CHAPTER III

EXPERIMENTAL

3.1 Materials

3.1.1 Chemicals

K-LTL-Zeolite (HSZ-500, SiO_2/Al_2O_3 ratio = 6, surface area = 280 m^2/g) was supplied from Tosoh (Tokyo, Japan).

Platinum (II) acetylacetonate ($[CH_3COCH=(-CO-)CH_3]_2Pt$) of 97% purity was supplied from Aldrich (Milwaukee, USA).

Tin (IV) bis(acetylacetonate) dichloride ($[CH_3COCH=(-CO-)CH_3]_2SnCl_2$) of 98% purity was supplied from Aldrich (Milwaukee, USA).

n-Octane (C_8H_{18}) of minimum 99% purity was obtained from Lab-Scan. Co., Ltd.

Platinum standard solution (1000 ppm) from Merck (Germany).

Tin standard solution (1000 ppm) from Carlo ERBA Reagent Co., Ltd.

3.1.2 Gases

Air (zero grade)

High purity (HP) nitrogen, 99.99%

High purity (HP) hydrogen, 99.99%

High purity (HP) helium, 99.99%

3 vol% carbon monoxide balance in helium

Air and N_2 gases were obtained from Thai Industrial Gas Public Co. Ltd. For H_2, He and 3 vol% CO balance in He gases were obtained from Praxair Co., Ltd.

3.2 Instruments and Equipment

3.2.1 Instruments

Glovebox

Dessicator

.3.2.2 Equipment

Gas Chromatograph, GC (Shimadzu, GC-17A)

Atomic Adsorption Spectrometer (Varian, SpectrAA-300)

Transmission Electron Microscope (JEOL, JEM-2000FX TEM)

Bio-Rad FTS-40 spectrometer

3.3 Experimental

3.3.1 Vapor Phase Impregnation Method (VPI)

3.3.1.1 Calcination of KL Zeolite

KL zeolite was calcined in the air flow rate of 100 cc/min/g of zeolite for 2 hours with a ramp temperature from ambient to 500°C and held for 5 hours. Then, the zeolite was cooled down to room temperature, after that it was removed and quickly transferred to inert atmosphere (in a glovebox with a flow of nitrogen).

3.3.1.2 Pt-Sn Loading

According to Chanajaranwit *et al.* (2002), it was found that 1wt% Pt loading on KL zeolite showed the highest catalyst activity among other percentage of Pt loading. Therefore, 1wt% Pt loading were selected to prepare the catalysts. Since the amount of Sn loading would play a role on n-octane aromatization, the appropriate amount of tin loading were investigated by varying its loading at 0.2, 0.5, 0.8, and 1wt%. The reaction testing and catalyst characterization techniques were performed.

The way of preparing the catalyst was important to investigate. Three different methods to synthesize the Pt-Sn/KL catalyst were: (A) coimpregnation of Pt and Sn; (B) two-step impregnation of KL catalyst, first by Pt, and then impregnation of Sn; (C) two-step impregnation, the same as (B) but in the reverse order.

For coimpregnation of Pt and Sn, the catalyst was prepared by physically mixing weighed platinum (II) acetylacetonate with tin (IV) bis (acetylacetonate) dichloride and a dry support under nitrogen atmosphere. The mixture was loaded into the reactor tube under a He flow of 2 cm^3 /min. The mixture was slowly ramped to 40°C and held there for 3 h and ramped again to 60°C and held again for 1 h. After that, it was further ramped to 100°C, at which temperature the mixture was held for 1 h to sublimate the $Pt(AcAc)_2$ and $C_{10}H_{14}C_{l2}O_4Sn$. After sublimation, the mixture was ramped to 110°C and held for 15min to ensure that the entire precursor was sublimed. The reactor was then, cooled to room temperature. After that, it was ramped to 350°C in flow of air for 2 h to decompose the Pt and Sn precursor. Finally the Pt-Sn/KL catalyst prepared by the VPI method was stored in a dessicator.

