CHAPTER III
EXPERIMENTAL

3.1 Materials

3.1.1 Chemicals

- Glycerol ($C_3H_8O_3$, reagent grade) was obtained from Fisher Chemical, UK.
- Palm fatty acid distillate (PFAD) was obtained from Thai Oleochemicals Company Limited (TOL).
- *n*–Pentane of min. 99% purity was obtained from RCI Labscan, Thailand.
- The commercial ZSM–5 zeolite (SiO_2/Al_2O_3 = 23, 30, 50, 80, and 280) was obtained from Zeolyst, USA.
- Zinc(II) nitrate hydrate ($Zn(NO_3)_2.xH_2O$) was obtained from T.S. Interlab Limited Partnership.
- Gallium(III) nitrate hydrate ($Ga(NO_3)_3.xH_2O$) was obtained from Aldrich, USA.
- Tetraethyl orthosilicate ($SiC_8H_{20}O_4$) was obtained from Aldrich, USA.
- Cyclohexane was obtained from Labscan, Thailand.
- Tetrapropylammonium hydroxide (TPAOH) was obtained from Aldrich, USA.
- Ammonium hydroxide (NH_4OH) was obtained from Aldrich, USA.

3.1.2 Gases

- Hydrogen (H_2, HP grade, 99.99 % purity) was used for the catalyst activity testing, and FID detector.
- Nitrogen (N_2, HP grade, 99.99 % purity)) was used for the catalyst activity testing.

- Helium (He, HP grade, 99.99 % purity) was used as carrier gas for gas chromatograph and for temperature–programmed desorption (TPD) measurement.
- The zero grade air was used for FID detector.
- 5 vol.% oxygen balance in helium was used for the temperature–programmed oxidation (TPO) measurement.
- 2 vol.% propylene balance in helium was used for the temperature–programmed desorption (TPD) measurement.
- 10 vol.% ammonia balance in helium was used for the temperature–programmed desorption (TPD) measurement.

All gases mentioned above were supplied from TIG, Thailand.

3.2 Experimental Procedure

3.2.1 Part I: Conversion of Glycerol to Aromatic Hydrocarbons over Zn–Promoted HZSM–5 Catalysts

3.2.1.1 Catalyst Preparation

In this part, the parent HZSM–5 with different SiO_2/Al_2O_3 ratios and Zn/HZSM–5 were used as catalysts. Two preparation methods, consisting of aqueous phase ion–exchange and incipient wetness impregnation was used to prepare Zn/HZSM–5 catalysts.

3.2.1.1.1 Preparation of Parent HZSM–5 Catalysts

The NH_4ZSM–5 zeolites with SiO_2/Al_2O_3 ratios of 23, 30, 50, 80,and 280 were provided by Zeolyst International. The powdered catalysts were pelletized and sieved to 20–40 mesh in order to attain the suitable catalyst packing in the reactor. The catalysts were calcined in air at 550 °C with a heating rate of 10 °C/min for 5 h. The obtained catalysts are denoted as HZSM–5(x), where x is the SiO_2/Al_2O_3 ratios of HZSM–5.

3.2.1.1.2 Preparation of Zn/HZSM–5 Catalysts

In order to study the effects of different Zn species, Zn–promoted HZSM–5 catalysts were prepared by IE and IWI methods

*y*Zn/HZSM–5 (IWI) catalysts were prepared by incipient wetness impregnation of HZSM–5 (30), where y refers to the Zn loading (wt %). The HZSM–5 (4 g) was impregnated with the aqueous solution containing desired amount of $Zn(NO_3)_2 \cdot H_2O$, followed by dried in an oven at 120 °C overnight and calcined at 550 °C (heating rate of 10 °C/min) in air for 5 h. *y*Zn/HZSM–5 (IE) catalysts were prepared by aqueous phase ion–exchange method. The HZSM–5 (30) was stirred in an aqueous solution of 0.005–0.05 $MZn(NO_3)_2 \cdot H_2O$ at 70 °C for 12 h. Subsequently, the obtained catalysts were washed with excess distilled water, followed by dried in an oven at 120 °C overnight and calcined at 550 °C (heating rate of 10 °C/min) in air for 5 h.

