A Comparative Study of n-Octane Aromatization over Modified MFI- and MEL-Type Zeolite Catalysts

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Abstract

The aromatization of n-octane was studied over modified MFI- (ZSM-5) and MEL- (ZSM-11) type zeolite catalysts as bifunctional catalysts to investigate the effect of pore geometry on their catalytic activity and product distribution. ZSM-5 and ZSM-11 zeolites were synthesized by the conventional method and characterized by using XRD, SEM, ICP-OES, and surface area analyzer. Zinc was loaded into the synthesized zeolites by ion exchange to prepare Zn/HZSM-5 and Zn/HZSM-11 catalysts which were then tested for aromatization at 500˚C under atmospheric pressure. Preliminary results revealed that Zn loaded into both zeolites provided a significant increase in total aromatics selectivity. The n-octane aromatization activity for such catalysts was found in the order of Zn/HZSM-11 > Zn/HZSM-5 > HZSM-5 > HZSM-11. This is due to the higher content of zinc on Zn/HZSM-11 catalysts. Regarding to C_8 Aromatics/Cracking ratio of HZSM-5 and HZSM-11 catalysts, it suggests that the aromatization of n-octane takes place preferentially in zigzag channels of ZSM-5 more than in straight channels of ZSM-11 since both zeolite catalysts contain similar acidity. Toluene was observed as a major aromatic product, followed by C_8 aromatics and benzene on Zn/HZSM-5 and Zn/HZSM-11 catalysts. However, HZSM-5 and HZSM-11 catalysts provided C_8 aromatics as the major aromatics product. Moreover, the *n*-octane aromatization over both zeolite catalysts occurs through similar reaction pathways. The aromatization will undergo via classical bifunctional reaction pathways over the zinc modified HZSM-5 and HZSM-11 catalysts.

Keywords: *n*-octane aromatization, ZSM-5, ZSM-11, zinc modified zeolite catalyst

Introduction

Aromatics are important raw materials for the production of a wide variety of petrochemicals. The alkane transformation into such chemicals is a big challenge in both scientific and practical points of view. MFI (ZSM-5) zeolite of the pentasil family is well known as a potential catalyst for the aromatization of lower alkanes (C_3-C_6 alkanes) [Biscardi et al., 1998 and Berndt et al., 1996]. It is known that ZSM-5 zeolite has bi-dimensional medium pore structure consisting of two intersecting channel systems. One channel system is zigzag having a cross section of 5.1 x 5.5 A^o. The other channel system has 5.3 x 5.6 A^o opening which run straight and perpendicular to the first channel system. The high activity and selectivity of ZSM-5 in alkane aromatization is attributed to its high acidity and correct pore geometry [Bhattachara and Sivasanker, 1995]. The addition of zinc (Zn) into the ZSM-5 zeolite has been reported in many literatures [Smieskova et al., 2004]. They reported that Zn supported ZSM-5 shows an excellent performance of aromatization due to its dehydrogenating function.

Extensive studies have been reported the utilization of MEL (ZSM-11) zeolite, one of medium pore opening containing straight channel system with similar diameter to ZSM-5, as a catalyst for aromatization of alkanes [Anuniziata et al., 2003]. Moreover, the modified ZSM11 with zinc has been successfully used for aromatization. Zn containing ZSM-11 catalysts were reported to exhibit good results in methane conversion to aromatics by using n-pentane and n-hexane as co-reactants [Anuniziata et al., 2003 and 2004].

However, the aromatization of higher alkane, for instance, *n*-octane, over such catalysts is still limited in the literature because many researches have been focused on the lower paraffin aromatization. Therefore, it is interesting to investigate the aromatization behavior of *n*-octane over the different pore structure zeolite catalysts. In this contribution, the aromatization of *n*-octane over Zn containing ZSM-5 and ZSM-11 zeolite catalysts was studied at 500 ^{o}C under atmospheric pressure. A comparative study of aromatization behavior was also performed to inverstigate the effect of pore geometry. Fresh and spent catalysts were characterized using several techniques, e.g. XRD, BET, SEM, ICP-OES, and Temperature Programmed Oxidation (TPO) technique.

