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Isopropylation of naphthalene over H-mordenite, H-Y, and H-beta zeolites: Roles of isopropylnaphthalene isomers

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Abstract−Isopropylation of naphthalene (NP) was examined over H-mordenite (MOR), H-Y zeolite (FAU), and H-Beta zeolite (BEA) in order to elucidate roles of isopropylnaphthalene (IPN) isomers during the catalysis. 2-IPN was the predominant isomer over MOR and works as a precursor for the selective formation of β,β-DIPN, particularly, 2,6-DIPN. In contrast, 1-IPN was predominant (with 2-IPN as a minor isomer) over FAU and BEA at low temperatures; dialkylation accompanied by the consumption of 1- and 2-IPN led to predominant formation of α,α- and α,β-DIPN. The formation of β,β-DIPN from 2-IPN was enhanced at higher temperatures. Bulky transition states of 1-IPN in IPN isomers and α,α- and α,β-DIPN among DIPN isomers were hindered by the interaction with MOR channels, resulting in the selective formation of β,β-DIPN, particularly 2,6-DIPN through the less bulky 2-IPN. FAU and BEA allow the formation of α,α- and α,β-DIPN from both of 1- and 2-IPN isomers because their channels are too large to exclude bulky transition states. The catalysis over FAU and BEA occurred under kinetic control at lower temperatures, and thermodynamic control also participates at higher temperatures.

Key words: Isopropylation, Naphthalene, Isopropylnaphthalene, Diisopropylnaphthalene, Mordenite, Y Zeolite, Beta Zeolite

INTRODUCTION

The isopropylation of polynuclear aromatic hydrocarbons, such as naphthalene (NP) and biphenyl (BP), is one of the targets for shape-selective catalysis over zeolites [1,2]. Steric restriction of the transition state of the products is an important factor in determining the products in these catalyses. Among the zeolites, H-mordenite (MOR) gives the highest selectivities for 2,6-diisopropylnaphalene (2,6-DIPN) [3-14]. The catalyses over MOR exclude the bulky transition states by steric interaction with the channels, resulting in predominant formation of the least bulky 2,6-DIPN. In contrast, the catalyses over zeolites such as H-Y zeolite (FAU) and H-Beta zeolite (BEA) [12-20], and mesoporous materials such as MCM-41, MCM-48, and SBA-1 [19,21-23] with large pores and channels, were non-selective against 2,6-DIPN because their pores and channels are too large to exclude the bulky DIPN isomers. The catalyses over these zeolites and mesoporous materials occur under kinetic control and/or under thermodynamic control depending on the reaction conditions [2,16].

It is crucial to elucidate the roles of intermediates, particularly isopropylnaphthalene (IPN) isomers, during the catalysis in order to understand the mechanism of shape-selective catalysis. In this paper, we discuss the roles of IPN isomers during the isopropylation of NP over MOR, FAU, and BEA on the basis of yields and selectivities of IPN and DIPN isomers.

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EXPERIMENTAL SECTION

1. Zeolites

MOR (SiO_2/Al_2O_3=10, 15, 20, 25, 30, 73, 110, 128, 206, and 220; Tosoh Corporation) [24], and FAU (SiO_2/Al_2O_3=30; Zeolyst CV) were obtained commercially. BEA (SiO_2/Al_2O_3=110) samples were synthesized according to the literature [25]. All zeolites were used in the H-form.

2. Alkylation of NP

Alkylation of NP was carried out in a 100-mL SUS-316 autoclave. Typical conditions for the isopropylation were: NP 6.42 g (50 mmol), catalyst 0.25 g, reaction temperature 150-325 °C, with a 4 h operating time under 0.8 MPa of propene pressure. The autoclave containing NP and the catalyst was flushed with nitrogen before heating. After the reaction temperature was reached, propene was introduced to the autoclave, and the reaction was started with agitation. Propene pressure was maintained as constant throughout the reaction. After the autoclave was cooled, the catalyst was filtered off and washed well with toluene. The liquid products were analyzed with a Shimadzu gas chromatograph GC-14A or GC-18A equipped with TC-17 (25 m×0.25 mm; GL Sciences) and/or HP-INNOWax (60 m×0.25 mm; Agilent Technologies) capillary columns. These products were also identified by using a Shimadzu GC-MS 5000 Gas Chromatograph-Mass Spectrometer using the above columns.

Analysis of encapsulated products in the catalyst used for the reac-

tion was typically carried out as follows: the catalyst was separated by filtration, washed well with 100 mL of acetone, and dried at 110 °C for 12 h. The catalyst (50 mg) was carefully dissolved using 3 mL of aqueous hydrofluoric acid (47%) at room temperature. The resulting solution was neutralized with solid potassium carbonate, and the organic layer was extracted three times with 20 mL of dichloromethane. After removal of the solvent *in vacuo*, the residue was dissolved in 5 ml of toluene, and then analyzed according to the procedure used for the bulk products.

The yields of each product were calculated on the basis of the amount of starting NP, and the selectivities for each IPN and DIPN isomer are expressed based on the total amounts of the IPN and DIPN isomers. α,α-, α,β-, and β,β-DIPN express the groups of the DIPN isomers: (1,4- and 1,5-), (1,3-, 1,6-, and 1,7-), and (2,6- and 2,7-), respectively.

RESULTS AND DISCUSSION

1. MOR

Fig. 1(a) shows the influence of SiO_2/Al_2O_3 ratio of MOR on the yields of IPN and DIPN isomers in the isopropylation of NP (reaction temperature: 250 °C; propene pressure: 0.8 MPa). Catalytic activities of MOR, expressed by reaction time reaching 80% NP conversion, were significantly decreased with the increase in SiO_2/Al_2O_3 ratio. MOR with low SiO_2/Al_2O_3 ratio (10-20) took long time for 80% NP conversion, yielding 2-IPN as a primary isomer and 1-IPN as a minor isomer. The yields of 2-IPN were increased with the ratio, accompanying those of 1-IPN, and maximized at around 50. 2-IPN was predominant over 1-IPN over all ratios. The predominant formation of α,α- and α,β-DIPN was observed over the MOR with the low ratios. The yields of β,β-DIPN were enhanced with the increase in the ratio from 10-25, and saturated with further increase in the ratio, even for 220. These results indicate that 2-IPN is the primary isomer for the formation of β,β-DIPN: 2,6- and 2,7-DIPN, and that the intrinsic catalytic properties of MOR, particularly shape-selective nature, appear in the isopropylation of NP after the dealumination. Similar features of the dealumination of MOR were also found in the isopropylation of BP [1,2,26].

