

## CHAPTER III

### EXPERIMENTAL

#### 3.1 Materials

##### 3.1.1 Gases

All gases used in this experiment were commercial grade obtained from Thai Industrial Gas Public Co., Ltd. and Praxair Korea Co., Ltd.

The high purity (HP) nitrogen was used for purging the glove box during catalyst preparation and FT-IR measurement.

The ultra high purity (UHP) hydrogen was used as fuel for FID detector in gas chromatography and as a reactant for n-hexane aromatization reaction.

The high purity (HP) helium was used for purging catalysts after reduction with hydrogen and adsorption with 3 vol% carbonmonoxide (CO) balance in helium during FT-IR measurement and as the carrier during the catalyst preparation by the chemical vapor deposition method.

The 3 vol % carbonmonoxide balance in helium was used as an adsorbate in FT-IR measurement.

The air zero grade was used as the oxidant in gas chromatography and the combustion gas in the calcination procedure which was one of the catalyst preparation procedures.

##### 3.1.2 Chemicals

n-Hexane (C<sub>6</sub>H<sub>14</sub>) of min. 99% purity was supplied from Merck (Darmstadt, Germany).

Thiophene (C<sub>4</sub>H<sub>4</sub>S) of 98% purity was supplied from Fluka (Steinheim, Switzerland).

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

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

Cerium(III) 2,4-pentanedionate ( $[\text{CH}_3\text{COCH}=(\text{CO}-)\text{CH}_3]_3\text{Ce}$ ) was supplied from Alfa Aesar (West Deptford, USA).

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).

## 3.2 Catalyst Preparation

In this work the catalysts were prepared at 1 wt % loading of platinum (Pt) and with and without 0.15 wt % loading of cerium (Ce). The platinum-supported catalysts were prepared by two methods; incipient wetness impregnation (IWI) and chemical vapor deposition (CVD) whereas the platinum-cerium zeolite catalysts were only prepared by CVD method. Before addition of the metal, the K-LTL zeolite was dried in an oven at 110°C overnight and calcined at 400°C in a dried air flow of 100 ml/min-g for 5 h.

### 3.2.1 Incipient Wetness Impregnation

Tetraammineplatinum(II) nitrate was weighed and dissolved in deionized water using a liquid/solid ratio of 0.69 ml/g. The dry support was then impregnated in a glove box under nitrogen atmosphere with an aqueous solution of platinum salt by adding a few drops to the L-zeolite and then the mixture was ground with a mortar and pestle. This procedure was repeated until all the water and salt had been added. Next, the mixture was covered by paraffin film to prevent the contaminations and left at room temperature for 4 h. The mixture covered by a watch glass was dried in an oven at 110°C overnight. The cool mixture was loaded into the reactor tube and calcined at

350°C in a dried air flow of 100 ml/min.g for 2 h and left cool to room temperature. The resultant catalysts were stored in a desiccator.

### 3.2.2 Chemical Vapor Deposition

Weighed platinum(II) acetylacetonate ( $\text{Pt}(\text{AcAc})_2$ ) was mixed physically with the dried zeolite under nitrogen atmosphere. The mixture was loaded into the reactor tube under a helium flow of 2 ml/min. The mixture was slowly ramped to 40°C and held there for 3 h, and then ramped again to 60°C and held again for 1 h. The procedure was repeated by increasing temperature to 80, 90 and 100°C, respectively. After further ramping to 100°C, the mixture was held for 1 h to sublime the  $\text{Pt}(\text{AcAc})_2$ . After sublimation, the mixture was ramped to 130°C and held for 15 minutes to ensure that virtually all of  $\text{Pt}(\text{AcAc})_2$  was sublimed. The reactor was cooled to room temperature, and the sample was removed. At this point, the sample was ramped to 350°C in flow of air for 2 h and calcined at that temperature for 2 h to decompose the platinum precursor. The resultant catalysts ( $\text{Pt}/\text{KL}$ ) were stored in a desiccator.

In the case of the platinum-cerium zeolite catalyst ( $\text{PtCe}/\text{KL}$ ), it was prepared using the same procedure as above but the calcined support was first mixed physically with cerium(III) 2,4-pentanedionate ( $\text{Ce}(\text{AcAc})_3$ ) and the mixture was then ramped up step by step until 130°C. After calcination in a dried air flow,  $\text{Ce}/\text{KL}$  was obtained.  $\text{Ce}/\text{KL}$  was then mixed physically again with  $\text{Pt}(\text{AcAc})_2$  and calcined in a dried air flow. Finally  $\text{PtCe}/\text{KL}$  was obtained.

