1. Introduction

The aromatization of light alkanes including ethane, propane, and \( n \)-hexane is an important process for producing value-added aromatic compounds, especially benzene, toluene, and xylenes (BTX), because the aromatization process can be adapted to use natural gas, to meet the increased demands for raw chemicals in the petrochemical industry in recent decades. For the aromatization of alkanes, various metal-loaded zeolite catalysts based on ZSM-5 \( \beta \) 14), MCM-22 15), ZSM-11 16), and L zeolite 17) \( \beta \) 21) have been extensively developed. In particular, Zn- or Ga-containing ZSM-5 provides high catalytic activities and selectivities for aromatic compounds because of the combination of the dehydrogenation over the metal species and Brønsted acidity of the ZSM-5 zeolite 1),3),5),6),10). Furthermore, the metal species are highly dispersed on ZSM-5 through the replacement of protons on ZSM-5 with the metal species by ion exchange and reducing-oxidizing treatment to provide active sites such as cationic metal species instead of bulk ZnO and Ga 2O 3 22) \( \beta \) 25). Since the aromatization of alkanes fundamentally proceeds via the dehydrogenation of alkanes, it is important to increase the number of active metal sites for improving the catalytic performances.

The incorporation of metal species into the framework of zeolite through the hydrothermal treatment leads to the formation of highly dispersed and isolated metal species in the zeolite. In addition, the incorporation of trivalent Ga species, instead of Al species, into the zeolite framework generates Brønsted acid sites with weaker acidity than those generated by the incorporation of Al species 24), resulting in a bifunctional catalyst for the aromatization of the cracked compounds to produce toluene and xylenes, whereas the selectivity for benzene was independent of the Ga content.

Keywords
MFI-type zeolite catalyst, MWW-type zeolite catalyst, Zinc, Gallium, \( n \)-Hexane, Aromatization

[Research Note]

Synthesis of Zeolite Catalysts Containing Zn and Ga for Aromatization of \( n \)-Hexane

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MFI-type zeolites and MWW-type zeolites containing Zn and/or Ga species were directly synthesized through the hydrothermal treatment of an amorphous gel containing Zn and/or Ga species with a high metal content in the absence of Al species. The metal-containing zeolites were applied to the aromatization of \( n \)-hexane to evaluate the catalytic performances. Ga-containing zeolites exhibited much higher catalytic activities than Zn-containing zeolites. The Ga-containing zeolites predominantly produced benzene through the dehydrocyclization of \( n \)-hexane among benzene, toluene, and xylenes (BTX), although cracked compounds were mainly produced. Higher crystallinity of the MFI zeolite containing both Zn and Ga species led to higher catalytic performances for both the dehydrocyclization and cracking. Furthermore, higher Ga content in the MFI zeolite containing both Zn and Ga species, which corresponds to lower Zn/Ga molar ratio, improved the catalytic activity for the aromatization of the cracked compounds to produce toluene and xylenes, whereas the selectivity for benzene was independent of the Ga content.

Keywords
MFI-type zeolite catalyst, MWW-type zeolite catalyst, Zinc, Gallium, \( n \)-Hexane, Aromatization

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lites containing two types of metal species, Zn and Ga species. The catalytic properties of the metal-containing zeolite catalysts were evaluated in the aromatization of n-hexane for the direct production of benzene through the dehydrocyclization. Zn and/or Ga-containing MWW-type zeolites were also hydrothermally synthesized to investigate their catalytic properties for the aromatization of n-hexane.

