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Effect of Type of Matrix on Formation of Aromatics by Cracking and Dehydrocyclization of \(n\)-Pentane Using ZnZSM-5 Metal Oxide Hierarchical Composite Catalysts

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ZnZSM-5 metal oxide hierarchical composite catalysts were made using Zn-exchanged ZSM-5 and various oxides by the conventional kneading method. The effects of these oxides as matrices on the activity and selectivity for aromatics in cracking and dehydrocyclization of \(n\)-pentane were investigated. ZnZSM-5 50-85 wt% was mixed with oxide 0-35 wt% and alumina-sol binder 15 wt% using the kneading method. \(\text{Al}_2\text{O}_3\) (A), \(\text{TiO}_2\) (T), \(\text{ZrO}_2\) (Zr) and kaolin (ka) were used as the oxide. Cracking and successive dehydrocyclization of \(n\)-pentane was carried out in a fixed-bed reactor under atmospheric \(\text{H}_2\) in the range 450-550 °C. Conversions of \(n\)-pentane at 550 °C decreased in the order ZnZSM/0A (85 wt% ZnZSM-5, 0 wt% \(\text{Al}_2\text{O}_3\), 15 wt% binder) \(\geq\) ZnZSM/10A > ZnZSM/10T > ZnZSM/10Zr > ZnZSM/10ka \(\geq\) ZnZSM/35A. The selectivity for aromatics at 550 °C decreased in the order ZnZSM/10A > ZnZSM/0A > ZnZSM/10Zr = ZnZSM/10T = ZnZSM/10ka > ZnZSM/35A. These results suggested that the use of both ZnZSM-5 and matrix with large porosity for this reaction would optimize the catalytic functions. The product distribution indicated that aromatization of olefins to benzene, toluene, and xylene occurred through the Diels-Alder reaction on Zn species in the ZSM-5.

Keywords
Dehydrocyclization, \(n\)-Pentane, Aromatization, Zn-exchanged ZSM-5, Mesoporous oxide, Matrix effect

1. Introduction

Atmospheric crude oil distillation produces excess quantities of the C5 and C6 fractions, so methods of transformation are highly desirable to more valuable compounds such as aromatics with high octane numbers, which can be used for not only petrochemical raw materials but also gasoline blending. Synthesis of aromatics from the C5 and C6 fractions is a type of catalytic reforming which could simultaneously provide hydrogen as a type of clean energy. Chlorine-doped Pt/\(\text{Al}_2\text{O}_3\) is usually used for the catalytic reforming process, but this type of catalyst may not promote selective dehydrocyclization\(^{1}\). \(\text{Zn}\)- and Ga-exchanged ZSM-5 catalysts are known to be active for the selective production of aromatics by dehydrocyclization of light hydrocarbons\(^{21-24}\) and related compounds\(^{25-34}\). Use of hierarchical catalysts is effective for catalytic conversions of hydrocarbons\(^{35}\), and our group reported that the hierarchical catalysts are active for the aromatization of \(n\)-pentane and \(n\)-hexane\(^{11,36}\). ZSM-5-based catalysts are expected to promote the aromatization of gaseous hydrocarbons\(^{37,38}\). Other zeolites than ZSM-5 could also promote aromatization of alkanes, but through a different mechanism from that of ZSM-5 and very few examples are known\(^{39-42}\). Acidic sites like ZnH or ZnOH\(^{13,44}\) or protonic acid sites\(^{45}\) may be active for the aromatization or isomerization of alkanes by hydrogen transfer on Zn/HZSM-5. However, the effects of the components and structure of catalysts on the activity and selectivity remain unknown. Furthermore, use of microporous zeolite introduces other problems with the diffusion of reactants and products. The matrix is essential for actual reactions with zeolites\(^{35}\), but the properties of the matrix for many catalytic reactions using zeolites have been little studied.