Experimental

Catalyst Preparation

ZSM-5 and ZSM-11 were synthesized using the conventional method indicated in the well-known patents [Argauer et al., 1979 and Chu, 1973] with some modifications. Tetrapropylammoniumhydroxide (TPAOH) and Tetrabutylammoniumhydroxide (TBAOH) were used as organic templates for ZSM-5 and ZSM-11, respectively. Moreover, the gel compositions were adjusted in order to obtain similar Si/Al ratios, and consequently the similar number of acidic sites of both zeolites. The synthesized zeolites were calcined at 600 ^{o}C for 5 h to decompose the organic templates. Na^+ ions in the synthesized zeolites were replaced with NH_4^+ ions by ion exchange with 1 M of NH_4NO_3 solution at 80 ^{o}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 ^{o}C for 5 h to produce the acidic form of the zeolites (HZSM-5, HZSM-11). Both HZSM-5 and HZSM-11 were exchanged with 0.0065 M of $Zn(NO_3)_2$ for 5 h at 80 ^{o}C using 50 ml per gram of zeolite to attain Zn/HZSM-5 and Zn/HZSM-11, respectively. Then, the exchanged samples were dried overnight at 110 ^{o}C and calcined at 500 ^{o}C for 5 h.

Catalytic Activity Measurements

The catalytic activity tests were performed for n-octane aromatization in a 0.5- inch pyrex glass tube at 500 ^{o}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 WSHV was studied at 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 catalysts were *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 detected using an online gas chromatograph (Shimadzu GC-17A) equipped with a capillary HP-Plot/Al_2O_3 “S” deactivated column, and a temperature program to obtain optimal product separation. In this work, the C_8 aromatics/cracking product ratio is defined as the selectivity for total aromatics divided by the selectivity for cracking products (C_1-C_6). The aromatics produced from this reaction are benzene, toluene, and C_8 aromatics.

Catalysts Characterization

XRD was employed to identify the phase of zeolite using a Rigaku X-Ray Diffractometer, with CuK_α line as incident radiation and a filter at a scanning rate of 5 °/s. Moreover, the crystal morphology and crystal size were investigated by using a JEOL 5200-2AE scanning electron microscope. Nitrogen adsorption was carried out to analyze the surface area and pore volume of the synthesized ZSM-5 and ZSM-11 zeolites. The adsorption isotherms were collected at 77K using a Thermo Finnigan Modeled Sorptomatic 1100 series. Elemental analyses were carried out in a Perkin-Elmer Optima 4300 DV inductively coupled plasma – optical emission spectrometer (ICP-OES).

Temperature Programmed Oxidation (TPO) was carried out to determine the amount and characteristics of coke formed on the spent catalysts. TPO profiles of the spent catalysts were performed in a continuous flow of 2% O_2/He while the temperature was linearly ramped to 800 ^{o}C with a heating rate of 12 ^{o}C/min. Thirty milligrams of sample were placed in a ¼" quartz fixed bed reactor. The CO_2 produced by the oxidation of coke was further converted to methane over 15% Ni/Al_2O_3 catalyst in the presence of hydrogen at 400 ^{o}C. The methane obtained was analyzed online by a FID detector. The amount of oxidized coke was calibrated using 100 μl pulses of pure CO_2.

Results and Discussion

Characterization of synthesized zeolites and fresh catalysts

Prior to the catalyst preparation, the synthesized ZSM-5 and ZSM-11 zeolites as catalyst supports were characterized by XRD to investigate the crystal structure, crystallinity, and purity of the samples. The XRD patterns of both synthesized zeolites shown in Figure 1 are similar. However, the synthesized ZSM-5 exhibits a characteristic peak at 2θ about 23 degrees which is not observed for the synthesized ZSM-11 zeolite. Furthermore, there is only a single peak appearing at 2θ around 45 degrees for the synthesized ZSM-11 zeolite while there are two combined peaks attained at this angle for the synthesized ZSM-5 zeolite. These results are in agreement with the XRD patterns indicated in the patents [Argauer et al., 1972 and Chu, 1973]. Therefore, it confirms that the crystalline structures of ZSM-5 and ZSM-11 zeolites were successfully synthesized. The nitrogen adsorption technique and SEM were used to investigate the surface area, crystal size, and morphology of all catalysts, respectively. The results in Table 1 and Figure 2 illustrated that the HZSM-11 catalysts provided higher surface area with smaller crystallite size compared to the HZSM-5 catalysts.

