



## CHAPTER III EXPERIMENTAL

### 3.1 Materials

*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 Alfa Aesar, USA. Colloidal silica (40wt% suspension) was obtained from Aldrich, Germany. Potassium hydroxide (KOH) and Barium hydroxide (Ba(OH)<sub>2</sub>) were supplied by Carlo Erba, Thailand. Aluminium hydroxide (Al(OH)<sub>3</sub>) of 99.8% purity was acquired from Merck, Germany. Tin (IV)bis acetylacetonate dichloride [CH<sub>3</sub>COCH=(CO-)CH<sub>3</sub>]<sub>2</sub>Sn<sub>4</sub>Cl<sub>2</sub>) was obtained from Aldrich, USA.

### 3.2 Methodology

#### 3.2.1 Synthesis of KL Zeolites

In this work, the KL zeolites were prepared by two methods which are conventional-heating treatment and microwave hydrothermal treatment. To study the effect of crystallite size of KL zeolite, the various sizes of KL zeolite were prepared by microwave-hydrothermal treatment. In the part of effect of morphology and channel length of KL zeolite, the KL zeolites were synthesized by conventional-hydrothermal treatment.

##### 3.2.1.1 *Synthesis of KL Zeolites by Microwave-Hydrothermal Treatment*

The KL zeolites were synthesized from a mixture of silicate and potassium aluminate solutions to attain the following composition: 2.65K<sub>2</sub>O: 0.0032BaO: 0.5Al<sub>2</sub>O<sub>3</sub>: 10SiO<sub>2</sub>: 159H<sub>2</sub>O. The potassium aluminate solution was prepared by dissolving 2.64 g of Al(OH)<sub>3</sub> in 8.15 M KOH solution. The silicate

solution was prepared by mixing colloidal silica with 2.8 mM Ba(OH)<sub>2</sub> solution and stirring for 15 min. The silicate and aluminate solutions were then mixed and stirred vigorously by a mechanical stirrer for different periods of ageing time at room temperature. After that, the gel mixture was transferred to a microwave vessel and heated using a MARS5 microwave machine up to 170°C within 2 min and maintained at that temperature for 15-50 h. In comparison, a conventionally synthesized L zeolite was aged for 24 h and transferred to a 250 ml Teflon-lined autoclave which was placed in an oven at 170°C and held at that temperature for 96 h. Moreover, the effects of adding barium (0-445 ppm) and seeding (0-8 wt%), based on the total weight of gel, were studied. The resultant material was washed with deionized water until a pH of 10 was attained before being centrifuged to separate the solid phase from the solution. The solid product was dried in an oven at 110°C overnight and then calcined at 500°C in flowing air. The synthesized zeolites are named by their synthesized conditions and compositions as listed in Table 1.

To reduce the particle size of KL zeolite into nanocluster, the gel composition was changed to 10K<sub>2</sub>O: Al<sub>2</sub>O<sub>3</sub>: 20SiO<sub>2</sub>: 400H<sub>2</sub>O (Tsapatsis *et al.*, 1994). The gel was aged for 17 h and heated using a MARS5 microwave machine up to 175°C within 2 min. and maintained at that temperature for 8 h to bring about the crystallization.

### 3.2.1.2 Synthesis of KL Zeolites by Conventional-Hydrothermal

#### *Treatment*

The different morphologies of KL zeolites were synthesized by following a patented procedure of Wortel (1985) and Verduijn (1991). The potassium aluminate solution was prepared by dissolving Al(OH)<sub>3</sub> in KOH solution. The silicate solution for hockey puck shape (HOC) was prepared by mixing colloidal silica with Ba(OH)<sub>2</sub> solution and being stirred for 15 min while there was no mixing of Ba(OH)<sub>2</sub> solution into colloidal silica for other morphologies. The silicate and aluminate solutions were then mixed and stirred vigorously to obtain the homogeneous gel mixture at ambient temperature. After that, the gel mixture was transferred into a Teflon-lined 250 ml autoclave for crystallization. The detail of gel composition, stirring and period of crystallization are depicted in Table 2. The

resultant material was washed with deionized water until a pH of 10 was attained before being centrifuged to separate the solid phase from the solution. The solid product was dried in an oven at 110°C overnight and then calcined at 500°C in flowing air.

