

## CHAPTER III EXPERIMENTAL

### 3.1 Materials

#### 3.1.1 Gases

The ultra high purity (UHP) hydrogen was used as reactant for n-C<sub>6</sub> and n-C<sub>8</sub> reaction testing, as fuel for FID detector, H<sub>2</sub> chemisorption measurement.

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

The high purity (HP) helium was used for purging catalysts after reaction testing, for the catalyst preparation during sublimation, and H<sub>2</sub> chemisorption measurement.

The air zero grade was used for FID detector and catalyst preparation during calcination and pretreatment.

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

The 5 volume % oxygen balance in helium was used for the temperature-programmed oxidation (TPO) measurement.

#### 3.1.2 Chemicals

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

n-Octane (C<sub>8</sub>H<sub>18</sub>) of min. 99% purity was obtained from Merck (Darmstadt, Germany).

Tetraammineplatinum(II)nitrate (Pt(NH<sub>3</sub>)<sub>4</sub>(NO<sub>3</sub>)<sub>2</sub>) was obtained from Aldrich (Milwaukee, USA).

Cerium (III) nitratehexahydrate ( $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ) was obtained from Aldrich (Milwaukee, USA).

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

Cerium (III) 2,4-pentanedionate ( $[\text{CH}_3\text{COCH}=(\text{CO}-)\text{CH}_3]_3\text{Ce}$ ) was obtained 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 obtained from Tosoh (Tokyo, Japan).

Thiophene ( $\text{C}_4\text{H}_4\text{S}$ ) of 98% purity was obtained from Fluka (Steinheim, Switzerland).

## 3.2 Catalyst Preparation

### 3.2.1 Incipient Wetness Impregnation

#### *I) Calcination of L-zeolite*

For a 3 gram batch, L-zeolite was put in tubular reactor and set aside only for calcination. The L-zeolite is heated in flow of air at 100 ml/min per gram of L-zeolite to drive off chemisorbed water. Temperature was set to reach 400°C in 2 hours and hold for 5 more hours. Then reactor was cooled to room temperature, the L-zeolite was reweighed and transferred to an inert atmosphere glove box to prevent water vapor from the atmosphere to be readsorbed in the pores of the L-zeolite.

#### *II) Addition of Pt salt*

Measure out 0.69 ml of water for each gram of L-zeolite used. Whereas, for a 1% Pt loading, dissolve in the water, 0.01985 gram of  $\text{Pt}(\text{NH}_3)_4(\text{NO}_3)_2$  per gram of L-zeolite. Stir the water containing Pt-salt until the salt dissolves. Add a few drops of solution to L-zeolite and grind the mix with a mortar and pestle to impregnate, after that, add a few more drops and grind the mix again. Repeat this procedure until all the water and salt have

been added. Cover the mortar with parafilm and leave it on the lab bench for 4 hours. Next, place the mortar in conventional oven at 110°C for 8 hours.

### *III) Pretreatments*

Load the mixture into calcination reactor, then calcine in flow of air at 100 ml/min per gram of catalyst, ramp to 350°C and hold for 2 hours. After that, let it cool to room temperature. The finished catalyst should be stored in vial with parafilm covering and keeping in a dessicator.

### 3.2.2 Vapor-Phase Impregnation

#### *I) Calcination of L-zeolite*

Calcined KL zeolite in flow of air (100 ml/min per gram of L-zeolite). Use 2 hours ramp to 400°C and hold for 5 hours at 400°C. Then cool in air, remove the zeolite and transfer to inert atmosphere (glove box with nitrogen flow).

#### *II) Addition of rare earth (VPI procedures)*

In the inert atmosphere, weigh out enough lanthanide acetylacetonate to yield 0.15% loading in KL zeolite and mix with a spatula to give uniformly mixture. The well mixed mixture was loaded into the reactor tube. To have inert atmosphere, flowing He (<10 ml/min per gram of catalyst), ramp to 40°C, hold for 3 hours. Slowly ramp to 60°C, 80°C, and 90°C each step hold to 1 hour to remove trace of water, ramp to 100°C, and hold for 1 hour to sublime the lanthanide acetylacetonate compound. Ramp again at 1° C/min to 130°C and hold for 15 minutes to make sure all the lanthanide acetylacetonate has vaporized. Next, the sample was removed and loaded back into calcination reactor.