3.2.1.2 Catalytic Activity Testing

The pure glycerol (>99.99%) was fed together with a N_2 carrier at a flowrate giving a molar ratio of N_2/glycerol of 10:1. The reaction was carried out at temperature of 400 °C, pressure of 300 psig, and W/F ranged from 0.07 to 1 h. The liquid products, including water, were collected in a cold trap and ana–lyzed by an Agilent 5890 gas chromatograph equipped with acapillary HP–INNOWAX column. Non–condensed products were analyzed online by a Shimadzu GC–17A gas chromatographequipped with a capillary HP–PLOT/Al_2O_3 "S" deactivated column. The schematic of the experiment set up is shown in Figure. 3.1 and Table 3.1.

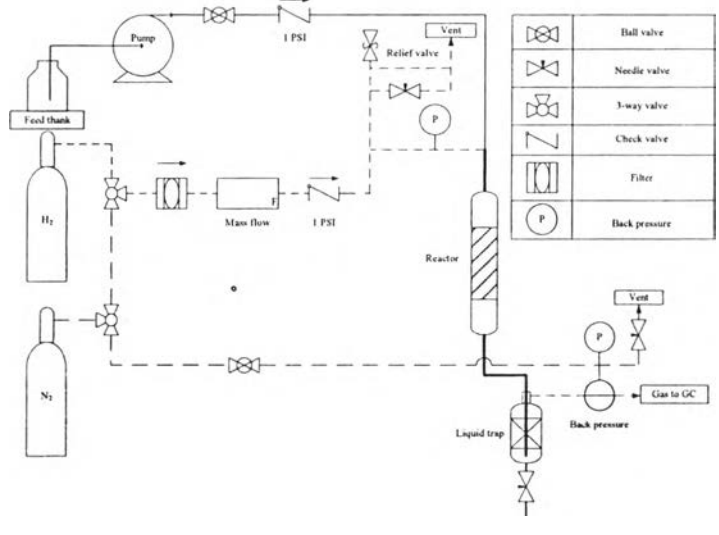

Figure 3.1 A schematic flow diagram of experimental setup.

Table 3.1 Description of flow diagram

No.	Items	Functions
1	V1	On-off valve for liquid from high pressure liquid pump
2	V2	Checking valve for avoiding the backward flow of liquid from high pressure pump
3	V3	Three-way valve for switching nitrogen gas to hydrogen gas
4	V4	Checking valve for avoiding the backward flow of hydrogen or nitrogen gas
5	V5	Three-way valve for switching direction of nitrogen flow
6	V6	Needle valve for controlling pressure in back pressure regulator
7	V7	Needle valve for releasing gas from the system
8	V8	Relief valve to release to pressure overload in the system
9	V9	On-off valve for releasing the pressure from back pressure Regulator
10	V10	Metering valve for releasing the product from condenser

3.2.2 Part II: The Effect of Ga and Zn over HZSM–5 on the Transformation Palm Fatty Acid Distillate (PFAD) to Aromatics

3.2.2.1 Catalyst Preparation

In this part, the parent HZSM–5 with different SiO_2/Al_2O_3 ratios and Zn contained HZSM–5 were used as catalysts. Two preparation methods, consisting of aqueous phase ion–exchange and incipient wetness impregnation were used to prepare Zn/HZSM–5 catalysts.

3.2.2.1.1 Preparation of Parent HZSM–5 Catalysts

The NH_4ZSM–5 zeolites with SiO_2/Al_2O_3 ratios of 23, 30, and 50 were obtained from Zeolyst International, USA. In order to convert to proton form, the catalysts were calcined in air at 550 °C for 5 h after that ground and sieved to the size between 20–40 mesh (450–850 μm).

3.2.2.1.2 Preparation of Ga/HZSM–5 and Zn/HZSM–5 Catalysts

The $Zn(NO_3)_2$ or $Ga(NO_3)_3$ precursors were loaded on 3 g HZSM–5 (SiO_2/Al_2O_3 = 30) by incipient wetness impregnation (IWI) method. After that, the catalysts were dried at 110 °C overnight and then calcined in air at 550 °C for 5 h. The resulting catalysts are denoted as xM/HZSM–5, where x represents amount of expected metal loading and M represents Ga or Zn.

