



CHAPTER III EXPERIMENTAL

3.1 Material

3.1.1 Chemicals

n-Octane (C₈H₁₈) of min. 99% purity was obtained from Merck, Germany.

The commercial K-LTL zeolite (HSZ-500, SiO₂/Al₂O₃ = 6, surface area = 280 m²/g) was obtained from Tosoh, Japan.

Platinum (II) acetylacetonate ([CH₃COCH=(CO-)CH₃]₂Pt) was obtained from Aldrich, USA.

Colloidal silica (40wt% suspension) was obtained from Aldrich, USA.

Potassium hydroxide (KOH) was supplied by Carlo Erba, Thailand.

Aluminium hydroxide (Al(OH)₃) of 99.8% purity was acquired from Merck, Germany.

Tin (IV) bisacetylacetonate dichloride [CH₃COCH=(CO-)CH₃]₂SnCl₂) was obtained from Aldrich, USA.

3.1.2 Gases

The ultra high purity (UHP) hydrogen was used for *n*-octane reaction testing, FID detector, H₂ chemisorption measurement, and reduction catalyst during XPS.

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 H₂ chemisorption measurement.

The air zero grade was used for FID detector and catalyst preparation during calcinations, pretreatment, and regeneration.

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

The 5 volume% hydrogen balanced in argon was used for the temperature-programmed reduction (TPR) measurements.

All gases as mentioned above were supplied from TIG, Thailand.

3.2 Equipment

MARS5 microwave machine

Rigaku X-Ray diffractometer (Cu K α , scanning rate of 5°/s)

Thermo Finnigan sorptomatic, 1100 series

Malvern 4700 DLS spectrophotometer equipped with Ar-ion laser as a light source

Thermo Finnigan modeled TPDRO 1900

JEOL JEM-2100 transmission electron microscope (TEM)

Temperature programmed reduction unit (TPR)

X-Ray photoelectron spectroscopy (XPS) by Physical Electronics PHI 5800 ESCA system

Temperature programmed oxidation unit (TPO)

Catalytic testing system consisting of gas cylinders, mass flow controller, furnace, and tube reactor

Shimadzu GC-17A gas chromatograph equipped with a capillary HP-PLOT/Al₂O₃ "S" deactivated column

3.3 Methodology

3.3.1 Synthesis of the Nano-crystalline KL Zeolite (NCL)

In the synthesis of the NCL, a gel composition of 10K₂O: 1Al₂O₃: 20SiO₂: 400H₂O was introduced following previously published method (Tsapatsis *et al.*, 1994). First, the silicate solution was prepared by mixing 54 g of colloidal silica with 60 ml of deionized water and stirring for 15 min. Then, the potassium aluminate solution was prepared by dissolving 2.8 g of Al(OH)₃ in the 36 ml of 11.5 M of KOH solution with stirring and heating at 80°C for 30 min. After that, the silicate and aluminate solutions were then mixed and stirred vigorously by a

mechanical stirrer for 17 h at ambient temperature. Next, the gel mixture was transferred to a Teflon-lined microwave vessel and heated at the power of 600 W, using a MARS5 microwave machine, up to 175°C within 12 min. and maintained at that temperature for 8 h to bring about the crystallization. After crystallization, the obtained material was washed with deionized water until reaching pH 10 and then centrifuged to separate the solution from the solid deposit, which was later dried in an oven at 110°C overnight and then calcined at 500°C in flowing air.

3.3.2 Catalyst Preparation

The bimetallic Pt-Sn supported on the synthesis NCL was prepared by vapor phase co-impregnation (VPCI) which was introduced following previously published method (Trakarnroek *et al.*, 2007). For this method, the nominal percentage of platinum is 1 wt%. Prior to impregnation, the synthesized NCL was dried in an oven at 110°C overnight and calcined at 500°C in flowing dry air of 100 cm³/min.g for 5 h. In the case of co-impregnation, the dried support was mixed physically with weighed platinum (II) acetylacetonate and tin (IV) bis acetylacetonate dichloride precursors under nitrogen atmosphere. The mixture was then loaded in a tube reactor before being subjected to a helium flow of 5 cm³/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 110°C where the mixture was held for 1 h to sublime the Pt(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 oxide form. To study the effect of the amount of tin, the nominal platinum loading was held constant at 1 wt% and the tin loading was varied.