2. Experimental

2.1. Catalyst Preparation

Zn- and/or Ga-containing MFI-type zeolites ([Zn]-MFI, [Ga]-MFI, and [Zn,Ga]-MFI) were hydrothermally synthesized using Ga(NO₃)₃·nH₂O (Mitsuwa Chemicals Co., Ltd.) and/or Zn(NO₃)₂·6H₂O (Junsei Chemical Co., Ltd.) as metal sources as previously described. Typically, a mixture of tetraethyl orthosilicate (TEOS; Tokyo Chemical Industry Co., Ltd.) and tetrapropylammonium hydroxide (TPAOH; 20-25 wt% in water, Tokyo Chemical Industry Co., Ltd.) was pretreated by stirring at 80 °C for 24 h. Then, NaOH (Kanto Chemical Co., Inc.) aqueous solution and an aqueous solution containing the metal salt(s) were added to the mixture to give rise to the starting gel with a molar composition of 1SiO₂ : 0.1Metal(s) : 0.26TPAOH : 0-0.2NaOH : 13H₂O. The prepared gel was hydrothermally treated at 175 °C for 24 h. The resultant solid was recovered by centrifugation, washed with deionized water, and dried at 90 °C, then calcined in air at 550 °C for 8 h. The MFI zeolite was hydrothermally synthesized without the pretreatment of the mixture of TEOS and TPAOH for comparison with the MFI zeolite synthesized through the pretreatment of the mixture of TEOS and TPAOH followed by the hydrothermal synthesis.

Zn-containing MWW-type zeolites were synthesized using boric acid ([Zn,B]-MWW) as described previously because boron species enhances the crystallization of metal-containing MWW-type zeolites.

First, for the use as a seed crystal in the synthesis of metal-containing MWW-type zeolite, boron-containing MWW-type zeolite ([B]-MWW) was synthesized through the hydrothermal treatment using fumed silica (Nippon Aerosil Co., Ltd.), hexamethylenimine (HMI; Sigma-Aldrich Co. LLC.), and boric acid (FUJIFILM Wako Pure Chemical Corp.) followed by the calcination. The synthesized [B]-MWW was acid-treated with an HNO₃ aqueous solution at 80 °C for 20 h to remove boron species for providing the seed crystal. In a typical synthesis of [Zn,B]-MWW, fumed silica as a silica source, boric acid, and HMI were added to an aqueous NaOH solution. After stirring for 2 h, Zn(NO₃)₂·6H₂O and the seed crystal were added to the mixture, then the mixture was further stirred for 5 h. The prepared starting gel with a molar composition of 1SiO₂ : 0.05Metal : 1HMI : 0.2H₃BO₃ : 0.1NaOH : 19H₂O was hydrothermally treated at 170 °C for 7 days.

For comparison with [Zn,B]-MWW, Zn- and/or Ga-containing MWW-type zeolites ([Zn]-MWW, [Ga]-MWW, and [Zn,Ga]-MWW) were synthesized without boric acid as previously described. A mixture of fumed silica as the silica source, NaOH, and HMI was stirred in an aqueous solution for 2 h. Then, the metal salt(s) and seed crystal were introduced into the mixture and stirred for 2 h. Then the mixture with a molar composition of 1SiO₂ : 0.05Metal(s) : 1HMI : 0.15NaOH : 45H₂O was hydrothermally treated at 135 °C for 11 days. In both these synthesis procedures above, the as-synthesized precursor was obtained by filtration, washed with deionized water, and dried at 90 °C. The obtained precursor was calcined in air at 600 °C for 8 h.

2.2. Characterization

The crystalline structure of the prepared materials was characterized by X-ray diffraction (XRD; Rigaku Corp., SmartLab) using a Cu Kα radiation source (45 kV and 200 mA). The metal content of the prepared zeolites was estimated by X-ray fluorescence (XRF; Rigaku Corp., NEX CG) analysis. The specific surface area (S_BET) and the micropore volume (V_mic) of the prepared zeolites were calculated based on the N₂ adsorption-desorption isotherm measured at −196 °C on a BELSORP-miniX instrument (MicrotracBEL Corp.). Prior to the measurements, the samples were heated under a vacuum at 350 °C for 2 h.

2.3. Conversion of n-Hexane to Aromatic Compounds

Zeolite catalysts hydrothermally synthesized in the presence of sodium cations were repeatedly ion-exchanged with 2 M ammonium nitrate solution (3 times) and were subsequently calcined at 550 °C for 3 h for the use in the aromatization of n-hexane.

