

CHAPTER III EXPERIMENTAL

3.1 Materials and Equipment

3.1.1 Feedstock

- *n*-Pentane 99 %purity was obtained from RCI Labscan Limited.
- Light naphtha was obtained from PTTGC.

3.1.2 Gases

- The ultra-high purity (UHP) hydrogen was used for reduction metal loading catalyst in aromatization and 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 is used for the temperature-programmed oxidation (TPO) measurement.
- The 5 vol. % hydrogen balanced in argon is used for the temperature-programmed reduction (TPR) measurement.

All gases mentioned above are supplied from Linde, Thailand.

3.1.3 Chemicals

- The commercial ZSM-5 zeolite ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 23$) was obtained from Zeolyst, USA.
- *n*-Pentane and *n*-hexane of min. 99 % purity was obtained from RCI Labscan, Thailand.
- Oxalic acid ($\text{C}_2\text{H}_2\text{O}_4$) of 99% purity was obtained from Merck, Thailand.
- Gallium(III) nitrate hydrate ($\text{Ga}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$) was obtained from Aldrich, USA.
- Tetraethyl orthosilicate ($\text{SiC}_8\text{H}_{20}\text{O}_4$) was obtained from Aldrich, USA.
- Cyclohexane was obtained from Labscan, Thailand.

- Glacial acetic acid was obtained from RCI Labscan Limited.
- Pseudoboehmite was obtained from Sasol, Germany.

3.1.4 Equipment

- Shimadzu GC-17A gas chromatograph equipped with a capillary HP-PLOT/Al₂O₃ “S” deactivated column.
- Agilent Model 6890N gas chromatograph equipped with a capillary Stabilwax column
- Rigaku X-ray diffractometer
- Temperature programmed desorption of IPA (TPD) apparatus
- Temperature programmed reduction (TPR) apparatus
- Temperature programmed oxidation (TPO) apparatus
- Cole-Parmer 74900 series syringe pump
- Mettler Toledo TGA/SDTA 851e machine
- Bulk density, attrition loss, and radial crushing strength machine

3.2 Methodology

3.2.1 Catalyst Preparation

3.2.1.1 *Dealumination*

The dealumination was performed on HZSM-5 catalysts by steaming and acid leaching. HZSM-5 was taken to leach with a 0.5 M oxalic acid solution (5 mL/g zeolite) at 80 °C for 10 h. Subsequently, the sample was filtered and washed repeatedly with deionized water, dried at 110 °C for overnight and then calcined with air at 550 °C for 5 h. The modified catalyst was designated as Ac/ZSM-5 or Z.

Next, the Ac/ZSM-5(Z) was further placed in the reactor and heated up to the pretreatment temperature (400 °C) in a flow of N₂. The optimum condition of steaming was determined by adjusting water flowrates corresponding to various water vapor pressures to be 5, 20 and 40 kPa, this resulted ZP5, ZP20 and ZP40. Another, temperatures of steaming were 350, 500 and 650 °C at vapor pressure of 26.75 kPa, which resulted ZT350, ZT500 and ZT650, respectively. The

water flowrate is added by a syringe pump during a treatment time of 4 h. Catalyst was quenched to room temperature. The calculation of water flowrate is shown in Appendix A. Lastly, ZP5, ZP20, ZP40, ZT350, ZT500 and ZT650 were acid leaching again, results are noted as Ac/ZP5, Ac/ZP20, Ac/ZP40, Ac/ZT350, Ac/ZT500 and Ac/ZT650, respectively.

3.2.1.2 Ion-exchange

The Ac/ZP5, Ac/ZP20, Ac/ZP40, Ac/ZT350, Ac/ZT500, and Ac/ZT650 were ion-exchanged with a 150 mL aqueous solutions containing precursor ($\text{Ga}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$) equivalent to 1 wt.% metal in zeolite, stirred for 12 h, washed with excess distilled water, dried at 110 °C overnight and then calcined with air at 550 °C for 5 h. The modified catalysts were noted as Ga/Ac/ZP5, Ga/Ac/ZP20, Ga/Ac/ZP40, Ga/Ac/ZT350, Ga/Ac/ZT500, and Ga/Ac/ZT650, respectively.

