Shape-Selective Alkylation of Biphenyl over H-[Al]-SSZ-24 Zeolites with AFI Topology

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H-[Al]-SSZ-24 zeolites with AFI topology were synthesized through the alumination of [B]-SSZ-24 zeolites, and applied for the alkylation of biphenyl (BP). H-[Al]-SSZ-24 zeolites have high activity for the isopropylation. The shape-selective formation of 4,4'-disopropylbiphenyl (4,4'-DIPB) occurred at moderate temperature; however, the selectivity for 4,4'-DIPB decreased with an increase in the reaction temperature. Isomerization of 4,4'-DIPB occurred at higher temperatures over internal and external acid sites when there are enough acid sites inside the channels. The channels can discriminate 4,4'-DIPB from the other DIPB isomers in their transition states; however, they can not prevent the isomerization of 4,4'-DIPB at higher temperatures. The selectivity for the least bulky 4,4'-dialkylbiphenyl increased with the bulkiness of alkylation agents in the order: isopropylation < s-butylation < t-butylation. These results strongly support the shape-selective formation of the least bulky products inside the channels of H-[Al]-SSZ-24 zeolites.

ZeoVites are the most promising microporous crystals for achieving highly shape-selective catalysis because their pores are uniformly distributed and have dimensions allowing both organic reactants and products to enter, to accommodate, and to leave.\(^\text{12}\) Large-pore molecular sieves (LPMS) are expected to be useful as catalysts in the alkylation of polynuclear aromatics.\(^\text{3–5}\) 4,4'-Disopropylbiphenyl (4,4'-DIPB) has been selectively produced from biphenyl (BP) over dealuminated H-mordenite (MOR).\(^\text{3–9}\) It is very interesting to elucidate the catalytic features of LPMS pores in the catalysis; however, there have been few very articles on the subject other than MOR. Our previous relevant findings on the subjects have been published on the alkylation of BP over H-[Al]-SSZ-31,\(^\text{10}\) H-[Al]-CIT-5,\(^\text{5,11}\) SAPO-5,\(^\text{12}\) and MAPO-5 (M: Mg, Ca, Sr, Ba, and Zn).\(^\text{13–15}\)

H-[Al]-SSZ-24 zeolite is a high-silica large-pore molecular sieve, which is isostructural with AlPO\(_4\)-5 (AFI topology),\(^\text{16}\) and is expected to work as a potential catalyst for shape-selective alkylation of polynuclear aromatics because of its straight twelve-membered ring (12-MR) channel structure. SSZ-24 zeolite was first synthesized by Zones as its pure-silica form using 1-trimethylammonioadamantane as a structure-directing agent (SDA).\(^\text{17}\) [B]-SSZ-24 zeolite in borosilicate version was subsequently synthesized using a calcined form of boron-substituted zeolite beta ([B]-BEA) as the boron and silicon sources.\(^\text{18}\) Lobo and Davis reported the synthesis of [B]-SSZ-24 zeolite using N\(^{\text{16}}\)-methylsparteinium (MeSPA\(^+\)) as SDA and using sodium borate as the source of boron.\(^\text{19}\) [B]-SSZ-24 zeolite was easily converted to H-[Al]-SSZ-24 zeolites by post-synthetic treatment with aluminum nitrate.\(^\text{19}\) This isomorphous substitution will be expressed as “alumination” in this paper.

It is important to know how zeolite structure influences shape-selective character of the alkylation of BP and how the bulkiness of alkylation agent influences shape-selective catalysis. These questions have led us to investigate the catalytic properties of H-[Al]-SSZ-24 zeolites. In this paper, we describe the isopropylation, s-butylation, and t-butylation of BP over H-[Al]-SSZ-24 zeolites to elucidate the relationships between their pore structure and shape-selective catalysis.