We previously investigated the effect of the matrix on various catalysts with zeolites used in petroleum refining. Alumina is the most common support for reforming catalysts and can also be used as a matrix component in FCC catalysts. This study investigated the use of various oxides as a matrix in catalytic alkane conversion and prepared composite materials using Zn-exchanged ZSM-5 and alumina-sol binder by the kneading method. The effects of the matrix oxides on the activity, selectivity and stability of catalysts for crack-
2. Experimental

2.1. Preparation and Characterization of Zn-exchanged ZSM-5 Oxide Hierarchical Composite Catalysts

Commercial HZSM-5 (SiO₂/Al₂O₃ = 24, Tosoh Corp., HSZ-822HOA) was ion-exchanged with aqueous zinc nitrate hexahydrate (Zn(NO₃)₂·6H₂O, Nakalai Tesque, Inc.), aqueous NH₃ (Nakalai Tesque, Inc.), and ion-exchanged water as described elsewhere 1),36). The catalysts prepared were named Zn(X)ZSM(24) where X was the exchange ratio of Zn (about 15, percent value of the ratio 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 XRF (Shimadzu EDX-720) measurement using a calibration curve with ZnO/SiO₂.

Zn-exchanged ZSM-5 oxide hierarchical composite catalysts were prepared by the conventional kneading method as described elsewhere 36)–38,46). The weight ratios of ZnZSM-5, oxide, and alumina-sol binder (15 wt%, cataloid AP-1, JGC Catalysts and Chemicals Ltd., about 70 % alumina included) were 50 : 35 : 15, 75 : 10 : 15, and 85 : 0 : 15. The particle size of the prepared catalyst was 600–355 μm (70 wt%) and 355–125 μm (30 wt%). For example, the sample was named ZnZSM(24)10A which included 10 wt% alumina. Titania (AEROXIDE TiO₂ P 25, 50 + 15 m²/g, crystal size 21 nm ≥), zirconia (Catalysis Society of Japan, JRC-ZRO-4, 203 nm crystal size, 29.8 m²/g), and kaolin (Hakutoutou, White clay, 7 m²/g, 0.04 cm³/g, FUJIFILM Wako Pure Chemical Corp.) were also used and were named T, Zr and ka, respectively.

X-ray diffraction (XRD, Ultima IV, Rigaku Corp.) was used to determine the crystal structure of a catalyst as described elsewhere 36)–38,46). The pore structure of the catalysts was measured by the nitrogen adsorption and desorption method (BELSORP-mini, MicrotracBEL Corp.), and the surface areas, pore volumes, and pore diameters were estimated by the BET and BJH methods. The acid property of the catalysts was estimated by temperature-programmed desorption of ammonia (NH₃-TPD) measured by GC-thermal conductivity detector (GC-TCD, GC-8A, Shimadzu Corp.).

2.2. Cracking and Dehydrocyclization of n-Pentane Using Zn-exchanged ZSM-5 Oxide Hierarchical Composite Catalysts

Figure 1 shows the experimental apparatus for cracking and dehydrocyclization of n-pentane. Catalyst 1 g was packed into the center of a fixed-bed flow reactor (ID 8 mm, OD 10 mm, stainless steel). Both sides of the catalyst bed were stopped with glass wool (Tosoh Corp., fine) and quartz sand was used to fill the far ends. n-Pentane (FUJIFILM Wako Pure Chemical Corp.) was introduced into the reactor using a syringe pump and hydrogen gas was introduced through a mass flow controller. The reaction conditions were WHSV 6.26 h⁻¹, H₂ 50 mL/min, H₂/feed 1.38 mol/mol, pressure 0.1 MPa, and heating rate 5 °C/min. Hydrogen was used to inhibit coke formation 1). Gas and liquid products were collected during every one-hour period in the gas-liquid separator, and the samples collected during the second period at the reaction temperature of 450, 500 or 550 °C were analyzed by GC-hydrogen-flame ionization detector (GC-FID). The reaction was then maintained at 550 °C for 4 h and samples collected during every one-hour period were also analyzed. Concentrations of components in the liquid and gas products were determined by GC-FID (GC-2014 and GC-2010, Shimadzu Corp.). The PONA solution system (GC-2010, Shimadzu Corp.) was used to determine the types of hydrocarbons, paraffins (P), olefins (O), naphthenes (N), and aromatics (A) 36)–38,46). To estimate the coke amount formed during the reaction, thermogravimetric and differential thermal analysis (TG-DTA) was performed (DTG-60AH, Shimadzu Corp.).

