



## CHAPTER III EXPERIMENTAL

### 3.1 Materials

#### 3.1.1 Gases

- Hydrogen (UHP grade) was used for *n*-octane reaction testing, FID detector, and H<sub>2</sub> chemisorption measurement.
- Nitrogen (HP grade) was used for purging the glove bag during catalyst preparation.
- Helium (HP grade) was used as carrier gas in Pt precursor sublimation process, H<sub>2</sub> chemisorption experiment, and purging catalyst after reaction testing.
- Air zero grade was used for FID detector and catalyst preparation during calcination and pretreatment.
- 5 % oxygen balanced in helium was used for the temperature-programmed oxidation (TPO) measurement.
- 5 % hydrogen balanced in argon was used for the temperature-programmed reduction (TPR) measurement.
- 5 % carbon monoxide balanced in helium was used for IR spectrometer.

#### 3.1.2 Chemicals

- *n*-Octane (C<sub>8</sub>H<sub>18</sub>) of min. 99% purity was obtained from Lab-scan, Thailand.
- Thiophene (C<sub>4</sub>H<sub>4</sub>S) of 98% purity was supplied by Aldrich, USA.
- 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 (Pt[CH<sub>3</sub>COCH=(CO-)CH<sub>3</sub>]<sub>2</sub>) was obtained from Aldrich, USA.

- Tin (IV) bisacetylacetonate dichloride ( $\text{SnCl}_2[\text{CH}_3\text{COCH}=(\text{CO}-\text{CH}_3)_2]$ ) was obtained from Aldrich, USA.
- Bis (2-carboxyethylgermanium sesquioxide) ( $\text{C}_6\text{H}_{10}\text{Ge}_2\text{O}_7$ ) was obtained from Aldrich, USA.

## 3.2 Equipment

1. JEOL JEM-2000FX transmission electron microscope (TEM)
2. Temperature programmed reduction apparatus (TPR)
3. Temperature programmed oxidation apparatus (TPO)
4. Hydrogen chemisorption apparatus
5. IR spectrometer (Bruker, Spectrum 100) equipped with a liquid nitrogen cooled MCT detector, a diffuse reflectance accessory (Praying Mantis, Harrick) and a high temperature cell (HVC, Harrick)
6. X-Ray Photoelectron Spectroscopy (XPS)
7. Catalytic testing system consisting of gas cylinders, mass flow controller, furnace, and tube reactor
8. 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

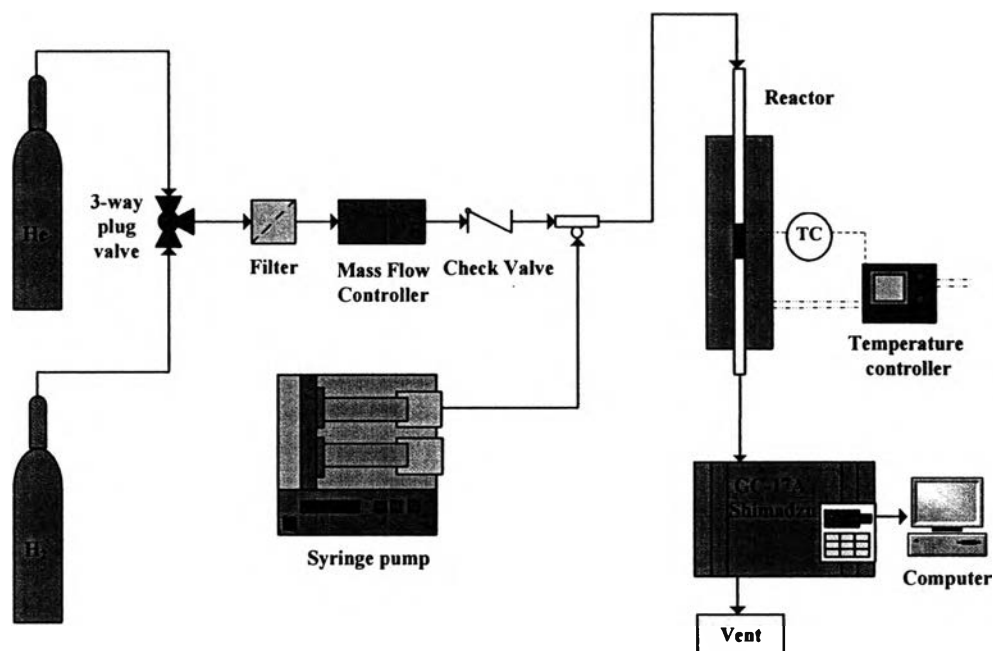
The bimetallic Pt–Sn and Pt–Ge supported on the commercial KL zeolite catalysts were prepared by vapor-phase co-impregnation (VPCI). The nominal percentage of platinum was 0.6 wt%. Prior to impregnation, the commercial KL zeolite was dried in an oven at 110 °C overnight and calcined at 500 °C in flowing dry air of 100 cm<sup>3</sup>/min.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) precursor for Pt–Sn/KL or bis (2-carboxyethylgermanium sesquioxide) (Aldrich) precursors for Pt–Ge/KL under nitrogen atmosphere. The mixture was then loaded in a tube reactor before being