Experimental

Synthesis of H-[Al]-SSZ-24 Zeolites. \(\text{N}^{[\text{16}]}\)-Methylsparteinium hydroxide ([MeSPA\(^+\)]OH\(^-\)) was synthesized by the quaternization of sparteine with methyl iodide, followed by ion-exchange with ion-exchange resin. The detailed procedure is reported elsewhere.\(^\text{20}\) [B]-SSZ-24 was hydrothermally synthesized from a gel having the composition 1.0SiO\(_2\)-0.04B\(_2\)O\(_3\)-0.2[MeSPA\(^+\)]OH\(^-\)-0.1NaOH-50H\(_2\)O.\(^\text{19}\) A typical procedure is as follows. After stirring the mixture of a NaOH solution (32 wt %, 375 mg), a [MeSPA\(^+\)]OH\(^-\) solution (0.700 mmol g\(^{-1}\), 14.3 g), and sodium borate decahydrate (Na\(_2\)B\(_4\)O\(_7\)-10H\(_2\)O, 381 mg) until the solution became clear, and then, 3.00 g of fumed silica (Cab-O-Sil M-5, Cabot) and 33.0 g of de-ionized water were added to the homogeneous mixture. A small amount (60 mg) of [B]-BEA seed was added to the mixture, which was further stirred for 3 h. The mixture was then transferred to a 23-mL Teflon-lined stainless autoclave. The autoclave was kept statically in a convection oven at 175 °C for 5 days. The crystals were collected by filtration, washed several times with de-ionized water, and dried overnight.

To remove the organic SDA occluded inside the [B]-SSZ-24 zeolite, the as-synthesized sample was kept in a muffle furnace, and heated stepwise in a flow of air (100 mL min\(^{-1}\)). The temperature was raised from room temperature to 650 °C over a period of 310 min, and maintained at the same temperature for 4 h. Finally, the calcined sample was cooled to room temperature under ambient conditions.

[B]-SSZ-24 zeolite was aluminated to H-[Al]-SSZ-24 zeolites.

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by heating in an aluminum nitrate solution at 80 °C for 18 h. The relative weight of components in this alumination process was zeolite:Al(NO₃)₃·H₂O = 1:1:50, and this process was repeated several times.

**Catalytic Reaction.** The alkylation of BP was carried out in a 100-mL SUS-316 autoclave under a pressure of the alkylating agent. Typical conditions of the isopropylation are: BP 50 mmol, zeolite 0.25 g, propane pressure 0.8 MPa, reaction temperature 150–250 °C, and reaction time 4 h. An autoclave containing BP and the zeolite was purged with N₂ before heating. After reaching the reaction temperature, propane was introduced to the autoclave, and the pressure kept constant throughout the reaction. After cooling the autoclave, the zeolite was filtered off, and bulk products were diluted with toluene. The products were analyzed by GC analysis was performed according to the same procedure as that for bulk products. The enantioselective analysis was difficult. The enantiomeric excess of each product was calculated on the basis of the amounts of IPBP and DIPB isomers, respectively.

![Table 1. Properties of H-[Al]-SSZ-24 Zeolites](image)

<table>
<thead>
<tr>
<th>Sample</th>
<th>SiO₂/B₂O₃</th>
<th>SiO₂/Al₂O₃</th>
<th>Surface area /m² g⁻¹</th>
<th>Pore volume /cm³ g⁻¹</th>
<th>h-Peak /°C</th>
<th>Acid amount /mmol g⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>[B]-SSZ-24</td>
<td>71</td>
<td>—</td>
<td>379</td>
<td>0.16</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>A₁</td>
<td>816</td>
<td>768</td>
<td>357</td>
<td>0.14</td>
<td>243</td>
<td>0.024</td>
</tr>
<tr>
<td>A₃</td>
<td>—</td>
<td>172</td>
<td>340</td>
<td>0.13</td>
<td>278</td>
<td>0.165</td>
</tr>
<tr>
<td>A₅</td>
<td>—</td>
<td>135</td>
<td>350</td>
<td>0.15</td>
<td>269</td>
<td>0.175</td>
</tr>
</tbody>
</table>

**Results and Discussion**

**Properties of H-[Al]-SSZ-24 Zeolites.** [B]-SSZ-24 zeolites were synthesized by the methods in the literature. Typical properties of the zeolites are shown in Table 1. [B]-SSZ-24 zeolite was converted from [B]-BEA using (MeSPA)⁺OH⁻ as the SDA under hydrothermal conditions. [B]-SSZ-24 zeolite had a SiO₂/B₂O₃ ratio of 71, specific surface area (379 m² g⁻¹), and pore volume (0.16 cm³ g⁻¹). H-[Al]-SSZ-24 zeolites were obtained from [B]-SSZ-24 by repeating the alumination process as described in the Experimental Section. Samples aluminated for n times are abbreviated as Aₙ (n: 1–8). Figure 1 shows the influences of the boron and aluminum contents on the alumination. Boron content of [B]-SSZ-24 zeolite decreased rapidly due to alumination; however, the aluminum content gradually increased with each repetition. From these samples, we chose samples, A₁, A₃, and A₅ of which the SiO₂/Al₂O₃ ratios were 768, 172, and 135, respectively.