Table 1 Analysis data of the synthesized catalysts

Catalysts	Si/Al (molar ratio)	Zn/Al (molar ratio)	Zn Loading (wt%)	Surface Area (m^2/g)	Pore Volume (cm^3/g)	Particle Size* (μm)
HZSM-5	36	-	-	380	0.26	3
HZSM-11	35	-	-	432	0.37	1
Zn/HZSM-5	36	0.12	0.3	364	0.24	3
Zn/HZSM-11	35	0.17	0.5	439	0.35	1

*Measured by SEM

In addition, the ICP-OES was employed to perform the elemental analysis. As shown in Table 1, the HZSM-5 and HZSM-11 have similar Si/Al molar ratios meaning that they provide similar concentration of acidic sites. Even though both catalysts have similar acidity and ion exchange parameters (time and metal concentration) were controlled, they still contain different contents of zinc (Zn). The Zn supported on HZSM-5 denoted as Zn/HZSM-5 contains 0.3 wt% of Zn, while the Zn supported on HZSM-11 denoted as Zn/HZSM-11 contains higher contents of Zn loading about 0.5 wt% corresponding to a higher Zn/Al molar ratio.

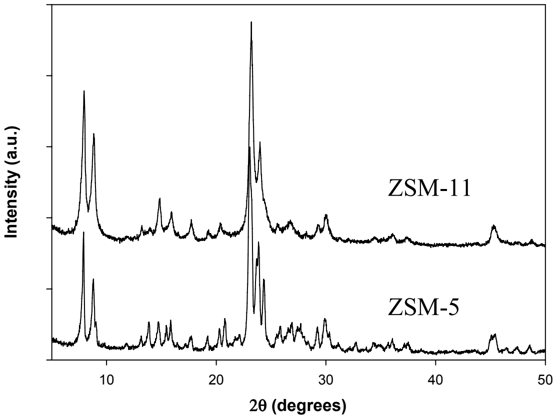
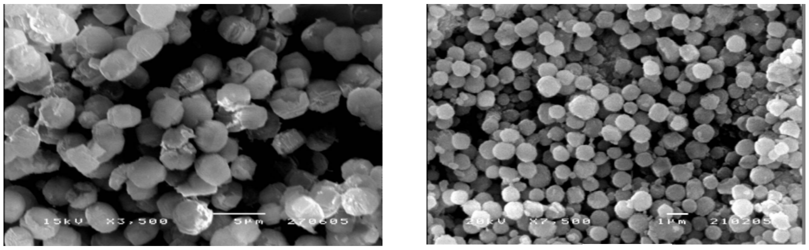


Figure 1 XRD patterns of the synthesized ZSM-5 and ZSM-11 zeolites.



(a) (b)

Figure 2 SEM photographs of the synthesized (a) ZSM-5 and (b) ZSM-11 zeolites

Catalyst Activity

The HZSM-5, HZSM-11, Zn/HZSM-5, and Zn/HZSM-11 catalysts were measured for their catalytic performance as a function of time on stream for the aromatization of *n*-octane at 500 ^{o}C under atmospheric pressure. The *n*-octane conversion and total aromatics selectivity are shown in Figures 3(a) and 3(b), respectively. The results showed that Zn/HZSM-11 exhibited the highest activity, as well as, the selectivity to total aromatics among the catalysts tested. Therefore, the catalyst supported on HZSM-11 zeolite seems to be a promising catalyst for aromatization of *n*-octane. The addition of Zn showed very much improvement in *n*-octane conversion over Zn/HZSM-11. Moreover, the total aromatics selectivity was significantly increased by the addition of Zn into HZSM-5 and HZSM-11 catalysts as illustrated in Figure 3(b). The higher total aromatics selectivity over Zn/HZSM-11 catalyst than that over Zn/HZSM-5 catalyst may be attributed to the higher content of zinc on the zeolite framework. It was reported that the olefinic fragments are the precursors for aromatics. The presence of zinc as dehydrogenation component facilitates the formation of a high concentration of these precursors leading to significant increase in the production of aromatics from *n*-heptane aromatization [Viswasanadham et al., 1996]. This may explain that ethane and propane are dehydrogenated into the corresponding olefins resulting in the decrease in the selectivities of ethane and propane over the zinc modified catalysts. Then, these olefinic compounds are consumed in the further reactions to produce the aromatics leading to the decrease in the selectivities of ethylene and propylene, as well as the increase in the total aromatic selectivity. Moreover, the properties of various catalysts tested of *n*-octane aromatization after 550 min time on stream summarized in Table 2 showed that C_8 aromatics were observed as a major product, followed by toluene and benzene on HZSM-5 and HZSM-11 catalysts. On the other hands, over zinc modified HZSM-5 and HZSM-11 catalysts, toluene was found as the major product followed by C_8 aromatics, and benzene.