The preparation method of two-step impregnation of Pt-Sn/KL catalyst can be described as follows: the Pt-Sn/KL catalyst prepared by physically mixing weighed platinum (II) acetylacetonate and a dry support under nitrogen atmosphere. The mixture was loaded into the reactor tube under a He flow of 2 cm^3 /min. The mixture was slowly lamped to 40°C and held there for 3 h and ramped to 60°C and held again for 1 h. After that it was further ramped to 100°C, at which temperature the mixture was held for sublimate the $Pt(AcAc)_2$. After sublimation, the mixture was ramped to 130°C and held for 15 min to ensure that the entire precursors are sublimed. The reactor will be cooled to room temperature. After that, it was ramped to 350°C in a flow of air for 2 h to decompose the Pt precursor. For loading Sn, physically mixing weighed Tin (IV) bis(acetylacetonate) dichloride with Pt/KL catalyst and then repeat the VPI method for loading Sn. Finally we got Pt-Sn/KL catalyst and kept in dessicator. For second path way, we did the preparation method like a first path way but in the reverse order of loading Pt and Sn into the support.

3.4 Reaction Testing

3.4.1 Reduction of Catalyst

The prepared catalyst was transferred to a reactor used for n-octane atomization. Then, its temperature was ramped to 500°C in the flow of H_2 (100cc/min per gram of catalyst) for 2 hours and held at this condition for 1 hour in order to reduce the catalyst.

3.4.2 Reaction Testing

Reaction test was conducted at atmospheric pressure by using continuous flow reactor in parallel. Each reactor consisted of a 0.5 inch stainless steel tube with an internal K-type thermocouple and the oven temperature was monitored with a K-type thermocouple. In each run, the experiment was conducted using 0.2 g of catalysts. The catalyst bed was supported on a bed of glass wool. The reactor was operated under flowing H_2, and n-octane was injected by using a syringe pump through a T-junction prior to the reactor. In all experiments, the molar ratio of H_2 to n-octane was kept at 6:1, the reaction was conducted at 500°C for 10 h, while the space velocity was fixed at 5 h^{-1}.

3.4.3 n-Octane Aromatization Product Analysis

An auto-sampling valve was used to send the product to a Shimadzu GC-17A gas chromatograph for analysis. Helium was sent to purge the effluent of reaction through the column to achieve product separation. The column was operated in a temperature-programmed mode by starting at 40°C for 10 minutes, and then it was ramped up to 195°C with a heating rate of 5°C/min and held for 30 min. The catalytic activities were defined in terms of conversion, selectivity and aromatics yield as follows:

$$\text{Conversion} = ([\text{n-Octane}]_{in} - [\text{n-Octane}]_{out}) / [\text{n-Octane}]_{in}$$

$$\text{Aromatic Selectivity} = [\text{Aromatics}] / ([\text{n-Octane}]_{in} - [\text{n-Octane}]_{out})$$

$$\text{Aromatics Yield} = \text{Conversion x Aromatic Selectivity}$$

where

$[\text{n-Octane}]_{in}$ = Total normalized product signals
$[\text{n-Octane}]_{out}$ = Normalized n-octane product signal
[Aromatics] = Normalized aromatics product signal

3.5 Catalyst Characterization

Fresh and spent samples were characterized by Atomic Adsorption Spectrometer (AAS), Fourier Transform Infrared Spectroscopy (FT-IR) with DRIFT of adsorbed CO, Hydrogen Chemisorption, Temperature Programmed Reduction (TPR), Temperature Programmed Oxidation (TPO), and Transmission Electron Microscopy (TEM).

3.5.1 Atomic Adsorption Spectrometer (AAS)

The metal content of the catalyst was determined by AAS. Five milliliter of aqua regia was added to the carefully measured samples and the metals were dissolved at 80°C. After cooling to room temperature the solution was filtered into a 50 ml volumetric flask. The metal concentrations of stock solutions were determined by atomic adsorption spectrometer. The Platinum and Tin standard solutions were diluter from 1000 mg/dm^3.

3.5.2 Fourier Transform Infrared Spectroscopy (FT-IR) with DRIFT of adsorbed CO

The fresh Pt/KL and Pt-Sn/KL catalysts were characterized by DRIFT using adsorbed CO as a probe in a Bio-Rad FTS-40 spectrometer equipped with an MCT detector. Experiments were performed in diffuse reflectance cell from Harrick Scientific, Type HVC-DR2, with ZnSe windows. For IR spectrum, 128 scans were taken at a resolution of 8 cm^{-1}. Prior to each spectrum being taken, a background was collected on the sample reduced in situ under a slow of H_2 at 300°C for 1 h and purged in He for 30 min at room temperature. Then a flow of 3% CO in He was sent over the sample for 30 min. After this treatment, the spectrum of adsorbed CO was collected.

