

Improved *p*-Xylene Selectivity of *n*-Pentane Aromatization over Silylated Ga-exchanged HZSM-5 Catalysts

Tunchanok Nitipan, Siriporn Jongpatiwut, Thirasak Rirksomboon, Boonyarach Kitiyanan, Tivaporn Apphakvan

Abstract—In this study, the conversion of *n*-pentane to aromatics is investigated on HZSM-5 zeolites modified by Ga ion-exchange and silylation using tetraethyl orthosilicate (TEOS) via chemical liquid deposition (CLD). The effect of SiO₂/Al₂O₃ ratios of HZSM-5 was also studied. Parameters in preparing catalysts i.e. TEOS loading and cycles of deposition were varied to obtain the optimal condition for enhancing *p*-xylene selectivity. The highest *p*-xylene selectivity 99.7% was achieved when the amount of TEOS was 20 vol.%. The catalysts were characterized by TPD, TPO, XRF, and BET. Results show that the conversion of *n*-pentane was influenced remarkably by the SiO₂/Al₂O₃ ratios of HZSM-5. The highest *p*-xylene selectivity 99.7% was achieved when the amount of TEOS was 20 vol.%. And cycles of deposition greatly improves HZSM-5 shape-selectivity.

Keywords—Aromatization, Chemical Liquid Deposition (CLD), *p*-Xylene, ZSM-5 Zeolite

I. INTRODUCTION

AROMATICS are one of the most important petrochemical products. Many items such as packaging, drug, transportation device, telecommunication device, cloth, and sport device in our everyday life are made from aromatics. The main aromatics are benzene, toluene, and xylene. Xylene is a clear, colorless, and sweet-smelling liquid that is flammable. It has 3 isomers, *p*-xylene, *o*-xylene, and *m*-xylene. In particular, *p*-xylene is the most valuable chemicals used to produce terephthalic acid as starting material for producing plastic PET bottles. The transformation of heavy naphtha (C₇-C₁₀) into aromatics takes place over Pt/Cl-Al₂O₃ catalysts. Unfortunately, the feedstock is limited to heavy naphtha which contains *n*-alkanes with carbon atom higher than 6 atoms because lower paraffin (C₃-C₆) are heavy converted into aromatics over these catalysts [1].

T. N. is with The Petroleum and Petrochemical College, Chulalongkorn University, Soi Chula 12, Phayathai Road, Pathumwan, Bangkok 10330, Thailand (e-mail: konahcnut@hotmail.com)

S. J. is with The Petroleum and Petrochemical College and Center for Petroleum, Petrochemicals, and Advanced Materials, Chulalongkorn University, Bangkok 10330, Thailand (e-mail: siriporn.j@chula.ac.th)

T. R. is with The Petroleum and Petrochemical College and Center for Petroleum, Petrochemicals, and Advanced Materials, Chulalongkorn University, Bangkok 10330, Thailand (e-mail: t.rirksomboon@unb.ca)

B. K. is with The Petroleum and Petrochemical College and Center for Petroleum, Petrochemicals, and Advanced Materials, Chulalongkorn University, Bangkok 10330, Thailand (e-mail: boonyarach.k@chula.ac.th)

T.A. is with PTT Global Chemical Public Company Limited, Thailand (e-mail: tivaporn.a@pttar.com)

ZSM-5 is known to be an excellent medium pore size zeolites and catalyst for the aromatization of lower alkanes [2]-[4]. The reactions involve cracking, oligomerization, and cyclization [5]. So the naphtha containing light paraffins can be also used as the feedstock for aromatic production [6].

As a result, many studies on the aromatization of light paraffin such as ethane, propane, butane and pentane over various catalysts have been investigated. ZSM-5 catalysts exhibited the highest conversion and selectivity to aromatics compared to other catalysts [7]-[8]. Gallium-loaded zeolites are known to be active for the aromatization of light paraffin upon the Cyclar process [9]-[12]. In order to obtain the high shape-selectivity of *p*-xylene over ZSM-5 zeolite, acidic sites on the external surface of the zeolite must be limited by silylation such as impregnation of metallic, pre-coking, chemical vapor deposition (CLD) of silica, and chemical liquid deposition (CLD) of silica which can cover acid sites on the external surface [13]-[15].

The objective of this present work is to study the aromatization of *n*-pentane over ZSM-5 zeolite catalysts modified by metal ion-exchange and silylation. The addition of Ga metal will be done by ion-exchange technique. The silylation will be performed by chemical liquid deposition (CLD). The effect of SiO₂/Al₂O₃ of zeolite, amount of deposition agent, and cycle of deposition will also be studied.