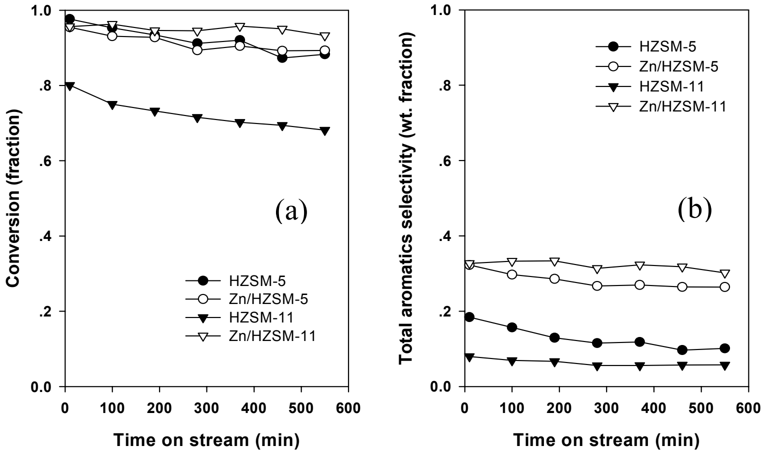


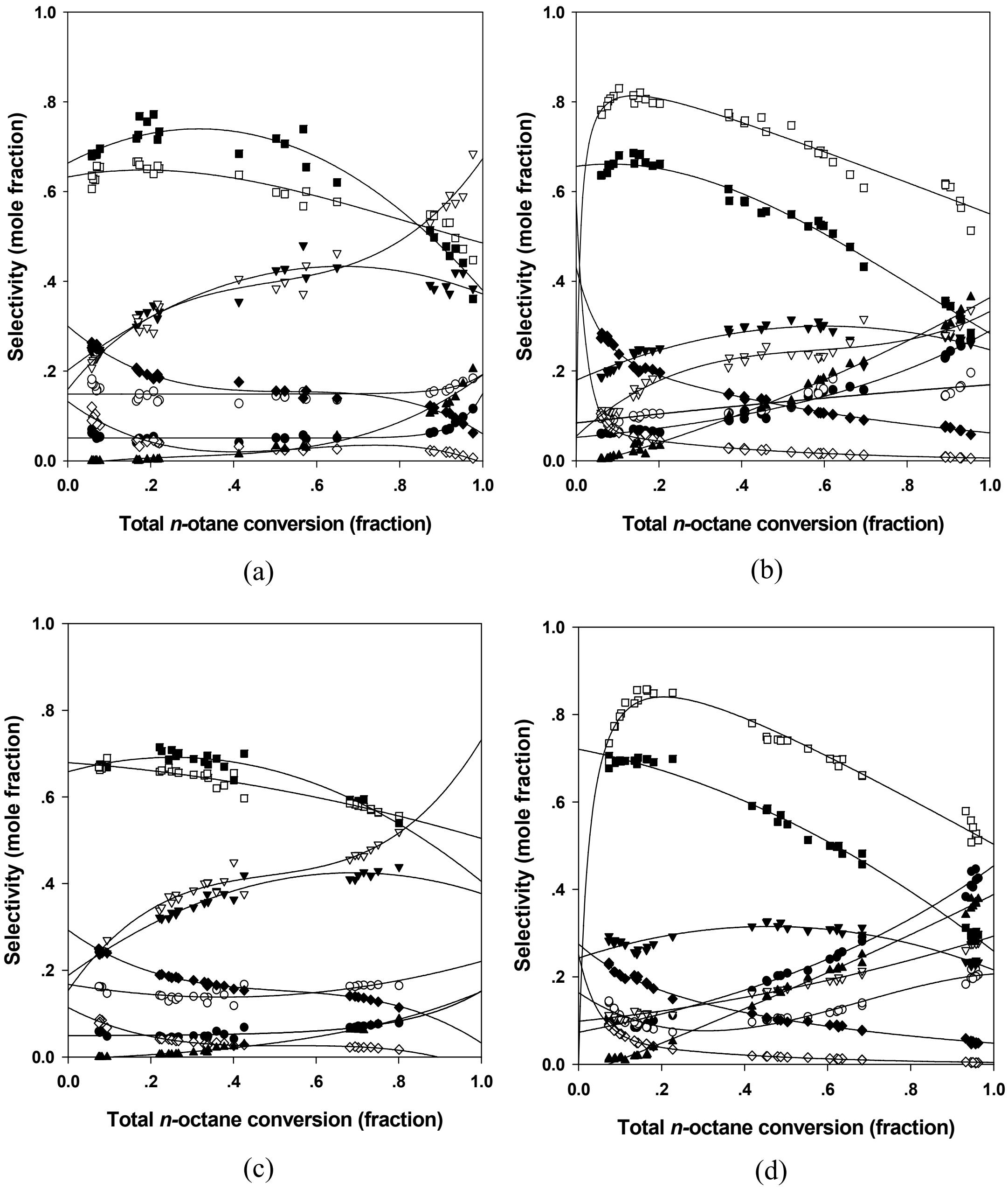
Figure 3 (a) *n*-Octane conversion and (b) Total aromatics selectivity as a function of time on stream over HZSM-5, HZSM-11, Zn/HSM-5, and Zn/HZSM-11 catalysts**:** reaction conditions: 500^{o}C, 1 atm, H_2: *n*-C_8 molar ratio 6:1, WHSV 5 h^{-1}