3.2.2.2 Catalytic Activity Testing

Palm fatty acid distillate (PFAD) was obtained from Thai Oleochemicals Company Limited (TOL), Thailand. The reaction activity was tested in a continuous flow fixed bed reactor. The reaction was carried out at 500 °C under atmospheric pressure. N_2 was used as a carrier gas with the flow rate of 55 mL/min. The PFAD was melted by preheating at 80 °C before feeding to the reactor. The gas products were analyzed on–line by using an Agilent Model 5890 gas chromatography equipped with a capillary HP–PLOT/Al_2O_3 "S" deactivated column for FID and Porapak N, 80–100 column for TCD detectors. The liquid products were analyzed by using an Agilent Model 6890 gas chromatography equipped with a capillary HP–INNOWAX column.

3.2.3 Part III: Generation of New Active ZnH^+ Species over Hydrogen–Treated Zn/HZSM–5 Catalysts for *n*–Pentane Aromatization

3.2.3.1 Catalyst Preparation

The NH_4ZSM–5 zeolite with SiO_2/Al_2O_3 ratio of 30 was obtained from Zeolyst International. In order to convert to proton form, the catalyst was calcined in air at 550 °C for 5 h. The Zn^{2+} were loaded on the HZSM–5 catalyst by aqueous phase ion–exchange. Briefly, the HZSM–5 (4 g) was stirred in 0.05 M $Zn(NO_3)_2$ solution (100 mL) at 70 °C for 12 h. The ion–exchanged sample was washed with excess deionized water, dried overnight at 120 °C, after that calcined at 550 °C in air for 5 h.

3.2.3.2 Catalytic Activity Testing

The catalytic activity was tested by using pulse reactor. 50 mg of catalyst was packed in ¼" Pyrex fixed–bed reactor. The catalyst was heated under flow of He at 500 °C for 1 h. After that, 0.25 mL of *n*–pentane vapor (at room temperature) was pulsed into the reactor with the He flow rate of 180 mL/h. In order

to study the effect of H_2, The carier gas was changed to H_2 and the catalyst was heated at 500 °C for 1 h after that the carier gas was changed to He again, the catalytic activity was tested by pulsing *n*–pentane under He atmosphere.

3.2.4 Part IV: Improved *n*-pentane conversion and *p*-xylene selectivity using Zn(II)ions/silicalite-1 coated on Zn/HZSM-5 catalysts

3.2.4.1 Catalyst Preparation

The NH_4ZSM–5 zeolite with SiO_2/Al_2O_3 ratio of 25 was calcined in air at 550 °C for 5 h the resulted catalyst was denoted as HZSM–5. The Zn^{2+} were loaded on the HZSM–5 catalyst by aqueous phase ion–exchange. Briefly, the HZSM–5 (4 g) was stirred in 0.05 M $Zn(NO_3)_2$ solution (100 mL) at 70 °C for 12 h. The ion–exchanged sample was washed with excess deionized water, dried overnight at 120 °C, after that calcined at 550 °C in air for 5 h, denoted as ZnHZSM–5 catalyst.

In order to coat silicalite–1 on the catalyst, Zn/HZSM–5 was used as a core. The precursor solution contained with TEOS, tetraprophylammonium hydroxide (TPAOH), ethanol (EtOH) and deionized water with the molar ratios of 0.5TPAOH: 120H_2O: 8EtOH: 2SiO_2. Approximately 1.0 g of Zn/HZSM–5 catalyst was immersed in 15 g of precursor solution. The solution was carried out in stainless steel vessel at 453 °C for 24 without agitation. The products were rinsed with deionized water and dried over night at 363 K, then, calcined in air at 773 K for 6 h at a heating rate of 1 K/min. The resulted catalysts was denoted as Sil–1/ZnHZSM–5 catalyst.

The dehydrogenation layer was grafted on Sil–1/ZnHZSM–5 catalyst by using strong electrostatic adsorption methodology. Approximately 1.0 g of Sil–1/ZnHZSM–5 was suspended in 5 mL of deionized water. The solution was adjusted to pH 11 by using 30% ammonium hydroxide (NH_4OH). In a separate flask, 0.16 g of $Zn(NO_3)_2.6H_2O$ (Sigma Aldrich) was dissolved in 1.6 mL of deionized water. The pH of the solution also adjusted to be 11 using ammonium hydroxide. The solution was added to the catalyst solution and stir for 10 min. Then the mixed solution was allowed to settle for 5 min. The resultant slurry was rinsed several times with deionized water. The resulted catalyst was vacuum filtered, dried overnight at 125 °C, and calcined in air with a heating rate of 5 °C/min to 300 °C, maintained for 3 h. The catalyst was denoted as Zn(II)ions/Sil–1/ZnHZSM–5 catalyst.

