Aromatization of *n*-Octane over ZSM-5 Zeolite Catalysts and Its Reaction Pathways

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Abstract

The aromatization of *n*-octane, one of the main components of light naphtha, has been investigated over HZSM-5 (Si/Al = 10, 36, 50, 100) and Zn/HZSM-5 catalysts prepared by the ion exchange method. The catalytic activity measurement was performed at 500^oC under atmospheric pressure. Results showed that the lower Si/Al ratio of HZSM-5 catalysts provided the higher selectivity to total aromatics since an increase in BrØnsted acid sites enhances for the greater availability of cracking intermediates to aromatics. The presence of zinc in Zn/HZSM-5 provided a significant increase in total aromatics selectivity due to the improvement of dehydrogenation activity by Zn incorporation. The Zn species facilitated the aromatization by converting the paraffins into corresponding olefins which, in turn, were the aromatics precursors. Therefore, both acidity and zinc incorporation played important roles in the aromatization of *n*-octane. The results revealed that the aromatics were generated from small olefins. The reaction pathways could be proposed based on the preliminary results as follows: the *n*-octane would be first decomposed to small olefins, followed by oligomerization and cyclization. In addition, toluene disproportionation and benzene alkylation would also take place for C_8 aromatics production. However, the direct dehydrocyclization of *n*-octane was not observed over Zn/HZSM-5.

Introduction

The aromatization of *n*-alkane is a profitable reaction for the transformation of naphtha to aromatics, which are more valuable components. Aromatics obtained can be used as essential raw materials for the production of a wide variety of petrochemicals. ZSM-5 (MFI) zeolite of the pentasil family is well known as a potential acidic catalyst for the aromatization of lower alkanes (C_3-C_5) [Biscardi *et al.*, 1998 and Berndt *et al*, 1996]. The high activity of HZSM-5 catalyst in the aromatization of alkane is attributed to its high acid strength and correct pore geometry [Bhattachara and Sivasanker, 1995]. Although the HZSM-5 catalyst provided a high conversion, the selectivity to aromatics was quite low due to the low dehydrogenation ability of HZSM-5. Therefore, the addition of metal on the HZSM-5 catalyst was introduced to improve the aromatics selectivity. The study on the aromatization of propane over HZSM-5 catalysts with the addition of Ga, Zn, and Pt indicated that the highest aromatics selectivity was observed on Ga/HZSM-5 or Zn/HZSM-5 catalysts [Meriaudeau *et al.*, 1991]. Nevertheless, Pt/HZSM-5 yielded less aromatics selectivity than HZSM-5. This might be due to the fact that the hydrogenolysis property of Pt leads to the production of a large amount of lower alkanes, especially for ethane.

Although the metal-modified HZSM-5 catalysts exhibit a significant improvement in the selectivity to total aromatics, the detailed reaction pathways of the aromatization on such catalysts have not yet been understood but extensively discussed. Giannetto *et al.* [1991] suggested that the direct aromatization of *n*-hexane and *n*-heptane yielding benzene and toluene, respectively, took place over Ga/HZSM-5 catalysts, thereby proposed that the direct aromatization occurred via the dehydrogenation step on metal sites, followed by

cyclization over acid sites. In contrast, recent reports on the aromatization of *n*-heptane over Zn/HZSM-5 and Ga/HZSM-5 catalysts proposed that the aromatization started with cracking of *n*-heptane, followed by oligomerization to higher alkenes, before the dehydrocyclization steps. Moreover, the direct dehydrocyclization of *n*-heptane to toluene could possibly occur on the Zn modified HZSM-5 [Viswanadham *et al.*, 1996 and Choudhary *et al.*, 2003].

The study on aromatization of *n*-octane over such catalysts has so far been limited. Therefore, it is essential to investigate the aromatization behavior of *n*-octane over HZSM-5 and modified HZSM-5 catalysts. The objectives of this study are to determine the reaction pathways of the *n*-octane aromatization and to study the effect of the Si/Al ratio of the catalysts. In this contribution, the aromatization of *n*-octane over HZSM-5 and Zn promoted ZSM-5 catalysts has been studied at 500 ^{o}C under atmospheric pressure.

