

## 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).

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

Platinum (II) acetylacetonate ( $[\text{CH}_3\text{COCH}=\text{C}(\text{O})\text{CH}_3]_2\text{Pt}$ ) 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.

#### 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. and Praxair Co., Ltd.

### 3.2 Catalyst Preparation via Vapor Phase Impregnation Method (VPI)

#### 3.2.1 Calcination of KL zeolite

KL zeolite was calcined in flow of air (100 ml/min/g. of KL zeolite). Then the temperature was ramped to  $500 \text{ }^\circ\text{C}$  in 2 h and held for 4 h. Then the zeolite

was cooled in air, and after that it was removed and quickly transferred to an inert atmosphere (used glove box with N<sub>2</sub> flow).

### 3.2.2 Loading Pt

In the inert atmosphere, platinum acetylacetonate was weighed to yield 1.0 % loading in KL zeolite and mixed uniformly using a spatula. The solid mixture was transferred into the reactor tube (sealed at one end). Helium (<10 ml/min/g) was performed to make inert atmosphere and the temperature was ramped to 40 °C and held for 3 h. After that temperature was slowly ramped to 60, 80, 90 °C. Then temperature was ramped to 100 °C and held for 1 h to sublime the Platinum acetylacetonate compound. Temperature was ramped again at 1°C/min to 130°C and held for 15 min to make sure that the platinum acetylacetonate had sublimed. After that the catalyst was ramped in flow of air (100ml/min/g) to 350 °C and held for 2 h for pretreatment. Finally, the reactor tube was cooled to room temperature and the sample was removed and kept in dessicator.

## 3.3 Reaction and Regeneration

The optimal conditions for regeneration of Pt/KL catalysts utilized for *n*-octane aromatization were studied by varying temperature of regeneration at 150°C - 400°C, time of regeneration at 0.5-8 h and air flow rate at 50-200 ml/min/g. of catalyst with which the same reaction testing were performed.

### 3.3.1 Catalyst Reduction

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

### 3.3.2 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 equipped with an internal type-K thermocouple. Furnace was controlled with a type-J thermocouple. In each run, the experiment was conducted using 0.2 g. of catalyst. The catalyst bed was enclosed by 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 prior to the reactor. In all experiments, the molar ratio of H<sub>2</sub> to n-octane and the space velocity was kept at 6:1 and 5 h<sup>-1</sup> respectively. The reaction was conducted at 500 °C for 12 h. Products were analyzed in every time on stream of 1.5 h.

### 3.3.3 Regeneration in Air

**Table 3.1** Regeneration procedures

Temperature of regeneration(°C)	Time of regeneration (h)	Air flow rate (ml/min/g.cat.)	Catalyst (code)
Effect of temperature of regeneration			
150	0.5	100	A
200	0.5	100	B
250	0.5	100	C
300	0.5	100	D
400	0.5	100	E
Effect of regeneration time			
250	0.5	100	C
250	2	100	F
250	8	100	G
Effect of air flow rate			
250	0.5	50	H
250	0.5	100	C
250	0.5	200	I
Spent Pt/KL without regeneration			S

Regeneration was performed in situ at atmospheric pressure continuously after the course of reaction. The preliminary step was performed with H<sub>2</sub>. The flow rate was kept constant at 21.4 ml/min. and temperature was fixed at 500 °C (reaction temperature) and held constant for 1 h. After this treatment the reactor was purged with He and the temperature was adjusted to the temperature of regeneration, in the range of 150-400 °C. The coke formed on the spent catalyst was oxidized by burning in the flow of air (50-200 ml/min/grams of catalysts). After coke oxidation, the regenerated catalyst was purged with He together with ramping the temperature back to the reaction temperature to begin the second reaction-regeneration cycle. Finally, the regenerated catalyst was conducted to the second reaction testing sequentially.

#### 3.3.4 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.

#### 3.3.5 Pt Redispersion

After the regeneration in air, the sample was first reduced under H<sub>2</sub> for 1 h at 500°C. Then, the sample was treated with air for 30 min at 400°C followed by an oxychlorination step to obtain the redispersion of Pt particles. CCl<sub>4</sub> was saturated with a continuous flow of N<sub>2</sub> through a gas bubbler and then diluted with a stream of air. After that, the sample was exposed to this mixture for 1.5 h. Finally, CCl<sub>4</sub> was switched off and the catalyst was allowed to oxidize in air for another 30 min.