The aromatization of n-hexane was performed in a 6 mm (O.D.) quartz tubular reactor loaded with 0.1 g of a catalyst. The catalyst was pretreated at 600 °C for 1 h in an air flow. Nitrogen was used as a carrier gas. After the introduction of n-hexane in the liquid phase followed by vaporization, a mixture of n-hexane and N₂ was supplied to the catalyst bed. The reaction temperature was escalated after the reaction of 1 h at each temperature. The catalyst weight to the flow rate ratio (W/F) is 15.7 g_cat h (mol_n-hexane)⁻¹, which corresponded to the weight hourly space velocity of n-hexane (WHSV) of 5.5 h⁻¹. The outlet gases were analyzed with an on-line gas chromatograph (Shimadzu GC-2014) equipped with a flame ionization detector (FID) and a capillary column (Ucon LB-550X).
3. Results and Discussion

3.1. Synthesis of Metal-containing MFI-type Zeolites

3.1.1. Synthesis of [Zn]-MFI and [Ga]-MFI Zeolites

Figure 3.1 shows XRD patterns of the calcined metal-containing MFI-type zeolites. As we previously reported, [Zn]-MFI was successfully synthesized with a low Si/Zn molar ratio of 10. Similarly, when the starting gel with a low Si/Ga molar ratio of 10 was used, only amorphous phase was obtained, indicating that the crystallization of gallosilicate was slower compared with zincoisilicate. [Ga]-MFI was successfully synthesized using the starting gel with higher Si/Ga molar ratios of 20 and 50 (Fig. 1(a)). The Ga content in the [Ga]-MFI zeolites was greater than that in the corresponding starting gels. In addition, the BET surface area and micropore volume of [Ga]-MFI (Si/Ga = 20) were estimated at 308 m² g⁻¹ and 0.11 cm³ g⁻¹, respectively, similar to those of [Zn]-MFI at 295 m² g⁻¹ and 0.09 cm³ g⁻¹. In contrast, only amorphous phase was obtained without the pretreatment of the mixture of TEOS and TPAOH even using the starting gel with the Si/Ga molar ratio of 20 (Fig. 1(b)). [Ga]-MFI was obtained even without the pretreatment when the Ga content in the starting gel was decreased (Si/Ga molar ratio of 50). These observations indicate that the pretreatment followed by the hydrothermal treatment is effective in the crystallization of the MFI zeolite with high metal content.

3.1.2. Synthesis of [Zn,Ga]-MFI Zeolites

To introduce the two types of catalytic functions into the zeolite catalyst, [Zn,Ga]-MFI was hydrothermally synthesized using the starting gel containing both Ga and Zn species at 175 °C for 24 h. The XRD patterns of the as-synthesized [Zn,Ga]-MFI are shown in Fig. 2(a). The MFI structure was obtained using the starting gel with a high metal content (Si/(Zn + Ga): 10 and Zn/Ga = 1/1) in the absence of sodium cations (Na/Si: 0 and HT: 24 h). However, the XRD pattern of the as-synthesized sample showed a broadened peak at around 6°, which was not observed in the XRD patterns of as-synthesized [Ga]-MFI. Therefore, Zn species in the starting gel caused the formation of the layered structure. To convert the layered structure to the MFI structure and to improve the crystallinity of [Zn,Ga]-MFI, the hydrothermal treatment was carried out in the presence of sodium cations. After the hydrothermal treatment of the starting gel with an Na/Si molar ratio of 0.1, the peak assigned to the layered structure was still observed at around 6° (Na/Si: 0.1 and HT: 24 h). However, higher content of sodium cations (Na/Si: 0.2 and HT: 24 h) led to the formation of the as-synthesized sample with only the MFI structure. The large amount of alkali cations would accelerate the transformation of the starting gel into the MFI structure in preference to the layered structure. In addition, to convert the starting gel with a low Na/Si molar ratio of 0.1 to the MFI structure, the starting gel was hydrothermally treated for 7 days. The layered structure was still obtained together with the MFI structure (Na/Si: 0.1 and HT: 7d). Thus, the addition of sodium cations is more effective in the crystallization of amorphous starting gel to the MFI structure compared with extended hydrothermal treatment.

Si/metal numbers correspond to molar ratios in the starting gel. Numbers in parentheses correspond to Si/metal molar ratios estimated by XRF measurement.