The selectivities for β,β- and 2,6-DIPN were significantly enhanced with the increase in the SiO_2/Al_2O_3 ratio as shown in Fig. 1(b). The selectivities for β,β- and 2,6-DIPN over un-dealuminated MOR (SiO_2/Al_2O_3 = 10) were only 46% and 29%, respectively. Other isomers were α,α- and α,β-DIPN in the selectivities 47% and 7%, respectively. The selectivities for β,β-DIPN, particularly 2,6-DIPN were significantly increased with the decrease in the selectivities for α,α- and α,β-DIPN by the increase of the ratio from 10 to 20, and further enhanced by the dealumination despite of the decrease of acid sites. They finally reached 91% and 65% for β,β- and 2,6-DIPN, respectively, in the shortest reaction time over highly dealuminated MOR with the ratio of 220. The selectivities for 2-IPN were similarly increased over MOR with SiO_2/Al_2O_3 ratio from 10 to 25, and remained constant over MOR with the higher ratios. Furthermore, they were in almost the same levels as those for β,β-DIPN. The selectivities for 2,6-DIPN in encapsulated products remained higher than those in bulk products: 23% and 50%, respectively, for SiO_2/Al_2O_3=10, and 63% and 70% for SiO_2/Al_2O_3=220 (reaction temperature: 250 °C; reaction time: 4 h) [6]. These results indicate that the formation of β,β-DIPN: 2,6- and 2,7-DIPN occurs from 2-IPN in the channels, and that MOR channels moderately favor 2,6-DIPN over 2,7-DIPN due to the difference in bulkiness of both isomers. Moreover, α,α- and α,β-DIPN forms at external acid sites of MORs with the low SiO_2/Al_2O_3 ratio.

Unusual features in the isopropylation of NP over MOR with low SiO_2/Al_2O_3 ratio are due to the deactivation by rapid coke deposition in MOR channels during the reaction. Fig. 2 shows the TG profiles of the catalysts used for the reaction. The coke-deposition, which appeared at 500-700 °C, was decreased by the dealumination because acid sites, on which coke deposits, were effectively eliminated [27-30]. External acid sites of MOR with the low SiO_2/Al_2O_3 ratio lead to non-selective reactions such as the formation of α,α- and α,β-DIPN because the most of the internal acid sites are rapidly deactivated by coke deposition. However, the dealumination

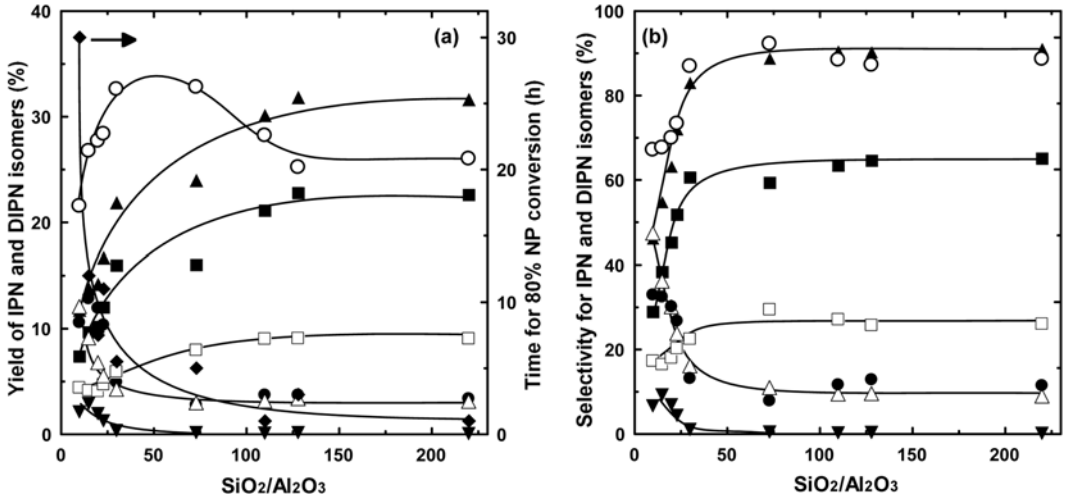

Fig. 1. Influence of SiO_2/Al_2O_3 ratio of MOR on the isopropylation of NP. (a) Yields of IPN and DIPN isomers. (b) Selectivities for IPN and DIPN isomers. Reaction conditions: NP: 50 mmol; MOR (SiO_2/Al_2O_3=10-206): 0.25 g; reaction temperature: 250 °C; propene pressure: 0.8 MPa. Legend: ○: 2-IPN; ●: 1-IPN; ■ : 2,6-DIPN; □: 2,7-DIPN; ▲: β,β-DIPN; △: α,β-DIPN; ▼: α,α-DIPN; ◆: Time for 80% NP conversion.

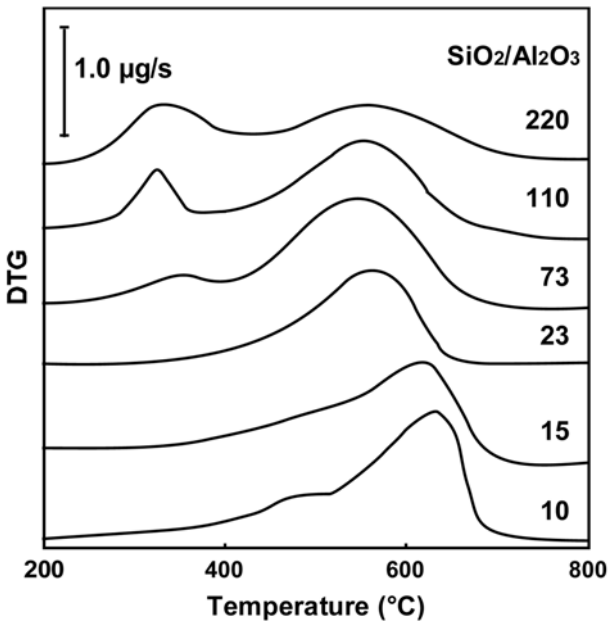

Fig. 2. Thermogravimetric (TG) profiles of MOR used for the reaction. TG conditions: MOR: 10 mg; programmed rate: 10 °C/min under air atmosphere. Reaction conditions: see Fig. 1.

enhances the alkylation at the internal acid sites due to the decrease in coke-deposition, yielding less bulky products: 2-IPN and *β,β*-DIPN, particularly 2,6-DIPN. Based on these results, MOR with SiO_2/Al_2O_3 of 128 and 220 was used as a typical catalyst for further investigation.

