

## CHAPTER III

### EXPERIMENTAL SECTION

The experimental section in this study can be divided into three parts: (a) catalyst preparation; (b) activity and selectivity measurements; and (c) catalyst characterization. The details of each part are described in the following sections.

#### 3.1 Catalyst Preparation

The impregnation technique was employed to prepare the catalysts. There are two impregnation methods used in this work:

1. Incipient wetness impregnation (IWI) method
2. Vapor phase impregnation (VPI) method or chemical vapor deposition (CVD) method

In the case of promoted catalyst, PtYb/KL, the catalyst was separately impregnated in the sequence of ytterbium and platinum, respectively.

##### 3.1.1 Materials

All chemicals used in this experiment were analytical grade.

(a) K-LTL zeolite powder (series TSZ-500, BET area 292 m<sup>2</sup>/g, SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio = 6) manufactured by Tosoh Corporation.

(b) Tetraammineplatinum (II) nitrate (Pt (NH<sub>3</sub>)<sub>4</sub> (NO<sub>3</sub>)<sub>2</sub>) manufactured by Aldrich Chemicals.

(c) Platinum (II) acetylacetonate ([CH<sub>3</sub>COCH=C(O-)CH<sub>3</sub>]<sub>2</sub>Pt) with Pt of 97% purity manufactured by Aldrich Chemicals.

(d) Ytterbium (II) acetylacetonate

Prax Air Company supplied gases used in this work.

(a) High purity helium gas (99.99%) was used in the VPI preparation method.

(b) High purity air zero (99.99%) was used for calcinating catalysts.

### 3.1.2 Methodology

Prior to incorporation of Pt metal, the zeolite powder was dried in an oven at 110°C for 12 h and calcined at 400°C for 5 h. All calcination steps were performed under a flow of air (100 ml/g zeolite), employing a temperature ramp of 3 °C/min. The incorporation of platinum metal into the zeolite was performed using the two methods.

#### *3.1.2.1 Incipient Wetness Impregnation (IWI) Method*

In the IWI procedure, the freshly calcined support was quickly transferred to an inert atmosphere and impregnated dropwise while grinding with an aqueous solution of platinum salt tetraamine platinum (II) nitrate. To achieve incipient wetness, a liquid/solid ratio of 0.69 ml/g was used. After impregnation, the samples were dried for 12 h at 110 °C and then calcined for 2 h in air at 350 °C. This sample was designated IWI.

#### *3.1.2.2 Chemical Vapor Deposition (CVD) Method*

The second method employed was VPI or CVD. After quickly transferring the freshly calcined support to an inert atmosphere, platinum acetylacetonate was physically mixed with KL, and then solid mixture was transferred to a continuous-flow reactor. The reactor consisted of a 0.5-inch diameter stainless steel pipe with an internal thermocouple. The solid mixture bed was supported on a bed of quartz glass wool. The reactor was operated under atmospheric pressure and a low flow rate of helium (< 10 ml/min). The catalyst was slowly ramped to 40 °C and held at this temperature

for 3 h for keep the pore with the inert atmosphere. After that the catalyst was slowly ramped to 60°C, 80°C, 90°C and held at each step for 1 h to remove the trace of water, and then ramped again to 100°C and held for 1 h for subliming the Pt(AcAc)<sub>2</sub>. After sublimation, the catalyst was ramped to 130 °C and held there for 15 min to ensure that virtually all of the Pt(AcAc)<sub>2</sub> was sublimed. The reactor was cooled to room temperature, and the sample was removed. At this point, the sample was light yellow in color, indicating that the Pt(AcAc)<sub>2</sub> did not decompose during the procedure. To decompose the platinum precursor the sample was ramped to 350 °C in flow of air and calcined for 2 h. This sample was designated CVD.

## 3.2 Activity and Selectivity Measurements

### 3.2.1 Materials

(a) The purity of 99.99% n-hexane (C<sub>6</sub>H<sub>14</sub>) from Merck was used as liquid feed for the study of the catalytic activity.

(b) The purity of > 98% thiophene (C<sub>4</sub>H<sub>4</sub>S) from Fluka was used as source of sulfur in the feed for the studying of sulfur effect on the deactivation of the catalysts.

(c) High purity hydrogen gas (99.99%) was used as a feed stream for n-hexane aromatization and for reducing catalyst before used.

### 3.2.2 Apparatus

The apparatus used for studying the activity and selectivity of Pt/KL and PtYb/KL catalysts on the n-hexane aromatization reaction was schematically shown in Figure 3.1.