Fig. 1 XRD Patterns of Calcined Products Synthesized through (a) Pretreatment Followed by Hydrothermal Treatment and (b) Direct Hydrothermal Treatment
XRD patterns typical of the MFI structure (Fig. 2(b)). Characterizations of the calcined [Zn,Ga]-MFI zeolites after the removal of Na⁺ by ion exchange are summarized in Table 1. The metal content in the zeolites was similar to that in the corresponding starting gels, whereas the Ga content was slightly larger than the Zn content in all the zeolites. [Zn,Ga]-MFI zeolite (Na/Si: 0.1 and HT: 7d) exhibited the highest specific surface area among the zeolites shown in Fig. 2(b), although the collapsed layered compound coexisted with the MFI structure. [Zn,Ga]-MFI zeolite (Na/Si: 0.2 and HT: 24 h) had the lowest specific surface area, although only the MFI structure was observed in the corresponding as-synthesized material.

To investigate the effect of the Zn/Ga molar ratio on the crystallization, MFI zeolites were hydrothermally synthesized with various Zn/Ga molar ratios and the Si/(Zn + Ga) molar ratio of 10. The MFI structure was successfully obtained using the starting gel with a high metal content, independent of the Zn/Ga molar ratio (Fig. 3(a)). However, the crystallization to the MFI structure was slow using the starting gel with the high Ga content (Zn/Ga = 1/10), which was consistent with the findings in the synthesis of [Ga]-MFI. Moreover, the MFI structure was successfully formed using the starting gel with the high Ga content (Zn/Ga = 1/10) in the presence of sodium cations (Na/Si = 0.1) through the hydrothermal treatment at 175 °C for 7 days (Fig. 3(b)). In addition, since higher crystalline MFI zeolites were obtained using Zn-rich starting gel, which corresponds to a high Zn/Ga molar ratio, Zn species is preferable to Ga species for the formation of the MFI zeolite. Furthermore, increasing the Zn/Ga molar ratio in the starting gel led to decreasing the Si/(Zn + Ga) molar ratio, which corresponded to an increase in the metal content. Using the Zn-rich starting gels, the Zn/Ga molar ratio of the calcined zeolite was smaller than that of the corresponding starting gel, suggesting that the introduction of Zn species to the zeolite was suppressed by coexisting Ga species.

3.2. Synthesis of Metal-containing MWW-type Zeolites

In the synthesis of metal-containing MWW-type zeolites, deboronated [B]-MWW was added as a seed crystal to the starting gel. The XRD pattern of the mixture of fumed silica and the seed mainly shows amorphous phase together with very small peaks derived from the MWW structure (Fig. 4), indicating that intense peaks attributed to the MWW structure in the products should be derived from the zeolite crystallized from the amorphous starting gel.

Figure 4 shows XRD patterns of the calcined metal-containing MWW-type zeolites. The XRD pattern of [Zn,B]-MWW contained sharp and intense

Table 1 Characteristics of Calcined [Zn,Ga]-MFI Catalysts

| Catalyst   | Si/(Zn + Ga) | Zn/Ga | S_{BET}^{\text{\(\text{m}^2 \text{g}^{-1}\)}} | \(V_{\text{micro}}^{\text{\(\text{cm}^3 \text{g}^{-1}\)}}\) |
|------------|--------------|-------|------------------------------------------|------------------------------------------|
| Na/Si: 0   | 9.1          | 0.9   | 259                                      | 0.06                                     |
| HT: 24h    |              |       |                                          |                                          |
| Na/Si: 0.1 | 8.9          | 0.8   | 277                                      | 0.10                                     |
| HT: 24h    |              |       |                                          |                                          |
| Na/Si: 0.2 | 8.8          | 1.0   | 211                                      | 0.08                                     |
| HT: 24h    |              |       |                                          |                                          |
| Na/Si: 0.1 | 11           | 0.7   | 349                                      | 0.13                                     |
| HT: 7d     |              |       |                                          |                                          |

a) Measured by XRF.
b) Estimated by N₂ adsorption method.
peaks derived from the MWW structure, indicating that a highly crystalline zeolite containing Zn species was formed using boron species. However, small peaks attributed to the MFI structure were also observed with those to the MWW structure. [Zn]-MWW was also successfully crystallized even in the absence of boron species under the synthesis conditions at a lower temperature of 135 °C for a longer hydrothermal period of 11 days. To investigate the effects of the seed crystal on the crystallization of the MWW zeolite, the starting gel was hydrothermally treated in the absence of the seed crystal under the same conditions as those for the synthesis of [Zn]-MWW. As shown in Fig. 4, only amorphous phase was obtained, indicating that the presence of the seed crystal during the hydrothermal synthesis was essential to the crystallization of the MWW zeolite containing Zn species.

