



## CHAPTER III EXPERIMENTAL

### 3.1 Materials

#### 3.1.1 Gases

- The ultra high purity (UHP) hydrogen was used for *n*-octane reaction testing, FID detector, and H<sub>2</sub> chemisorption measurement.
- The high purity (HP) nitrogen was used for purging the glove box during catalyst preparation.
- 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 zero grade air was used for FID detector and catalyst preparation during calcination and pretreatment.
- The 5% oxygen balanced in helium was used for the temperature-programmed oxidation (TPO) measurement.
- The 5% hydrogen balanced in argon was used for the temperature-programmed reduction (TPR) measurement.

All gases were supplied from TIG, Thailand.

#### 3.1.2 Chemicals

- *n*-Octane (C<sub>8</sub>H<sub>18</sub>) of min. 99% purity was obtained from Merck, Germany.
- The commercial K-LTL zeolite (HSZ-500, SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> = 6, surface area = 280 m<sup>2</sup>/g) was obtained from Tosoh, Japan.
- Platinum (II) acetylacetonate ([CH<sub>3</sub>COCH=(CO-)CH<sub>3</sub>]<sub>2</sub>Pt) was obtained from Aldrich, USA.
- Tin (IV) bisacetylacetonate dichloride [CH<sub>3</sub>COCH=(CO-)CH<sub>3</sub>]<sub>2</sub>SnCl<sub>2</sub>) was obtained from Aldrich, USA.

- Thulium 2, 4-pentanedionate ( $\text{Tm}[\text{CH}_3\text{COCHCOCH}_3]_3$ ) of 99.9% purity was supplied by Alfa, USA.
- Cerium (2,4-pentanedionate ( $\text{Ce}[\text{CH}_3\text{COCHCOCH}_3]_3$ ) of 98% purity was supplied by Alfa, USA.
- Thiophene ( $\text{C}_4\text{H}_4\text{S}$ ) of 98% purity was supplied by Fluka, USA.

## 3.2 Equipment

- JEOL JEM-2000FX transmission electron microscope (TEM)
- Temperature programmed reduction (TPR)
- Temperature programmed oxidation (TPO)
- Catalytic testing system consisting of cylinders, mass flow controllers, furnace and tube reactors
- Shimadzu GC-17A gas chromatograph equipped with a capillary HP-PLOT/ $\text{Al}_2\text{O}_3$  "S" deactivated column

## 3.3 Methodology

### 3.3.1 Catalyst Preparation

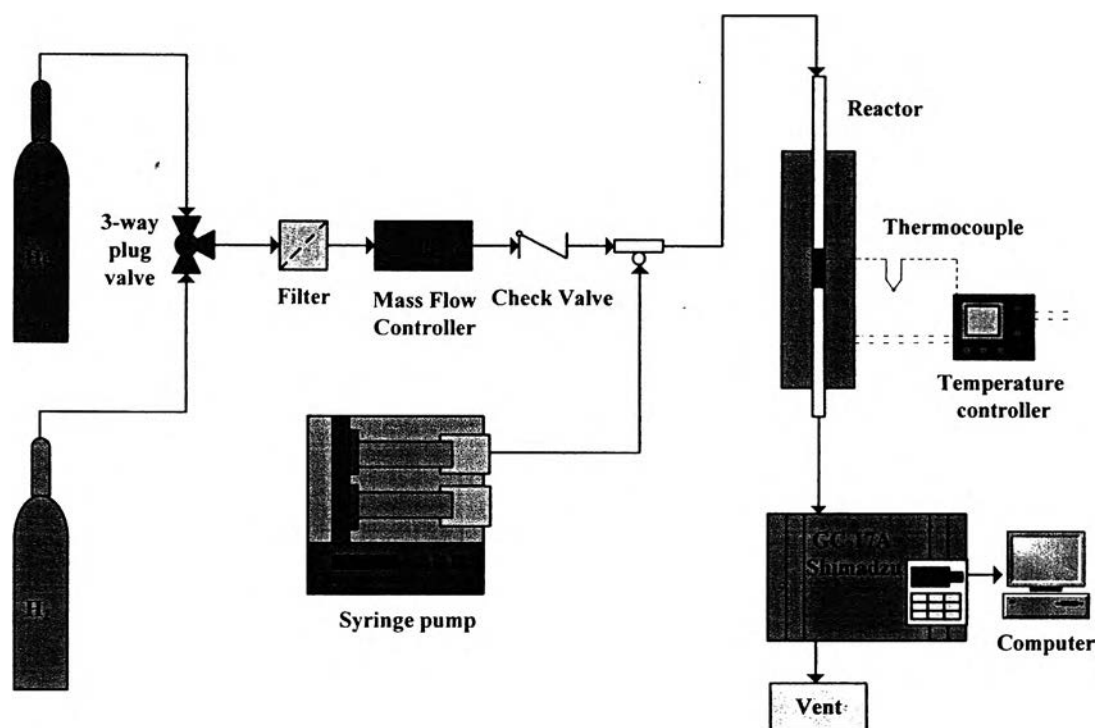
The bimetallic Pt-Sn supported on the commercial KL zeolite was prepared by vapor-phase co-impregnation (VPCI) which was introduced following previously published method (Trakarnroek *et al.*, 2006). For this method, the nominal percentage of platinum is 1 wt%. Prior to impregnation, the commercial KL zeolite was dried in an oven at 110°C overnight and calcined at 500°C in flowing dry air of 100  $\text{cm}^3/\text{min}\cdot\text{g}$  for 5 h. In the case of co-impregnation, the dried support was mixed physically with weighed platinum (II) acetylacetonate (Aldrich) and tin (IV) bisacetylacetonate dichloride (Aldrich) precursors under nitrogen atmosphere. The mixture was then loaded in a tube reactor before being subjected to a helium flow of 5  $\text{cm}^3/\text{min}\cdot\text{g}$ . The reactor was gradually ramped to 40°C and held for 3 h, and ramped again to 60°C and held for 1 h. After that it was further ramped to 110°C where the mixture was held for 1 h to sublime the  $\text{Pt}(\text{AcAc})_2$ . After being cooled down to room

temperature, it was ramped to 350°C in flowing air for 2 h to decompose the platinum precursor. The resulting materials were stored in the oxidic form.