### 3.4 Characterization of Catalysts

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.

#### 3.4.1 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  $\text{H}_2$  for 1 h at  $500^\circ\text{C}$ , cooled under Helium flow, and purged by Helium at room temperature for 30 min. The  $\text{N}_2$  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 min and was purged with Helium for 30 min to remove weakly adsorbed CO.  $\text{N}_2$  was flowed in chamber to collect IR spectra.

#### 3.4.2 Temperature Programmed Oxidation (TPO)

The spent catalyst was performed in a continuous flow of 5%  $\text{O}_2$  balance with He while the temperature was linearly increased at a heating rate of  $12^\circ\text{C}/\text{min}$ . Before conducting the TPO on a 0.05 g sample placed in a  $\frac{1}{4}$ " quartz fixed-bed reactor, the spent catalyst was dried at  $110^\circ\text{C}$  overnight and weighed. The catalyst was then flushed by 5%  $\text{O}_2$  balance with He for 30 min before the temperature ramp was started. The  $\text{CO}_2$  produced by the oxidation of coke species was monitored by a mass spectrometer. The amount of coke was calibrated by using 100  $\mu\text{l}$  pulses of pure  $\text{CO}_2$ . The evolved  $\text{CO}_2$  partial pressure was normalized by the total pressure and the maximum signal in the pulses of  $\text{CO}_2$ .

### 3.5 Apparatus

The experimental apparatus is schematically shown in Figure 3.1.