[Ga]-MWW was also hydrothermally synthesized with the Si/Ga ratio of 20 by the same manner as that for [Zn]-MWW. [Ga]-MWW exhibited a similar XRD pattern to that of [Zn]-MWW with very small peaks attributed to the MFI structure. [Zn,Ga]-MWW with only the MWW structure was also successfully synthesized using the starting gel containing both Zn and Ga species (Si/(Zn + Ga) 1/20 and Zn/Ga 1/1) in the presence of the seed crystal. As shown in Table 2, both [Zn]-MWW and [Ga]-MWW exhibited a lower Si/Metal molar ratio than the corresponding starting gels, and had similar specific surface areas and micropore volumes. In contrast, [Zn,Ga]-MWW had a higher Si/(Zn + Ga) molar ratio than the corresponding starting gel, suggesting that the introduction of metal species into the MWW structure was suppressed by the coexistence of different metal species in the starting gel.

Table 2 Characteristics of Calcined MWW Zeolites

| Catalyst      | Si/(Zn + Ga) | Zn/Ga | \(S_{\text{BET}}\) | \(V_{\text{mic}}\) |
|---------------|-------------|-------|-----------------|-----------------|
| [Zn,B]-MWW    | 14          | 440   | 0.16            | 0.12            |
| [Zn]-MWW      | 12          | 357   | 0.12            | 0.12            |
| [Ga]-MWW      | 13          | 367   | 0.12            | 0.12            |
| [Zn,Ga]-MWW   | 60          | 519   | 0.18            | 0.12            |

a) Measured by XRF.
b) Estimated by N\(_2\) adsorption method.
3.3. Aromatization of n-Hexane over Metal-containing MFI Zeolites

The aromatization of n-hexane was carried out over the synthesized metal-containing MFI zeolites. Benzene is directly produced through the dehydrocyclization of n-hexane, while other aromatic compounds such as toluene and xylenes are formed through multi-step reactions including the cracking of n-hexane followed by the oligomerization and cyclization of the cracked products\(^\text{[16]}\). The formation of benzene is desirable in the conversion of n-hexane because the carbon number of n-hexane is maintained. The zeolite catalysts synthesized with sodium cations were ion-exchanged with NH\(_4\)NO\(_3\) aqueous solution; subsequently, activated by calcination prior to the reaction. Figure 5 shows the results obtained after the reaction time of 1 h at each reaction temperature. [Zn]-MFI (Si/Zn = 10) exhibited low catalytic activities at every reaction temperature, although [Zn]-MFI exhibited high catalytic properties in the dehydrogenation of n-butane to selectively produce 1,3-butadiene\(^\text{[31]}\). Isomerized and dehydrogenated compounds with the carbon number of 6 (C\(_6\)) were produced even at a low temperature of 450 °C, indicating that the dehydrogenation of n-hexane predominantly proceeded on [Zn]-MFI. The yields of aromatic compounds and cracked products (C1-C5) increased with an increase in the reaction temperature. In the aromatization of alkane over Zn-loaded ZSM-5, the BTX compounds were competitively produced through the cracking of alkane followed by the aromatization of the cracked products\(^\text{[37]}\). However, benzene was predominantly produced among the aromatic compounds during the reaction, suggesting that benzene was directly produced through the dehydrocyclization of n-hexane on [Zn]-MFI.