Table 2 Properties of various catalysts tested for n-octane aromatization after 550 min

	HZSM-5	**HZSM-11**	**Zn/HZSM-5**	**Zn/HZSM-11**
Conversion	88.3	68.2	89.3	93.2
Product Selectivity (wt%)				
Methane	0.8	0.8	3.0	4.8
Ethane	3.9	4.1	3.6	4.6
Ethylene	9.6	10.3	7.0	5.9
Propane	20.7	17.1	10.5	9.8
Propylene	18.7	22.3	13.3	11.7
C_4	27.3	29.2	30.8	28.9
C_5	7.4	8.8	4.8	3.7
C_6	1.6	1.7	0.6	0.4
Benzene	1.0	0.6	5.2	6.4
Toluene	4.0	2.5	12.5	13.0
Ethylbenzene	0.3	0.0	0.7	1.0
m-, p-Xylene	4.0	2.1	6.6	7.7
o-Xylene	0.7	0.5	1.4	2.1
Total C_8 Aromatics	5.0	2.6	8.7	10.8
Total Aromatics	10.0	5.7	26.4	30.2
C_8 Aromatics/Cracking Product Ratio	0.05	0.03	0.10	0.12

Reaction conditions: 500^{o}C, 1 atm, H_2: *n*-C_8 ratio 6:1, WHSV 5 h^{-1}

Furthermore, a new parameter of C_8 aromatics/cracking product ratio is introduced in this work to correlate the favorable pore geometry for *n*-octane aromatization. It showed that the higher C_8 aromatics/cracking product ratio of HZSM-5 catalyst compared to HZSM-11 catalyst was obtained. This may suggest that the aromatization of n-octane takes place preferentially in zigzag channels of ZSM-5 more than in straight channels of ZSM-11. Besides, the lower cracking products were attained over zinc modified catalysts, while the aromatics were increased. This may indicate that the cracking activity was suppressed resulting in higher aromatization activity.



(a) (b)

(c) (d)

Figure 4 Product selectivities as a function of total *n*-octane conversion during aromatization over (a) HZSM-5, (b) Zn/HZSM-5, (c) HZSM-11, and (d) Zn/HZSM-11 catalysts: ● Methane ○ Ethane ▼ Ethylene ▽ Propane ■ Propylene □ C_4 ◆ C_5 ◇C_6 ▲ Total Aromatics: Reaction conditions: 500°C, 1 atm, H_2: *n*-C_8 ratio 6:1, WHSV 5, 25, 100, and 200 h^{-1}.

