Effects of a Matrix on Formation of Aromatic Compounds by Dehydrocyclization of n-Pentane Using ZnZSM-5–Al₂O₃ Composite Catalysts

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ABSTRACT: In this study, the effects of the combination of a mesoporous material and Zn-exchanged ZSM-5 on the activity and selectivity of aromatic compounds in dehydrocyclization of n-pentane were investigated. A total of 65–85 wt % of ZnZSM-5 was mixed with 0–20 wt % of Al₂O₃ and 15 wt % of the alumina-sol binder using a conventional kneading method. Dehydrocyclization of n-pentane was performed using a fixed-bed reactor under the conditions of a H₂ atmosphere and the temperature range of 450–550 °C. Conversions of n-pentane tended to increase upon increasing the amounts of zeolite content and ZnZSM/0A (85 wt % ZnZSM-5, 0 wt % Al₂O₃, and 15 wt % binder) exhibited the highest value. The selectivity for toluene and benzene increased with increasing temperature, while it decreased in the order ZnZSM/10A > ZnZSM/0A > ZnZSM/20A in comparison at the same temperature. Upon changing the carrier gas, the conversion decreased in the order CH₄ > H₂ > H₂ + N₂ > N₂. Although the selectivity for aromatics was higher under CH₄ and N₂ atmospheres, the conversions decreased at 550 °C with time, suggesting that the deactivation would proceed by coke formation. Furthermore, the selectivity for aromatics of ZnZSM/10A was higher than that of HZSM-5 while the catalyst was deactivated rapidly at 600 °C.

1. INTRODUCTION

Surplus C₅ and C₆ fractions from a topper can be reformed to valuable aromatic compounds with high octane numbers, one of the basic raw materials in the petrochemical industry, and hydrogen without environmental load. Although Pt/Al₂O₃–Cl is used for the catalytic reforming process and the content of Cl may change the activity and the selectivity of the reactions included, acidic properties other than those of Cl and metallic properties other than those of Pt were not investigated extensively. Furthermore, dehydrocyclization will not proceed selectively using Pt and Al₂O₃-based catalysts. Since the late 1980s, it has been reported that Zn- and Ga-exchanged zeolite catalysts are effective for the selective formation of aromatics in cyclization of saturated hydrocarbons and specifically HZSM-5 is known for promoting the aromatization of light alkanes, alkene, and oxygen-containing compounds. Ono et al. reported that Zn- and Ga-exchanged ZSM-5 would include metal cations, which possess not only Bronsted acid sites derived from HZSM-5 but also dehydrogenation activity and produce butadiene from butenes and allylic species from propene leading to aromatics. Yashima et al. and Nagamatsu et al. reported aromatization of n-butane and n-hexane, respectively, on Zn- and Ga-modified ZSM-5 catalysts. Inui reported the high selectivity of aromatics in propane conversion on Zn-modified ZSM-5 while the catalyst was deactivated rapidly at 600 °C. Ga-silicate and Zn-silicate were also more effective for aromatization of pentane than other metal-silicates. Recently, it was reported that in order to achieve higher aromatic yields, a certain amount of acid sites was enough in the co-impregnated Zn–Ga-H-ZSM5 catalyst while the increase in the amount of acid sites was required in the H-ZSM-5 without Zn and Ga. Although Zn-modified H-[Fe]ZSM-5 was not able to activate hexane, temperature-programmed desorption (TPD)—thermogravimetric analysis (TGA)—of adsorbed propene on the catalyst showed the strong interaction between Zn and propene and the formation of benzene, suggesting that this observation might be strongly related to the dehydrocyclization of light alkanes.
alkanes in Zn-exchanged H-[Al]ZSM-5.\textsuperscript{22} Ga\textsubscript{2}O\textsubscript{3}/ZSM-5 hollow fibers, which are a class of hierarchical catalysts,\textsuperscript{29} were effective for the formation of aromatics and light olefins in n-butane conversion.\textsuperscript{23} H-ZSM-5/oxide composite catalysts were used for aromatization of isobutene.\textsuperscript{24} Some oxygen-containing compounds have been converted to aromatic hydrocarbons using Zn-modified ZSM-5 catalysts.\textsuperscript{25–26} Catalysts other than ZSM-5 were also used for aromatization of alkanes while examples were very few\textsuperscript{30–33} and their reaction mechanisms may be different from those of the ZSM-5-based catalysts, which would mainly catalyze the aromatization of gaseous hydrocarbons.\textsuperscript{34,35}