In the part of trimetallic PtSnRE/KL, the catalysts were firstly prepared vapor-phase impregnation of RE into KL zeolite, then co-impregnated Pt and Sn. After that, the preparation followed by the same procedures and using the same conditions.

### 3.3.2 Catalytic Activity Testing

The catalytic activity studies were conducted at atmospheric pressure in a 0.5 inch diameter glass tube reactor equipped with an internal K-type thermocouple for temperature measurements. To avoid unwanted contamination, independent systems were used for runs using clean feeds and runs using sulfur-containing feeds. In the continuous-flow reactor 0.2 g of fresh catalyst was used in each run. Prior to reaction, the catalyst was slowly ramped in flowing H<sub>2</sub> for 2 h up to 500°C and in-situ reduced at that temperature for 1 h. The *n*-octane feed was continuously injected from a syringe pump, keeping in all the experiments hydrogen to *n*-octane molar ratio of 6:1. For the sulfur deactivation studies, thiophene was pre-mixed in *n*-octane at the proper amount to obtain 2.5 ppm S in the reaction mixture. The equipment for sulfur-free and sulfur-containing feed was completely segregated. The products were analyzed by gas chromatography using a Shimadzu 17A-GC equipped with an HP-PLOT/Al<sub>2</sub>O<sub>3</sub> “S” deactivated capillary column. The GC column temperature was programmed to obtain an adequate separation of the products. The temperature was first kept constant at 40°C for 10 min and then, linearly ramped to 195°C and held for 30 min. The schematic of the experiment set up is shown in Figure 3.1 (Jongpatiwut *et al.*, 2001; Trakarnroek *et al.*, 2006).



**Figure 3.1** Schematic of the experimental set-up for *n*-alkane aromatization

### 3.3.3 Catalyst Characterization

#### 3.3.3.1 *Hydrogen Chemisorption*

This technique was employed to characterize the bimetallic PtSn/KL and trimetallic PtSnRE/KL catalyst dispersion including Pt agglomeration. Hydrogen uptake and degree of dispersion were determined by using a pulse technique. Prior to the pulse chemisorption, the sample is reduced in H<sub>2</sub> atmosphere at 500°C for 1 h. Consecutively, it was purged with N<sub>2</sub> at 500°C for 30 min and cooled down to 50°C in flowing N<sub>2</sub>. H<sub>2</sub> pulses (purged H<sub>2</sub>, 20 μl) were injected onto the sample at 50°C until the saturation was observed.

#### 3.3.3.2 *Transmission Electron Microscopy (TEM)*

This technique was employed to characterize metal size distribution of the bimetallic PtSn/KL and trimetallic PtSnRE/KL catalysts. The TEM images of the catalysts were acquired in a JEOL JEM-2000FX electron microscope. The pre-reduced catalyst samples were ultrasonicated for 5 min in isopropanol until a homo-

geneous suspension was formed. In each determination, one drop of this mixture was placed over a TEM copper grid and subsequently dried before the analysis.

#### 3.3.3.3 *Temperature Programmed Reduction (TPR)*

This technique was employed to investigate the reducibility of samples. Temperature programmed reduction was performed on the fresh catalysts. For each run, the samples were weighted 50 mg. TPR runs were conducted using a heating rate of 10°C/min in a flow of 5% H<sub>2</sub>/Ar (30 ml/min) up to 800°C. An ice trap was used to eliminate water during the operation.

To prove that sulfur would break metal interaction, mild decoking was firstly operated at 350°C for 30 min in a flowing of 5% H<sub>2</sub>/Ar in order to remove coke deposited on the spent catalysts. For each run, the spent samples were weighted 50 mg and placed in a quartz reactor. Afterward, the decoking catalyst was further employed in temperature programmed reduction (TPR) up to 800°C to see the reducibility of the catalyst after mild decoking.

#### 3.3.3.4 *Temperature Programmed Oxidation (TPO)*

This technique was employed to analyze the amount and characteristics of the coke deposited on the catalysts during reaction and obtain information about how the coke distributes over the catalyst. TPO of the spent catalysts was performed in a continuous flow of 2% O<sub>2</sub> in He while the temperature was linearly increased with a heating rate of 12°C/min. The oxidation was conducted in a ¼ in. quartz fixed-bed reactor after the spent catalyst has been dried at 110°C overnight, weighted (30 mg), and placed between two layers of quartz wool inside the quartz tube. The sample was further purged at room temperature by flowing 2% O<sub>2</sub> in He for 30 min before the TPO was started. The CO<sub>2</sub> produced by the oxidation of the coke species was converted to methane using a methanizer filled with 15% Ni/Al<sub>2</sub>O<sub>3</sub> and operated at 400°C. The evolution of methane was analyzed using an FID detector.

#### 3.3.4 Product Obtained from *n*-Octane Aromatization Analysis

The products was analyzed in a Shimadzu GC-17A gas chromatograph 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 at 195°C for 30 min. Helium was sent to carry the effluent of each reaction 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 including product yield which was defined as conversion multiplied by selectivity.