The details of the experimental equipment were described as follows:

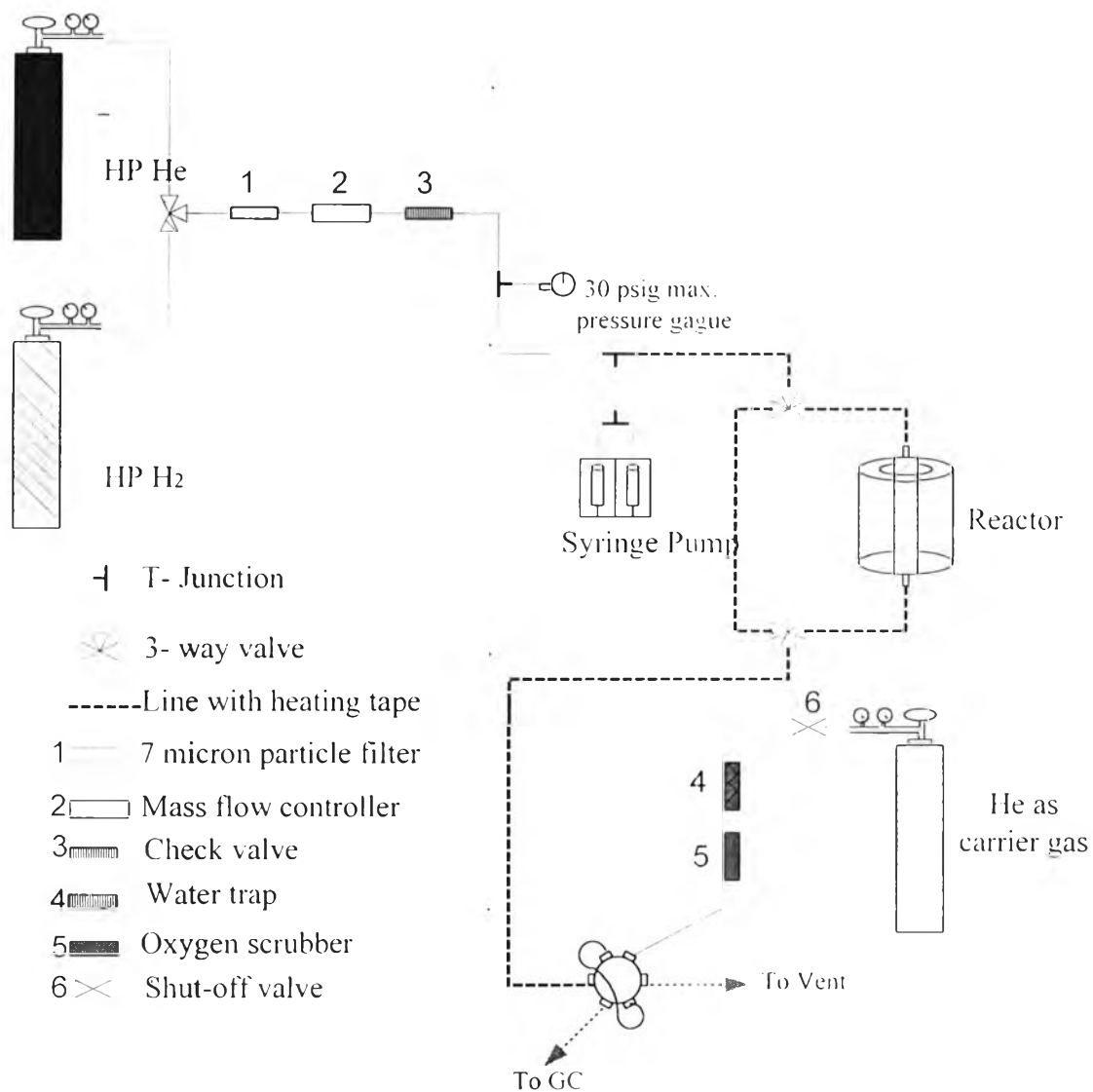


Figure 3.1 The schematic diagram of the reaction system.

(a) Reactor: The reactor was an I.D. 0.5-inch and length 40 cm stainless steel pipe.

(b) Gas chromatograph: The compositions of feed and product streams were analyzed by a GC-17A Shimadzu gas chromatograph equipped with C-R8A Chromatopac, the data plotter. Its specifications and operating conditions are given in Table 3.1.

**Table 3.1** Gas chromatography specifications and operating conditions

Item	Specifications and operating conditions
Column	the HP-PLOT/Al <sub>2</sub> O <sub>3</sub> "S" deactivated capillary column
Temp.	Held at 40 °C for 10 min and then ramped (5 °C/min) to 195 °C. Held at 195 °C for 9 min
Carrier	37 cc/min of helium
Detector Temp.	Flame ionization detector (FID), 250 °C
Injector Temp.	250 °C

(c) Mass flow module: The flow controllers from Cole-Parmer Instrument Company were used to control the flow rates of hydrogen and helium.

(d) Temperature controller: The temperature controller consisted of a variable voltage transformer and a temperature controller manufactured by Yamatake-Honeywell model SDC 10 as well as a type-K thermocouple from Cole Palmer, probeflex 2521-mini was used.