Furthermore, it was suggested that Zn species on catalysts would react with hydrogen to give ZnH or ZnOH generating new acid sites, which contribute to making aromatics.\textsuperscript{36,37} Protonic acid sites were also active for the isomerization of n-pentane through hydrogen spillover behavior of Zn/HZSM-5.\textsuperscript{38,39} It has been reported that the use of pressurized methane of 3 MPa would increase the selectivity for aromatics in naphtha reforming catalyzed by Pt–Zn/HZSM-5 catalysts.\textsuperscript{40–43} In the conversion of methanol with pentane, hexane, or cyclohexane using Zn/ZSM-5 in a fluidized bed reactor, it was confirmed that the use of the exothermic conversion of methanol increased the endothermic aromatization of C5 to C6 hydrocarbons.\textsuperscript{44} However, it is not necessarily clarified how components and the structure of catalysts would affect their activity and selectivity. Furthermore, although in the use of microporous zeolites, the diffusion of reactants and products always attracts interest, and a matrix would be needed to apply zeolites in the actual processes,\textsuperscript{29} there are very few reports related to the reactivity and the effectiveness of the matrices for various catalytic reactions by zeolites. Mesoporous alumina is usually used as a support of reforming catalysts and is also used as a matrix of FCC catalysts. In this situation, we investigate the effect of a matrix on various catalyses with zeolites in petroleum refining.

In this study, mesoporous alumina was used as a matrix component and composite materials were prepared with Zn-exchanged ZSM-5 and the alumina-sol binder using the kneading method. In dehydrocyclization of n-pentane to make aromatic compounds selectively, the effects of the structure, acid properties, and Zn-exchange ratio of catalysts on their activity, selectivity, and stability were investigated. Furthermore, the effect of the atmosphere on the reaction was also investigated using not only hydrogen but also hydrogen/nitrogen, nitrogen, and methane as carrier gases.

**2. RESULTS AND DISCUSSION**

**2.1. Characterization of Zn-Exchanged ZSM-5–Al\textsubscript{2}O\textsubscript{3} Composite Catalysts.** Figures 1 and S1 show X-ray diffraction (XRD) patterns of fresh ZnZSM-5–Al\textsubscript{2}O\textsubscript{3} composite catalysts. Only signals of zeolite crystals and alumina were detected and they did not change before and after the reaction. ZSM-5 signals were not affected by the presence of Zn. Zn species were not observed for every catalyst, suggesting that Zn species would be dispersed on ZSM-5 and that the presence of Zn might not affect the original structure of ZSM-5–Al\textsubscript{2}O\textsubscript{3} composite catalysts.\textsuperscript{34,35}

