

CHAPTER III EXPERIMENTAL

3.1 Materials and Equipment

3.1.1 Feedstocks

- Palm fatty acid distillate (PFAD) was obtained from Thai Oleochemicals Company Limited (TOL).

3.1.2 Gases

- The ultra-high purity (UHP) hydrogen was used for aromatization of light hydrocarbon testing, and for FID detector.

- The high purity (HP) helium was used for purging catalysts after reaction testing and carrier gas.

- The zero grade air was used for FID detector.

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

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

All gases mentioned above were supplied from Linde, Thailand.

3.1.3 Chemicals and Others

- The commercial ZSM-5 zeolite ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 23,50,80$) were obtained from Zeolyst, USA.

- Zinc(II) nitrate hydrate ($\text{Zn}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$) was obtained from T.S. Interlab Limited Partnership.

- Gallium(III) nitrate hydrate ($\text{Ga}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$) was obtained from Aldrich, USA.

- Distilled water

3.1.4 Equipment

- Continuous packed-bed flow reactor system consisting of:
 - Mass flow controller (Brooks instrument 5850E)
 - High pressure liquid pump (Water 515 HPLC)
 - $\frac{3}{4}$ " O.D. stainless steel reactor
 - Tubular furnace with a temperature controller
- Rigaku X-ray diffractometer
- Surface area analyzer (SAA, Quantachrome/Autosorb1)
- Thermo Finnigan sorptomatic, 1100 series
- X-ray absorption spectroscopy (XAS)
- Atomic absorption spectroscopy (AAS, Varian)
- Temperature programmed desorption (TPD) apparatus
- Temperature programmed reduction (TPR) apparatus
- Temperature programmed oxidation (TPO) apparatus
- Agilent Model 5890 equipped with a capillary HP-PLOT/ Al_2O_3 "S" deactivated column
- Agilent Model 6890 gas chromatograph equipped with a capillary HP-INNOWAX column

3.2 Methodology

3.2.1 Catalyst Preparation

3.2.1.1 *Incipient wetness impregnation (IWI)*

- *Zn/HZSM5*
 $(\text{Zn}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O})$ precursor was loading on HZSM-5 zeolite by incipient wetness impregnation (IWI). After that catalyst was dried at 110 °C overnight and then calcined with air at 550 °C for 5 h. The modified catalyst was noted as Zn/HZSM-5.

- *Ga/HZSM5*
 $(\text{Ga}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O})$ precursor was loading on HZSM-5 zeolite by incipient wetness impregnation (IWI). After that catalyst was dried at 110 °C

overnight and then calcined with air at 550 °C for 5 h. The modified catalyst was noted as Zn/HZSM-5.

3.2.2 Catalytic Activity Testing

The aromatization of PFAD was carried out in a continuous flow reactor. First 1.5 g of catalyst was loaded into the reactor. The reaction was carried out at 500 °C under atmospheric pressure. The PFAD was preheated at 80 °C by heater before putting in the reactor. The gas products were analyzed by gas chromatography using a Agilent Model 5890 equipped with a capillary HP-PLOT/Al₂O₃ “S” deactivated column and TCD detector. The liquid products were analyzed by gas chromatography using an Agilent Model 6890 gas chromatograph equipped with a capillary HP-INNOWAX column. The schematic of the experiment set up is shown in Figure 3.1.

The conversion of feed and selectivity is defined as follows;

$$\text{Conversion (\%)} = \frac{\text{wt. of feed converted}}{\text{wt. of feed input}} \times 100$$

$$\text{Selectivity to product i (\%)} = \frac{\text{wt. of product i}}{\text{Total wt. of products}} \times 100$$