The product selectivities over the four catalysts as a function of *n*-octane conversion are shown in Figure 4. It should be noted that the selectivities of the products as a function of *n*-octane conversion over HZSM-5 and HZSM-11 catalysts are very similar pattern. It was observed that the main products are propylene and C_4 at low *n*-octane conversion. From this finding, it may be taken as the indication that the primary reaction involves in the decomposition of *n*-octane. It is well known the presence of acidic site of the catalysts favor to the cracking, oligomerization, and cyclization activity [Meriaudeau and Naccache, 1997]. Therefore, it is believed that *n*-octane was cracked into small hydrocarbons at the first stage, and then these compounds were consumed in the further reaction. The high selectivities of propylene and C_4 hydrocarbon at low conversion and the decrease in those of both compounds at higher conversion can confirm this postulation.

In addition, ethylene, propylene, C_4, C_5, and C_6 were found to be the intermediate products because their selectivities decreased with increasing conversion of *n*-octane. This observation may explain the reductions in the selectivities of these compounds in over Zn/HZSM-5 and Zn/HZSM-11 shown in Table 2 that these compounds may be consumed in the further reaction to produce the aromatics product. Regarding to figure 4, the inactive intermediates were methane, and ethane since their selectivities increased as the conversion increased. The appearance of zinc incorporated in the zeolite catalysts enhanced the dehydrogenation function of the catalysts resulting in lower selectivities of the inactive intermediates over Zn/HZSM-5 and Zn/HZSM-11 catalysts.

Since the product distribution as a function of *n*-octane conversion over HZSM-5 and HZSM-11 catalysts showed similar patterns. Therefore, it was believed that the *n*-octane aromatization over both catalysts takes place through similar pathways. This may be proposed that *n*-octane is firstly cracked into small hydrocarbons over the acidic sites. Then, these cracking products are further oligomerized. After that, the oligomers will undergo dehydrocyclization to produce the corresponding aromatics. The presence of zinc makes the greater availability of olefinic compounds leading to higher selectivity of total aromatics. This corresponds to the reaction pathways of n-heptane aromatization proposed by Viswanadham et al. [1996]. However, the in-depth investigation will be further performed to confirm such a proposed mechanism.

Characterization of Spent Catalysts

All spent catalysts were analyzed by TPO after the reaction to determine the nature and amount of coke deposited during the reaction. Figure 5 shows the TPO profiles of coke deposited on each different catalyst. The weight percent of the coke formed on HZSM-5, HZSM-11, Zn/HZSM-5, and Zn/HZSM-11 were 2.4, 2.5, 2.6, and 3.0, respectively. It illustrated that the coke formed on all four catalysts can be removed at the temperature around 600-630 ^{o}C. The higher amount of coke deposited on zinc modified HZSM-5 and HZSM-11 catalysts compared to the catalysts in the absence of zinc may be due to less catalytic activity. Furthermore, the presence of zinc helped the oxidation of coke easier leading to the shift of the signal to lower temperature.

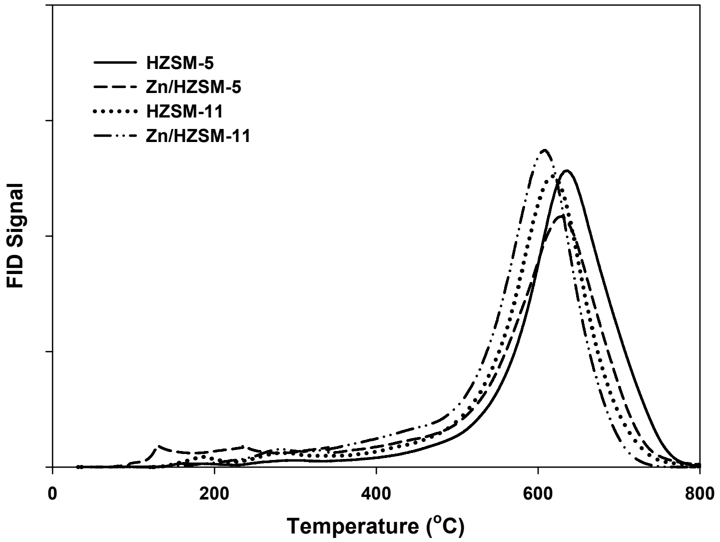


Figure 5 Temperature programmed oxidation profiles of coke deposited on (a) HZSM-5, (b) Zn/HZSM-5, (c) HZSM-11, and (d) Zn/HZSM-11 after the reaction at 500 °C, 1 atm, 550 min on stream