## 3.3 Catalyst Characterization

### 3.3.1 Hydrogen Chemisorption Measurement

The Autosorb-1-MP was used for hydrogen chemisorption measurement. The experiments were conducted on several of the powder preparation catalysts in a static volumetric Pyrex adsorption system, equipped with a high capacity, high vacuum pumping station. The catalyst was loaded into the quartz tube and undergone a reduction under hydrogen flow at 500°C for 1 h. The physisorbed hydrogen at the platinum surface was then removed by helium flow at the reduction temperature for 30 min and evacuated for 1.5 h. After that, the catalyst was cooled down to 40°C and evacuated at the same time. At this step, all hydrogen was removed from the surface of platinum to quantify reabsorbing hydrogen incrementally. The hydrogen was incrementally added at 40°C at elevated pressure. The extrapolation back to zero pressure method was used to calculate the volume adsorbed. To quantify the amount of reversibly adsorbed hydrogen, after obtaining the first isotherm, the sample was evacuated for 5 min at 40°C to remove the weakly adsorbed (physisorbed) and a second isotherm was determined. The amount of irreversible H/Pt was obtained by subtracting from the two isotherms.

### 3.3.2 Fourier Transform-Infrared Spectroscopy

The platinum clusters loaded in the catalysts 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 of Spectra-Tech with ZnSe windows that allowed to perform *in-situ* thermal pretreatments. For each IR spectrum, taken at a resolution of 8 cm<sup>-1</sup>, 128 scans were added. Sample was *in-situ* reduced in a flow of H<sub>2</sub> for 30 min at either 400°C or 500°C for 1 h, cooled under He flow, and purged by using He at room temperature for 30 minutes. The N<sub>2</sub> was flowed in a chamber of the instrument to remove the moisture and CO<sub>2</sub> prior to background collection. The background was recorded at this time. The catalyst was then exposed to a flow of 3 % CO in

He for 30 minutes at room temperature and purged in He for 30 minutes, prior to obtaining the scans, to remove the contribution from gas phase and weakly adsorbed CO. N<sub>2</sub> gas was flowed in a chamber before collecting IR spectrum.

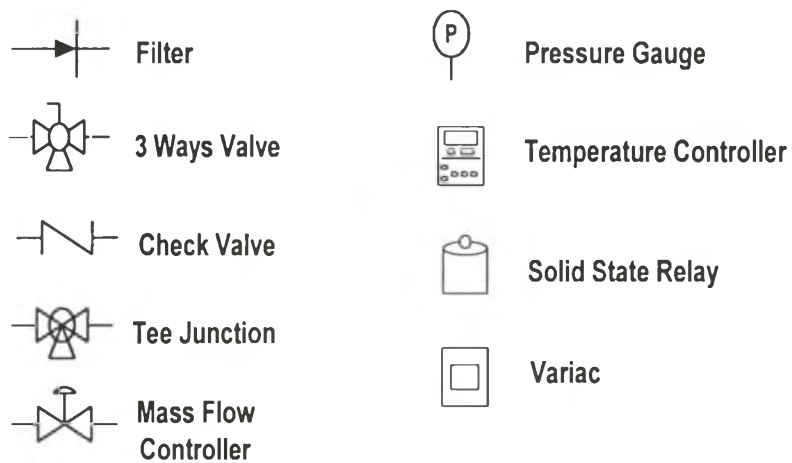
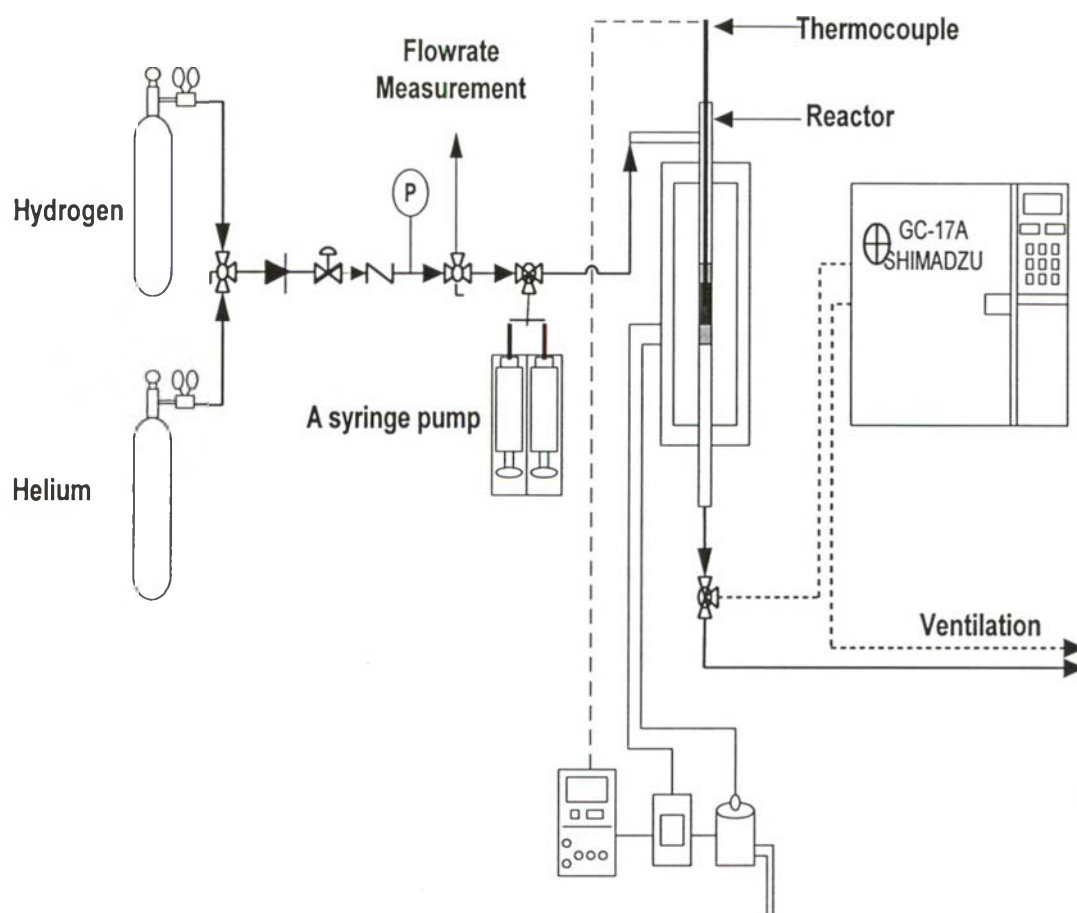
### 3.3.3 Temperature Programmed Oxidation