(e) Fittings and tubing system: The stainless steel and brass fittings and tubing system having outside diameters of 1/4" and 1/8" were utilized and obtained from SWAGELOCK Co., Ltd.

(f) Regulator: The regulators for all gases were obtained from Praxair Co., Ltd.

(g) Heating tape: The heating tapes that were used for controlling the temperature of reactants and products flowing in the tubing system over 90 °C to avoid the gas condensation.

(f) Syringe tubing and pumping: The syringe pump from Cole-Parmer Instrument Company that was equipped with a 50 ml. syringe from Hamilton Co., Ltd. was used to inject the n-hexane to the reaction system. The syringe was separately used in the case of injection of n-hexane mixed with thiophene.

### 3.2.3 Methodology

Four hundred milligrams of catalyst was placed in the 0.5-inch stainless steel tube reactor with an internal thermocouple and sealed with quartz glass wool at the top and bottom of the catalyst bed that was supported by a quartz inserted tube. The operating temperature and pressure were maintained at 400°C or 500 °C and 1 atm in the continuous flow reactor. The reactant was operated under hydrogen flow. The liquid n-hexane was added by infusion with a syringe pump through a tee-junction prior to the reactor. In all experiments, the hydrogen/n-hexane ratio was kept at 6. Prior to reaction, the catalyst was slowly ramped in flowing hydrogen at 100 ml/ g catalyst for 2 h to a temperature of 400°C or 500°C and reduced for 1 h at that temperature. The reaction testing was conducted at the same temperature with the reduction temperature at a weight hourly space velocity (WHSV) of 5 h<sup>-1</sup>.

#### 3.2.3.1 *Selectivity Testing*

The WHSV was increased for observing the selectivity at the low conversion of the catalyst. In order to increase the WHSV of reactant feed, the catalyst weight was decreased while the flow of n-hexane feed was fixed at 3.03 ml/h to obtained values of WHSV that were showed in Table 3.2.

**Table 3.2** Varying weight of catalysts at different WHSV ( $\text{h}^{-1}$ )

WHSV ( $\text{h}^{-1}$ )	Weight of catalyst (g)
5	0.3993
10	0.1997
15	0.1331
20	0.0998
25	0.0799
30	0.0665
35	0.0570
40	0.0499

The WHSV can be calculated by using this following formula;

$$WHSV(\text{h}^{-1}) = \frac{n\text{-hexane flowrate (cc/h)} \times \text{density of } n\text{-hexane (g/cc)}}{\text{grams of catalyst (g)}}$$

### 3.2.3.2 Sulfur Tolerance

The thiophene was mixed with n-hexane feed at the concentration of sulfur 0.6 ppm and 2.5 ppm for testing the sulfur tolerance of the catalyst. To prevent the contamination from sulfur, the reaction line from feed point to the entrance of the reactor including reactor and syringe were used separately from free sulfur reaction runs.

## 3.3 Catalyst Characterization

### 3.3.1 Hydrogen Chemisorption Measurement

The Autosorb-1-c is used for hydrogen chemisorption measurement. The experiments were conducted on several of the powder preparation catalysts in a static volumetric adsorption Pyrex system, equipped

with a high capacity, high vacuum pumping station. First, the catalyst was loaded into the quartz tube and performed a reduction under hydrogen flow for 1 h at 500°C. Second, the hydrogen at the platinum surface was removed by helium flow at the reduction temperature for 30 min and then evacuated for 1.5 h. After that the catalyst was cooled to 40°C and evacuated at the same time. At this step, all hydrogen was removed from the surface of platinum, which was reabsorbed hydrogen incrementally. The hydrogen was incrementally dosed at 40 °C at elevated pressure. The extrapolation back to zero pressure method was used to calculate the adsorbed volume. To quantify the amount of reversibly adsorbed hydrogen, after obtaining the first isotherm, the sample was evacuated for 5 min at 40 °C to removed the weakly adsorbed (physisorbed) and a second isotherm was determined. The irreversible H/Pt was obtained by subtracting the two isotherms.

### 3.3.2 Infrared Spectroscopy

Infrared spectroscopy of adsorbed CO was performed on Nicolet Avatar 360 spectrometer equipped with a DTGS detector. Experiments were conducted in a diffuse reflectance cell Spectra-Tech that allowed in-situ thermal pretreatment performance. For each IR spectrum, taken at a resolution of 8 cm<sup>-1</sup>, 128 scans were added. Samples were in-situ reduced under H<sub>2</sub> flow at either 400°C or 500°C for 1.30 h. Prior to each spectrum, the catalyst was purged in He for 30 min. The background was recorded at this time. Then the catalyst was exposed to a flow of 3 % CO in He for 30 min at room temperature and purged in He for 30 min, prior to obtaining the scans, to remove the contributions from gas phase and weakly adsorbed CO.