3. Results and Discussion

3.1. Characterization of Zn-exchanged ZSM-5 Oxide Hierarchical Composite Catalysts

Figures 2 shows the XRD patterns of fresh ZnZSM-5-Al₂O₃ hierarchical composite catalysts. Only the signals of zeolite and oxides crystals were observed and were almost the same before and after the reaction. Zn species were not detected in any catalysts, indicating that Zn species were dispersed on ZSM-5 and did not influence the original structure of the catalysts prepared 36)–38,46).

Tables 1 and 2 show the information about the pore structure of fresh and used catalysts measured by N₂
adsorption and desorption, respectively. The BJH method was utilized to evaluate the mesopores larger than 3.3 nm in diameter of the ZSM-5 used. BET surface area (SA), total pore volume (TPV), BJH surface area (BJH-SA), and BJH pore volume (BJH-PV) were 388 m²/g, 0.30 cm³/g, 34 m³/g, and 0.14 cm³/g, respectively. Decrease in zeolite content and increase in Al₂O₃ content for 0A, 10A and 35A resulted in decreased BET-SA and increased BJH-SA and BJH-PV for mesopores and increased TPV caused by the large mesopores of Al₂O₃. The effects of TiO₂, ZrO₂ and kaolin on BET-SA and TPV were rather small, as BJH-SA and BJH-PV decreased compared with Al₂O₃. The values of TPV, BJH-SA, and BJH-PV were almost the same even after the reaction because the mesopores of oxides were hardly affected by coke formation. For example, TPV, BJH-SA and BJH-PV of the catalyst with TiO₂ before the reaction were 0.35 cm³/g, 84 m³/g, and 0.28 cm³/g, respectively, and were 0.36 cm³/g, 81 m³/g, and 0.30 cm³/g after the reaction. In contrast, BET-SA of 342 m²/g before the reaction decreased to 303 m²/g after the reaction, and the same trend was observed for all catalysts probably because of coke formation near the pore mouths of ZSM-5.

Table 3 shows the amounts of NH₃ desorbed and Fig. 3 shows the NH₃-TPD profiles. NH₃-TPD in the range 350-650 °C was regarded as indicating the strong acid sites of ZSM-5. Values for catalysts with Al₂O₃ decreased from 3.3 to 2.6 (10⁻⁴ mol/g) with higher Al₂O₃ content but the difference between Al₂O₃ and other oxides was rather small. Amounts of strong acid sites at the same content of matrix were distributed in the range 3.1-3.7 (10⁻⁴ mol/g). Presumably the values of NH₃-TPD in the range of 100-350 °C were derived from the weak acid sites of ZSM-5 including physical adsorption by ZnZSM-5 and oxides.

Table 1 Pore Properties of Fresh ZnZSM-5 Oxide Hierarchical Composite Catalyst Measured by N₂ Adsorption and Desorption

| Catalysts         | BET SA* [m²/g] | Total PV* [cm³/g] | Average PD* [nm] | BJH SA* [m²/g] | PV* [cm³/g] | PD* [nm] |
|-------------------|----------------|-------------------|------------------|----------------|-------------|----------|
| ZSM-5             | 388            | 0.30              | 3.1              | 36             | 0.14        | 3.7      |
| Zn(13)ZSM(24)/0A  | 386            | 0.32              | 3.3              | 92             | 0.19        | 3.7      |
| Zn(15)ZSM(24)/10A | 362            | 0.36              | 4.0              | 120            | 0.29        | 3.7      |
| Zn(15)ZSM(24)/35A | 324            | 0.49              | 6.1              | 206            | 0.44        | 10.6     |
| Zn(13)ZSM(24)/10T | 342            | 0.35              | 4.1              | 84             | 0.28        | 3.7      |
| Zn(18)ZSM(24)/10Zr| 342            | 0.30              | 3.5              | 80             | 0.19        | 3.7      |
| Zn(18)ZSM(24)/10ka| 390            | 0.33              | 3.4              | 91             | 0.20        | 3.7      |

*: SA; surface area, PV; pore volume, PD; pore diameter.