Fig. 3(a) shows the influence of time course on yields of IPN and DIPN in the isopropylation over MOR (SiO_2/Al_2O_3=220; reaction temperature: 250 °C; propene pressure: 0.8 MPa). 2-IPN was the primary isomer at the early stage, and then, the yield of 2-IPN was decreased with the increase in the NP conversion, while the yields of 1-IPN remained almost constant except in the early stages. Predominant formation of 2-IPN is due to the exclusion of bulky 1-IPN from MOR channels. Preferential disappearance of 2-IPN also indicates that 2-IPN is a primary precursor of *β,β*-DIPN, particularly 2,6-DIPN.

The selectivities for DIPN isomers remained constant during the prolonged reaction time as shown in Fig. 3(b). The selectivities for *β,β*- and 2,6-DIPN were 90% and 65%, respectively, during the reaction, although *α,β*-DIPN was accompanied less than 10% in selectivities. The selectivities for 2-IPN were also higher than 90% at the early stage; however, they decreased with prolonged reaction time. These features correspond to the preferential formation of 2-IPN from NP due to steric limitation of MOR channels, and the consequent formation of *β,β*-DIPN occurs *via* 2-IPN.

Fig. 4(a) shows the influence of reaction temperature on the yields of IPN and DIPN isomers (SiO_2/Al_2O_3=128, reaction temperature: 200-325 °C; propene pressure: 0.8 MPa; reaction time: 4 h). 2-IPN were the primary product at low temperatures, and the yield of 2-IPN was decreased with the increase in temperature, while the yields of 1-IPN remained almost constant even at high temperatures. The yields of *β,β*-DIPN, particularly 2,6-DIPN, were increased with the increase in reaction temperatures, accompanying the decrease in that of 2-IPN, and were maximal around at 275-300 °C. These results suggest that the isopropylation occurred by a consecutive reaction mechanism: NP to 2-IPN, and 2-IPN to *β,β*-DIPN: 2,6- and 2,7-DIPN at moderate temperatures. Then, the decrease in the yields of *β,β*-DIPN, the decrease in the yields of 2,6-DIPN and the saturation of those of 2,7-DIPN, were observed with further increase in reaction temperatures, accompanying the increase in the yields of 2-IPN. The changes of the yields of *β,β*-DIPN are due to the de-alkylation to 2-IPN and the isomerization of 2,6-DIPN to 2,7-DIPN. Further alkylation to triisopropylnaphthalene (TriIPN) and tetraisopropylnaphthalene (TetraIPN) isomers were also found in small amounts at higher temperatures above 300 °C (see Fig. S1 in Appendix).

As shown in Fig. 4(b), the selectivities for *β,β*- and 2,6-DIPN were around 85% and 65%, respectively, with gradual decrease in the selectivities for 2-IPN at low and moderate temperatures. These features indicate that the preferential formation of 2-IPN from NP,

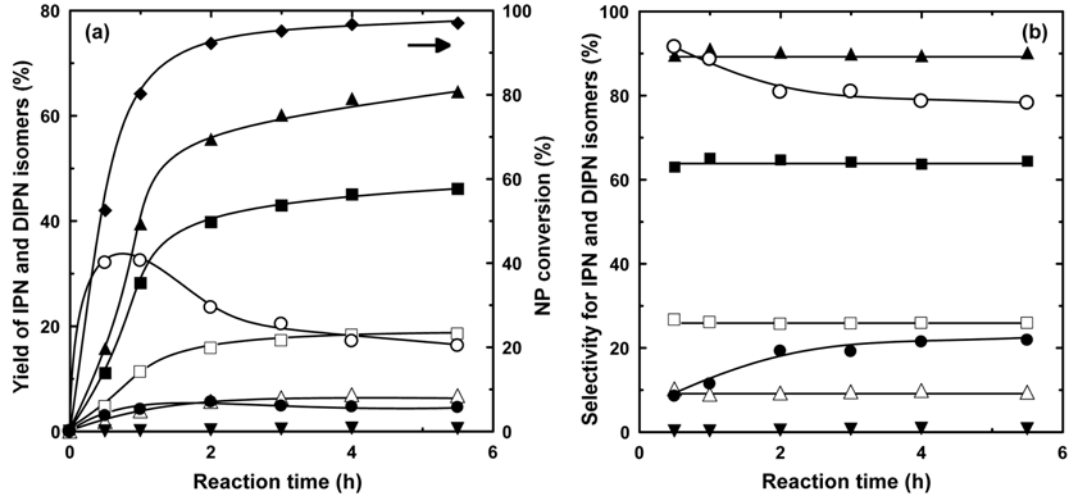

Fig. 3. Influence of reaction time on the isopropylation of NP over MOR. (a) Yields of IPN and DIPN isomers. (b) Selectivities for IPN and DIPN isomers. Reaction conditions: NP: 50 mmol; MOR (SiO_2/Al_2O_3=128): 0.25 g; reaction temperature: 250 °C; propene pressure: 0.8 MPa. Legend: ○: 2-IPN; ●: 1-IPN; ■ : 2,6-DIPN; □: 2,7-DIPN; ▲: *β,β*-DIPN; △: *α,β*-DIPN; ▼: *α,α*-DIPN; ◆: NP conversion.