Experimental

Catalyst Preparation

ZSM-5 zeolites were synthesized using the conventional method indicated in the recognized patents [Argauer *et al.*, 1979] with some modifications. Tetrapropylammonium-bromide (TPA-Br) was utilized as organic templates. In addition, the silicon and aluminum compositions in the gel solution were adjusted in order to yield the desired Si/Al ratios. The synthesized zeolites were calcined at 600°C for 5 h to decompose the organic templates. Na$^+$ ions in the synthesized zeolites were replaced with NH$_4^+$ ions by ion exchange method with 1 M of NH$_4$NO$_3$ solution at 80°C for 10 h using 100 ml per gram of zeolite. Then, the zeolites were separated from the solution by filtering and washing. The exchange procedure was repeated three times to complete the Na$^+$ ion exchange. After that, the catalysts were dried overnight at 110 ^{o}C and calcined in flowing dry air (100 ml/min per gram of zeolite) at 500°C for 5 h to produce the acidic form of the zeolites (HZSM-5). HZSM-5 (36) was exchanged with 0.0065 M of Zn(NO$_3$)$_2$ for 5 h at 80°C using 50 ml per gram of zeolite to attain 0.3Zn/HZSM-5 (36) catalyst. Then, the exchanged samples were dried overnight at 110 ^{o}C and calcined at 500°C for 5 h.

Catalyst Characterization

The fresh catalysts were characterized using several techniques. Nitrogen adsorption was carried out to analyze the surface area and pore volume of the synthesized ZSM-5 zeolites. The adsorption isotherms were collected at 77K using a Thermo Finnigan modeled Sorptomatic 1100 series surface area analyzer. Elemental analyses were carried out in a Perkin-Elmer Optima 4300 DV inductively coupled plasma – optical emission spectrometer (ICP-OES).

The acidity of all samples was determined by the temperature programmed desorption of propylamine technique [Parrillo *et al.*, 1990]. 30 mg of the sample was preteated in a flow of He at 773 K for 1 h. After that, the sample was cooled in flowing He to room temperature. Then, 10 μl of propylamine was injected over the sample each time until the sample was saturated. The saturation of propylamine adsorption was monitored using a mass spectrometer. After the removal of the excess propylamine by flowing He for 3 h, the sample was linearly heated to 973 K at a ramping rate of 10 K/min. The mass to charge ratios (m/z) of 17, 30, and 41 were monitored to determine the evolution of

ammonia, propylamine, and propylene, respectively. The amount of desorbed propylene was calibrated with a 5 ml pulse of 2% propylene in He.

Catalytic Activity Measurements

The catalytic activity measurements were carried out for n-octane aromatization in a 0.5- inch pyrex glass reactor at 500°C under atmospheric pressure with a WHSV of 5 h^{-1}. To investigate the selectivities of the products as a function of total *n*-octane conversion, the WHSV was also varied at 15, 25, 100, and 200 h^{-1}. The reactor was a single-pass continuous flow type packed with a catalyst bed of 0.2 g. Prior to the reaction, the catalyst was *in situ* reduced for 1 h. *n*-Octane was injected using a syringe pump. The molar ratio of hydrogen to *n*-octane was kept at 6:1 in all experiments. The products were analyzed using an online gas chromatograph (Shimadzu GC-17A) equipped with a capillary HP-Plot/Al$_2$O$_3$ "S" deactivated column.

Results and Discussion

Characterization of Fresh Catalysts

The elemental analysis carried out using ICP-OES technique is reported in Table 1. The numbers indicated in the parentheses represent the Si/Al ratio of the catalysts. In addition, 0.3 wt% of Zn loaded to HZSM-5 at Si/Al ratio of 36 is denoted as 0.3Zn/HZSM-5 (36). As shown in Table 1, it exhibits that the amount of Brønsted acid sites decreased with increasing Si/Al ratio. This is consistent with the fact that the Brønsted acidity is created by the amount of Al content in the zeolite framework. Furthermore, the addition of Zn to the HZSM-5 (36) catalyst resulted in the significant loss in the density of Brønsted acid sites, as observed by others [Ono, 1992 and Smiešková *et al.*, 2004]. This is because the Brønsted acid sites are converted to Lewis acid sites.