Table 2 Pore Properties of Used ZnZSM-5 Oxide Hierarchical Composite Catalyst Measured by N₂ Adsorption and Desorption

| Catalysts         | BET SA* [m²/g] | Total PV* [cm³/g] | Average PD* [nm] | BJH SA* [m²/g] | PV* [cm³/g] | PD* [nm] |
|-------------------|----------------|-------------------|------------------|----------------|-------------|----------|
| Zn(13)ZSM(24)/0A  | 332            | 0.29              | 3.5              | 85             | 0.22        | 3.7      |
| Zn(15)ZSM(24)/10A | 288            | 0.29              | 4.4              | 112            | 0.26        | 3.7      |
| Zn(15)ZSM(24)/35A | 284            | 0.49              | 6.9              | 205            | 0.45        | 10.6     |
| Zn(13)ZSM(24)/10T | 303            | 0.36              | 4.7              | 81             | 0.30        | 3.7      |
| Zn(18)ZSM(24)/10Zr| 301            | 0.27              | 3.5              | 74             | 0.17        | 3.7      |
| Zn(18)ZSM(24)/10ka| 305            | 0.27              | 3.6              | 77             | 0.18        | 3.7      |

*: SA; surface area, PV; pore volume, PD; pore diameter.
3.2. Production of Aromatics by Cracking and Dehydrocyclization of \textit{n}-Pentane Using ZnZSM-5 Oxide Hierarchical Composite Catalysts

The effect of matrix on production of aromatics from \textit{n}-pentane was investigated in Zn-exchanged ZSM-5 oxide hierarchical composite catalysts. Figure 4 shows the changes in conversion of \textit{n}-pentane with temperature. Conversion increased with higher temperature and ZSM-5 content, in the order ZnZSM/0A \textless\textless ZnZSM/10A \textless\textless ZnZSM/10T \textless\textless ZnZSM/10Zr \textless\textless ZnZSM/10ka \textless\textless ZnZSM/35A. Comparison of the change in conversion with reaction time at 550 °C found a slight decrease in conversion during 3 h for 35A catalyst, but stable conversion with reaction time for the other catalysts as shown in Fig. 5. The results suggested that the use of both ZnZSM-5 and matrix with large porosity would optimize the catalytic activity of the catalyst.

Figures 6 and 7 show the changes in selectivity for benzene and toluene with temperature. Selectivity for aromatics was significantly low at 450 °C, but increased markedly with higher temperature. On the other hand, conversion reached more than 60 % even at 450 °C (Fig. 4) and gradually increased with higher temperature. The difference in behavior between cracking and aromatization suggested that these reactions occurred at separate active sites. The effect of the amounts of ZnZSM-5 and alumina on the selectivity appeared clearly and selectivity for both benzene and toluene increased in the order 35A < 0A < 10A at 550 °C. 35A catalyst exhibited higher selectivity for benzene and toluene, and ZSM-5 content, in the order ZnZSM/0A \textless\textless ZnZSM/10A \textless\textless ZnZSM/10T \textless\textless ZnZSM/10Zr \textless\textless ZnZSM/10ka \textless\textless ZnZSM/35A. Comparison of the change in conversion with reaction time at 550 °C found a slight decrease in conversion during 3 h for 35A catalyst, but stable conversion with reaction time for the other catalysts as shown in Fig. 5. The results suggested that the use of both ZnZSM-5 and matrix with large porosity would optimize the catalytic activity of the catalyst.