**Table 3.1** Synthesis condition for KL zeolites by microwave-hydrothermal treatment

Zeolites	Ageing time (h)	Cryst. time (h)	Amount of Ba (ppm)	Amount of seeding (wt%)
A17/C30/B1 <sup>1*</sup>	17	30	115	0
A24/C30/B1 <sup>1*</sup>	24	30	115	0
A30/C30/B1 <sup>1*</sup>	30	30	115	0
A24/C30/B2 <sup>1*</sup>	24	30	230	0
A24/C30/B3 <sup>1*</sup>	24	25	345	0
A24/C25/B1/S2 <sup>1*</sup>	24	25	115	2
A24/C25/B1/S5 <sup>1*</sup>	24	25	115	5
A24/C25/B1/S8 <sup>1*</sup>	24	25	115	8
A24/C96/B1 <sup>1**</sup>	24	96	115	0
A17/C8/B0 <sup>2*</sup>	17	8	0	0

When <sup>1\*</sup> represents the gel composition: 2.65K<sub>2</sub>O: 0.0032BaO: 0.5Al<sub>2</sub>O<sub>3</sub>: 10SiO<sub>2</sub>: 159H<sub>2</sub>O and synthesis by microwave-hydrothermal treatment, whereas <sup>1\*\*</sup> represents the gel composition: 2.65K<sub>2</sub>O: 0.0032BaO: 0.5Al<sub>2</sub>O<sub>3</sub>: 10SiO<sub>2</sub>: 159H<sub>2</sub>O and synthesis by conventional-hydrothermal treatment. <sup>2\*</sup> represents the gel composition: 10K<sub>2</sub>O: Al<sub>2</sub>O<sub>3</sub>: 20SiO<sub>2</sub>: 400H<sub>2</sub>O and synthesis by microwave-hydrothermal treatment.

**Table 3.2** Gel compositions and synthesis conditions for KL zeolites by conventional-hydrothermal treatment

Morphologies of KL zeolites	Gel composition (mole)					Stirring time (h)	Cryst. time (h)	Temp. (°C)
	K <sub>2</sub> O	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	H <sub>2</sub> O	BaO			
Hockey puck (HOC)	2.62	0.50	0	160.0	0.0032	17	96	170
Cylinder (CYL)	2.62	1	10	160.0	0	24	120	150
Long channel length cylinder (LCYL)	2.21	1	9	164.4	0	24	96	175
Clam (CLAM)	3.5	1	10	160.0	0	24	120	150

### 3.2.2 Characterization of Synthesized KL Zeolites

The zeolite structures of synthesized KL zeolites were characterized using a Rigaku X-ray diffractometer, with Cu-K line as incident radiation and a filter at a scanning rate of 5°/s. The Si/Al ratio was measured by an SRS 3400 Bruker X-ray fluorescence spectroscopy, with 99.8% boric acid as binder. The crystal morphology was investigated using a JEOL 5200-2AE scanning electron microscope. A Malvern 4700 DLS spectrophotometer equipped with Ar-ion laser as a light source was used to determine the average particle size. The detector was fixed at 60° with respect to incident beam direction. The photomultiplier aperture used was 150 µm. Nitrogen adsorption was employed to analyze the surface area and pore volume of synthesized KL zeolites. The adsorption isotherms were collected at 77K using a Thermo Finnigan sorptomatic modeled 1100 series.

### 3.2.3 Catalyst Preparation

Pt/KL catalysts were prepared by vapor phase impregnation (VPI). Prior to impregnation, the support 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.

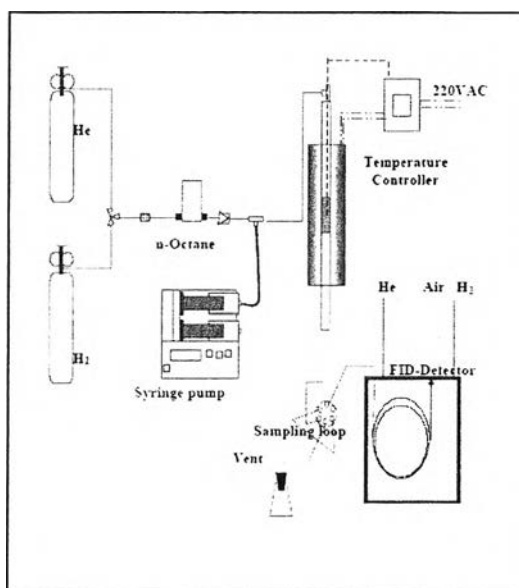
The Pt/KL catalysts were prepared by physical mixing weighed platinum (II) acetylacetonate (Pt(acac)<sub>2</sub>) with the dried support under nitrogen atmosphere. The mixture was then loaded in a tube reactor before being subject to a helium flow of 5 cm<sup>3</sup>/min.g. The reactor was gradually 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 100°C at which the mixture was held for 1 h to sublime the Pt(acac)<sub>2</sub>. After being cooled down to room temperature, it was ramped to 350°C in flowing air and held for 2 h to decompose the platinum precursor.