#### *III) Addition of Pt salts and pretreatments*

To pretreatment, ramp the catalyst in flow of air again (100 ml/min per gram catalyst) to 350°C and hold for 2 hours. Repeat VPI procedures (step2), by adding 1% loading of Pt(AcAc)<sub>2</sub> to the lanthanide/KL.

Calcine the Pt/lanthanide-KL catalyst by ramping for 2 hours in air (100 ml/min per gram catalyst) and holding for 2 hours at 350°C. The finished catalyst should be stored in vial with parafilm covering and keeping in a dessicator.

### 3.3 Catalytic Activity Measurements

#### 3.3.1 Priority to Reaction Testing

To reduce the catalyst for 3 hours by following procedures. Transfer the prepared catalyst to the reactor that using for n-hexane (or n-octane) reaction testing. Ramp the catalyst in the flowing of H<sub>2</sub> (100 ml/min per gram of catalyst) for 2 hours to 500°C. Reduce *in situ* in the flowing of H<sub>2</sub> (100 ml/min per gram of catalyst) for 1 hour at 500°C.

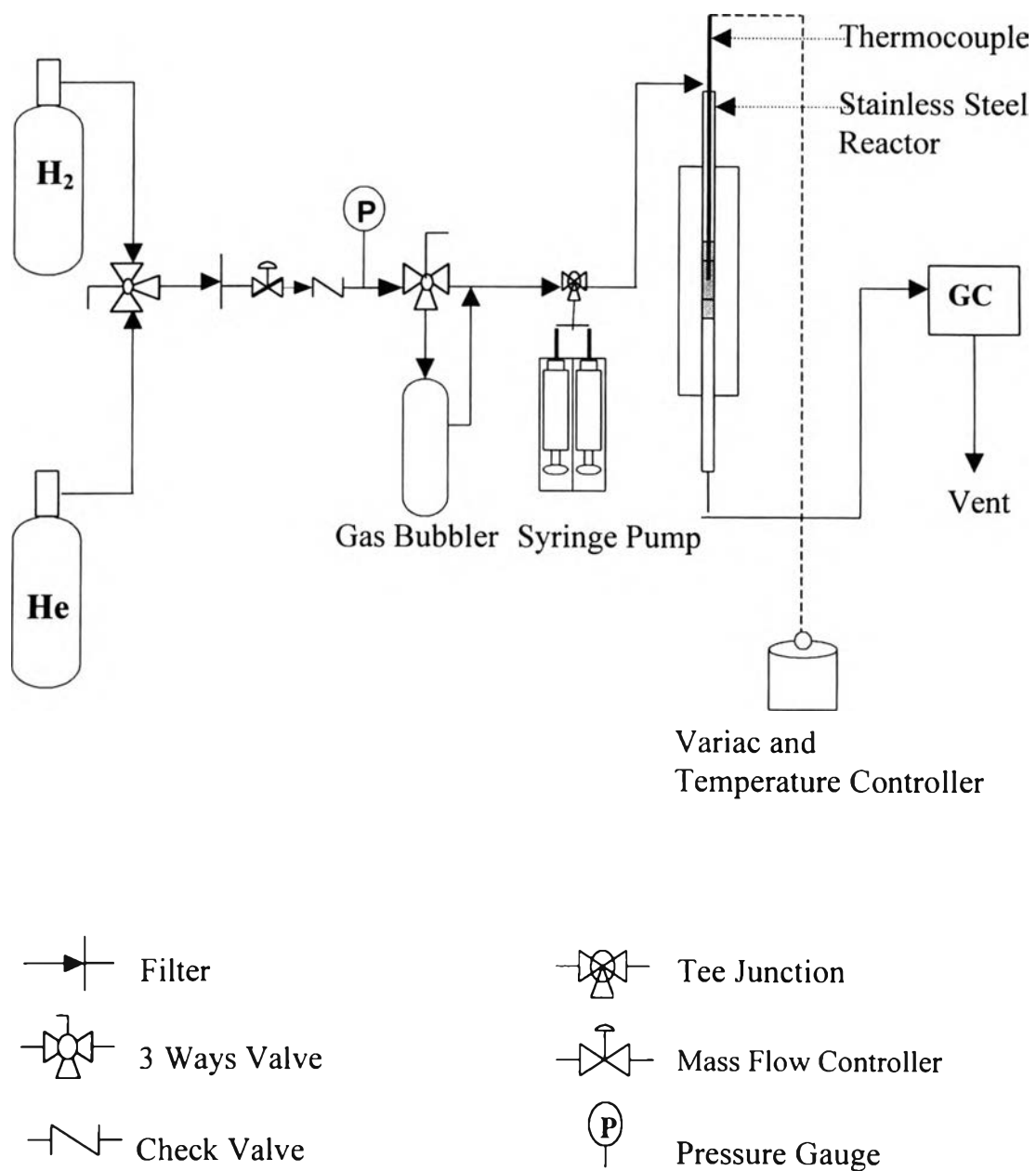
#### 3.3.2 Reaction Testing

Reaction test were conducted at atmospheric pressure using two fixed-bed, single pass and continuous flow reactors in parallel. One reactor was only used for sulfur free n-hexane (or n-octane) runs, while the other reactor was only used for sulfur deactivation studies (sulfur-containing feeds). To avoid contamination of clean runs, all lines leading to each reactor were kept segregated. By using 0.5-inch stainless steel tube with an internal K-type thermocouple and the oven was controlled with a J-type thermocouple. In each run, the experiments were conducted using 0.40 gram of catalyst. The catalyst bed was supported on a bed of quartz wool. The reactor was operated under flowing of H<sub>2</sub>, and n-hexane (or 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> and n-hexane (or n-octane) was kept at 6.0 and reactions were conducted at 500°C or 400°C while the space velocity was varied to achieve different conversions and selectivity of product for study. For sulfur

poisoning studies, thiophene was mixed into n-hexane (or n-octane), feed prior to reaction. Furthermore, for the water poisoning studies, water vapor was fed by a gas bubbler. The schematic diagram of the reaction testing was shown in Figure 3.1.

### 3.3.3 Product Analysis of n-Hexane (or n-Octane) Aromatization

A purge valve was used to send sample to a Shimadzu GC-17A for analysis. The GC utilized He as the carrier gas and sent purged products of reaction through the column (HP-PLOT/Al<sub>2</sub>O<sub>3</sub> “S” Deactivation) to achieve product separation and incorporates with flame ionization detector (FID). A temperature ramp program provided the means for adequate peak separation in the GC column. The column was operated in a temperature-programmed mode by starting at 40°C for 10 minutes, and then the temperature was ramped to 195°C with a heating rate of 5°C/min and held at this temperature. To determine the signal/abundance ratio and quantify the concentration of each component in the products, normalized curves were obtained by using pure component.



