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The alkylation of naphthalene over three-dimensional large pore zeolites: The influence of zeolite structure and alkylating agent on the selectivity for dialkylnaphthalenes

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Abstract

In order to elucidate how zeolite structure and alkylating agent play roles in the shape-selective catalysis, the alkylation, *i.e.*, isopropylation, *sec*-butylation, and *tert*-butylation, of naphthalene (NP) was examined over three-dimensional twelve-membered (12-MR) zeolites, Y (FAU), Beta (BEA), and CIT-1 (CON), and compared to that of H-mordenite (MOR). The β,β-selectivities (for β,β-dialkylnapthalene (β,β-DAN)) and the 2,6-selctivities (for 2,6-dialkylnaphthalene (2,6-DAN)) among DAN isomers varied with the types of zeolites and alkylating agents. FAU, BEA, and CON gave only low selectivities for 2,6-diisopropylnaphthalene (2,6-DIPN) in the isopropylation, and predominant isomers were bulky and thermodynamically unstable α,β-DIPN (1,3-, 1,6-, and 1,7-DIPN) and α,α-DIPN (1,4- and 1,5-DIPN) at lower temperatures, and the formation of the less bulky and thermodynamically stable β,β-DIPN (2,6- and 2,7-DIPN) increased with increasing the temperature: they have quite different features from the shape-selective catalysis over MOR. These results suggest that FAU, BEA, and CON are not shape-selective in the isopropylation, and that the isopropylation is principally controlled kinetically at lower temperatures, and thermodynamically at higher temperatures.

The β,β-selectivities over FAU, BEA, and CON increased with increasing the bulkiness of alkylating agents, and were almost 100% in the *tert*-butylation. On the other hand, the 2,6-selectivities over these zeolites were much lower than those over MOR at a typically moderate temperature, 250 °C. These results mean that FAU, BEA, and CON have the shape-selective nature to give the less bulky isomers, β,β-DAN, in the *sec*-butylation and *tert*-butylation by using bulkier alkylating agents, particularly 2-methyl-2-propene: they can differentiate β,β-DAN from their isomers at the transition states by the steric restriction of zeolite channels. However, the channels of these zeolites are too large for differentiating 2,6- and 2,7-DAN even with 2-methyl-2-propene.

Keywords: FAU; BEA; CON; Alkylation; Naphthalene; Shape-selective catalysis; β,β-Dialkylnaphthalene; 2,6-Dialkylnaphthalene

1. Introduction

The shape-selective catalyses by zeolites occur by differentiating reactants, products, and/or reaction intermediates according to their shape and size in sterically restricted environments of the zeolite [1–6]. Only molecules of which dimensions are less than the pore-entrances of zeolites can enter their channels, and react at the internal catalytic sites of zeolites. The bulky molecules, which cannot accommodate in the channels are excluded from the zeolite, and only molecules which can diffuse through the channels appear in the products, thus resulting in the formation of the slimmest isomers. In these catalyses, the selectivities for the least bulky isomers are determined by the steric differentiation of the bulky isomers at transition states in the channels: this is so called ‘‘restricted transition state selectivity’’ [1]. Besides this selectivity, there are also ‘‘product selectivity’’ by the preferential diffusion from zeolite in the catalysis, and ‘‘reactant selectivity’’ by the differentiation of bulkiness of the reactants to enter the zeolites [1]. The appearance of the shape-selectivities was highly influenced by the types of zeolites and bulkiness of reagents. If the spaces of zeolite channels are large enough to accommodate

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the reactant and/or the products, or if the reactants and the products are smaller than the spaces in the channels, the shape-selective catalysis is not operated because the transition states of bulky isomers are also allowed in the channels. The catalysis over such a zeolite is controlled kinetically by the reactivity of each position at lower temperatures, and by the thermodynamic stability of the products at higher temperatures [1–3]. These considerations indicate that the extent of the exclusion of bulky molecules from the channels is one of the key factors for the shape-selective catalysis, and that it depends on the types of zeolites and alkylating agents.

The isopropylation of polynuclear hydrocarbons, such as naphthalene (NP) and biphenyl (BP) is a typical acid-catalyzed reaction for demonstrating shape-selective nature of zeolite [4–15]. The selective formation of the least bulky 2,6-diisopropylnaphthalene (2,6-DIPN) and 4,4′-diisopropylbiphenyl (4,4′-DIPB) should be facilitated over zeolites if the catalytic sites are sterically restricted. In the previous paper, we described that 2,6-DIPN was selectively produced from NP over dealuminated H-mordenite (MOR) [9]. MOR effectively excludes the transition states of bulky DIPN isomers from the channels, thus resulting in the selective formation of the least bulky 2,6-DIPN. On the other hand, many of large pore zeolites, such as Y, Beta, and L zeolites, gave the mixtures of DIPN isomers, and the selectivities for 2,6-DIPN were much lower than MOR [16–21]: these results are due to the large reaction spaces in their channels. However, there are several works that the shape-selective formation of 2,6-di-*tert*-butylnapthalene (2,6-DTBN) occurred when 2-methyl-2-propanol or 2-methylpropene was used as an alkylating agent [22–24]. These results prompted us to study how the type of zeolites, particularly, dimensionality, structures of pore-entrance and channels, *etc.*, and of alkylating agents influence on transition states to lead shape-selective catalysis in zeolite channels.