\begin{table}[h]
\centering
\caption{NH\textsubscript{3} Temperature Programmed Desorption of ZnZSM-5 Oxide Hierarchical Composite Catalysts before Use}
\begin{tabular}{|c|c|c|c|}
\hline
Catalysts & NH\textsubscript{3} desorption [10\textsuperscript{-4} mol/g] & & \\
& Total acid site & Weak acid site & Strong acid site \\
& (100-350 °C) & (350-650 °C) & (100-350 °C) \\
\hline
Zn(13)ZSM(24)/0A & 8.6 & 5.3 & 3.3 \\
Zn(15)ZSM(24)/10A & 8.4 & 5.2 & 3.2 \\
Zn(13)ZSM(24)/35A & 7.6 & 5.0 & 2.6 \\
Zn(13)ZSM(24)/10T & 10.3 & 6.6 & 3.7 \\
Zn(18)ZSM(24)/10Zr & 8.7 & 5.6 & 3.1 \\
Zn(18)ZSM(24)/10ka & 9.3 & 6.0 & 3.3 \\
\hline
\end{tabular}
\end{table}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig3.png}
\caption{NH\textsubscript{3}-TPD Curves of Fresh ZnZSM-5 Oxide Hierarchical Composite Catalysts}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig4.png}
\caption{Change in Conversion with Temperature}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig5.png}
\caption{Change in Conversion with Time on Stream at 550 °C}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig6.png}
\caption{Change in Selectivity for Benzene with Temperature}
\end{figure}
toluene at 500 °C compared to other catalysts, suggesting that a small amount of ZnZSM-5 would inhibit significant cracking of \( n \)-pentane and promote the aromatization of formed olefins. Significant cracking also apparently promoted hydrogen transfer to olefins, which may have decreased the aromatization of olefins. The selectivity for aromatics at 550 °C decreased in the order ZnZSM/10A > ZnZSM/0A > ZnZSM/10Zr = ZnZSM/10T > ZnZSM/10ka > ZnZSM/35A. Consequently, use of both ZnZSM-5 and matrix with large porosity would be optimum to achieve maximum product selectivity.

Table 4 shows the olefin and paraffin (O/P) ratios in C2-C4 fractions. O/P ratios tended to decrease with higher ZnZSM-5 and lower Al2O3 content, indicating that a higher amount of ZnZSM-5 would consume larger amounts of olefins leading to the higher ratio of aromatics or paraffins and the lower ratio of olefins. That is, ZnZSM-5 had two major functions, dehydrocyclization of olefins to aromatics and hydrogenation of olefins to paraffins by hydrogen transfer. Hydrogen transfer apparently proceeded more preferentially for 0A catalyst than for 10A catalyst because of the higher concentration of ZnZSM-5, and cyclization of olefins to aromatics was suppressed for 35A catalyst because of the lower concentration of ZnZSM-5. However, this high promotion of hydrogen transfer slightly decreased the selectivity of aromatics for 0A catalyst compared with 10A catalyst. These results suggested that addition of appropriate amounts of matrix could optimize the functions of cracking and aromatization in the catalyst.

The selectivity for benzene and toluene did not change with reaction time and remained constant for 3 h. This result differed from the finding of slightly decreased conversion for 35A catalyst, suggesting that cracking of \( n \)-pentane and cyclization of olefins occur at separate active sites, and that the olefin cyclization sites of Zn-derived species were not deactivated whereas the acid sites for cracking of \( n \)-pentane were deactivated by coke deposition.

Figures 8 and 9 show the distributions of paraffins, olefins, and aromatics. Methane formation was similar for all catalysts and no significant cracking occurred. These results suggested that most \( n \)-pentane was cracked without isomerization, and that cracking of C2-C4 fractions did not occur.

| Catalyst            | C2   | C3   | C4   |
|---------------------|------|------|------|
| Zn(13)ZSM(24)0A    | 0.213| 0.083| 0.190|
| Zn(15)ZSM(24)10A   | 0.291| 0.119| 0.319|
| Zn(15)ZSM(24)35A   | 0.483| 0.181| 0.255|
| Zn(13)ZSM(24)10T   | 0.255| 0.091| 0.174|
| Zn(18)ZSM(24)10Zr  | 0.320| 0.130| 0.202|
| Zn(18)ZSM(24)10ka  | 0.334| 0.147| 0.229|