subjected to a helium flow of 5 cm<sup>3</sup>/min-g. The reactor was gradually ramped to 40 °C with the ramping rate of 0.5 °C/min and held for 3 h; and ramped again to 60 °C with the ramping rate of 0.5 °C/min and held for 1 h; and ramped again to 80 °C with the ramping rate of 0.5 °C/min and held for 1 h; and ramped again to 90 °C with the ramping rate of 0.5 °C/min and held for 1 h. After that it was further ramped to 110 °C with a heating rate of 0.5 °C/min where the mixture was held for 1 h to sublime the precursors. After being cooled down to room temperature, it was ramped to 350 °C with a heating rate of 3 °C/min in flowing air for 2 h to decompose the precursors. The resulting materials were stored in the oxidic form.

### 3.3.2 Catalytic Activity Testing

The catalytic activity testings were conducted at 500 °C and atmospheric pressure in a 0.5 inch diameter glass tube reactor equipped with an internal K-type thermocoupl. To avoid unwanted contaminations, 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 with a heating rate of 4 °C/min and in-situ reduced at that temperature for 1 h. The *n*-octane feed was continuously injected by 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 25 ppm S in the reaction mixture. 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 then, linearly ramped to 150 °C with the ramping rate of 5 °C/min and held for 5 min and then, linearly ramped to 180 °C with the ramping rate of 1 °C/min and held for 10 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 including product yield which was defined as conversion multiplied by selectivity. 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*-octane aromatization.

### 3.3.3 Catalyst Characterization

#### 3.3.3.1 *Hydrogen Chemisorption*

Hydrogen chemisorption was employed to characterize the bimetallic Pt–Sn/KL and Pt–Ge/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 was 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 30 °C until the saturation was observed.

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

TEM was employed to characterize the metal size distribution of the bimetallic Pt–Sn/KL and Pt–Ge/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

homogeneous suspension was obtained. 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) of Fresh and Spent Catalysts*

TPR 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. The ice trap was used to eliminate water during the operation. To prove that sulfur might break metal interaction, mild decoking was firstly operated at 350 °C for 30 min in a flowing of 2% O<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 decoked catalyst was further employed in temperature programmed reduction (TPR) up to 800 °C to investigate the reducibility of samples after mild-decoking.

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

TPO 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 is 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> in the presence of H<sub>2</sub> flow and operated at 400 °C. The evolution of methane as a function of temperature was analyzed by an FID detector.

#### *3.3.3.5 Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) of Adsorbed CO*

DRIFTS of adsorbed CO was employed to investigate the size and location of platinum cluster inside zeolite channel. Diffuse reflectance

infrared Fourier transform (DRIFT) spectra of adsorbed carbon monoxide were recorded by using an IR spectrometer (Bruker, Spectrum 100) equipped with a liquid nitrogen cooled MCT detector, a diffuse reflectance accessory (Praying Mantis, Harrick) and a high temperature cell (HVC, Harrick). The cell was fitted with two CaF<sub>2</sub> windows. Briefly, 50 mg of sample powder was loaded in the sample cup of high temperature cell. The sample was reduced in situ at 250 °C for 1 h under 30 ml/min of H<sub>2</sub> gas and then purged with He gas for another 30 min at the same temperature. After that, the sample was cooled down to room temperature (30 °C), and the background spectrum was recorded. Then, 5% CO in He was introduced to the sample for approximately 30 min (30 ml/min) followed by a purge of non-adsorbed CO by a flow of He for 30 min. After that, the spectra of adsorbed CO were recorded at a resolution of 4 cm<sup>-1</sup> and 256 scans accumulation.

#### 3.3.3.6 X-Ray Photoelectron Spectroscopy (XPS)

This technique is employed in order to obtain information about the oxidation states of the metal. XPS data were achieved on a Physical Electronics PHI 5800 ESCA system using monochromatic Al K<sub>1s</sub> excitation (1486.6 eV) with an energy resolution of 125 meV under a background pressure of approximately 2.0×10<sup>-9</sup> Torr. The electron takeoff angle was 45° with respect to the sample surface, and pass energy of 23 eV was typically used for the analysis. The energy scale of the instrument was calibrated using the Ag 3d<sub>5/2</sub> line at binding energy of 368.2 eV. The binding energy values reported below are all referenced to the Fermi level. Quantification of the surface composition was carried out by integrating the peaks corresponding to each element with aid of the Shirley background subtraction algorithm, and then converting these peak areas to atomic composition by using the sensitivity factors provided for each element by the PHI 5800 system software. The reduction treatment was carried out under a hydrogen flow at 500 °C for 1 h. After that, the sample was transferred into the XPS holder under a He flow to avoid any contact with air.