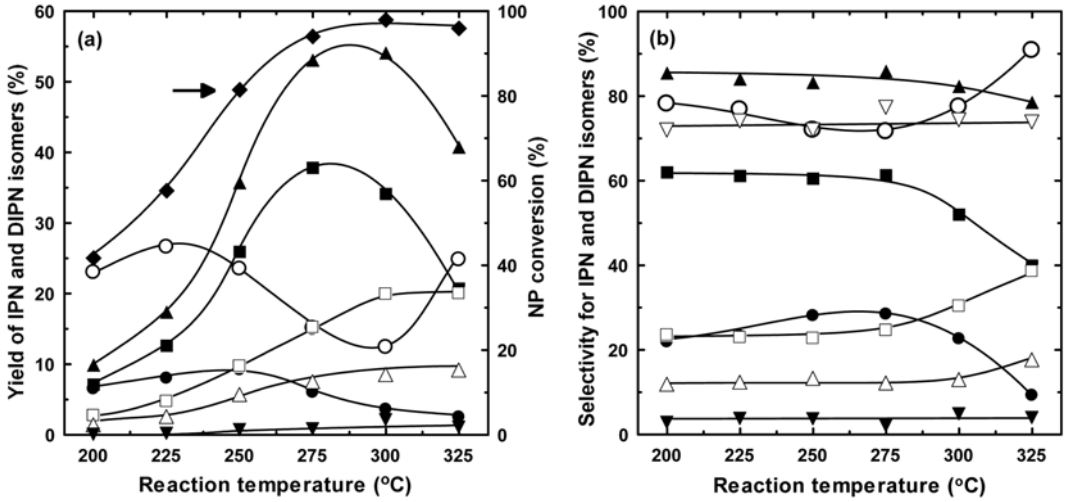

Fig. 4. Influence of reaction temperature on the isopropylation of NP over MOR. (a) Yields of IPN and DIPN isomers. (b) Selectivities for IPN and DIPN isomers. Reaction conditions: NP: 50 mmol; MOR (SiO_2/Al_2O_3=128): 0.25 g; reaction time: 4 h; propene pressure: 0.8 MPa. Legends: Legend: ○: 2-IPN; ●: 1-IPN; ■ : 2,6-DIPN; □: 2,7-DIPN; ▲: *β,β*-DIPN; △: *α,β*-DIPN; ▼: *α,α*-DIPN; ▽: 2,6-DIPN in encapsulated products; ◆: NP conversion.

and that the selective formation of *β,β*-DIPN occurs from 2-IPN inside the MOR channels under their steric limitation. However, the selectivities for 2,6-DIPN began to decrease at around 275 °C: 61% for 275 °C and 43% at 325 °C, accompanying the increase in the selectivities for 2,7-DIPN. Meanwhile, the selectivities for *β,β*-DIPN gradually decreased: 86% for 275 °C and 79% at 325 °C. These results show that the decrease in the selectivities for 2,6-DIPN is principally due to the isomerization of 2,6-DIPN to 2,7-DIPN because 2,6- and 2,7-DIPN have almost the same stabilities in their equilibrium at high temperatures. The selectivities for 2-IPN were rapidly increased again at high temperatures as 325 °C, accompanying rapid increase in the selectivity for 1-IPN. This is due to the de-alkylation of *β,β*-DIPN to 2-IPN.

Fig. 4(b) also shows the selectivities for 2,6-DIPN in encapsulated products. They remained constant in the range from 200 to 325 °C. These results show that *β,β*-DIPN: 2,6- and 2,7-DIPN are formed inside the MOR channels, and that the isomerization of 2,6-DIPN to 2,7-DIPN occurs at external acid sites. It is unclear why these selectivities were slightly higher than the bulk products. One possible explanation is that there are different steric restrictions due to the depth of the channels: active sites near the pore mouth should give lower restriction compared with the deeper ones, resulting in higher selectivities for 2,6-DIPN in encapsulated products. Further studies are necessary for clarification of the discrepancies.

Fig. 5(a) shows the influence of the catalyst amounts (NP/MOR ratio (mmol/g)) on the yield of IPN and DIPN isomers (SiO_2/Al_2O_3= 128; reaction temperature: 250 °C; reaction time: 4 h). 2-IPN was the primary IPN isomer at the high ratio, *i.e.*, in the presence of a

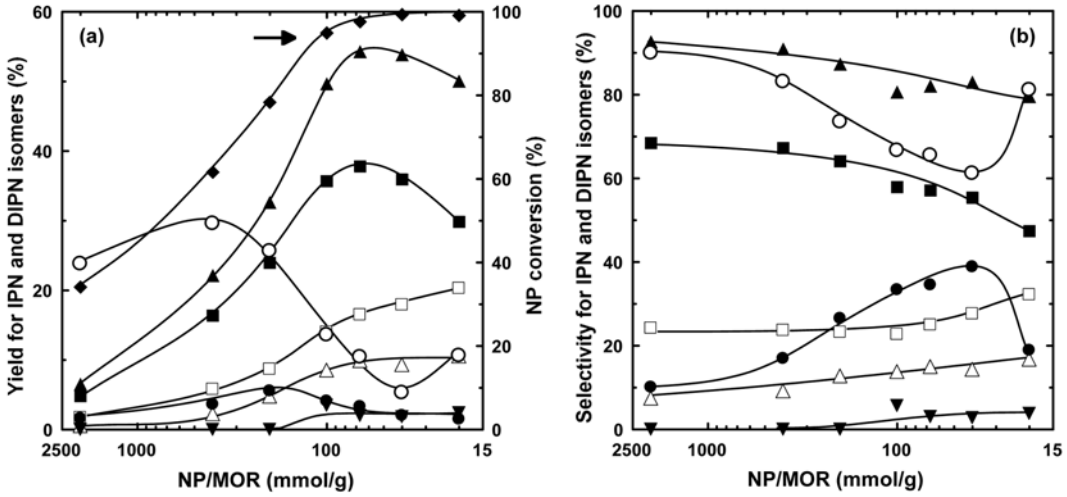

Fig. 5. Influence of catalyst amount (NP/MOR ratio) on the isopropylation of NP. (a) Yields of IPN and DIPN isomers. (b) Selectivities for IPN and DIPN isomers. Reaction conditions: NP: 50 mmol; MOR (SiO_2/Al_2O_3=128): 10-400 mg; NP/MOR: 20-2,000 mmol/g; reaction temperature: 250 °C; reaction time: 4 h; propene pressure: 0.8 MPa. Legends: see Fig. 3.