Tables S1 and S2 show the pore properties of the fresh and used catalysts measured using the N\textsubscript{2} adsorption and desorption isotherm, respectively. Examples of N\textsubscript{2} adsorption and desorption isotherms and the BJH pore size distribution for Zn(15)ZSM(24)/10A catalyst are given in Figure S2a,b, respectively. The Barrett–Joyner–Halenda (BJH) method was used to evaluate mesopores larger than 3.3 nm of the catalyst. The Brunauer–Emmett–Teller (BET) surface area (SA), total pore volume (PV), BJH SA, and BJH PV of ZSM-5 used are 388 m\textsuperscript{2}/g, 0.30 cm\textsuperscript{3}/g, 34 m\textsuperscript{2}/g, and 0.14 cm\textsuperscript{3}/g, respectively. As the alumina-sol binder was added even for Zn(3)ZSM(24)/10A, mesopores estimated by BJH were observed and its BJH-SA and BJH-PV were 92 m\textsuperscript{2}/g and 0.19 cm\textsuperscript{3}/g, respectively. BET SA decreased, BJH SA increased, and PVs increased with increasing alumina content, indicating that the amounts of microporous ZSM-5 would contribute to the size of BET SA and that the amounts of mesoporous alumina would contribute to the sizes of BJH SA and PV. When the alumina content increased in the order 0, 10, and 20 A, the content of ZnZSM-5 decreased in the order 85, 75, and 65 wt %. As the difference in the content of ZnZSM-5 between catalysts was rather small, the decrease in BET SA was small with increasing alumina content. The increase in the amount of Zn added only slightly decreased BET and BJH PVS and SAs. There was a slight decrease in BJH SA and PV after the reaction, indicating that the mesoporous alumina part was hardly affected. However, when the reaction was performed under the atmosphere of N\textsubscript{2} and CH\textsubscript{4}, a marked decrease was observed in BET SA and total PV, indicating that coke deposition would occur in the surface of microporous ZSM-5.

Table S1 also shows the amounts of NH\textsubscript{3} adsorbed and desorbed and Figure S3 shows the NH\textsubscript{3}-TPD profiles. The amounts of NH\textsubscript{3} desorbed in the higher temperature range of 350–650 °C could be attributed to the strong acid sites of ZSM-5 and tended to decrease with increasing amounts of alumina and with increasing amounts of Zn added. The amounts of NH\textsubscript{3} desorbed in the lower temperature range of 100–350 °C could be attributed to the weak acid sites of ZSM-5 and physical adsorption by alumina as they tended to decrease slightly with increasing amounts of alumina and decreased with a higher amount of Zn added.

**2.2. Production of Aromatic Compounds by Dehydrocyclization of n-Pentane Using ZnZSM-5–Alumina Composite Catalysts.** In order to estimate the effect of the alumina matrix on the production of aromatic compounds from n-pentane, Zn-exchanged ZSM-5–alumina composite catalysts were used. Figure S2a shows the changes in conversion of n-pentane with temperature. The conversion increased with increasing temperature and with increasing content of ZSM-5. When the higher content of Zn was used in Zn(30)ZSM(24)/10A, the conversion decreased noticeably. As shown in Table S1, the amounts of strong acid sites in NH\textsubscript{3}-TPD for Zn(30)ZSM(24)/10A were significantly lower than those of other catalysts, suggesting that as believed in general, the amounts of strong acid sites would affect the activity. When the
The effect of the atmosphere on the conversion was compared, the conversion decreased in the order CH₄ > H₂ > H₂/N₂ = 1:1 > N₂, suggesting that the presence of hydrogen atoms in molecules of carrier gas would affect the activation of n-pentane molecules. When the effect of reaction time on the conversion at 550 °C was investigated in Figure 2b, the clear deactivations were observed during 3 h in the atmosphere of CH₄, N₂, and H₂/N₂ = 1:1, indicating that the presence of large amounts of hydrogen inhibited the deactivation of the catalysts probably because of the inhibition of coke formation. Although the pressurized methane was effective in the aromatization of n-pentane catalyzed by Pt–Zn/ZSM-5, the absence of Pt in our system did not bring about the stability of the catalyst.