The spent catalyst was performed in a continuous flow of 5 % O<sub>2</sub> in He while the temperature was linearly increased. The reaction was conducted in a quartz fixed bed reactor and 40-50 mg of spent catalyst was placed on a bed of quartz glass wool. The catalyst was flushed by He at least for 30 minutes before performing the TPO. The evolution of CO<sub>2</sub> produced by the oxidation of the carbon species was monitored by a mass spectrometer. Quantification of the CO<sub>2</sub> produced was calibrated with 100-ml pulse 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>.

## 3.4 Apparatus

### 3.4.1 Gas Blending System

Figure 3.1 showed a schematic flow diagram of the experimental system. A gas flow rate was controlled by a mass flow controller from Cole-Parmer. Helium gas was used for cooling the reactor to room temperature. H<sub>2</sub> was flowed into the reactor for *in-situ* reduction and as a reactant gas. All gases were passed through a micron filter, and the mass flow controller at a constant pressure. A check valve was installed to prevent the back flow of gases. n-Hexane was introduced into the reaction system by a syringe pump (Cole-Parmer, model 74900) with a constant flow rate. In the study of sulfur effect, thiophene was mixed homogeneously with n-hexane and the mixture was fed into the reaction system.



**Figure 3.1** Schematic flow diagram

### 3.4.2 Catalytic Reactor

The reactor was 0.50-inch diameter stainless steel tube operated at atmospheric pressure. The catalysts were loaded between quartz wool plugs in the middle of reactor. An electrical heater was used to heat the reactor. The reaction temperature was controlled by PID controller using a K-type thermocouple inserted into the heater at the same level of catalyst bed. The reaction temperature was monitored by using a K-type thermocouple inserted in the middle of catalyst bed. The controller, connected to the thermocouple, was a Yamatake-Honeywell model SDC10.

### 3.4.3 Gas Chromatograph

A Shimadzu GC-17A gas chromatograph with an HP-PLOT/Al<sub>2</sub>O<sub>3</sub> “S” Deactivated, was used for measuring the composition of reactor effluent stream qualitatively and quantitatively. The products were analyzed by FID detector. The column was operated in a temperature programmed mode. The temperature was started at 40°C for 10 minutes, then the temperature was ramped to 200°C with a heating rate of 5°C/min and held at this temperature for 9 minutes. The injection and detector were operated at the same temperature, 250°C.

0.10 ml of gas sample was drawn by a 1.0 ml gas-tight syringe and injected at first 10 minutes and every 1 h into the gas chromatography for the analysis.

## 3.5 **Catalytic Activity Measurements**

The tests for catalytic reaction were conducted at atmospheric pressure in a 0.5-inch stainless steel tube with an internal K-type thermocouple for temperature measurement. The reactor was a single pass and continuous-flow type. The reactors were kept segregated for clean n-hexane runs while the

other reactor was only used for sulfur deactivation studies. The 0.40 g of catalysts were conducted in each run. The catalyst bed was supported on a bed of quartz glass wool. Prior to reaction, the catalyst was slowly ramped in flowing hydrogen at 100 ml/min.g for 2 h to a temperature of 400°C or 500°C and *in-situ* reduced at that temperature in flowing hydrogen at 100 ml/min.g for 1 h. The catalyst was kept at the reduction temperature and n-hexane was added by infusion with a syringe pump through a T-junction prior to the reactor. In all experiments, the hydrogen/n-hexane ratio was kept at 6.0. All signals were normalized to quantify concentration of each product. The catalytic activities were defined in the terms of conversion, selectivity, benzene yield and hexenes yield as follows:

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

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

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

$$\text{Hexenes Yield} = \sum [\text{Hexene}]_i$$

where

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

$$[\text{n-Hexane}]_{\text{out}} = \text{Normalized n-hexane product signal}$$

$$[\text{Benzene}] = \text{Normalized benzene product signal}$$

$$[\text{Hexene}]_i = \text{Normalized each hexene product signal}$$