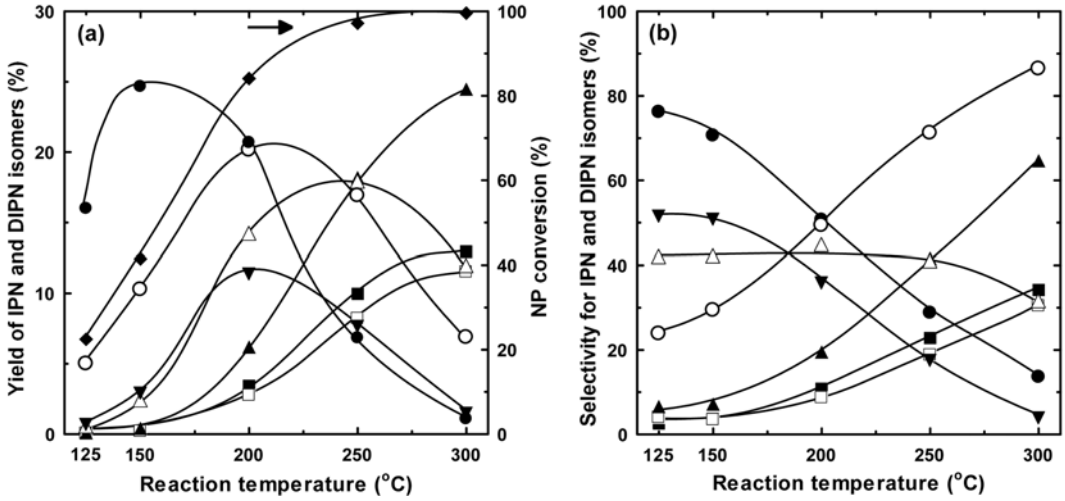

Fig. 6. Influence of reaction temperature on the isopropylation of NP over FAU. (a) Yields of IPN and DIPN isomers. (b) Selectivities for IPN and DIPN isomers. Reaction conditions: NP: 50 mmol; FAU (SiO_2/Al_2O_3=30): 0.25 g; reaction time: 4 h; propene pressure: 0.8 MPa. Legends: see Fig. 3.

small amount of catalyst. The yields of DIPN isomers, particularly *β,β*-DIPN, were increased with decreases in the ratio, *i.e.*, by using a large amount of catalyst, accompanying the decrease in the yield of 2-IPN. These features show that 2-IPN is a primary precursor of *β,β*-DIPN: 2,6- and 2,7-DIPN. The yields of *β,β*-DIPN reached maxima in the range of 75-100 of the ratio, and then decreased with further decrease in the ratio accompanying the increase in the yield of 2-IPN; however, the yields of *α,α*- and *α,β*-DIPN increased at low ratios, *i.e.*, by using large amount of catalyst. The increase in the yield of 2-IPN and the decrease in the yield of *β,β*-DIPN suggest the de-alkylation of *β,β*-DIPN, particularly 2,6-DIPN, at external acid site by using large amount of catalyst.

As shown in Fig. 5(b), the selectivities for 2,6-DIPN were gradually decreased with the decrease in NP/MOR ratio, *i.e.*, the increase in catalyst amount: 68% at 2000, 58% at 100, and 47% at 20 of the ratio, accompanying the increase in the selectivities for 2,7-DIPN. The selectivities for 2-IPN were rapidly decreased with the increase in catalyst amount, which correspond to the predominant consumption of 2-IPN to form *β,β*-DIPN, particularly, 2,6-DIPN, inside the MOR channels. The decrease in the selectivities for 2,6-DIPN means that the isomerization of 2,6-DIPN to 2,7-DIPN occurs at external acid sites. Meanwhile, the selectivities for *β,β*-DIPN were gradually decreased with the decrease in NP/MOR ratio: 93% at 2000 and 80% at 100 with the increase in the selectivities for *α,β*-DIPN (7% at 2000 and 17% at 100) and *α,α*-DIPN: (0% at 2000 and 4% at 100). A significant increase in the selectivity for 2-IPN was observed at 20 of NP/MOR ratio, probably due to the de-alkylation of *β,β*-DIPN. These results indicate that the external acid sites are also active for non-selective formation of *α,β*-DIPN and de-alkylation of *β,β*-DIPN.

These results obtained from the different reaction parameters (reaction time, reaction temperature, and catalyst amount) in the isopropylation of NP over MOR indicate that 2-IPN was the primary isomer for the formation of *β,β*-DIPN in the MOR channels by a consecutive mechanism: NP to 2-IPN; 2-IPN to *β,β*-DIPN under moderate reaction conditions. The MOR channels restrict the transition state to form the bulky isomers, resulting in the selective formation of less bulky isomers (2-IPN in IPN isomers and *β,β*-DIPN among DIPN isomers). Moreover, MOR favored 2,6-DIPN over 2,7-DIPN, the second least bulky isomer among DIPN isomers according to the difference of their bulkiness, in particular, at the their transition states.

2. FAU

The catalytic features of FAU (SiO_2/Al_2O_3=30) were quite different from those of MOR as shown in Fig. 6. The high catalytic activities appeared at temperatures as low as 125 °C, and higher isopropylated products, TriIPN and TetraIPN isomers, were observed in large amounts as well as IPN and DIPN with the increase in temperatures (see also Fig. S2 in Appendix).

Fig. 6(a) shows the influence of reaction temperature on yields for IPN and DIPN isomers over FAU zeolites. Product distribution was highly dependent on reaction temperature: the isopropylation did not operate by shape-selective catalysis but under kinetic and/or thermodynamic controls. Thermodynamically unstable 1-IPN, which yields under kinetic control by electrophilic attack of isopropyl cation against the electron-rich *α*-position, was the primary isomer at low temperatures. The yield of 1-IPN was increased with reaction temperatures and reached a maximum at 150-175 °C but decreased with a further increase in temperature. Thermodynamically stable 2-IPN was a minor isomer at 125-175 °C; however, the yield of 2-IPN was increased with a maximum at 200-225 °C, and then decreased with further increase in reaction temperature. 2-IPN was more predominant than 1-IPN at higher temperatures because of the differences in the stabilities of both isomers.