In the part of adding Sn into Pt/KL catalysts, tin (IV) bis (acetylacetonate) dichloride (Cl<sub>2</sub>Sn(acac)<sub>2</sub>) was used as the precursor. The Sn/KL catalyst was prepared using the same VPI and calcination procedures as described for the loading of Pt, using the same temperature and heating rate. However, in this part the steps for loading which were loading Sn before Pt, loading Pt before Sn, and Co-impregnation of Sn and Pt were studied. The actual metal contents were analyzed by a Varian modeled SpectraA-300 atomic absorption spectroscopy.

### 3.2.4 Catalytic Activity Measurement: n-Hexane and n-Octane

#### Aromatization

The catalytic activity studies were conducted at atmospheric pressure in a 0.5-inch glass tube inserted with an internal K-type thermocouple for temperature measurement and control. The reactor was a single pass and continuous-flow type. Two hundred milligrams of catalysts were used in each run. Prior to the reaction, the catalyst was slowly ramped in flowing  $H_2$  for 2 h up to  $500^\circ C$  and in-situ reduced at that temperature for 1 h. The feed, n-Hexane or n-Octane, was introduced to the system using a syringe pump. For all experiments, the hydrogen-to-hydrocarbon feed molar ratio was maintained at 6:1. The products were analyzed using a Shimadzu 17A-GC equipped with an HP-PLOT/ $Al_2O_3$  "S" deactivated capillary column. The GC column temperature was programmed to obtain an adequate separation of the products. The GC oven temperature was first kept constant at  $40^\circ C$  for 10 min and then it was linearly ramped with a heating rate of  $5^\circ C/min$  to  $195^\circ C$  and held for 30 min. The schematic diagram of the experiment set-up is shown in Figure 3.1.



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

### 3.2.5 Catalyst Characterization

Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) of adsorbed CO: The fresh Pt/commercial KL and Pt/synthesized KL catalysts were characterized by DRIFTS using CO as a probe in a Bruker Equinox 55 spectrometer equipped with an MCT detector. Experiments were performed in a diffuse reflectance cell from Harrick Scientific typed HVC-DR2, with ZnSe windows. For each IR spectrum, a background was collected on the sample reduced in situ under a flow of H<sub>2</sub> at 300°C for 1 h and purged in He for 30 min at ambient temperature. Then, a flow of 5%CO in He was passed through the sample for 30 min, followed by a purge in He flow for 30 min. After such a treatment, the spectrum of adsorbed CO was collected.

Hydrogen Chemisorption: H<sub>2</sub> uptake and degree of dispersion were determined by using a pulse technique (Thermo Finnigan modeled TPDRO 1100). 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>, 0.4 ml) were injected onto the sample at 50°C until the saturation was observed.

Temperature Programmed Oxidation (TPO): This technique was employed to analyze the amount and characteristics of coke formation on the spent catalysts. TPO of the spent catalysts was performed in a continuous flow gas of 2% O<sub>2</sub> in He and the temperature was linearly increased with a heating rate of 12°C/min. The oxidation reaction was conducted in a ¼" quartz fixed-bed reactor. The spent catalyst was dried at 110°C overnight. Thirty milligrams of dried sample were placed in between the layers of quartz wool. The sample was flushed by flowing 2% O<sub>2</sub> in He for 30 min before the TPO was performed. CO<sub>2</sub> produced by the oxidation of coke species was further converted to methane using a methanizer filled with 15% Ni/Al<sub>2</sub>O<sub>3</sub> and operated at 400°C. The methane was analyzed as a function of temperature using an FID detector.