Table 3.1 List of mono- and bi- metallic Pt-Sn/KL catalysts investigated

Catalysts	Pt (wt%)	Sn (wt%)	Pt:Sn Molar ratio
1Pt/NCL	1	-	1:0
1Pt/COM	1	-	1:0
1Pt1Sn/COM	1	1	1:1.65
1Pt0.6Sn/NCL	1	0.6	1:0.99
1Pt1Sn/NCL	1	1	1:1.65
1Sn/NCL	-	1	0:1

In the part of regeneration, the Pt-Sn catalyst supported on the commercial KL zeolites was prepared using the same VPCI and calcinations procedures as described for the loading of Pt, using the same temperature and heating rate.

3.3.3 Characterization of Synthesized KL Zeolites and Catalysts

3.3.3.1 *X-Ray Diffraction (XRD)*

The zeolite structures of the synthesized KL zeolites were characterized in a Rigaku X-Ray diffractometer (Cu K α , scanning rate of 5°/s). The sample was delicately crushed in a mortar. After that, the obtained sample (20 mg) was packed in an aluminium plate and then was covered by glass plate. The 2 theta (degrees) is in the range from 3 to 50.

3.3.3.2 *Dynamic Light Scattering (DLS)*

The scattering of light passing through a medium is a result of refractive index heterogeneities in the medium. Particle within the colloidal size range, 1-1000 nm, exhibit random motion due to collisions with the surrounding medium (Brownian motion) and as a result, the particles (or heterogeneities) present in these suspensions give rise to random fluctuations in the intensity of scattered light upon irradiation (Schoeman *et al.*, 1995). The average particle size of the synthesized KL zeolites were analyzed by a Malvern 4700 DLS spectrophotometer equipped with

Ar-ion laser as a light source. The detector was fixed at 60° with respect to incident beam direction. The photomultiplier aperture used was $150\ \mu\text{m}$. First of all, the distilled water was filtrated through filter paper, Whatman-Cellulose Nitrate (pore size = $0.45\ \mu\text{m}$) in order to eliminate the dust and then the samples were delicately crushed in a mortar and weighted $0.01\ \text{g}$. Next, those samples were dispersed with $10\ \text{ml}$ of distilled water. After that, the samples as described above were ultrasonicated for $30\ \text{minutes}$ in order to get the colloidal suspension. Prior to analysis, the ultrasonicated samples were diluted with distilled water (the ultrasonicated samples: distilled water; $1\ \text{ml}: 5\ \text{ml}$). The obtained samples were decanted in a glass cell until reaching level $2/3$ of glass cell. Finally, the glass cell was replaced in the analyzed aperture.

3.3.3.3 *Hydrogen Chemisorption*

This technique was employed to characterize the bimetallic Pt-Sn catalyst dispersion. Hydrogen uptake and degree of dispersion were determined by using a pulse technique (Thermo Finnigan modeled TPDR0 1100). Prior to the pulse chemisorption, the sample was reduced in H_2 atmosphere at 500°C for $1\ \text{h}$. Consecutively, it was purged with N_2 at 500°C for $30\ \text{min}$ and cooled down to 50°C in flowing N_2 . H_2 pulses (purged H_2 , $0.4\ \text{ml}$) were injected onto the sample at 50°C until the saturation was observed.