3.2.1.3 Silylation

In this study, the silylation was performed on Ga/Ac/ZP5, Ga/Ac/ZP20, Ga/Ac/ZP40, Ga/Ac/ZT350, Ga/Ac/ZT500, and Ga/Ac/ZT650 catalysts by chemical liquid deposition. A gram of modified catalyst was obtained by impregnating with 1 mL tetraethyl orthosilicate (TEOS) dissolved in 4 mL cyclohexane at room temperature for 12 h, dried at 110 °C for overnight and then calcined at 550 °C for 5 h. The modified catalysts were noted as CLD/Ga/Ac/ZP5, CLD/Ga/Ac/ZP20, CLD/Ga/Ac/ZP40, CLD/Ga/Ac/ZT350, CLD/Ga/Ac/ZT500 and CLD/Ga/Ac/ZT650, respectively.

3.2.2 Modified Catalyst Formulation

Shaping selected modified HZSM-5 powder samples was carried out by mixing an inert alumina binder, pseudoboehmite. Three factors were varied; ratios of zeolite to pseudoboehmite, concentration of peptizing agent, and calcined temperature. Firstly, mass ratios of zeolite to pseudoboehmite were 80:20 and 60:40 wt%. Secondly, the concentration of glacial acetic acid was varied from 1 to 5 vol%. Lastly, calcined temperatures were varied from 500 to 650 °C for 4 h. The mixture was extruded through a 2 mm diameter size syringe in cylindrical form, wet extrudates were allowed to get dry at room temperature overnight and further dried at 100 °C for 7 h followed by calcination.

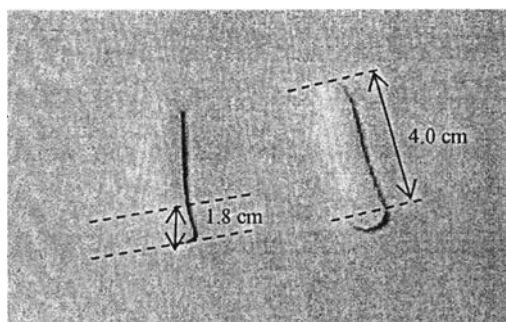


Figure 3.1 The extruded CLD/Ga/Ac/ZP5 catalysts.

3.2.3 Catalytic Activity Testing

The aromatization of *n*-pentane was carried out in a continuous flow fixed-bed reactor at 500 °C under atmospheric pressure. In the continuous-flow reactor, 0.20 g based on zeolite content of fresh catalyst was used in each run. Water was vaporized from pseudoboehmite and acetic solution after drying. The dried extrudates properties showed in Table 4.3. The purpose of this experiment was to compare the activity between before and after shaping.

Prior to aromatization reaction, the modified catalyst was reduced with H₂ at 500 °C for 3 h. The *n*-pentane was continuously injected from a syringe pump. Helium was a carried gas with flow rate 40 mL/min, WHSV= 5 h⁻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 in Table 3.1. The schematic of the experiment set up is shown in Figure 3.2. The fraction of xylene isomers was independently analyzed by an Agilent Model 6890N gas chromatograph equipped with a capillary Stabilwax column.

Table 3.1 Shimadzu 17A-GC column oven temperature programmed

Rate (°C/min)	Temperature (°C)	Hold time (min)
-	40.0	3.0
15.0	70.0	0.0
5.0	170.0	0.0
1.0	190.0	13.0

Table 3.2 Agilent Model 6890N-GC column oven temperature programmed

Rate (°C/min)	Temperature (°C)	Hold time (min)
-	60	1.0
9.0	190.0	4.0

The conversion of feed and selectivity is defined as following;

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

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

$$p\text{-Xylene selectivity in xylenes (wt\%)} = \frac{p\text{-Xylene} \times 100}{p\text{-Xylene} + m\text{-Xylene} + o\text{-Xylene}}$$

3.2.4 Catalyst Characterization

3.2.4.1 *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.

3.2.4.2 *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.