Figures 3 and 4 show the changes in selectivity of benzene and toluene with temperature. The selectivity for aromatics was rather low at 450 °C but increased remarkably with temperature while the conversions have already reached more than 70% even at 550 °C. Conversions were almost 100% at 550 °C for most of the catalysts and the C5 products were in trace amounts, suggesting that cracking of n-pentane would occur preferentially to C4 fractions. The O/P ratios of 20 A and 10 A were very similar to each other but were larger than those of 0 A, indicating that the ability of hydrogen transfer for 0 A was higher than those of 20 A and 10 A because of the high concentration of ZnZSM-5. However, it seems that this high ability of hydrogen transfer would decrease the selectivity for aromatics. The lower selectivity of aromatics for 20 A may be ascribed to the lower concentration of ZnZSM-5. Thus, it is likely that matrix alumina would play a role in drawing the maximum catalytic functions such as cracking and aromatization. The selectivity decreased with the increasing Zn-exchange ratio while it was affected by the carrier gas largely and increased in the order H₂/N₂ = 1:1 ≤ N₂ < CH₄. When the effects of reaction time on the selectivity of benzene and toluene were investigated in Figures S4 and S5, the selectivity did not decrease so largely as the conversion and was kept constant during 3 h, suggesting that the activation of n-pentane and aromatization by cyclization would occur separately. It is probable that the cyclization sites would not be disturbed by coke deposition, which may be a major factor causing damage and deactivation of the acid sites in the activation process of n-pentane.
while isomerization hardly occurred. Overcracking hardly occurred as the selectivity of methane was almost the same between the catalysts, indicating that not cracking of the C2–C4 product fractions but only n-pentane cracking occurred preferentially and that the presence of the matrix inhibited overcracking by ZnZSM-5 and made its action more effective. Furthermore, thermal cracking hardly occurs at 550 °C. It has been reported that only trace amounts of products were observed even at 650 °C in the pyrolysis of n-pentane.46

When it is assumed that cracking of n-pentane could occur, the reaction routes can be illustrated as shown in Figure 6.

Furthermore, 3% of pentane was also used to produce C9 and more than C9 aromatics, which were not illustrated in Figure 6. Therefore, 57% of pentane would undergo cracking to produce 23% of C2 and 34% of C3 fractions by route 1. The differences between these values and the actually produced C2 and C3 fractions must be consistent with the amounts of ethene and propene used to form benzene and toluene with C4 fractions, respectively. Calculated yields of benzene and toluene were 13 and 20%, respectively, which were almost completely consistent with the actually produced values. When all the remaining C4 are used for xylene formation, the yield of xylene is calculated to be 8%, which was also almost completely consistent with the actually produced value. As the calculated values of the BTX yields were consistent with actual yields, it can be suggested that the reaction of n-pentane on ZnZSM-5–alumina composite catalysts would proceed through the routes illustrated in Figure 6. The ratio of routes 1 and 2 would be derived from the difference in the stability of ethyl and methyl cations formed in routes 1 and 2, respectively. It seems that cracking of C4 and less than C4 fractions could not occur in the presence of n-pentane. Furthermore, it also seems that Zn-exchanged ZSM-5 could promote cyclization of olefins forming aromatics. It is assumed that the initial isomerization of n-pentane to isopentane would not occur in the present study because the conversion of isopentane is known to give much larger amounts of CH4 and C4H8 than those of C2H6 and C3H6.11 As shown in Table S3, olefin/paraffin ratios were lower under a hydrogen atmosphere than under H2/N2 = 1:1, N2, or a CH4 atmosphere, which would lead to the inhibition of cyclization and the decrease in yields of aromatics under a hydrogen atmosphere while the significant coke formation and successive deactivation of catalysts could be avoided. In Table S4, the amount of coke formation of each catalyst was estimated from weight loss in thermogravimetric and differential thermal analysis (TG–DTA) measurement because significant weight losses and exothermic profiles were observed in the range 400–600 °C in Figure S7. When the reaction was performed under a H2/N2 = 1:1, N2, or CH4 atmosphere, the significant coke formation was observed, which would lead to the deactivation of catalysts. It was shown that, when the yields of aromatics were smaller under the hydrogen atmosphere, the coke formations were also smaller. Although it was reported that the reforming of light straight run naphtha and pentane in CH4 and C3H8 environments using Pt–Zn/HZSM-5 reduced coking, enhanced liquid yield, and increased BTX selectivity, the presence of Pt and pressurized methane of 3 MPa may affect the positive effect of methane.50,47 As alkanes formed could not react further under the conditions, they have to be recycled in another unit. Furthermore, optimal ratios of Zn, ZSM-5, alumina, and hydrogen could be selected to increase the aromatic yields.