3.3.3.4 *Transmission Electron Microscopy (TEM)*

This technique was employed to characterize size of the zeolite crystals, morphology of the zeolite crystals, and particle size distribution of the bimetallic Pt-Sn/KL catalysts. The TEM images of the catalysts were acquired in a JEOL JEM-2100 electron microscope. The pre-reduced catalyst samples were ultrasonicated for $5\ \text{min}$ in isopropanol until a homogeneous suspension was formed. In each determination, one drop of this mixture was placed over a TEM copper grid and subsequently dried before the analysis.

3.3.3.5 *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 $50\ \text{mg}$. TPR runs were conducted using a

heating rate of 10°C/min in a flow of 5% H_2 /Ar (30 ml/min) up to 900°C. The ice trap was used to eliminate water during the operation.

3.3.3.6 *X-Ray Photoelectron Spectroscopy (XPS)*

This technique was employed in order to obtain information about the oxidation states of the metal phased (Pt and/or Sn). XPS data were achieved on a Physical Electronics PHI 5800 ESCA system using monochromatic Al $\text{K}_{1\alpha}$ excitation (1486.6 eV) with an energy resolution of 125 meV under a background pressure of approximately 2.0×10^{-8} Torr. The electron take off angle is 45° with respect to the sample surface, and pass energy of 58.7 eV was typically used for the analysis. The energy scale of the instrument was calibrated using the Ag $3d_{5/2}$ line at binding energy of 368.3 eV. The binding energy values reported below were 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 back ground subtraction algorithm, and then converting these peak areas to atomic composition by using the sensitivity factors provided for the 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.

3.3.3.7 *Temperature Programmed Oxidation (TPO)*

This technique was employed to analyze the amount and characteristics of the coke deposited on the catalysts during the course of reaction. TPO of the spent catalysts was performed in a continuous flow of 2% O_2 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 was dried at 110°C overnight, weighed (30 mg), and placed between two layers of quartz wool. The sample was further purged at room temperature by flowing 2% O_2 in He for 30 min before the TPO was started. The CO_2 produced by the oxidation of the coke species was converted to methane using a methanizer filled with 15% Ni/ Al_2O_3 and operated at 400°C. The evolution of methane was analyzed using an FID detector.

3.3.4 Catalytic Activity Testing

The catalytic activity was tested at atmospheric pressure and 500°C in a ½ inch diameter glass tube reactor equipped with an internal K-type thermocouple for temperature measurements. 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 H₂ 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. The products were analyzed by gas chromatography using a Shimadzu 17A-GC equipped with an HP-PLOT/Al₂O₃ “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 diagram of the experiment set up is shown in Figure 3.1 (Trakarnroek *et al.*, 2007).