Table 1 Analysis data of the synthesized catalysts

| Catalysts	Si/Al (molar ratio)	Zn loading (wt%)	Surface area (m^2/g)	Particle size [a] (μm)	Brønsted Acidity [b] (μmol/g$_{cat}$)
HZSM-5 (10)	10	-	413	~ 1	582
HZSM-5 (36)	36	-	377	~ 3	382
HZSM-5 (50)	50	-	496	~ 3	266
HZSM-5 (100)	100	-	439	~ 3	163
0.3Zn/HZSM-5 (36)	36	0.3	364	~ 3	218

[a] Measured by SEM
[b] Measured by TPD of propylamine

Catalytic Activity

The HZSM-5 with various Si/Al ratios and 0.3Zn/HZSM-5 (36) catalysts were tested their catalytic performance on the aromatization of *n*-octane conversion at 500°C under atmospheric pressure. Figure 1 illustrates the *n*-octane conversion and total aromatics selectivity as a function of time on stream. It shows that at a given time on stream both *n*-octane conversion and total aromatics selectivity increased with decreasing Si/Al ratio. Moreover, most of which decreased with time on stream. Since the acid sites are responsible for cracking, oligomerization, and cyclization [Meriadeau and Naccache, 1997],

the lower Si/Al of the catalyst provides the higher availability of active sites for aromatization, thus resulting in higher total aromatics selectivity. This can be confirmed by the observation attained in Figure 2. It obviously exhibits that the *n*-octane conversion and the selectivity to total aromatics increased with increasing density of Brønsted acid sites.
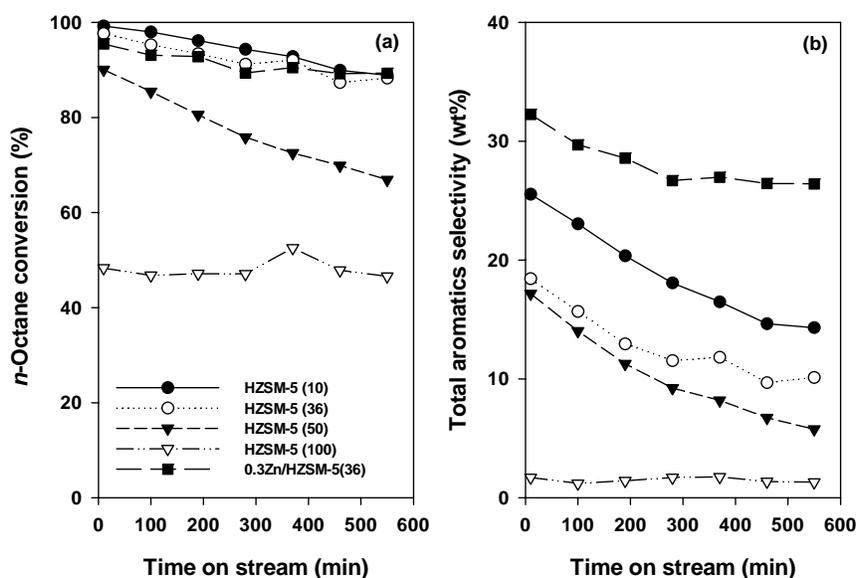
Figure 1 (a) *n*-Octane conversion and (b) total aromatics selectivity as a function of time on stream over various catalysts. Reaction conditions: 500°C, 1 atm, H_2 to *n*-C_8 ratio 6:1, WHSV 5 h^{-1}.
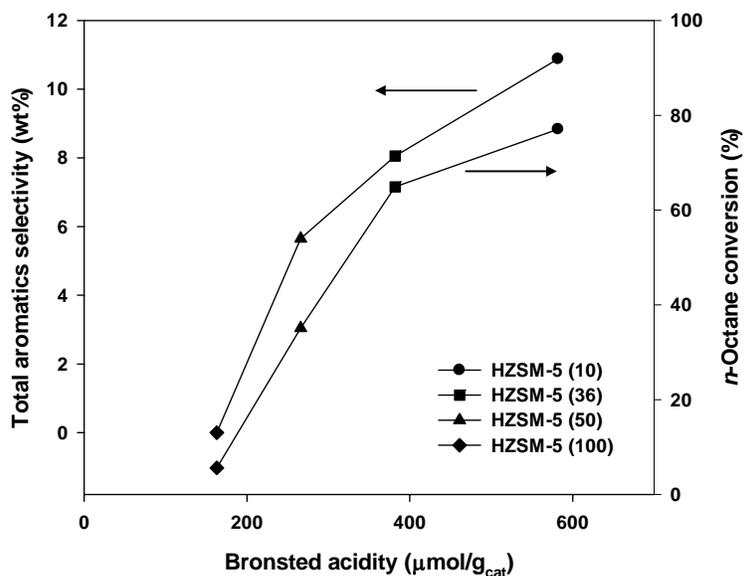
Figure 2 Total *n*-octane conversion and total aromatics selectivity as a function of amounts of Brønsted acid sites over various catalysts. Reaction conditions: 500°C, 1 atm, H_2 to *n*-C_8 ratio 6:1, WHSV 5 h^{-1}.