![Fig. 1. The isomorphous substitution of boron in [B]-SSZ-24 zeolites with aluminum. Abbreviation: S: starting gel; A: as-synthesized sample; C: calcined sample; Arabic numerals: numbers 1–8 correspond to the sample A₁–A₅, respectively as defined in the text. A₁, A₃, and A₅ were used for the catalysis.](image)
SEM images of [B]-SSZ-24 and H-[Al]-SSZ-24 zeolites A₁, A₃, and A₅. These results show that the structures of H-[Al]-SSZ-24 zeolites were retained during the alumination.

NH₃-TPD spectra of H-[Al]-SSZ-24 zeolites are shown in Fig. 4. They have two types of desorption peak, so-called l- and h-peaks, at 160–180 and 260–280 °C, respectively. The h-peak is due to desorbed NH₃ from Brønsted acidic sites, which work in solid acid catalysis. On the other hand, the l-peak is due to physisorbed NH₃, which plays no important role in solid acid catalysis. The acid amounts are 0.024, 0.165, and 0.175 mmol g⁻¹ for A₁, A₃, and A₅ zeolites, respectively. These results show that the introduction of aluminum to nest silanol groups, formed by the deboronation, was almost saturated by the alumination for three times.

Figure 5 shows solid¹¹B,²⁷Al, and²⁹Si MAS NMR spectra of H-[Al]-SSZ-24 zeolites during the alumination.¹¹B MAS NMR spectra of as-synthesized [B]-SSZ-24 (not shown) gave only a peak at −3.7 ppm corresponding to tetrahedral boron. Upon calcination, a minor broad peak assignable to trigonal boron appeared at around 6.1 ppm in addition to an intense, sharp peak at −3.7 ppm. The signals of these boron species almost disappeared after the first treatment with aluminum nitrate. The signals due to tetrahedral aluminum in the²⁷Al MAS NMR spectra gradually developed during repeated alumination over three repetitions. The spectra were taken in...
such a manner that the intensity reflects the amount. The major tetrahedral peaks were accompanied by minor octahedral peaks at an approximately constant ratio during the repeated aluminations. \(^{29}\)Si MAS NMR spectra showed that the Q\(^3\) species were predominant in all H-[Al]-SSZ-24 zeolites during the aluminations. Almost no Q\(^3\) species was found in calcined [B]-SSZ-24 zeolite; however, small but significant amounts of the aluminations. Almost no Q\(^3\) species appeared in A\(_1\) and A\(_3\) zeolites. These results are consistent with the presence of residual silanol nests which are caused by the almost complete deboronation of [B]-SSZ-24 zeolite and a partial insertion of Al\(^{3+}\) into framework.

**The Isopropylation of BP over H-[Al]-SSZ-24 Zeolites.**

Figure 6 shows the influence of reaction temperature on the products composition in the isopropylation of BP over A\(_1\), A\(_3\), and A\(_5\) zeolites. [B]-SSZ-24 zeolite had no activity towards the isopropylation of BP at 250 °C; however, the amorphous substitution of boron in [B]-SSZ-24 with aluminum enhanced the catalytic activity for the isopropylation. Particularly, A\(_3\) and A\(_5\) zeolites had very high activities affording isopropylbiphenyl (IPBP), diisopropylbiphenyl (DIPB), and triisopropylbiphenyl (TriIPB) isomers. These zeolites gave TriIPB in large amounts even at 200 °C. Catalytic activities of A\(_1\) zeolite appeared at higher temperatures than those of A\(_3\) and A\(_5\) zeolites. However, the profiles of the yield of IPBP, DIPB, and TriIPB isomers over A\(_1\) zeolite versus reaction temperature are quite resembled to A\(_3\) and A\(_5\) zeolites: the maximum yield of DIPB isomers over the A\(_3\) and A\(_5\) zeolites occurred about 300 °C higher than that of IPBP isomers of the A\(_1\) zeolite. These results show that the isopropylation of BP proceeds through the consecutive mechanism, i.e., BP to IPBP, IPBP to DIPB, and DIPB to TriIPB, and that the channels of H-[Al]-SSZ-24 with relatively high amounts of acid such as A\(_3\) and A\(_5\) zeolites can enhance the formation of bulky TriIPB isomers. On the other hand, the formation of TriIPB isomers was quite negligible over H-MOR. These differences may be due to the slightly larger channels of H-[Al]-SSZ-24 zeolites compared to H-MOR.