The yields of *α,α*- and *α,β*-DIPN isomers were increased with the increase in reaction temperature. The yields of *α,α*-DIPN were maximized, at around 200 °C, and then, rapidly decreased with the increase in reaction temperatures. The yields of *α,β*-DIPN reached maxima at 250 °C. Then, further increase in reaction temperature enhanced the formation of *β,β*-DIPN with decrease in *α,α*- and *α,β*-DIPN although *α,β*-DIPN was still predominant at high temperature as 300 °C. This increase and decrease of *α,α*- and *α,β*-DIPN

isomers is reflected the yields of 1- and 2-IPN isomers. The changes of the IPN and DIPN isomers indicate that kinetic control is operating at lower temperatures, resulting in the formation of α,α- and α,β-DIPN, and that the participation of thermodynamic control at higher reaction temperature enhances the formation of β,β- and α,β-DIPN because the stabilities of DIPN isomers increase in the order: α,α-DIPN<α,β-DIPN<β,β-DIPN. Under these conditions, 2,6- and 2,7-DIPN were formed in almost the same amounts because these isomers have similar thermodynamic stabilities and reactivities of the β-position in 2-IPN.

The influence of reaction temperature on the selectivities for IPN and DIPN isomers is shown in Fig. 6(b). The selectivities of IPN and DIPN isomers correspond well to their yields. The decrease in the selectivities for 1-IPN occurs with the increase in the reaction temperature, with the compensation of the selectivities for 2-IPN. The selectivities for α,α- and α,β-DIPN were almost in the similar level and those for β,β-DIPN were also low at low temperatures. However, the selectivities for β,β-DIPN were increased with the increase in reaction temperatures, accompanying the decrease in those for the most unstable α,α-DIPN. Moreover, the selectivities for α,β-DIPN remained constant until 250 °C, and decreased the selectivities for α,β-DIPN with further increase in temperature. These results can be summarized as follows. The most bulky and unstable α,α-DIPN were predominantly obtained at lower temperatures, the intermediately bulky and stable α,β-DIPN was increased with increasing temperature, and finally the least bulky and most stable β,β-DIPN increased at higher temperatures: kinetic control operates at low temperatures, yielding predominantly, 1-IPN in IPN isomers, and α,α- and α,β-DIPN among DIPN isomers; however, thermodynamic control participates in the catalysis with an increase in reaction temperatures, resulting in the increase in the formation of 2-IPN and β,β-DIPN. Moreover, there are possibilities of the formation of 2-IPN from 1-IPN and β,β-DIPN from α,α- and α,β-DIPN through the isomerization of α,α- and α,β-DIPN by de-alkylation-alkylation as well as direct formation from 2-IPN.

Previously, Toba and co-workers described changes of the selectivities of DIPN isomers by a prolonged reaction time at 250 °C [1,4]. Initially, α,α-DIPN is primarily obtained, then transferred to α,β-DIPN, and finally β,β-DIPN became predominant after prolonged reaction time. These results indicate that kinetic control operates at the initial stages, resulting in predominant formation of 1,4-DIPN, and that the formation of 1,3-DIPN is enhanced by the participation of thermodynamic control. Finally, the most stable β,β-DIPN becomes a predominant product in the almost equal amounts of 2,6- and 2,7-DIPN.

These results indicate that the active acid sites in FAU channels are much less sterically hindered than those in MOR channels. The catalyses are operating under kinetic and/or thermodynamic controls because FAU channels are large enough for the formation of bulky products.

3. BEA

The catalytic features of BEA (SiO_2/Al_2O_3=110) are similar to those of FAU, but not to those of MOR as shown in Fig. 7. The higher products, particularly TriIPN, were observed in large amounts as well as IPN and DIPN at higher temperatures (see also Fig. S3 in Appendix).

Fig. 7(a) shows the influence of reaction temperature on the yields of IPN and DIPN isomers over BEA. For IPN isomers, 1-IPN was the primary isomer at low temperatures. Its yield was increased with reaction temperature, reached a maximum at 200 °C, and then rapidly decreased with further increase of reaction temperature. The yield of 2-IPN, which is a minor at lower temperatures, was also increased with the increase in the temperature and reached a maximum at 225-275 °C. Then, it gradually decreased with a further increase in reaction temperature. 2-IPN was predominant over 1-IPN at higher temperatures.

The alkylation of IPN isomers to α,α- and α,β-DIPN was gradually increased with the increase in reaction temperature and maximized at 250 °C. α,β-DIPN was predominant over α,α-DIPN at all temperatures. The yields of β,β-DIPN were enhanced with the increase in reaction temperature accompanying the decrease in those in α,α- and α,β-DIPN, although α,β-DIPN was still predominant

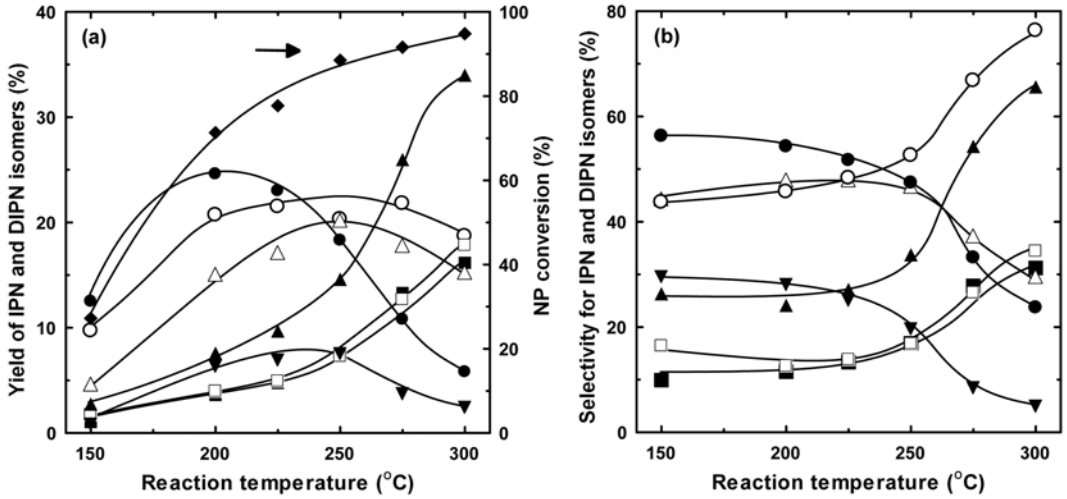

Fig. 7. Influence of reaction temperature on the isopropylation of NP over BEA. (a) Yields of IPN and DIPN isomers. (b) Selectivities for IPN and DIPN isomers. Reaction conditions: NP: 50 mmol; BEA (SiO_2/Al_2O_3=110): 0.25 g; reaction time: 4 h; propene pressure: 0.8 MPa. Legends: see Fig. 3.

over α,α-DIPN even at 300 °C. The increase in the yields of α,α- and α,β-DIPN corresponds to the increase in the yields of 1- and 2-IPN, respectively, at lower temperatures where the catalysis occurs under kinetic control. Further increase in reaction temperature enhanced the formation of β,β-DIPN, accompanying the decrease of α,α- and α,β-DIPN. These results indicate that 1- and 2-IPN are precursors of α,α- and α,β-DIPN at lower temperatures, and that the formation of β,β-DIPN occurs under thermodynamic control at high temperatures.