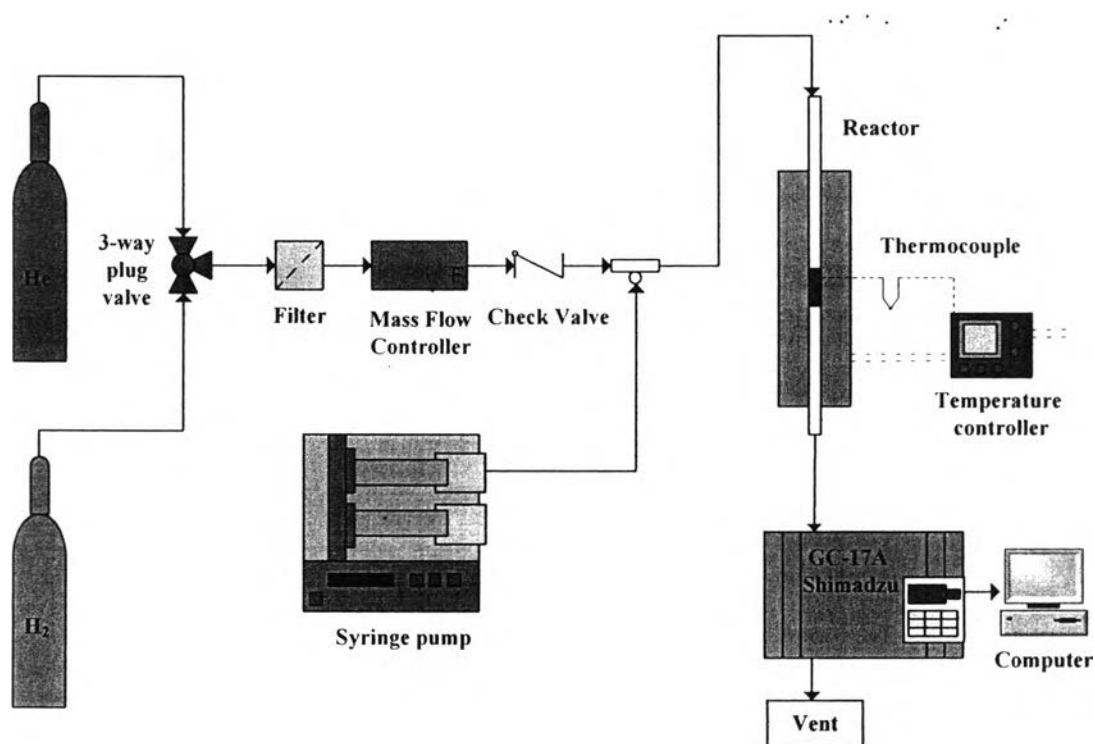


Figure 3.1 Schematic diagram of the experimental set-up for *n*-alkane aromatization.

3.3.5 Regeneration in Air

Regeneration was performed in situ at atmospheric pressure continuously after the course of reaction, using 0.2 g of catalyst in fixed-bed reactor. Table 3.1 summarizes the regeneration processes used. The experimental procedures were performed in three steps as following (Afonso *et al.*, 1997).

Table 3.2 Regeneration conditions

Temperature of Regeneration (°C)	Time of regeneration (min)	Air flow rate (ml/min)	Catalyst (Code)
Effect of temperature of regeneration			
300	30	20	A
350	30	20	B
400	30	20	C
450	30	20	D
500	30	20	E
Effect of regeneration time			
400	15	20	F
400	30	20	C
400	60	20	G
400	120	20	H
Effect of regeneration air flow rate			
400	60	10	J
400	60	20	G
400	60	40	K
Spent 1Pt1Sn/COM			S

3.3.5.1 Pretreatment

This was performed with H₂ continuously after the first reaction-regeneration cycle. The flow rate was kept constant at 22.4 ml min⁻¹ and temperature was fixed at 500°C (reaction temperature) and held constant for 1 h. After

pretreatment, the reactor was purged with high purity (HP) helium and the temperature was adjusted to the temperature of regeneration, in the range of 300-500°C.

3.3.5.2 *Coke oxidation*

Air zero grade was used as the oxidant agent for the regeneration procedure. In all case, the regeneration temperature was in the range of 300-500°C according to heating rate (10°C min⁻¹). The coke formed on the spent catalyst was oxidized by burning in the flow of air (10-40 ml min⁻¹) for a certain time (Table 3.1). The temperature of the catalytic bed during the regeneration procedure was measured by a thermocouple placed directly in the catalytic bed. After coke oxidation, the regenerated catalyst was purged with high purity (HP) helium together with ramping the temperature back to the reaction temperature to begin the second reaction-regeneration cycle.

3.3.5.3 *Final reduction*

The final reduction was performed before the second reaction-regeneration cycle with pure H₂ (22.4 ml min⁻¹) at 500°C for 1 h. The fresh catalyst, pretreated with H₂, was also submitted to regeneration processes 500°C.

Finally, the regenerated catalyst was tested for its activity and selectivity in the second cycle.

3.3.6 The Product of *n*-Octane Aromatization Analysis

The products was analyzed using a Shimadzu GC-17A gas chromatograph equipped with a capillary HP-PLOT/Al₂O₃ "S" deactivated column, with 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 were defined as conversion multiplied by selectivity.