By contrast, [Ga]-MFI (Si/Ga = 20) exhibited higher catalytic activity than [Zn]-MFI. Cracked products were mainly produced even at the low temperature of 450 °C. Moreover, [Ga]-MFI selectively produced benzene among the aromatic compounds at every temperature, although [Ga]-MFI produced larger amounts of toluene and xylenes at high temperatures compared with [Zn]-MFI. C\(_6\) compounds were not observed above 500 °C, indicating that Ga species in the zeolite significantly enhanced the dehydrogenation of alkanes followed by the aromatization compared with Zn species, which is agreement with the previous findings of the aromatization of alkanes over Ga or Zn species impregnated on ZSM-5\(^\text{[1]}\). The cracking of alkane preferably proceeds over Ga-loaded ZSM-5, resulting in the production of the BTX compounds through the aromatization of the cracked products\(^\text{[38]}\). Although the cracking process was favorable on [Ga]-MFI, a high selectivity for benzene among the aromatic compounds was observed, suggesting that the dehydrocyclization of n-hexane was preferable to the aromatization of cracked alkane.
products over [Ga]-MFI. To investigate the effect of Ga species on the catalytic properties, Ga species was loaded on [Zn]-MFI by the impregnation method (Ga/ [Zn]-MFI; Si/Zn = 10 and Zn/Ga = 1/1). Ga/[Zn]-MFI showed a lower catalytic activity than [Zn]-MFI, and produced negligible amounts of aromatic compounds even at high temperatures. Since active Ga species are formed based on strong Brønsted acid sites on H-ZSM-5, Ga-loaded ZSM-5 has high catalytic activity for the aromatization of n-hexane. Therefore, it is assumed that Ga species loaded on [Zn]-MFI without Brønsted acid sites would remain as inactive residues such as bulk Ga2O3; in addition, active Zn sites in [Zn]-MFI were covered with inactive Ga species, resulting in the low catalytic activity.

In contrast to [Zn]-MFI and [Ga]-MFI, [Zn,Ga]-MFI (Si/(Zn + Ga) = 10 and Zn/Ga = 1/1) showed quite low catalytic activity for the conversion of n-hexane, although Ga species was introduced into the zeolite. Considering influences of the crystallinity of zeolite catalysts in the catalytic properties, we investigated the catalytic properties of [Zn,Ga]-MFI (Si/(Zn + Ga) = 10 and Zn/ Ga = 1/1) prepared using sodium cations (Fig. 6). The crystallinity of the MFI zeolite was improved by increasing the amount of sodium cations in the hydrothermal treatment, and only the MFI structure was obtained in the as-synthesized product when the Na/Si molar ratio was increased up to 0.2 (Fig. 2). [Zn,Ga]-MFI prepared in the absence of sodium cations showed quite low catalytic activity (Fig. 6). When sodium cations was used in the preparation of [Zn,Ga]-MFI, the catalytic performances were considerably improved. Furthermore, [Zn,Ga]-MFI prepared with the Na/Si ratio of 0.1 exhibited higher catalytic activity and yield of benzene than [Ga]-MFI. In addition, the cracked products were mainly obtained, and benzene was selectively produced among the aromatic compounds, similar to the findings for [Ga]-MFI. However, the catalytic activity was drastically decreased for [Zn,Ga]-MFI prepared with a larger Na/Si ratio of 0.2. These observations suggest that the improvement in the crystallinity of the MFI zeolite would improve the catalytic activity for the aromatization of alkane, whereas highly crystalline MFI zeolite prepared with a large amount of sodium cations is not favorable for the aromatization of alkane.

Figure 7 shows the effect of the Zn/Ga molar ratio on the product distribution of [Zn,Ga]-MFI, which was synthesized with the Si/(Zn + Ga) molar ratio of 10 in the presence of sodium cations at 175 °C for 7 days. Higher Ga content, which corresponds to lower Zn/Ga ratio, resulted in greater catalytic activity and higher yields of the BTX products. All the [Zn,Ga]-MFI zeolites showed similar selectivities for benzene (21-26 %), whereas the selectivity for benzene in the BTX product was decreased by increasing the Ga content; 88, 67, 62, 61, and 61 % for the Zn/Ga ratio of 10/1, 5/1, 2/1, 1/5, and 1/10, respectively. In addition, the selectivity for the cracked products decreased with the increase in the Ga content; 76, 65, 56, 61, and 54 % for the Zn/Ga ratio of 10/1, 5/1, 2/1, 1/5, and 1/10, respectively. These observations suggest that increased Ga sites in the zeolite containing both Zn and Ga sites enhanced the aromatization through the C–C bond formation and cyclization of the cracked products in comparison with the direct production of benzene from n-hexane.