Fig. 7 Change in Selectivity for Toluene with Temperature

Fig. 8 Distribution of Paraffins, Olefins, and Aromatics (550 °C)

Fig. 9 Carbon Number Distribution of Products (550 °C)
whereas cracking of n-pentane occurred preferentially. The presence of matrix oxide apparently suppressed over-cracking by zeolite resulting in the effective function. Thermal cracking is known to hardly occur at 550 °C\(^{47}\).

**Figure 10** shows the reaction routes to produce aromatics assuming that primary cracking of n-pentane occurs on Zn(15)ZSM(24)\(\text{10A}^{1}\). Carbenium ions are formed on the β-carbon and γ-carbon of n-pentane. The β-carbenium ion is cracked to C2 and C3 fractions whereas the γ-carbenium ion is cracked to C1 and C4 fractions. Assuming that C2-C4 fractions could not be cracked further, and that C1 could be formed only by cracking of C5, the observed amount of C4 was much less than that predicted based on the amount of C1 formed. This indicates that most of the C4 fraction was used for BTX formation catalyzed by ZnZSM-5. Furthermore, the amount of the C4 fraction formed was much less than those of the C2 and C3 fractions, suggesting that benzene, toluene, and xylene were produced from the reactions of ethene, propene, and butene with butene, respectively, as shown in **Fig. 10**. This assumption was confirmed by the calculation based on the yield of methane which was 8 % (C.%) for most catalysts. This 8 % yield of methane indicates the formation of 32 % yield of C4 fraction. However, the detected yield of the C4 fraction was only 4 %, so that 28 % of C4 was presumably used for BTX formation. This route 2 used a total of 40 % of pentane. Furthermore, the yield of C9 and higher aromatics was 3 % in **Fig. 10**. Therefore, the remainder of pentane 57 % was cracked to 23 % of C2 and 34 % of C3 fractions through route 1. However, the observed C2 and C3 fractions were only 19 % and 26 %, so the balances of C2 and C3, 4 % and 8 %, must be used with C4 to form benzene and toluene, respectively. Yields of benzene and toluene calculated using these values were almost consistent with the observed values, 12 % and 20 %, respectively. The observed yield of xylene was 8 %, which was consistent with the balance of C4 not used for benzene and toluene formation. Calculated BTX yields were almost consistent with observed yields, suggesting that the reaction proceeded through primary cracking of n-pentane and successive dehydrocyclization of formed olefins on ZnZSM-5 oxide hierarchical composite catalysts as shown in **Fig. 10**. The selectivities of routes 1 and 2 may be related to the difference in the stability of ethyl and methyl cations formed in routes 1 and 2. Cracking of the C4 and lower fractions possibly could not proceed in the presence of n-pentane because n-pentane has higher adsorption equilibrium constant\(^{48}\). The initial isomerization of n-pentane to isopentane could not occur since cracking of isopentane occurs more easily than that of n-pentane and would form much larger amounts of CH\(_4\) and C\(_4\)H\(_8\) than those of C\(_2\)H\(_6\) and C\(_3\)H\(_6\)\(^3\).

% Numbers surrounded by a square were observed values of selectivity for products and were used for this calculation. The selectivity of aromatics was consistent with the values calculated on the basis of 8 % of methane and values of C2-C4 fractions observed using Zn(15)ZSM(24)\(\text{10A}^{1}\) catalyst. Rounding of values to the nearest 1 % may cause differences.  

**Table 5** shows the amount of coke formation on used catalysts estimated from the weight loss measured by TG-DTA. Significant weight losses and exothermic profiles were observed in the range 400-600 °C as shown in **Fig. 11**. Higher yields of aromatics were associated with greater coke formation. The alkanes formed could not react further under the conditions, but could be recycled in another unit. Furthermore, olefins still persisted and could be cyclized to form the maximum yield of aromatics by selecting the optimal ratios of Zn, ZSM-5, oxide, and hydrogen.  