3.2.4.2 Catalytic Activity Testing

In each test, 0.1 g of catalyst was packed in a ¼" Pyrex fixed–bed reactor. The catalyst was heated under a flow of N_2 at 500 °C for 1 h. The *n*–pentane feed–stock was continuously injected from a syringe pump with WHSV of 10 h^{-1}. The condition reaction was at 500 °C under 1 atm of 20 ml/min of N_2 flow. The products were analyzed by gas chromatography using a Shimadzu 17A–GC equipped with an HP–PLOT/Al_2O_3 "*S*" deactivated capillary column.

3.3 Catalyst Characterization

3.3.1 Temperature Programmed Reduction (TPR)

This technique wasa employed to study the reducibility of samples. For each run, 50 mg of catalysts were packed in the ¼" quartz tube reactor. The temperature was heated with the rate of 10 °C/min under 5% H_2/Ar (30 mL/min) to 800 °C.

3.3.2 Temperature Programmed Desorption (TPD) of Isopropylamine (IPA) and Ammonia (NH_3)

Temperature Programmed Desorption (TPD) were performed in a homemade apparatus using a quarter inch quartz tube reactor connected to an online MS detector (MKS Cirrus series 903). The IPA–TPD were carried out in the range of 30–800 °C at a heating rate of 10 °C/min, whereas NH_3–TPD experiment was monitored at the range of 100–700 °C. The MS signal of *m/e* 44, 41, and 17 were monitored to determine the evolution of isopropylamine, propylene, and ammonia, respectively. In the case of IPA–TPD, the amount of Brønsted site was determined by the amount of propylene observed which was calibrated by pure propylene. While the total acid site was calculated from total amount of NH_3 in NH_3–TPD.

3.3.3 X–ray Diffraction (XRD)

The relative crystallinities of the ZSM–5 zeolite before and after silylation were analyzed by a Rigaku X–ray diffractometer with Cu tube for generating CuKα radiation (λ= 1.5418 A°) at room temperature. The 20 is in the range between 5 and 80 with a scanning rate of 10°/min. This analysis is generally preformed 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.

3.3.4 N_2 Adsorption/Desorption Measurements

Surface areas, micropore, and mesopore volumes of the samples were measured using BET method on a Quantachrom instrument. The sample was first outgassed to remove the humidity and volatile adsorbents adsorbed on surface under vacuum at 150 °C for 12 h prior to the analysis. And then, N_2 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.

3.3.5 UV–vis Spectrophotometer

The measurements were performed on air–exposed samples at an ambient temperature of between 200 and 800 nm. The absorption intensity was expressed using the Kubelka–Munk function.

$$F(R\infty) = \frac{(1 - R_\infty)^2}{2R_\infty}$$

where R∞ is the diffuse reflectance from a semi–infinite layer.

3.3.6 X–ray Absorption Near Edge Structure (XANES) and Extended X–ray Absorption Fine Structure (EXAFS)

X–ray absorption near edge structure (XANES) and Extended X–ray absorption fine structure (EXAFS) of Zn (9659 eV) K–edge were performed at beamline 8, Synchrotron Light Research Institute (SLRI), Thailand. The samples were measured in the fluorescence mode using Ge(220) double crystal monochromator at room temperature. The data analysis was performed by Arthena version 0.9.18.2.

3.3.7 X–ray Photoelectron Spectroscopy (XPS)

X–ray photoelectron spectroscopy (XPS) was recorded by a Kratos Ultra X–ray photoelectron spectrometer. The monochromatic AlKα was used as an X–ray source (anode HT = 15 kV). The XPS peaks were referenced to the binding energy of C (1s) peak at 285 eV. In order to study the effects of hydrogen treatment, Zn/HZSM–5 catalysts were heated under Ar or H_2 flowing at various temperature for 1 h in an XPS catalyst reaction cell. The catalysts were then cooled down under the treated gas and then transferred to the XPS chamber for the analysis.