3.4. Aromatization of n-Hexane over Metal-containing MWW Zeolites

The synthesized metal-containing MWW zeolites were applied to the aromatization of n-hexane. Both [Zn,B]-MWW and [Zn]-MWW showed a low catalytic activity including the dehydrogenation and cracking of n-hexane (Fig. 8). By contrast, [Ga]-MWW exhibited a higher catalytic activity than [Zn,B]-MWW and [Zn]-MWW, and mainly produced cracked products followed by benzene. Similar to [Ga]-MFI, the dehydrocyclization of n-hexane for direct formation of benzene took place on Ga sites in the MWW structure, although the cracking of n-hexane preferably proceeded.
MWW (Si/(Zn + Ga) = 20 and Zn/Ga = 1/1) mainly produced the cracked products followed by benzene at high temperatures. In contrast to [Ga]-MWW, dehydrogenated C6 compounds were obtained by introducing Zn species in the zeolite at every reaction temperature, suggesting that Zn sites in the zeolite catalyzed the dehydrogenation; successively, the dehydrogenated compounds were transformed to benzene on Ga sites in the zeolite.

4. Conclusions

Ga-containing MFI-type zeolites with high Ga content were synthesized through the pretreatment of the mixture of TEOS and TPAOH followed by the hydrothermal treatment in the absence of sodium cations. Furthermore, MFI-type zeolites containing both Zn and Ga species were directly synthesized through the pretreatment followed by the hydrothermal treatment. Both Zn and Ga species were simultaneously introduced into the MWW structure through the hydrothermal treatment of the starting gel containing both Zn and Ga species in the presence of a seed crystal.

Ga sites in the MFI and MWW zeolites exhibited a higher catalytic activity for the aromatization of n-hexane than Zn sites in the zeolites. The dehydrogenation as well as the dehydrocyclization of n-hexane for directly producing benzene took place on the Zn sites, while the cracking of n-hexane as well as the aromatization of the cracked products to toluene and xylenes proceeded together with the dehydrocyclization of n-hexane on the Ga sites. The catalytic activity of the MFI zeolite increased with higher crystallinity of the [Zn,Ga]-MFI zeolite, whereas the catalytic performances were suppressed on a highly crystalline zeolite synthesized with a large amount of sodium cations. The catalytic activity was further improved upon the increased Ga sites in the [Zn,Ga]-MFI zeolite.

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要 旨

$n$-ヘキサンから芳香族化合物の生成のための亜鉛およびガリウムを含有するゼオライト触媒の合成

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Zn および Ga を含有する MFI 型および MWW 型ゼオライトは、Al 源を使用せずに、ゼオライト合成ガルの低温加熱処理と続く水熱合成を通じて直接生成された。この手法により、Zn および Ga の高い含有量のゼオライト合成ガルからもゼオライト合成が可能となった。ゼオライト中では、Zn および Ga 種は金属酸化物などで存在せず、高分散状態になっている。合成した金属含有ゼオライトを $n$-ヘキサンの芳香族化合物への変換反応に用いたところ、MFI 型および MWW 型ゼオライトのどちらにおいても、Ga 含有ゼオライトは Zn 含有ゼオライトよりも高い触媒活性を示した。また、Ga 含有ゼオライトでは、炭素数が 6 および 7 の芳香族化合物に多く生成したが、ペンゼン、トルエン、キシレン (BTX) のうち、ペンゼンが選択的に生成した。Zn と Ga を含有する MFI 型ゼオライトでは、ゼオライトの結晶性の向上により、$n$-ヘキサンの脱水素環化および分解反応に対する触媒性能の向上が見られた。さらに、Ga の含有割合を増加させることで、分解生成物の芳香族化により生成するトルエンやキシレンの生成量の増加が見られた。一方で、ペンゼンの選択率は Ga 含有割合に依存しなかった。