The influence of \(\text{SiO}_2/\text{Al}_2\text{O}_3\) ratio of H-[Al]-SSZ-24 zeolites on the catalytic activity and selectivity for 4,4'-DIPB are shown in Fig. 7. The activities appeared at low temperatures, such as 150 °C over A\(_1\) and A\(_3\) zeolites, and the conversion reached 100% at 225–250 °C. The selectivity for 4,4'-DIPB was around 70% at 150–225 °C, and it decreased with an increase in reaction temperature. A similar change in activity and selectivity were observed over A\(_1\) zeolite, which has very small amount of acid sites. The catalytic activity appeared from 200 °C, and increased with the increase in reaction temperature. The selectivity for 4,4'-DIPB were around 75% at temperatures lower than 300 °C. The decrease in the selectivity occurred with the further increase in temperature. These high selectivities for 4,4'-DIPB in the level of 70–80% over A\(_1\), A\(_3\), and A\(_5\) zeolites mean that the formation of 4,4'-DIPB occurred inside the channels of H-[Al]-SSZ-24 zeolites, and that the channels can discriminate 4,4'-DIPB from other isomers in the transition state. The difference in temperature for decreasing the selectivity is due to the acid amount in the zeolites, and not to the change of the pore structure of the zeolite.

The influences of reaction temperature on the selectivity for DIPB over A\(_1\) and A\(_3\) zeolites, which have \(\text{SiO}_2/\text{Al}_2\text{O}_3\) ratio of 172 and 768, respectively, are also shown in Figs. 8 and 9. The selectivities for 4,4'-DIPB of bulk products were around 70% for both A\(_1\) and A\(_3\) zeolites: at the lower temperatures

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**Fig. 5. Solid \(^{11}\)B, \(^{27}\)Al, and \(^{29}\)Si MAS NMR spectra during the aluminatation of H-[Al]-SSZ-24 zeolites. \(^*\) shows spinning side band peaks.**
than 200 °C for A₃ zeolite, and lower than 300 °C for A₁ zeolite. However, the selectivities of 4,4'-DIPB decreased with increasing reaction temperatures over both zeolites, and the selectivities for 3,4'-DIPB increased at higher temperatures. The decrease in the selectivity started at 225–250 °C for the A₃ zeolite, and at 300–325 °C for the A₁ zeolite. These results suggest that H-[Al]-SSZ-24 zeolites have high shape-selectivity for the isopropylation of BP at moderate temperatures, although it is lower than that of H-MOR as previously discussed.³⁻⁸ However, quite different features were observed in the encapsulated products, i.e., the selectivity for 4,4'-DIPB in encapsulated products for A₃ zeolite was as high as those in bulk products below 250 °C, and it decreased rapidly at temperatures higher than 250 °C. These results means that isomerization of 4,4'-DIPB occurred over acid sites inside the channels and probably also at the external acid sites. On the other hand, the selectivity for 4,4'-DIPB for A₁ zeolite was as high as 70–80% even at higher temperatures, such as 300 °C, although the selectivity for 4,4'-DIPB in bulk products decreased at 325 °C. However, the selectivity for 4,4'-DIPB in encapsulated products were remained almost constant even at 325 °C. Therefore, the decrease in the selectivity for 4,4'-DIPB in bulk products over the A₁ zeolite is due to the isomerization at external acid sites. Thus, acid sites inside the channels of A₁ zeolite did not work as the catalysts of isomerization of 4,4'-DIPB because they have not enough amounts for the reaction. These
results also show that the channels of SSZ-24 zeolite are large enough for the isomerization of 4,4'-DIPB and that the isomerization of 4,4'-DIPB occurred both at the external and internal acid sites although it depends on acid amounts. In contrast, no isomerization of 4,4'-DIPB occurred at the internal acid sites over H-MOR.3–5 These selectivities for 4,4'-DIPB of SSZ-24 zeolites are in the similar level to those of SAPO-5 and MAPO-5 molecular sieves with the AFI topology,11,13–15 whereas the selectivity for 4,4'-DIPB is lower than those for H-MOR.4–8 The differences in the selectivity for 4,4'-DIPB are due to the structural difference between H-MOR and molecular sieves with AFI topology.

Fig. 9. The influence of reaction temperature on the selectivity for DIPB isomers in the isopropylation of BP over H-[Al]-SSZ-24 zeolite. Reaction conditions: zeolite: A1, 0.25 g; BP, 50 mmol; propene, 0.8 MPa; temperature: 150–275 °C; period, 4 h.