3.5.3 Transmission Electron Microscope (TEM)

Before preparing the sample, the catalyst was reduced under H2 flow at 500°C for 1h. After that, the reduce catalyst was suspended in 2-propanol and stirred with ultrasound for 5 min. A few drops of resulting suspension were deposited on a TEM grid and subsequently dried and evacuated before the analysis. The TEM images were obtained with a JEOL JEM-2000FX TEM.

3.5.4 Temperature Programmed Oxidation (TPO)

Temperature Programmed Oxidation was employed to analyze the amount and characteristics of the coke deposits on spent catalysts. TPO of the spent catalysts was performed in a continuous flow of 5% O_2/He while the temperature was linearly increased at a heating rate of 12°C/min. Before the TPO was conducted on a 0.03g sample placed in a ¼" quartz fixed-bed reactor, the spent catalyst was dried at 110°C overnight and weighed. The catalyst was then flushed by 5% O_2 in He for 30 min before the temperature ramp was started. The CO_2 produced by the oxidation of coke species was further converted to methane on a 15% Ni/Al_2O_3 catalyst in the presences of hydrogen at 400°C. The methane thus obtained was analyzed online by a FID detector. The amount of coke was calibrated using 100-μl pulses of pure CO_2.

3.5.5 Temperature Programmed Reduction (TPR)

The sample was heated up to 900°C in the flow of H_2/Ar at a heating rate of 10°C/min.

3.5.6 Hydrogen Chemisorption

H_2 uptake and degree of dispersion were determined by using pulse technique. Prior to pulse chemisorption, the sample was reduce in H_2 atmosphere at 500 °C for 1 h. Then the sample was purged with N_2 at 500°C for 30 min and cooled to 30°C in flowing N_2. A H_2 pulse (pure H_2, 10μl) was injected to the sample at 30°C.

3.6 Apparatus

The experimental apparatus is schematically shown in Figure 3.1.

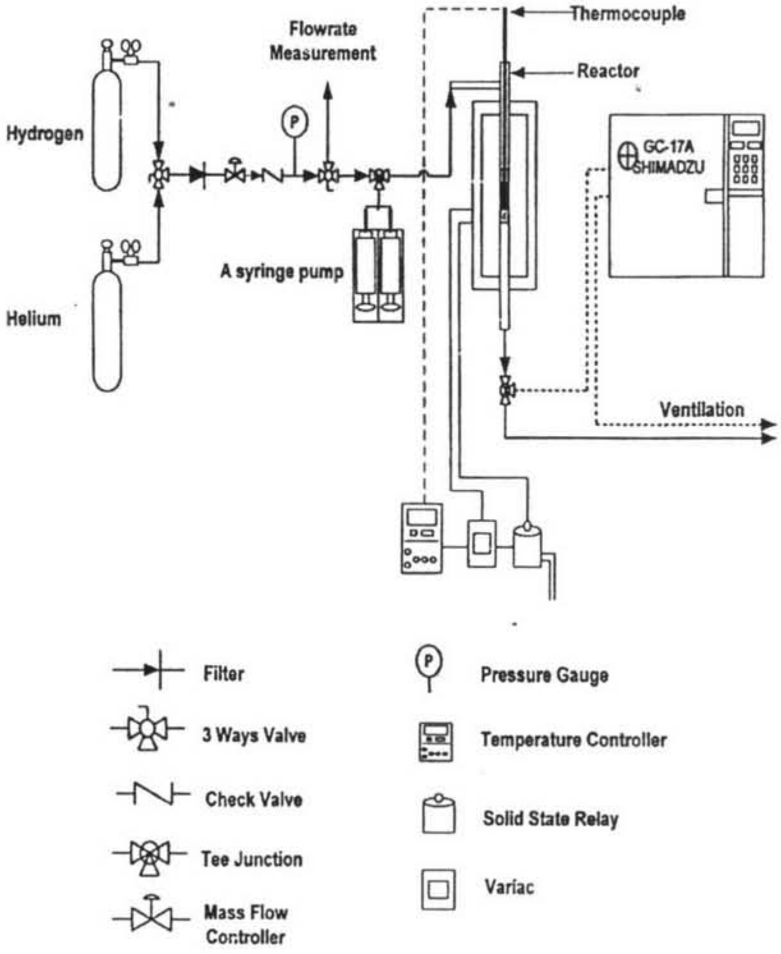

Figure 3.1 Schematic of the experimental set up.