II. EXPERIMENTAL

A. Catalyst Preparation

1. Ion-exchange

HZSM-5 is ion-exchanged with 150 mL aqueous solutions containing precursor (Ga(NO₃)₃.xH₂O) 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. Various SiO₂/Al₂O₃ ratio of ZSM-5 zeolites (23, 30, 50, and 80) were changed to investigate their influences on the performance of catalysts.

2. Silylation

The silylation will be performed on HZSM-5 and metal-exchange ZSM-5 catalysts by chemical liquid deposition. Various parameters i.e. amount of deposition agent and cycles of deposition are investigated. The modified catalysts are obtained by impregnating the HZSM-5 with tetraethyl orthosilicate (TEOS) dissolved in cyclohexane at room temperature for 7 h, dried at 120 °C for 2 h and then calcined at 550 °C for 5 h.

B. Catalytic Activity Testing

The aromatization of *n*-pentane is carried out in a continuous flow fixed-bed reactor at atmospheric pressure. In the continuous-flow reactor, 0.2 g of fresh catalyst is used in each run. Prior to aromatization reaction, the modified catalyst is reduced with H₂ at 500 °C for 3 h. The naphtha feed is continuously injected from a syringe pump and preheated at 70 °C with flow rate 0.01 mL/min. Helium is a carried gas with flow rate 40 mL/min, WHSV = 2.5 h⁻¹. The products are analyzed by gas chromatography using a Shimadzu 17A-GC equipped with an HP-PLOT/Al₂O₃ "S" deactivated capillary column. The GC column temperature is programmed to obtain an adequate separation of the products. The temperature is first kept constant at 40 °C for 10 min and then, linearly ramped to 195 °C and held for 30 min.

C. Catalyst Characterization

Surface areas and micropore 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, 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 was then measured. The solid sample was maintained at a constant temperature of the sample cell until the equilibrium was established. This volume-pressure data was used to calculate the BET surface area.

III. RESULT AND DISCUSSION

A. Effect of SiO₂/Al₂O₃ ratio of HZSM-5 zeolite

HZSM-5 zeolite with different SiO₂/Al₂O₃ ratios; HZSM-5(23), HZSM-5(30), HZSM-5(50), and HZSM-5(80) was tested in aromatization of *n*-pentane for their catalytic performances. Fig. 1 shows *n*-pentane conversion, aromatic selectivity, and *p*-xylene selectivity in xylene over unmodified HZSM-5 zeolite at fifth hour of time on stream. The results indicated that for all catalysts, the *p*-xylene selectivity was about 24%. While HZSM-5(80) did not give any *p*-xylene product. For the conversion, it generally decreased with the increase of SiO₂/Al₂O₃ ratio. HZSM-5(23) provided high conversion around 95%. HZSM-5(80) exhibited the low conversion around 20%. It is the fact that the increase of SiO₂/Al₂O₃ ratio would result in the decrease of the acid sites, which facilitate the *n*-pentane aromatization [16]. The result showed that HZSM-5(23), HZSM-5(30), and HZSM-5(50) catalysts gave aromatics as main products. Among the aromatic products, toluene was the dominant one. HZSM-5(80) gave a high amount of light hydrocarbon. Consequently, HZSM-5 zeolite with SiO₂/Al₂O₃ ratio of 23 was selected for the following Ga-exchange and chemical liquid deposition (CLD) process due to the highest conversion.

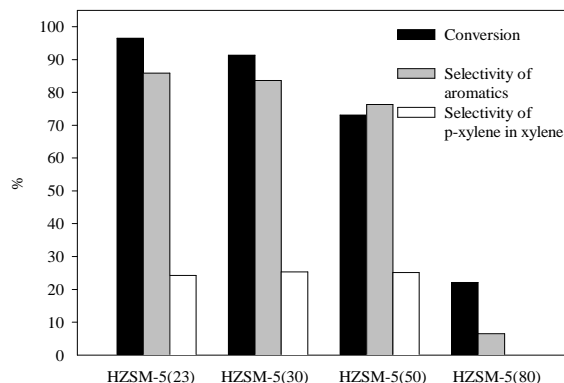


Fig. 1 Effect of SiO₂/Al₂O₃ ratio of HZSM-5 zeolite on the *n*-pentane conversion, aromatic selectivity, and *p*-xylene selectivity (Reaction condition: 500 °C, 1 atm, WHSV = 5 h⁻¹, and TOS = 5 h)