**Figure 3.1** Schematic diagram of the reaction testing.

### 3.4 Catalyst Characterization

#### 3.4.1 Hydrogen Chemisorption Measurement

The dispersion of Pt particles (irreversible H/Pt) was identified by using hydrogen chemisorption techniques. The experiments were conducted on the Pt/KL catalysts in a static volumetric Pyrex adsorption system, equipped with a high capacity vacuum pumping station (Varian SD-91) that provided vacuum on the order of  $10^{-9}$ - $10^{-7}$  Torr. The 0.30 grams of catalyst was loaded into the quartz sample cell and reduced under hydrogen at 400°C and 500°C for 1 h. Evacuated at high temperature (300°C) for 20 min in order to remove all adsorbed species. Next, the catalyst was cooled down to room temperature and evacuated at the same time. Readsorbing hydrogen incrementally at elevated pressure. The first obtained isotherm represented the total adsorption. After that, the catalyst was evacuated for 10 min at room temperature to remove the weakly adsorbed (physisorbed), and the second isotherm was obtained. The chemisorption isotherm that represents the H/Pt was determined by subtractions the two isotherms.

#### 3.4.2 Fourier Transform-Infrared Spectroscopy of Adsorbed CO

In order to obtain the distribution of Pt cluster size and location 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 performing *in-situ* thermal pretreatments. For each IR spectrum, taken at a resolution of  $8\text{ cm}^{-1}$ , 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 hr, 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.

### 3.4.3 Temperature-Programmed Oxidation

The amount of coke formation and the nature of the coke deposition were performed by temperature-programmed oxidation (TPO) techniques. The 0.030-0.040 gram of spent catalyst was loaded in quartz fixed-bed reactor supported by quartz wool. The different conditions of spent catalysts were conducted under flow of 5 % O<sub>2</sub> in He with the linear temperature increasing from room temperature to 800°C for 1 h. The evolution of CO<sub>2</sub> produced by the oxidation of the carbon species was monitored by a Balzers TCP 121 mass spectrometer to perform the profile of partial pressure of product gas with temperature. After that, the pure CO<sub>2</sub> was introduced into system to calibrate with 100 µl pulses in order to obtain the quantity of the CO<sub>2</sub> produced. 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>.