Conclusions

The preliminary results showed that the incorporation of Zn into HZSM-5 and HZSM-11 zeolite catalysts could enhance the *n*-octane aromatization reaction leading to the increase in total aromatics selectivity. The Zn/HZSM-11 catalyst provided the highest *n*-octane aromatization activity because of the higher content of zinc loaded into the zeolite. Zn/HZSM-11 seems to be a promising catalyst to aromatize *n*-octane. C_8 aromatics was found as the major aromatics product followed by toluene and benzene over HZSM-5 and HZSM-11 catalysts. However, Zn/HZSM-5 and Zn/HZSM-11 provided toluene as the major product followed by C_8 aromatics, and benzene. Considering to the C_8 aromatics/cracking product ratios over HZSM-5 and HZSM-11, it suggests that the aromatization of n-octane prefers to occur in zigzag channels of ZSM-5 more than in straight channels of ZSM-11. Moreover, the *n*-octane aromatization over HZSM-5 and HZSM-11 catalysts took place through similar pathways. However, the presence of zinc resulting in increasing dehydrogenation function might affect on different pathway. The in-depth investigation will be further performed to confirm the proposed mechanism.

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Literature Cited

Anunziata O. A., Griselda G., Gonzalez Mercado G. V., Pierella L. B., Catalytic activation of methane using *n*-pentane as co-reactant over Zn/H-ZSM-11 zeolite, Catal. Lett., 87, 167-171, 2003.

Anunziata O. A. G., Gonzalez Mercado G. V., Pierella L. B., Improvement of methane activation using *n*-hexane as co-reactant over Zn/H-ZSM-11 zeolite, Catal. Comm., 5, 401-405, 2004.

Argauer R. J., and Landolt G. R., Crystalline zeolite ZSM-5 and method of preparing the same, US Pat. 3 702 886, 1972.

Berndt H., Lietz G., Lucke B., Volter J., Zinc promoted HZSM-5 catalysts for conversion of propane to aromatics: I. Acidity and activity, App. Catal. A, 146, 351-363, 1996.

Bhattacharya D., Sivasanker S., A comparison of aromatization activities of the medium pore zeolites, ZSM-5, ZSM-22, and EU-1, J. Catal., 153, 353-355, 1995.

Biscardi J. A., Iglesia E., Reaction pathways and rate-determining steps in reaction of alkanes on HZSM-5 and Zn/HZSM-5 catalysts., J. Catal., 182, 117-128, 1998.

Biscardi J. A., Meitzner G. D., Iglesia E., Structure and density of active Zn species in Zn/HZSM-5 propane aromatization catalysts, J. Catal., 179, 192-202, 1998.

Chu P., Crystalline zeolite ZSM-11, US Pat. 3 709 979, 1973.

Meriaudeau P., Naccache C., Dehydrocyclization of alkanes over zeolite-supported metal catalysts: Monofunctional or bifunctional route, Catal. Rev.-Sci. Eng., 39 (1&2), 5-48, 1997.

Smieskova A., Rojasova E., Hudec P., Sabo L., Aromatization of light alkanes over ZSM-5 catalysts: Influence of the particle properties of Zn, App. Catal. A, 268, 235-240, 2004.

Viswanadham N., Muralidhar G., Prasada Rao T.S.R., Cracking and aromatization properties of some metal modified ZSM-5 catalysts for light alkane conversions, J. Mol. Catal. A, 223, 269-274, 2004.

Viswanadham N., Pradhan A.R., Ray N., Vishnoi S.C., Shanker U., and Prosada Rao T.S.R., Reaction pathways for the aromatization of paraffins in the presence of HZSM-5 and Zn/ZSM-5, App. Catal. A, 137, 225-233, 1996.