B. Effect of Ga-exchanged HZSM-5 zeolite

It is well known that the presence of Ga could accelerate the aromatization by improving dehydrogenation activity. In this work, the combined effects of Ga ion-exchange and silylation were investigated. For investigation on Ga-loaded HZSM-5, Ga metal was ion-exchanged with HZSM-5(23). Fig. 2 shows *n*-pentane conversion, aromatic selectivity, and *p*-xylene selectivity over unmodified HZSM-5(23) and Ga/HZSM-5(23). It can be seen that Ga/HZSM-5(23) exhibited higher aromatic selectivity than unmodified HZSM-5(23). Ga/HZSM-5 reduces the selectivity of light paraffin, resulting in more selectivity towards aromatics. This can be explained by the fact that Ga-modification enhances HZSM-5 dehydrogenation, leading to higher concentration of aromatics. The Ga metal provides an alternative path for the formation of olefins and aromatics and controls the formation of lower paraffins cracking and dehydrogenation. For the conversion of both catalysts, they almost reached 100%. Ga/HZSM-5(23) presented *p*-xylene selectivity about 24%, a value closed to that of unmodified HZSM-5(23).

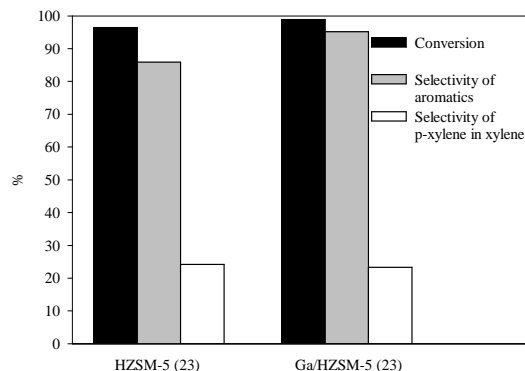


Fig. 2 Effect of Ga-exchange HZSM-5 zeolite on the *n*-pentane conversion, aromatic selectivity, and *p*-xylene selectivity (Reaction condition: 500 °C, 1 atm, WHSV = 5 h⁻¹, and TOS = 5 h)

C. Effect of TEOS loading on Ga/HZSM-5 catalyst

The enhanced *p*-xylene selectivity was due to the deposition of inert silica on the external surface of HZSM-5 zeolite. The effect of TEOS loading by chemical liquid deposition was investigated. Different TEOS concentrations (0 vol.%, 5 vol.%, 10 vol.%, 15 vol.% and 20 vol.% denoted as HZSM-5(23), CLD5, CLD15, and CLD20, respectively) were prepared in cyclohexane as silylating solution. The conversion and *p*-xylene selectivity of silylated zeolite in *n*-pentane aromatization are shown in Fig. 3. It can be seen that the *p*-xylene selectivity was quickly enhanced with increasing the amount of TEOS. The highest *p*-xylene selectivity 99.7% was achieved when the amount of TEOS was 20 vol.%. On the other hand, the conversion of *n*-pentane decreased with the increase of TEOS. In fact, chemical vapor deposition results in deactivation of external acid sites and also reducing surface areas of zeolite, which affects the diffusion of *m*- and *o*-xylene. Both *m*- and *o*-xylene are transformed to *p*-xylene by isomerization before escaping the pores. It was proposed that a low amount of TEOS resulted in a low coverage of deposited silica, which was not able to influence the *p*-xylene selectivity.

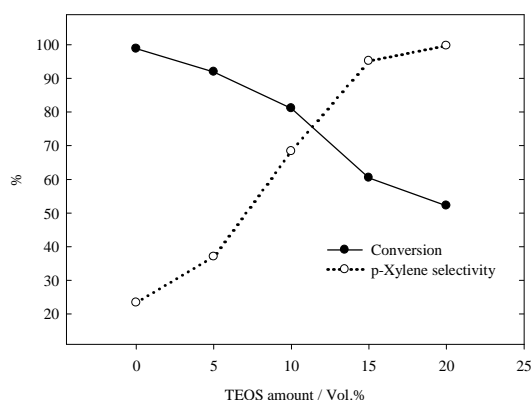


Fig. 3 Effect of TEOS loading on the conversion of *n*-pentane and *p*-xylene selectivity (Reaction condition: 500 °C, 1 atm, WHSV = 5 h⁻¹, and TOS = 5 h)

The deposited silica of silylated HZSM-5 was analyzed by XRF. Table I showed that the SiO₂ amount increased with increasing TEOS loading. The decrease in catalytic conversion and increase in *p*-xylene selectivity were proportional to the SiO₂ amount, but it is not a linear relationship.