In general, hydrocarbons with a higher carbon number have higher reactivity for cracking. This was explained by the higher adsorption equilibrium constant.47 As n-pentane has the higher adsorption equilibrium constant than those of C1–C4 hydrocarbons and has remarkably higher concentration as a sole feed in the system compared with those of products, it is likely that n-pentane would react preferentially to produce all hydrocarbons from C1 to C4. As it was assumed, Figure 6 was drawn as a mechanism-proposing reaction routes to aromatics.

As for the effect of the amount of Zn added, it was thought that the experiment of Zn(30) would have the effect of the amount of Zn compared with that of Zn(15) or Zn(13). The amounts of strong acid sites decreased with increasing the
content of Zn and the content of alumina as shown in Table S1 and Figure S3. The decrease in the amounts of strong acid sites decreased the conversion. The aromatic selectivity for Zn(30) was lower than that for Zn(15), indicating that the effect of the amount of Zn on the selectivity for aromatics would be rather low and that small amount of Zn was enough to complete cyclization of olefins forming aromatics. As for the active site of Zn on the composite catalyst, Zn cations would be exchanged with H⁺ of HZSM-5 as the initial ion-exchange of HZSM-5 using Zn on the composite catalyst, Zn cations would be exchanged low and that small amount of Zn was enough to complete the aqueous NH₃ solution. The amount of Zn incorporated into ZSM-5 was about 15 or 30 mol % of Al included in HZSM-5. Therefore, it seems that most of Zn would be dispersed in the inside of micropores for ZSM-5, and that, under the hydrogen atmosphere, a part of Zn would be reduced and become active for cyclization of olefins like the Diels–Alder reaction. Zn in the inside of ZSM-5 may be oxidized under the calcination conditions. However, the exchange ratio of Zn was about 15 or 30 mol % and therefore it may be dispersed in the inside of ZSM-5. It is likely that, under the reaction conditions of the hydrogen atmosphere, Zn species would be reduced again. Ono et al. have already proposed in pentane reforming that Zn-ions would promote the dehydrogenation activity and that the coupling of butadiene or allylic species, which are produced from butenes and propene, respectively, may produce aromatics.3–6 Furthermore, the transition metal like Pt-incorporation may promote dehydrogenation to produce olefins first and aromatization of smaller alkanes like propane than n-pentane would proceed through dehydrogenation first.21,22 Although the Zn-incorporation may promote the dehydrogenation of butenes to butadiene in the present study, it is thought that the dehydrogenation of n-pentene forming pentenes would not occur first because the aromatization mechanism of olefins started by cracking of n-pentane was consistent with the yields of BTX as shown in Figure 6. Furthermore, it was reported that while metal sites in Zn- and Ga-exchanged H-[Fe]ZSM-5 could not activate alkanes, they interacted with olefins and formed aromatics from olefins. It was also reported that protonic acidic sites formed on the Zn species of Zn/HZSM-5 would be active for cracking but for isomerization of n-pentane and only Brønsted acidic sites on HZSM-5 without Zn was active for cracking.3 In our present study, as all the acidic sites of HZSM-5 were not covered by the Zn species, some Brønsted sites remaining on HZSM-5 were active for n-pentane cracking. Furthermore, it seems that alkanes like ethane, propane, and butanes lighter than n-pentane would not be cracked in the presence of n-pentane because the cracking reactivity of n-pentane was much higher than those of n-butane, propane, and ethane when compared under the same conditions using Pt and Zn or Pt and Ga polyfunctional metallosilicate catalyst systems.17 It also seems that Zn species would act as a catalyst not for cracking but for olefin aromatization. On the other hand, the reactivity of Ga may be different from that of Zn. Wannapakdee et al. reported that catalysts treated with hydrogen increased the selectivity of aromatics compared to catalysts without hydrogen treatment in pentane aromatization using hierarchical galloaluminosilicate zeolites with the MFI structure.20 It was assumed that Ga species reduced under the hydrogen atmosphere might have served as active sites for dehydrogenation. Furthermore, the presence of a hierarchical structure increased the activity and aromatic yields. We would also like to report the effect of the matrix on Ga-incorporated catalysts in near future.