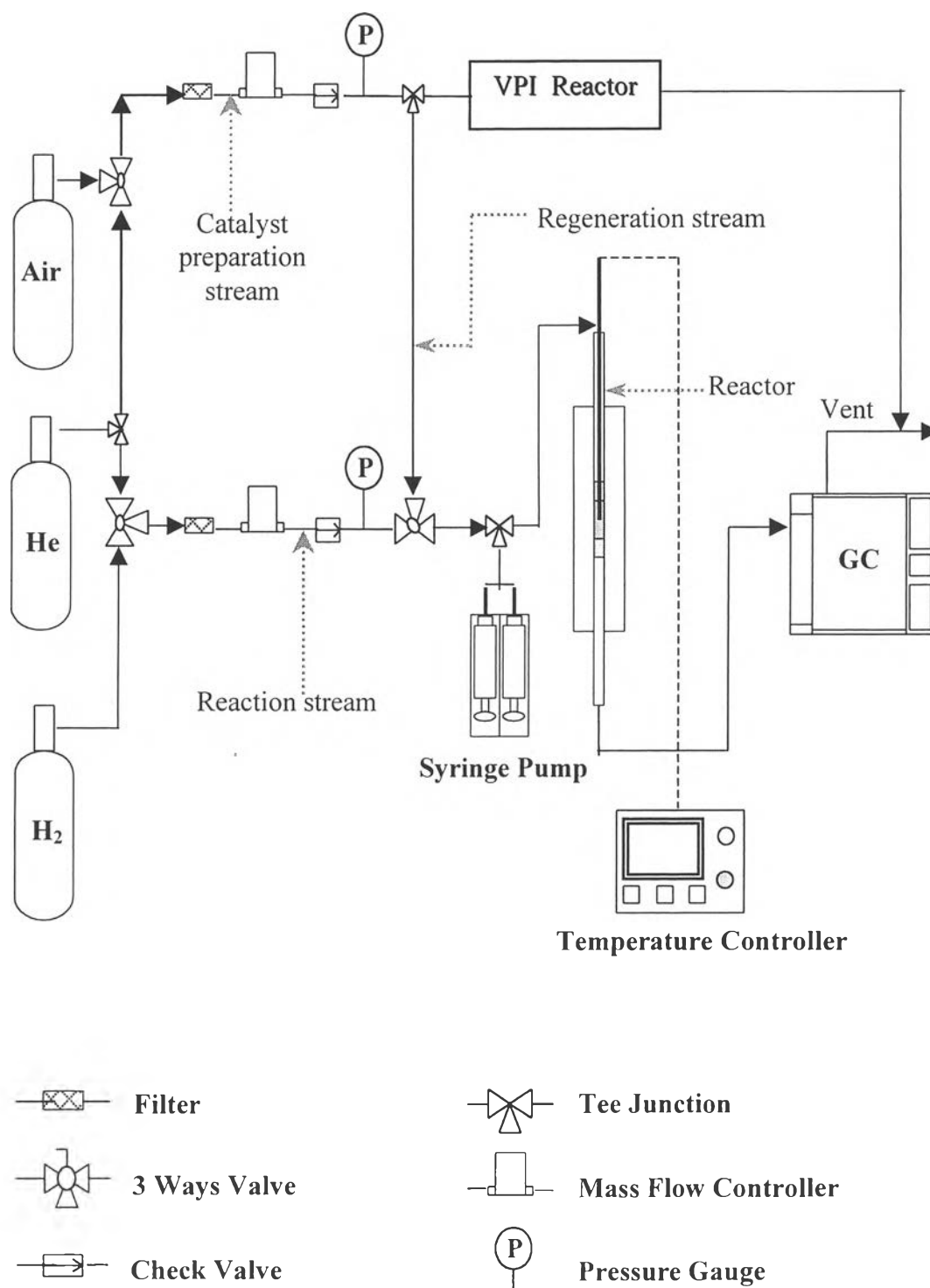
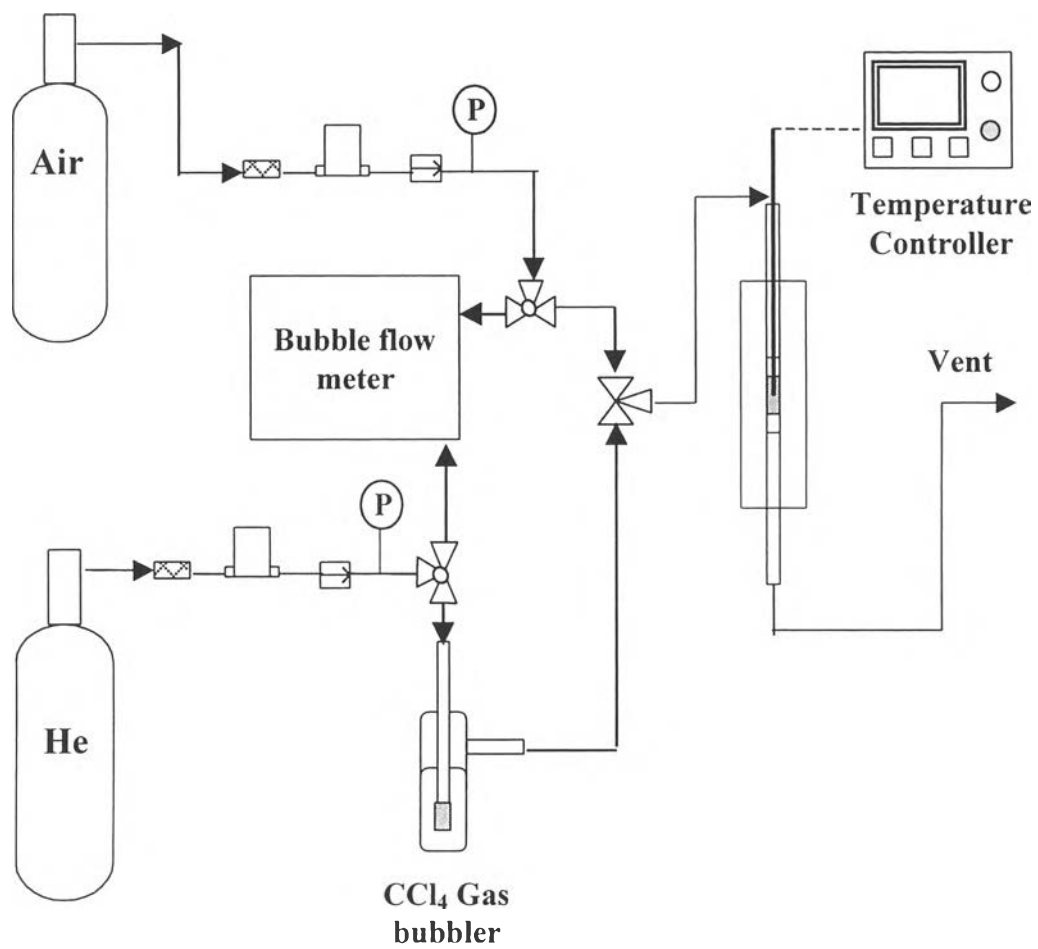


Figure 3.1 Schematic of the experimental set up



**Figure 3.2** Schematic of Pt Redispersion set up (in hood).