The product distributions over the various HZSM-5 and 0.3Zn/HZSM-5 (36) catalysts are reported in Table 1. The addition of Zn on the HZSM-5 (36) catalyst significantly increased the total aromatics selectivity (also shown in Figure 1). This may be attributed to the improvement of dehydrogenation activity of the catalyst by the presence of Zn species leading to the greater availability of olefin pool, which is the intermediate for aromatization [Smiešková A. *et al.,* 2004]. Nevertheless, as compared to the parent HZSM-5 (36) catalysts, the lower selectivities of ethylene, propylene, butenes, and C_5 hydrocarbons were obtained from the 0.3Zn/HZSM-5 (36) catalyst. This may imply that these compounds are consumed in the further reactions, such as oligomerization and cyclization leading to the higher total aromatics selectivity for the 0.3Zn/HZSM-5 (36) catalyst.

In addition, toluene was yielded as the main aromatic product, followed by C_8 aromatics, and benzene from all the catalysts tested. If the direct dehydrocyclization of *n*-octane had taken place over the catalysts tested, either *o*-xylene or ethylbenzene should be observed as the main C_8 aromatics product. However, among C_8 aromatics, *m*-and *p*-xylenes were found as the dominant C_8 aromatics obtained from both HZSM-5 and Zn promoted HZSM-5 catalysts. Only small amount of *o*-xylene, and ethylbenzene was observed. This indicates that the direct aromatization of *n*-octane does not occur under the conditions used in our investigation. Furthermore, the presence of Zn species in the HZSM-5 catalysts does not affect the aromatics distribution, in which toluene is still observed as dominant aromatic product for the 0.3Zn/HZSM-5 (36) catalyst.

Table 1 Product distributions of *n*-octane aromatization over various catalysts

Catalysts	HZSM-5 (10)	HZSM-5 (36)	HZSM-5 (50)	HZSM-5 (100)	0.3Zn/HZSM-5 (36)
Conversion	99.2	97.6	90.0	48.3	82.7
Product Selectivity (wt%)					
Methane	3.2	1.5	1.2	0.6	2.9
Ethane	6.7	4.6	3.8	3.8	4.6
Ethylene	7.5	9.6	8.3	8.7	6.2
Propane	30.3	25.7	24.8	14.0	13.5
Propylene	9.1	13.5	13.9	26.0	11.2
C_4	11.7	16.0	16.9	14.0	24.2
Butenes	3.8	6.3	7.8	17.6	6.0
C_5	2.0	3.9	5.1	11.1	4.7
C_6	0.2	0.5	1.0	2.5	0.6
Benzene	4.6	2.3	2.0	0.2	4.5
Toluene	12.4	8.5	8.1	0.9	12.7
Ethylbenzene	0.5	0.3	0.4	0.0	0.6
m-,p-xylene	6.5	6.0	5.8	0.6	6.9
o-xylene	1.5	1.3	0.9	0.0	1.4
C_8 aromatics	**8.5**	**7.6**	**7.1**	**0.6**	**8.9**
Total aromatics	**25.5**	**18.4**	**17.2**	**1.7**	**26.1**

Reaction Conditions: 500 $^\circ$C, 1 atm, H_2 : *n*-C_8 molar ratio 6 : 1, WHSV 5 h^{-1}, 10 min on stream