TABLE I
THE AMOUNT OF DEPOSITED SILICA ON THE UNTREATED AND SILYLATED Ga/HZSM-5(23) ZEOLITES

| Catalyst | Conversion (%) | <i>p</i> -Xylene Selectivity (%) | Silica Content (wt.%) |
|------------|----------------|----------------------------------|-----------------------|
| HZSM-5(23) | 97.6 | 23.4 | 89.1 |
| CLD5 | 91.9 | 37.0 | 90.5 |
| CLD10 | 81.1 | 68.3 | 91.5 |
| CLD15 | 60.5 | 95.2 | 92.3 |
| CLD20 | 52.2 | 99.7 | 93.2 |

D. Effect of CLD cycle

From the previous studies, silylations were based on the one-cycle CLD process. However, it was known that multi-cycle deposition not only increased the amount of silica deposited on the external surface of HZSM-5, but also improved the uniformity of the silica layer [17]. Table II lists the performance of catalysts modified with different CLD cycle at time on stream of 5 h. The catalyst names are defined by the number of cycle followed by TEOS concentration. For example, the catalyst silylated with 5% TEOS in cyclohexane for 2 cycles is noted as 2CLD5. It could be seen that repeated CLD treatments could improve *p*-xylene selectivity obviously. In detail, the selectivity of *p*-xylene increased up to 87.8% over the modified Ga/HZSM-5 2 cycles of CLD5 modification compared to 68.3% *p*-xylene selectivity of 1 cycle of CLD5 modification. However, the conversion was much lower for 2CLD5 (63.8%) compared to CLD10 (81.1%). In the same way, the selectivity of *p*-xylene of 3CLD5 increased up to 100% compared to 95.1% *p*-xylene selectivity of CLD15, and the conversion was much lower for 3CLD5 (21.9%) compared to CLD15 (60.4%).

TABLE II
EFFECT OF CLD CYCLE NUMBER OF Ga/HZSM-5 ZEOLITE ON THE *n*-PENTANE CONVERSION, *p*-XYLENE SELECTIVITY AND AMOUNT OF DEPOSITED SILICA (REACTION CONDITION: 500 °C, 1 ATM, WHSV = 5 h⁻¹, AND TOS = 5 h)

| Catalyst | Conversion (%) | <i>p</i> -Xylene Selectivity (%) |
|----------|----------------|----------------------------------|
| CLD10 | 81.1 | 68.3 |
| 2CLD5 | 63.8 | 87.8 |
| CLD15 | 60.4 | 95.1 |
| 3CLD5 | 21.9 | 100 |
| CLD20 | 52.2 | 99.7 |

E. BET analysis

BET was used to investigate the surface area and pore volume. Surface area and pore volume of the silylated HZSM-5 and untreated HZSM-5 are summarized in Table III. Deposition of an inert silica layer on the external surface of HZSM-5 by method of CLD has changed area and pore volume of the catalysts. It led to the decrease in both surface area and micropore volume. However, the pore diameters were unchanged. The results indicated that the addition of SiO₂ could block the pore of the zeolite. However, the silylation did not modify the pore opening of the zeolite. The surface area and pore volume decreased in the following order; HZSM-5 > Ga/HZSM-5 > CLD5 > CLD10 > CLD15 > CLD20. At the same TEOS loading, but different repeated CLD, 2CLD5 catalyst exhibited lower surface and pore volume. The surface area of 3CLD5 catalyst was lower than that of the CLD15 catalyst and even the surface area of CLD20 that has higher than TEOS loading.

TABLE III
BET SURFACE AREA, PORE DIAMETER, AND
MICROPOROUS VOLUME OF THE SILYLATED ZEOLITES

| Catalysts | Surface Area (m ² g ⁻¹) | Total pore vol. (ml g ⁻¹) | Pore Diameter* (Å) |
|-----------|---|--|--------------------------|
| HZSM-5 | 495 | 0.278 | 6.14 |
| Ga/HZSM-5 | 485 | 0.272 | 6.14 |
| CLD5 | 467 | 0.231 | 6.14 |
| CLD10 | 423 | 0.215 | 6.14 |
| CLD15 | 344 | 0.167 | 6.14 |
| CLD20 | 318 | 0.164 | 6.14 |
| 2CLD5 | 367 | 0.173 | 6.14 |
| 3CLD5 | 281 | 0.135 | 6.14 |

*Using NLDFT method

IV. CONCLUSIONS

The conversion of *n*-pentane was influenced remarkably by the SiO₂/Al₂O₃ ratios of HZSM-5. It decreased with the increase of SiO₂/Al₂O₃ ratio. The HZSM-5 with low SiO₂/Al₂O₃ ratios exhibited *p*-xylene selectivity of about 24%. The ZSM-5 zeolite modified by CLD with TEOS as the deposition agent are demonstrated to be shape-selective catalysts towards *p*-xylene for the aromatization of *n*-pentane. After the TEOS-CLD treatment, a layer of inert silica is deposited onto the surface of ZSM-5 zeolite crystals, which eliminates the external acid sites, and is responsible for the improved shape-selective performance. The catalyst, CLD20 prepared under the suitable conditions presents a high *p*-xylene selectivity 99.7% with a considerable high conversion 52.2%.

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