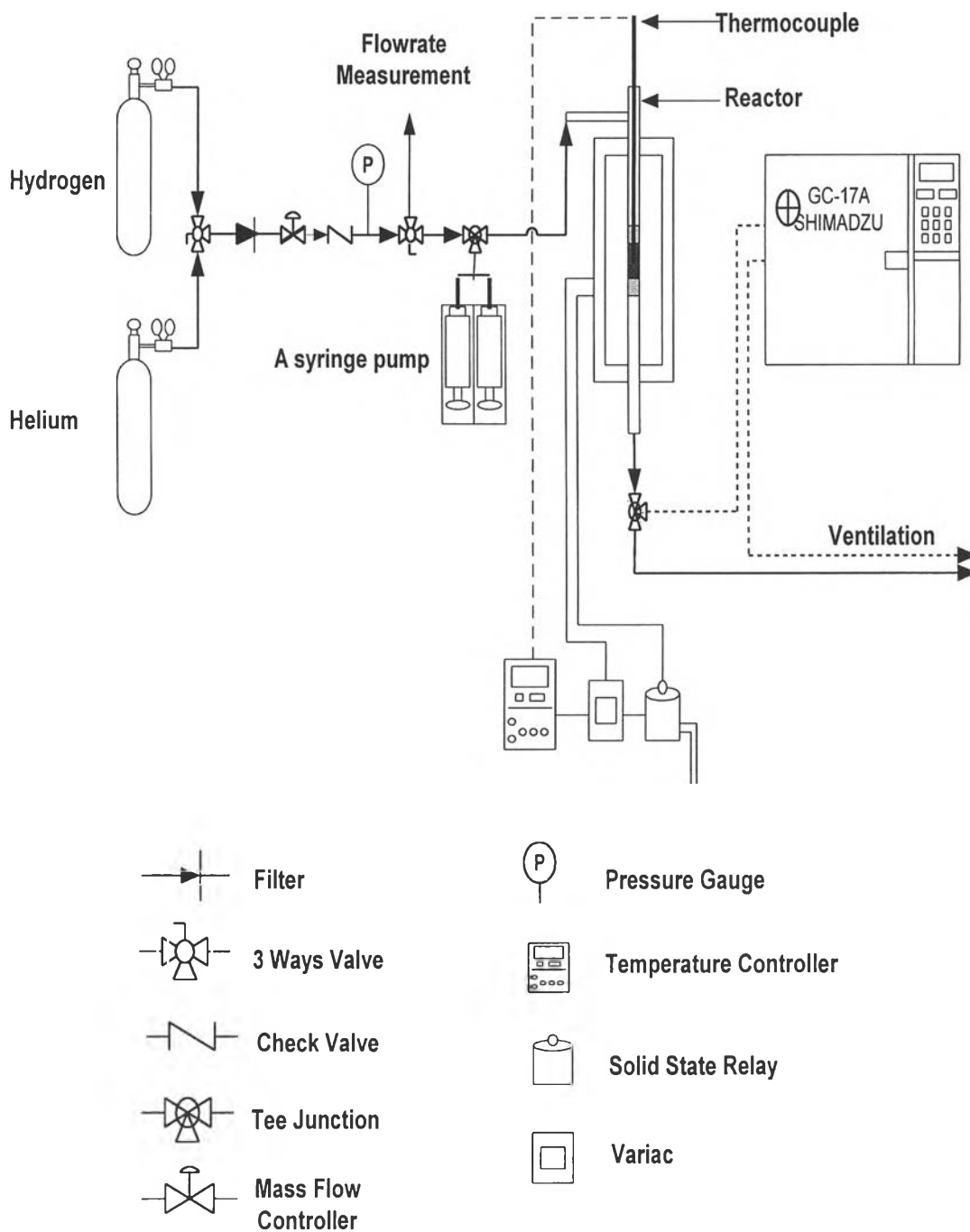


Figure 3.1 Experimental set up