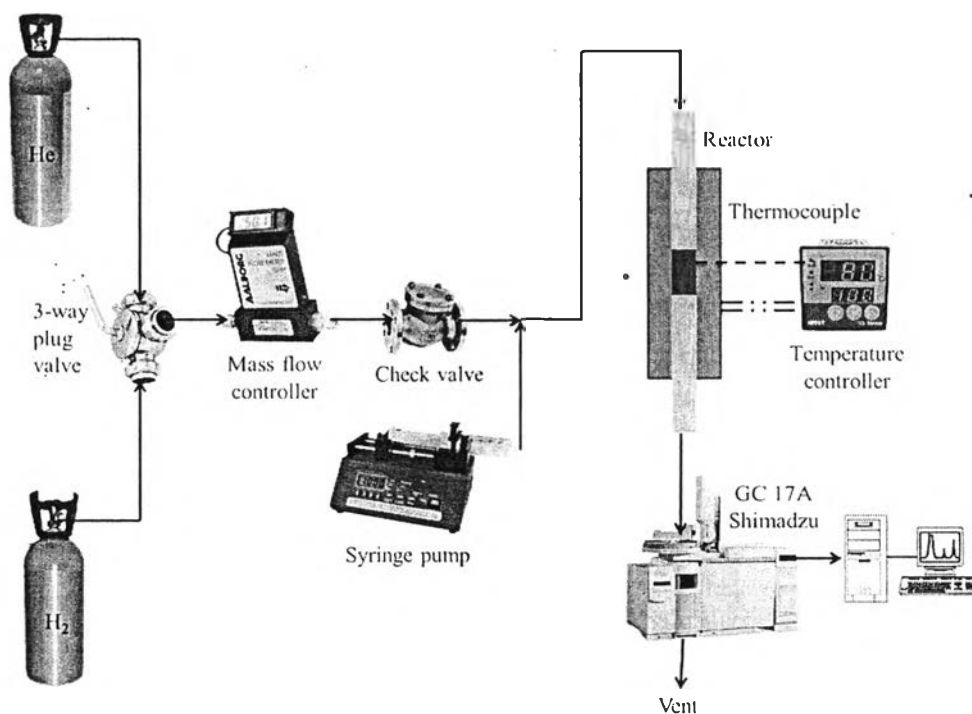


Figure 3.2 Schematic of the experiment for aromatization of *n*-pentane.

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.

3.2.4.3 Temperature Programmed Desorption (TPD)

The acidity of HZSM-5 and modified ZSM-5 was tested by the isopropylamine (IPA) TPD technique. First, 50 mg of sample was pretreated at 500 °C in a flow of He for 1 h. 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 20 °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 *N₂ Adsorption/Desorption Measurement*

Surface area and pore 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.

3.2.4.5 *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 10 and 80 with a scanning rate of 10 °/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.

3.2.4.6 *Scanning Electron Microscope (SEM)*

This technique is employed to investigate the morphology of the ZSM-5 zeolite and modified HZSM-5. The samples were first placed on the stub and coated with a thin layer of platinum. The SEM images of the catalysts were acquired in a JEOL 5200-2AE scanning electron microscope attached with energy dispersive X-ray spectrometer.

3.2.4.7 *Bulk Density*

Bulk density followed ASTM B527-93. Firstly, the sample was dried at 150 °C at least 3 h, followed cool the test samples in a desiccator to eliminate the possibility of moisture adsorption prior to test. The test specimen was weighed 100 g, which was recorded as M, into the graduated 100 cm³ cylinder. The tapping device started working and stopped until the level of sample in cylinder unchanged. This volume was recorded as V which was nearest 1 mL by estimating

the average level of the catalyst surface in the cylinder. Calculate the bulk density (g/cm^3) = M/V .

3.2.4.8 Attrition Loss

Attrition loss followed ASTM D4058-96. Firstly, the test cylinder needs to be cleaned and then lid of the apparatus using a fine-bristle brush. The sample was weighed 100 to the nearest 0.01 g and it was recorded as *A*. The sample was poured into the test cylinder. Cover of cylinder was sealed for rotation at 60 rpm of 1800 revolutions. After finishing the rotation, the test cylinder allowed the fines to settle to the bottom of the test cylinder. The test sample was carefully removed into a No.20 (850- μm) ASTM sieves with pan. The sieve was gently shaken by hand. The test sample in sieve was weighed and recorded weight as *B*. Calculate the percent loss on attrition % = $(A - B)/A \times 100$.

3.2.4.9 Radial Crushing Strength

A test sample was dried at 150 °C at least 3 h and then it was cooled the test samples in a desiccator. The test sample of 50 individual pieces was prepared. Each extruded catalyst need to measure the length and diameter. Next, it was placed between the anvils of the compression testing device. The machine forced on sample with 500 N until the pellet crushed or collapsed. The maximum compressive force was recorded in Newton unit and the radial crushing strength was calculated in N/cm unit.

3.2.4.10 Thermogravimetry Analysis

Mettler Toledo TGA/SDTA 851e machine, dried extruded samples was used for determination mass loss behavior at the heating rate of 10 °C/min with N_2 flow.