3. CONCLUSIONS

In this study, the effects of a mesoporous matrix on the activity and selectivity of aromatic compounds in dehydrocyclization of n-pentane catalyzed by the ZnZSM-5–alumina composite catalysts were investigated. The effect of the alumina matrix appeared and the selectivity for toluene and benzene decreased in the order 10 A > 0 A > 20 A at the same temperature. Although the selectivity for aromatics was higher under CH₄ and N₂ atmospheres than under H₂, the conversions decreased at 550 °C with the elapse of time, suggesting that the deactivation would proceed. It could be assumed that after initial cracking of n-pentane on Brønsted acidic sites to C1 to C4 fractions, C2–C4 olefins formed brought about the cyclization forming aromatics on the Zn active species, where the reactions of ethene, propene, and butene with butene produced benzene, toluene, and xylene, respectively.

4. EXPERIMENTAL SECTION

4.1. Preparation of Zn-Exchanged ZSM-5–Alumina Composite Catalysts. HZSM-5 used was commercially available (SiO₂/Al₂O₃ = 24, Tosoh, HSZ-822HOA) and was ion-exchanged with aqueous zinc nitrate hexahydrate (Nakalai Tesque. Co Ltd.), aqueous NH₃ (Nakalai Tesque), and ion-exchanged water. HZSM-5 was stirred in the ion-exchanged water and aqueous ammonia was added dropwise to adjust the pH value to 9. Zn(NO₃)₂·6H₂O was dissolved in water and was added into the suspension of HZSM-5. The mixture was stirred at 88 °C for 4 h. After filtration, washing with 10 mL water three times and drying, the resulting solid was calcined under the air atmosphere at a heating rate of 2 °C/min, at 500 °C for 3 h. The sample prepared was named Zn(exchange ratio)ZSM(24) − where the exchange ratio of Zn was about 15 (%) or 30 (%), (that is, the percentage value of the ratio of Zn/Al (mol/mol) in ZSM-5), ZSM was ZSM-5, and 24 was the ratio of SiO₂/Al₂O₃ (mol/mol). The amount of Zn was determined by X-ray fluorescence (Shimadzu EDX-720) measurement where a calibration curve of ZnO/SiO₂ prepared by a conventional impregnation was obtained.

Zn-exchanged ZSM-5–alumina composite catalysts were prepared using the conventional kneading method.25,34,35,45 5–75 wt % of ZnZSM-5, 10 wt % of alumina for industrial use (provided by Nippon Ketjen), and 15 wt % of the alumina-sol binder (cataloid AP-1, Nikki Shokubai Kasei Co Ltd., about 70% alumina included) were mixed and kneaded in a mortar with water until a clay-like solid was obtained. The solid was pelletized into extrudates, which were calcined under the air atmosphere, at a heating rate of 2 °C/m, and at 500 °C for 3 h. Calcined samples were crushed into 70 wt % of size 600–355 μm and 30 wt % of size 355–125 μm and were named ZnZSM(24)10A as it included 10 wt % alumina. The particle size of original ZSM-5 used is 5 μm, too small to use in the catalytic reaction using a fixed bed reactor. Even when alumina for industrial use was not added, 15 wt % of the alumina-sol binder was added and the catalyst was pelletized and crushed similarly.