The influence of reaction temperature on the selectivities for IPN and DIPN isomers is shown in Fig. 7(b). The changes of the selectivities of these isomers began at around 250 °C. The selectivities for 1- and 2-IPN remained almost constant below 250 °C; however, those for 2-IPN rapidly increased at higher temperatures with the decrease in those for 1-IPN. The selectivities for α,α- and α,β-DIPN also remained constant under low and moderate temperatures. The increase in reaction temperature above 250 °C enhanced the selectivities for β,β-DIPN. These results suggest that the catalyses are principally operating under kinetic control at low and moderate temperatures below 250 °C, and that the participation of thermodynamic control is enhanced at higher temperatures. The isomerization of 1-IPN to 2-IPN also occurs during the catalysis at high temperatures, and both isomers act as the precursor of DIPN isomers. Moreover, there are possibilities of the formation of β,β-DIPN through the isomerization of α,α- and α,β-DIPN by de-alkylation-alkylation as well as direct formation from 2-IPN.

These results indicate that the channels of BEA have similar reaction circumstances to FAU, and are much larger than those of MOR. As a result, BEA channels are large enough for the shape-selective isopropylation of NP.

4. Mechanistic Aspects of the Roles of Isopropylnapthalene Isomers

The catalytic features of MOR in the isopropylation of NP were quite different from those of FAU and BEA as discussed in previous chapters. These differences appear by the difference of the channel structures of the zeolites [31]. MOR has a two-dimensional diagonal pore system: 12-MR straight channels (0.65×0.70 nm) and 8-MR side pockets (0.26×0.57 nm). FAU has three-dimensional channels with entrances (0.74 nm) and super cages (1.3 nm). BEA also has three-dimensional with entrances (0.66×0.71 nm, 0.56×0.56 nm). The latter two zeolites have large reaction sites at the crossing sites of their channels. These differences of the zeolites afford the different steric interaction of the intermediate at the transition states in the isopropylation of NP. Particularly, 1- and 2-IPN play different roles in their formation and following isopropylation to DIPN isomers among the zeolites. Here, we would like to discuss the roles of IPN isomers in the isopropylation of NP over MOR, FAU, and BEA on the basis of yields and selectivities of IPN and DIPN isomers.

2-IPN was a primary product in the isopropylation over MOR. The selectivities for β,β-DIPN were more than 90% over MOR under moderate reaction conditions, and those for α,β-DIPN less than 10%. These results indicate that selective formation of β,β-DIPN occurs *via* 2-IPN from NP at internal acid sites in the 12-MR straight channels of MOR by a *restricted transition mechanism* and by a *reactant selectivity mechanism*. Thus, the MOR channels exclude transition states to the bulky isomers (1-IPN in IPN isomers, and α,α- and α,β-DIPN among DIPN isomers), resulting in the selective formation of less bulky isomers: 2-IPN in IPN isomers, and β,β-DIPN among DIPN isomers. MOR favored 2,6-DIPN over 2,7-DIPN, the second least bulky isomer among DIPN isomers, in the selectivities, 65% and 30%, respectively. These results mean that the MOR channels moderately differentiate 2,6- and 2,7-DIPN of β,β-DIPN isomers.

The selectivities for 2,6-DIPN were decreased with the increase in reaction temperature in the isopropylation over MOR although the selectivities for 2,6-DIPN in encapsulated product and for β,β-DIPN remained constant. A similar decrease in the selectivities for 2,6-DIPN was observed by the influence of catalyst amount. These decreases in the selectivities are explained by the isomerization of 2,6-DIPN to 2,7-DIPN at the external acid sites.

These characteristic features of the isopropylation over MOR indicate that internal acid sites are primary reaction sites, and that external acid sites are deactivated for the non-selective catalyses, such as the isopropylation of NP, the isomerization of 2,6-DIPN, de-alkylation under moderate reaction conditions. The deactivation is explained by the preferential adsorption of propene at the external acid sites. The direct adsorption of NP and its derivatives is essential for their reactions at the acid sites. Propene strongly adsorbs and occupies the external acid sites, resulting in prevention of access of NP and its derivatives, particularly 2,6-DIPN, under moderate reaction conditions. However, high temperatures and/or the use of a large amount of the catalyst allows the direct adsorption of 2,6-DIPN, resulting in the isomerization of 2,6-DIPN to 2,7-DIPN as discussed above, although the formation of 2,6- and 2,7-DIPN still occurs in the channels. Similar features of the catalysis were also found in the isopropylation of BP over MOR [2,6].