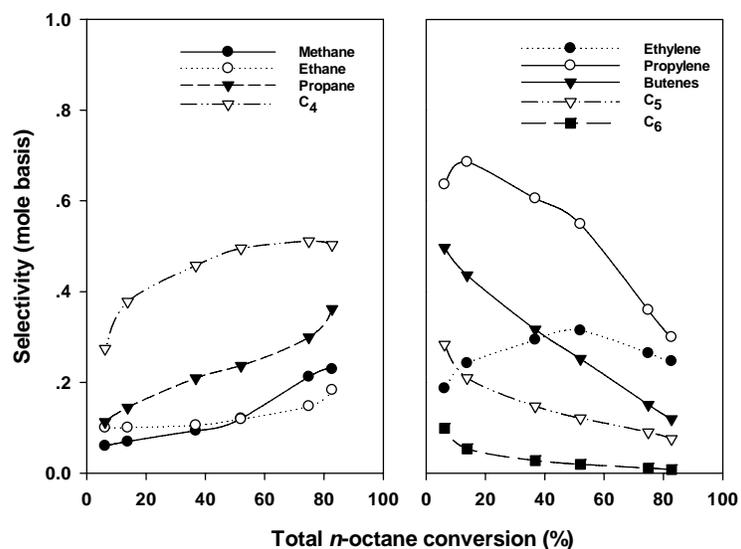## Products Distribution as a Function of *n*-Octane Conversion

To study the reaction pathways, WHSV was varied to obtain the product distributions at different conversion. Figure 3 and 4 illustrate the product distributions as a function of *n*-octane conversion obtained from the HZSM-5 (36) and 0.3Zn/HZSM-5 (36) catalysts, respectively. They illustrate in Figure 3 and 4 that the selectivities of methane, ethane, propane, and C_4 hydrocarbons increased with increasing *n*-octane conversion. It suggests that these components are inactive intermediates. In addition, the presence of Zn cation in the HZSM-5 (36) catalyst lowers the selectivities of ethane and propane by transformation of them into the corresponding olefins, aromatic intermediates, leading to higher aromatics selectivity. In contrast, the increase in the selectivity to methane was observed over the Zn modified HZSM-5 catalyst. This observation might be resulted from the presence of Zn species. Biscardi *et al.* [1998] concluded that the presence of Zn cation also increased the removal rate of intermediates to more stable products, such as aromatics, and methane.

Furthermore, they show that ethylene and propylene were initially produced at low conversion and decreased with further increasing conversion over both catalysts. This observation suggests that the primary reaction was involved in cracking of *n*-octane at first step. Moreover, butenes, C_5, and C_6 hydrocarbons decreased with increasing conversion. This result indicates that ethylene, propylene, butenes, C_5, and C_6 hydrocarbons were active intermediates, which were converted in subsequent reaction, such as, oligomerization and cyclization.
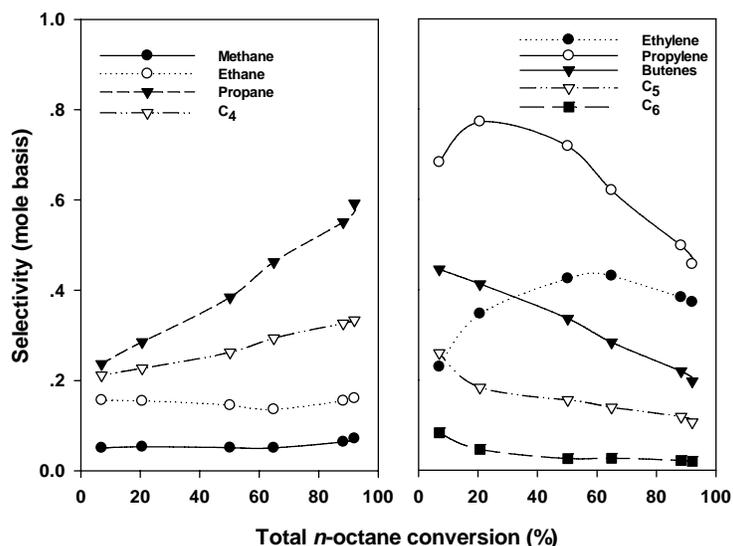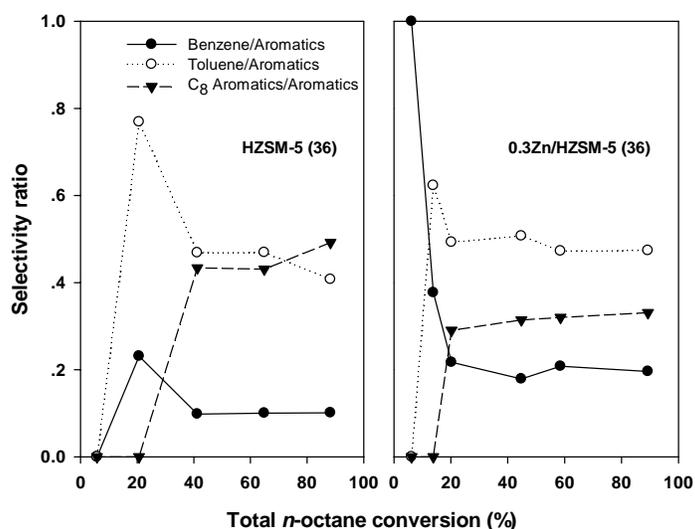