4.2. Characterization of Composite Catalysts. The crystal structure was analyzed by XRD (Rigaku Ultima IV) under the conditions: Ni filtered single-colored Cu Kα₁ radiation (λ = 0.15418 nm); sample, 0.10 g; 2θ = 10–70°; voltage, 40 kV; current, 20 mA; scan mode, continuous; scan speed, 1°/min; present time, 1 s; scattering slit, 2/3°; detecting slit, 2/3°; radiation slit, 0.45 mm. The pore structure of the
catalysts was measured by the nitrogen adsorption and desorption method using BELSORP (mini I-MSP, MicrortacBel Co. Ltd.) and SAs, PVs, and pore diameters were estimated using BET and BJH methods. About 0.07 g of each catalyst was degassed before measurement by BELPREP (vacII, MicrortacBel co. Ltd.). In order to estimate the acid properties of catalysts, NH3-TPD was measured by GC−TCD (Shimadzu GC-8A) under the conditions: catalyst, about 0.04 g; the injection and detector temperatures, 170 °C; column, 140 °C; attenuation, 16; current, 100 mA; carrier gas, 10 mL/min.

4.3. Dehydrocyclization of n-Pentane. Dehydrocyclization of n-pentane was performed using a fixed-bed flow reactor (ID 8 mm, OD 10 mm, and stainless steel) as shown in Figure S8. Into the center of the reactor was packed a 1 g catalyst and both near ends of the catalyst bed were closed by some glass wool (Tosoh, fine) and both far ends were by quartz sands. A thermocouple was set in the center of the catalyst bed. n-Pentane (Wako) was introduced into the reactor using a syringe pump. The reaction was performed under the conditions: WHSV, 6.26 h\(^{-1}\); \(H_2\), 50 mL/min; \(H_2/\text{feed}\), 1.38 mol/mol; pressure, 0.1 MPa; and heating rate, 5 °C/min. After the reaction temperature reached 450, 500, or 550 °C, gas and liquid samples were collected every 1 h in the gas—liquid separator and the samples collected during another 1 h at the same temperature were analyzed by GC-FID. The reaction was held at 550 °C for 4 h and samples collected every 1 h were also analyzed, respectively. Liquid samples were analyzed under the conditions: GC-2014 (Shimadzu), auto-sampler (Shimadzu, AOCS-20i), the initial column temp. 50 °C for 3 min, the final column temp. 200 °C, the injection temp. 250 °C, detector temp. 250 °C, 53 min, pressure 122 kPa, total flow rate 370 mL/min, column flow rate 1.81 mL/min, line speed 40 cm/s, split ratio 200, and capillary column BP-1 (length 60 m, ID 0.25 mm, and film thickness 0.50 μm). Gas samples were analyzed using GC-2010FID (Shimadzu). A detailed analysis of liquid samples was performed to estimate the types of hydrocarbon products, paraffins (P), olefins (O), naphthenes (N), and aromatics (A), using a GC-2010 PONA solution system (Shimadzu). In order to determine the amount of coke formed during the reaction, TG−DTA was carried out using a DTG-60AH (Shimadzu) under the conditions; sample weight, 10 mg; heating rate, 10 °C/min at 600 °C; an aluminum pan; carrier gas, \(O_2\); and gas flow rate, 100 mL/min.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c01147.

Pore properties of each fresh catalyst, pore properties of each used catalyst, olefin/paraffin ratios at 550 °C, weight loss of the used catalysts in TG−DTA measurement (mg), XRD patterns of the used catalysts, N\(_2\) adsorption and desorption isotherms, BJH pore size distribution. Catalyst: Zn(15)ZSM(24)/10A, NH\(_3\)-TPD curves of the fresh catalysts, changes in selectivity of benzene with time on stream at 550 °C, changes in selectivity of toluene with time on stream at 550 °C, paraffin, olefin, and aromatic distribution of products at 550 °C, TGA and DTA measurements on the used catalysts. a = Zn(13)Z(24)10A, b = Zn(30)Z(24)10A, c = Zn(15)Z(24)10A, d = Zn(13)Z(24)20A, e = Zn(13)Z(24)10A H\(_2\) + N\(_2\), f = Zn(13)Z(24)10A N\(_2\), and g = Zn(13)Z(24)10A CH\(_4\) and reaction apparatus for selective dehydrocyclization (PDF).

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Notes

The authors declare no competing financial interest.

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