The influence of reaction time on the selectivities for isopropylates in the isopropylation of BP over A3 zeolite at 175 °C is shown in Fig. 10. The catalytic activity and the yield of isopropylates in the bulk products during the catalysis are shown in Fig. 10a. The yield of DIPB and TriIPB isomers increased with a decrease in that of the IPBP isomers. These results suggest the consecutive formation of isopropylates as discussed above. However, the selectivities for isopropylates in the encapsulated products shown in Fig. 10b indicate that the selectivities of isopropylates did not significantly vary during the catalysis. The selectivities of DIPB isomers were almost constant during the catalysis, and the selectivities for IPBP isomers decreased slightly with an increase in that for TriIPB isomers. These results show that the formation of DIPB and IPBP isomers occurred inside the pores, and the products formed inside the pores rapidly diffused out. The product distribution of the encapsulated products shows that the catalysis steadily occurs inside pores.

Figure 11 shows the influences of reaction period on the selectivities for IPBP and DIPB isomers in bulk and encapsulated products in the isopropylation of BP over A3 zeolite. The influences of the selectivities for IPBP and DIPB isomers in bulk products are shown in Fig. 11a. The selectivities for 4,4',3,4', and 3,3'-DIPB were almost constant during the catalysis; however, the selectivity for 4-IPBP decreased with an increase in the selectivity for 3-IPBP. These results suggest that 3-IPBP accumulated because of rapid consumption of the highly reactive 4-IPBP, and that the formation of 4,4'-DIPB occurred predominantly through 4-IPBP. These results mean that “product selectivity” is operated in the catalysis.1–5 Figure 11b shows the selectivities for 4,4'-DIPB and 4-IPBP were almost constant in the encapsulated products during the catalysis. These results suggest that the AFI channels can discriminate the transition state of 4,4'-DIPB from those of the other isomers resulting in the selective formation of the least bulky 4,4'-DIPB. It is worthy to note that the selectivity for
4-IPBP among IPBP isomers was as high as 80% in the encapsulated products during the catalysis. These results mean that the products rapidly diffuse inside the channels and that the shape-selective catalysis steadily occurs. The less bulky 4-IPBP can be accommodated easier than 3-IPBP inside channels, and thus, predominantly isopropylated to 4,4'-DIPB inside the channels. Similar exclusion of 3-IPBP was observed during the isopropylation of BP over H-MOR.10

The TG profiles of the zeolites used for the reactions are shown in Figs. 12 and 13. Figure 12 shows the influences of reaction temperature over A3 zeolite. Coke appeared on the zeolite used for the reaction even at 150 °C: the peaks at 200–300 °C are assigned to encapsulated products and the peaks at 500–600 °C to coke. The amounts of coke gradually increased at higher temperature, and encapsulated products disappeared. These results suggest that the channels of H-[Al]-SSZ-24 zeolites were gradually choked by the coke-deposition, and organic chemicals cannot come out of the channels by heating the zeolites for TG measurements. Figure 13 shows the influences of reaction time on coke formation over A3 zeolite at 175 °C. Coke appeared just after the reaction started; however, the amount of coke was almost constant during the catalysis. From these results, coke formation inside the channels was not severe towards the isopropylation of BP because acid sites are highly dispersed in the zeolites. Similar results were also observed in the isopropylation over highly dealuminated H-MOR.3–8

**Fig. 11.** The influence of reaction time on the selectivity for IPBP and DIPB isomers in the isopropylation of BP over H-[Al]-SSZ-24 zeolite. (a) Selectivity for IPBP and DIPB isomers in bulk products. (b) Selectivity for IPBP and DIPB isomers in encapsulated products. Reaction conditions: see Fig. 10. Legends: DIPB isomers: □, 4,4'-; ■, 3,4'-; ▲, 3,3'-; IPBP isomers: ○, 4-; △, 3-; ⊿, 2-.

**Fig. 12.** The influence of reaction temperature on TG profiles of the zeolite used for the isopropylation of BP. Reaction conditions: see Fig. 8.