Figure 3 Product distributions as a function of total *n*-octane conversion on the HZSM-5 (36) catalyst. Reaction conditions: $500^{\circ}C$, 1 atm, H_2 to n-C_8 ratio 6:1.

An important aspect observed in the aromatic products distributions is the decreases in the selectivity ratios of benzene to total aromatics and toluene to total aromatics at low conversion as shown in Figure 5. However, the C_8 aromatics to total aromatics ratio increased with increasing *n*-octane conversion. These results may be implied that benzene and toluene are involved in secondary reactions for the production of the C_8 aromatics, such as benzene alkylation and toluene disproportionation.

Figure 4 Product distributions as a function of total *n*-octane conversion on the 0.3Zn/HZSM-5 (36) catalysts. Reaction conditions: 500°C, 1 atm, H₂ to *n*-C₈ ratio 6:1.

Figure 5 Product selectivity ratio as a function of total *n*-octane conversion during on HZSM-5 (36) and 0.3Zn/HZSM-5 (36) catalysts. Reaction conditions: 500°C, 1 atm, H₂ to *n*-C₈ ratio 6:1.

The results shown in Figure 5 also confirm the discussion about the direct dehydrocyclization of *n*-octane mentioned in previous section. The graph exhibits that benzene and toluene were initially produced at very low conversion (~10%) whereas C₈ aromatics were not observed. Therefore, it suggests that the direct aromatization of *n*-octane did not take place either on the HZSM-5 or the Zn promoted HZSM-5 catalysts.

Based on the preliminary results, the reaction pathways of the *n*-octane aromatization over the HZSM-5 and the Zn/HZSM-5 catalysts might be proposed as follows: *n*-octane would be initially cracked to small paraffins and olefins. Only olefins undergo the oligomerization, followed cyclization to form aromatics. Zn species facilitate the

aromatization by the transfromation of paraffins, inactive intermediates, to olefins which are aromatic precursors. This results in the greater olefin mixtures. In addition, toluene disproportionation and benzene alkylation would also take place for C_8 aromatics production. Moreover, the addition of Zn does not provide an alternative route for the aromatization because the direct dehydrocyclization of *n*-octane was not observed over the Zn/HZSM-5 catalyst. However, the in-depth investigation will be further performed to confirm such a proposed mechanism.

Conclusions

The results can be concluded that the density of BrØnsted acid sites and dehydrogenation activity play essential roles in the aromatization of *n*-octane. The addition of Zn could significantly enhance the selectivity to total aromatics. However, Zn species did not provide the alternative reaction route for aromatization. It helps in providing the greater olefin mixture, aromatic precursors. Based on the preliminary results the reaction pathways could be proposed as follows: the *n*-octane would be first cracked to small olefins, followed by oligomerization and cyclization. In addition, toluene disproportionation and benzene alkylation would also take place for C_8 aromatics production.

Acknowledgements

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