The catalyses over FAU and BEA are quite different from those of MOR. Product distribution was highly dependent on the reaction temperature: the isopropylation is not operating by shape-selective catalysis but under kinetic and/or thermodynamic controls. FAU and BEA allow formation and accommodation of 1-IPN as well as 2-IPN because their pores and channels are too large to exclude the formation of bulky 1-IPN. The primary isomer is 1-IPN at low temperatures over these zeolites. The yields of 1- and 2-IPN increased with reaction temperatures and reached maxima at around 200 °C and 225-250 °C for FAU and 200 °C and 200-275 °C for BEA. Then, they decreased with further increase in reaction temperatures, and 2-IPN was predominant over 1-IPN under the conditions. The selectivities for 2-IPN were increased with the increase in reaction temperatures over these zeolites, accompanying the decrease in those for 1-IPN. The dialkylation of IPN isomers to α,α- and α,β-DIPN increased with the increase in reaction temperature and reached maxima (FAU: 200 °C for α,α-DIPN; 225-250 °C for α,β-DIPN, and BEA: 225 °C for α,α-DIPN; 250 °C for α,β-DIPN). Further increase in reaction temperature enhanced the formation of β,β-DIPN accompanying the decrease of α,α- and α,β-DIPN. These results suggest that the catalyses are principally operating under kinetic control at low and moderate temperatures below 250 °C resulting in the formation of α,α- and α,β-DIPN, and that the participation of thermodynamic control was enhanced at higher temperatures, resulting in the preference of α,β- and β,β-DIPN. The isomerization of 1-IPN to 2-IPN also occurs during the catalysis at high temperatures, and both isomers act as the precursor of DIPN isomers. Moreover, there are possibilities of the formation of β,β-DIPN through the iso-

merization of α,α- and α,β-DIPN by de-alkylation-alkylation as well as direct formation from 2-IPN.

The results of FAU and BEA indicate that these zeolites have no shape-selective natures in the isopropylation of NP: they allow the formation of bulky α,α- and α,β-DIPN under kinetic control at low temperatures, and enhance the preference of stable β,β-DIPN by the participation of thermodynamic control at high temperatures because their channels are large enough for accommodation: the isomerization of α,α- and α,β-DIPN occurs in addition to direct formation of β,β-DIPN in their channels. The roles of 1- and 2-IPN are common in the isopropylation of NP over these zeolites, although there are some differences in the features of appearance and disappearance of IPN and DIPN isomers. We have also to remind that the differences between FAU and BEA reflect the differences of SiO_2/Al_2O_3 ratio in addition to the structural reasons as discussed.

CONCLUSION

The isopropylation of NP was examined over MOR, FAU, and BEA as typical examples of zeolite in order to understand the roles of IPN intermediates in the catalysis. 2-IPN was the primary isomer only over MOR, and acts as a precursor for the dialkylation, resulting in selective formation of β,β-DIPN, particularly the least bulky 2,6-DIPN. These catalyses occur through the sterically restricted transition state in the MOR channels by exclusion of the bulky transition state of α,α- and α,β-DIPN. The results indicate that product selectivity and restricted transition state mechanisms are operating in the isopropylation of NP. The isomerization at external acid sites occurred at high temperatures and in the presence of a large amount of catalyst, resulting in a decrease in selectivities for 2,6-DIPN and an increase in selectivities for 2,7-DIPN.

The formation of 1-IPN was predominant at low temperatures over FAU and BEA, and the dialkylation to α,α- and α,β-DIPN occurs by the consumption of 1-IPN and also minor product 2-IPN. However, the formation of β,β-DIPN from 2-IPN was enhanced at higher temperatures. There are possibilities that β,β-DIPN are through de-alkylation-isomerization of α,α- and α,β-DIPN in addition to direct formation from 2-IPN. These results indicate that the catalyses over FAU and BEA occur under kinetic and thermodynamic controls depending on the reaction conditions. FAU and BEA allow the formation of the bulky products because their channels are large enough to accommodate their bulky transition states.

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APPENDIX

The influences of reaction temperature on the yield of isopropylated napthalenes in the Isopropylation of NP

Fig. S1 MOR.

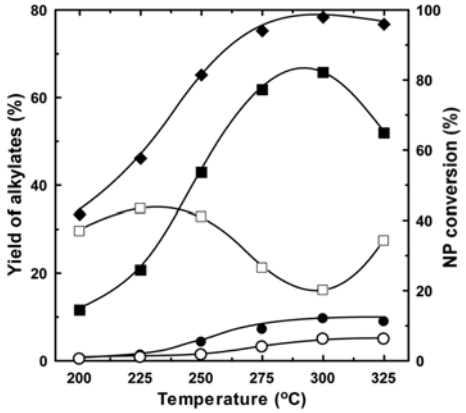

Fig. S1. The influences of reaction temperature on the yield of isopropylated napthalenes in the isopropylation of NP over MOR. Reaction conditions: NP: 50 mmol; MOR(128): 0.25 g; reaction time: 4 h; propene pressure: 0.8 MPa. Legend: □: IPN; ■: DIPN; ●: TriIPN; ○: TetraIPN; ◆: NP conversion.

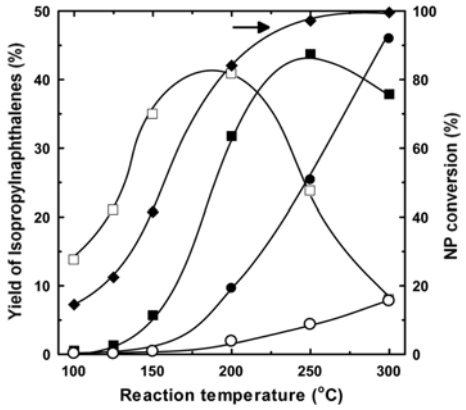

Fig. S2. The influences of reaction temperature on the yield of isopropylated napthalenes in the isopropylation of NP over FAU. Reaction conditions: NP: 50 mmol; FAU(30): 0.25 g; reaction time: 4 h; propene pressure: 0.8 MPa. Legend: the same as Fig. S1.

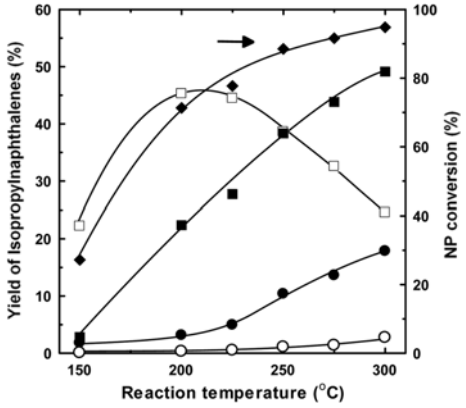

Fig. S3. The influences of reaction temperature on the yield of isopropylated napthalenes in the isopropylation of NP over BEA. Reaction conditions: NP: 50 mmol; FAU(30): 0.25 g; reaction time: 4 h; propene pressure: 0.8 MPa. Legend: the same as Fig. S1.

Fig. S2 FAU.
Fig. S3 BEA.

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