**Fig. 13.** The influence of reaction time on TG profiles of the zeolite used for the isopropylation of BP. Reaction conditions: see Fig. 10.
on catalytic activity and the selectivity for 4,4'-di-s-butylbiphenyl (4,4'-DSBB) and 4,4'-di-t-butylbiphenyl (4,4'-DTBB) in the s- and t-butylation of BP over A3 zeolite. Although the catalytic activities were low, s- and t-butylation of BP yielded selectively the least bulky products, 4,4'-DIPB. These molecular sieves have straight channel with similar pore entrance: 0.72 × 0.72 nm for SAPO-5, 0.56 × 0.82 nm for H-[Al]-SSZ-31, and 0.72 × 0.75 nm for CIT-5.

The selectivity for 4,4'-DIPB in encapsulated DIPB isomers over H-[Al]-SSZ-24 zeolite was influenced by the SiO2/Al2O3 ratio, i.e. the amounts of acid sites. The selectivity decreased at higher temperatures during the isopropylation of BP over the zeolites with high acid amounts. In these zeolites, the isomerization of 4,4'-DIPB occurs at internal acid sites because the channels are large enough to allow the isomerization of 4,4'-DIPB. However, the isomerization of 4,4'-DIPB did not occur inside the channels of H-[Al]-SSZ-24 zeolites with high SiO2/Al2O3 ratio, whereas a decrease in the selectivity for 4,4'-DIPB in the bulk products was observed due to isomerization at external acid sites. From these considerations, we can conclude that the internal and external acid sites of H-[Al]-SSZ-24 zeolites are active in the isomerization of 4,4'-DIPB resulting in the decrease in the selectivity for 4,4'-DIPB in the isopropylation of BP. These features over H-[Al]-SSZ-24 zeolites are quite different from those of H-MOR: no isomerization occurred inside the pore of H-MOR because of the steric restriction. A similar decrease in the selectivity for 4,4'-DIPB occurred for MAPO-5 (M: Mg and Zn) with AFI topology. However, no isomerization of 4,4'-DIPB was found in the encapsulated products for SAPO-5 although it has AFI topology. This may be due to its weak acidity.

There is another mechanism for the decrease in the selectivity for 4,4'-DIPB in the encapsulated products due to the change of pore structure of H-[Al]-SSZ-24 zeolites. A fluctuation in the channel width at higher temperatures could cause a decrease in the steric restriction of the transition state to form 4,4'-DIPB resulting the decrease in the shape-selective nature of H-[Al]-SSZ-24 zeolites. However, this mechanism is not probable because A3 zeolite had high selectivity for 4,4'-DIPB.
even at 300 °C and because the isomerization of 4,4′-DIPB did not occur even at 325 °C.

The selectivity for the least bulky 4,4′-dialkylbiphenyl were increased in the order: 4,4′-DIPB < 4,4′-DSBB < 4,4′-DTBB. These differences reflect the differences in steric constraint at the transition states inside the channels, and the predominance of the least bulky products increases with the bulkiness of the alkylating agent.

Conclusion

H-[Al]-SSZ-24 zeolites with AFI topology were synthesized from [B]-SSZ-24 zeolites, and applied for the alkylation of BP. The alumination enhanced the catalytic activity. Shape-selective formation of 4,4′-DIPB occurred at moderate temperature; however, the selectivity for 4,4′-DIPB decreased with an increase in the reaction temperature. Isomerization of 4,4′-DIPB occurred at higher temperatures over internal and external acid sites of the zeolites when there are enough acid sites inside the channels. However, no isomerization was observed inside the channels of the zeolite with high SiO₂/Al₂O₃ ratio although isomerization occurred at the external acid sites. These results suggest that the AFI channels can discriminate 4,4′-DIPB from the other DIPB isomers at their transition states and that the channels allowed the isomerization of 4,4′-DIPB at higher temperatures.

H-[Al]-SSZ-24 zeolites gave lower selectivity for 4,4′-DIPB than H-MOR zeolites. These differences of H-[Al]-SSZ-24 zeolites and H-MOR are due to the pore structures. The former zeolite has a slightly larger channels than the latter, and the discrimination of the transition states of 4,4′-DIPB from other bulkier isomers by the former zeolite is looser than that by the latter.

The s- and t-butylations of BP yielded almost selectively the least bulky products, 4,4′-DSBB and 4,4′-DTTB over H-[Al]-SSZ-24 zeolites, and the selectivities were higher than those of the isopropylation. These differences in the selectivity for 4,4′-dialkylbiphenyl show that the shape-selective catalysis occurred inside the channels, and governed by steric constraints of transition states.

Further aspects on the influences of the shape-selective catalysis on the zeolite structures are under investigation. The details will be discussed in near future.

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References