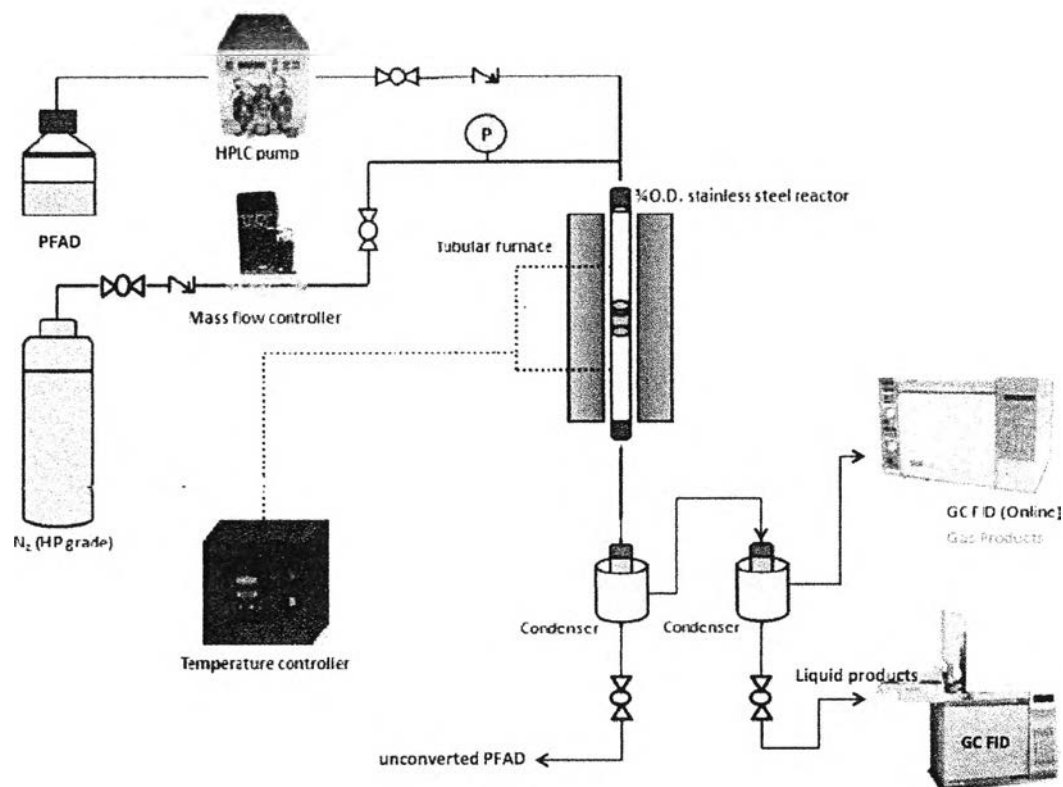


Figure 3.1 Schematic of the experimental set-up for aromatization of naphtha.

3.2.3 Catalyst Characterization

3.2.3.1 Temperature Programmed Reduction (TPR)

This technique was employed to investigate the reducibility of samples. Temperature programmed reduction (TPR) was performed on the fresh calcined catalysts. For each run, 50 mg of sample was packed in a 0.25" O.D quartz tube reactor. TPR runs were conducted using a heating rate of 10 °C/min in a flow of 5% H₂/Ar (30 ml/min) up to 800 °C.

3.2.3.2 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% O₂ in He while the temperature was linearly increased to 900°C with a heating rate of 10 °C/min. The oxidation was conducted in a 0.25" quartz tube fixed-bed reactor. Prior to the test, the spent catalyst

was dried at 110 °C overnight, weighted (10 mg), and placed between two layers of quartz wool inside the quartz tube. The sample was further purged at room temperature by flowing 2% O₂ in He for 30 min before the TPO is started. The CO₂ produced by the oxidation of the coke species was converted to methane in a separate methanizer filled with 15% Ni/Al₂O₃ and operated at 415 °C. The evolution of methane was analyzed using an FID detector.

3.2.3.3 *Temperature Programmed Desorption (TPD)*

The acidity of HZSM-5 and modified ZSM-5 was tested by the isopropylamine (IPA) TPD technique. After the pretreatment, the sample was cooled in He to 30 °C and then 5 µl pulses of isopropylamine were injected over the sample, until the sample was saturated. The saturation of isopropylamine adsorption was confirmed by mass spectrometry (MKS Cirrus). After removing the excess of isopropylamine by flowing He for 30 min, the sample was linearly heated to 800 °C at a heating rate of 10 °C/min. The MS signal of *m/e* 44, 41, and 17 were monitored to determine the evolution of isopropylamine, propylene, and ammonia, respectively. The amount of Brønsted site was determined by the amount of propylene observed which was calibrated by pure propylene.

3.2.3.4 *Brunaure-Emmett-Tellett Method (BET)*

Surface area and micropore volume of the samples were measured using BET method on a Quantachrom/Autosorb 1-MP instrument. The sample was first outgassed to remove the humidity and volatile adsorbents adsorbed on surface under vacuum at 300 °C for 12 h prior to the analysis. And then, N₂ was purged to adsorb on surface. The quantity of gas adsorbed onto or desorbed from their solid surface at some equilibrium vapor pressure by static volumetric method will be then measured. The solid sample was maintained at a constant temperature of the sample cell until the equilibrium is established. This volume-pressure data was used to calculate the BET surface area.

3.2.3.5 *X-ray Diffraction (XRD)*

The relative crystallinities of the ZSM-5 zeolite and modified ZSM-5 were analyzed by a Rigaku X-ray diffractometer with Cu tube for generating CuK α radiation ($\lambda = 1.5418 \text{ \AA}$) at room temperature. The 2θ is in the range between 5 and 80 with a scanning rate of $10^\circ/\text{min}$. This analysis is generally performed based on the fact that an X-ray diffraction pattern is unique for each crystalline substance, chemical identity can be assumed. It is also possible to make a relatively quantitative analysis by comparing substance of different samples, the higher intensity indicates the higher content.

3.2.3.6 *Atomic Absorption Spectroscopy (AAS)*

Atomic absorption spectroscopy (Varian SpectrAA 300) was used to determine the Zn and Ga contents in the prepared catalysts. Metals absorbed ultraviolet light when they were excited by heat. Each metal had a characteristic wavelength that was absorbed. The AAS instrument seek for a particular metal by focusing a beam of UV light at a specific wavelength through a flame and into a detector. The sample of interest was aspirated into the flame. If that metal was present in the sample, it absorbed some of the light, thus reducing its intensity. The instrument measured the change in intensity. A computer data system converted the change in intensity into an absorbance. As a concentration increases, an absorbance increases. A standard calibration curve was constructed by standard solutions at various concentrations.

3.2.2.7 *X-ray Absorption Spectroscopy (XAS)*

The electronic structure of the catalysts was study by using X-ray absorption spectroscopic measurements perform with synchrotron radiation at beam line BL8 station of the photon factory, operated at 2.5 GeV with about 10^6 - 10^8 mA of ring current. The data were recorded in transmission mode at room temperature using Ge (220) double crystal monochrometer. Energy was calibrated with Cu K-edge absorption (8981.0 eV) and energy step of measurement in the XANES region was 0.3 eV. For the extended X-ray absorption fine structure (EXAFS) analysis, the oscillation was normalized by edge height around 50 eV

higher than the absorption edge. The data analysis was performed using the Arthena version 0.9.18.2.