Zn species on the hierarchical composite catalyst would initially be exchanged with H\(^+\) of HZSM-5. As the exchange ratio of Zn was about 15 mol% of H\(^+\) in HZSM-5, most Zn was dispersed inside the micropo-
rous ZSM-5 and a part of Zn would be reduced to active species for dehydrocyclization of olefins through the Diels-Alder reaction.

Zn ions are reported to promote the dehydrogenation of butenes and propene in pentane reforming, and coupling of the butadiene or allylic species formed may produce aromatics. Transition metals such as Pt may also promote dehydrogenation to produce olefins and aromatization of smaller alkanes such as propane would proceed through initial dehydrogenation. Addition of Zn may promote the dehydrogenation of butenes to butadiene. However, the dehydrogenation of n-pentane forming pentenes may not occur first because neither isomerization of n-pentane nor excess formation of methane were observed. Furthermore, the aromatization mechanism involving olefins formed by cracking of n-pentane was consistent with the yields of BTX as shown in Fig. 10. Metal species of Zn- and Ga-exchanged HZSM-5 do not promote the dehydrogenation of alkanes but could interact with olefins to form aromatics. Protonic sites formed on Zn species are not active for cracking. In the present study, the Zn species did not cover all acid sites of ZSM-5, so any remaining Brønsted sites would be active for n-pentane cracking.

4. Conclusions

The present study investigated the effects of mesoporous matrix on the activity and selectivity of aromatic compounds in the dehydrocyclization of n-pentane catalyzed by ZnZSM-5 oxide hierarchical composite catalysts. Modification of the matrix oxide changed the activity and the selectivity for aromatics. Al2O3 matrix exhibited the highest conversion and selectivity for aromatics whereas the conversion of n-pentane and the selectivity for each product depended on the type of matrix oxide. We propose that initial cracking of n-pentane to C1 to C4 fractions occurred on Brønsted acidic sites, then dehydrocyclization of the formed C2-C4 olefins proceeded on Zn active species, where benzene, toluene and xylene were formed by the Diels-Alder reactions of ethene with butene, propene with butene, and butene with butene, respectively.

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ZnZSM-5-金属酸化物間層構造触媒を用いた n-ペンタンの分解および環化脱水素反応による芳香族生成に及ぼすマトリックスの影響

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ZnZSM-5- 金属酸化物間層構造触媒を Zn イオン交換 ZSM-5 と様々な酸化物を用いて混練法で調製した。n-ペンタンの分解および環化脱水素反応におけるマトリックスとしてのこれら酸化物の活性および芳香族選択性に及ぼす影響を検討した。混練法による触媒調製では、50 - 85 wt% の ZnZSM-5 を 0 - 35 wt% の酸化物および 15 wt% のアルミナゾルバインダーと混合した。酸化物として Al₂O₃ (A), TiO₂ (T), ZrO₂ (Zr) および kaolin (ka) を用いた。n-ペンタンの分解および続く環化脱水素反応は 450 〜 550 ℃ の温度範囲で、水素雰囲気下、固定床反応器を用いて行った。550 ℃ での n-ペンタンの転化率は、ZnZSM/0A (85 wt% ZnZSM-5, 0 wt% Al₂O₃, 15 wt% binder) が最も高く、ZnZSM/10A > ZnZSM/10T > ZnZSM/10Zr > ZnZSM/10ka > ZnZSM/35A の順に減少した。550 ℃ での芳香族選択性は、ZnZSM/10A > ZnZSM/10Zr = ZnZSM/10T = ZnZSM/10ka > ZnZSM/35A の順に減少した。これらの結果は、この反応において ZnZSM-5 と大きな細孔を持つマトリックスの使用が触媒機能を最大限に引き出すために必要であることを示唆した。ペンゼン、トルエンおよびキシレンを形成するオレフィンの芳香族化が ZSM-5 中の Zn 種上における Diels-Alder 反応を通して進行することが、生成物分布から予想された。

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