In this paper, we describe the alkylation, *i.e.*, isopropylation, *sec*-butylation, and *tert*-butylation of NP, over some three-dimensional zeolites, Y (FAU; 12 × 12 × 12-MR channels with super cages), Beta (BEA; 12 × 12 × 12-MR channels), and CIT-1 (CON; 12 × 12 × 10-MR channels) [25], and compare to the catalyses over MOR from view points how the types of the zeolite and alkylating agents affect the shape-selective catalysis. The discussion in the paper was based on the selectivities for DAN isomers. The abbreviation of zeolites is expressed by Framework Type Code (FTC) from IZA Structure Commission [25]: MOR for mordenite, FAU for Y zeolite, BEA for Beta zeolite, and CON for CIT-1 zeolite.

2. Experimental

2.1. Zeolites

BEA and CON were synthesized according to the literatures [26,27]. MOR ($SiO_2/Al_2O_3 = 128$; TSZ-690HOA; Tosoh Corporation) and FAU ($SiO_2/Al_2O_3 = 30$; CBVZ720, Zeolyst CV) were obtained commercially. All zeolites were used as H-form, and calcined at 550 °C before the use. Table 1 shows typical properties of the zeolites related to the catalytic alkylation of NP.

2.2. The alkylation of NP

The alkylation of NP was carried out in a 100-mL SUS-316 autoclave. Typical conditions of the isopropylation are NP 6.42 g (50 mmol), catalyst 0.25 g, reaction temperature 150–350 °C, and 4 h of operating period under 0.8 MPa of propene pressure (0.4 MPa of 1-butene in the *sec*-butylation and of 2-methylpropene in the *tert*-butylation). An autoclave containing NP and the catalyst was flushed with nitrogen before heating. After reaching the reaction temperature, propene was introduced to the autoclave, and the reaction was started with agitation. The pressure maintained constant throughout the reaction. After cooling the autoclave, the catalyst was filtered off, and washed well with toluene. The liquid products were analyzed by using a gas chromatograph GC-14A (Shimadzu Corporation) equipped with TC-17 (25 m × 0.25 mm; Agilent Technologies) and/or HP-INNOWax (60 m × 0.25 mm; Agilent Technologies) capillary columns. They were also identified by using a Shimadzu GC–MS 5000 Gas Chromatograph–Mass Spectrometer by using the above columns.

Dialkylnapthathalene is generally expressed as DAN: DIPN, DSBN, and DTBN for the isopropylation, *sec*-butylation, and *tert*-butylation, respectively. β,β-, α,β-, and α,α-DAN also

Table 1
Properties of zeolites

Zeolite	Topology (FTC)	Dimension	Pore system	Pore opening (nm)	SiO_2/ Al_2O_3	Surface area (m^2/g)	Pore volume (mL/g)	NH_3-TPD peak temperature (°C)	Acid amount (mmol/g)	Note
Mordenite	MOR	2	12–8	12-MR: 0.65 × 0.70 (0 0 1)[a] 8-MR: 0.34 × 0.48 (0 1 0)	128	460	0.16	389	0.20	8-MR: Side pocket
Y	FAU	3	12–12–12	12-MR: 0.74 × 0.74 (1 1 1)	30	810	0.29	254	0.18	Super cage
Beta	BEA	3	12–12–12	12-MR: 0.66 × 0.77 (1 0 0, 0 1 0) 12-MR: 0.56 × 0.56 (0 0 1)	111	660	0.28	304	0.18	
CIT-1	CON	3	12–12–10	12-MR: 0.64 × 0.70 (0 0 1) 12-MR: 0.59 × 0.70 (1 0 0) 10-MR: 0.45 × 0.51 (0 1 0)	40	538	0.22	303	0.23	

[a] Plane index.

Table 2
Estimation of equilibrium of DIPN isomers at 300 °C

Period (min)	Conversion (%)	Isopropylates (%)				DIPN composition (%)			
		IPN	DIPN	TriIPN	TetraIPN	2,6-	2,7-	α,β-	α,α-
20	99.3	9.8	53.4	17.3	19.6	38.3	36.7	22.2	2.8
60	99.3	29.7	53.0	8.1	9.2	36.4	38.4	22.2	2.9
300	100	2.9	33.2	31.4	32.5	37.4	38.9	20.1	3.6

Reaction conditions: 2,6-DIPN, 12.5 mmol; catalysts, H–Y ($SiO_2/Al_2O_3 = 30$); temperature, 300 °C; propene pressure, 0.8 MPa.

express, sum of 2,6- and 2,7-DAN, 1,3-, 1,6-, and 1,7-DAN, and 1,4- and 1,6-DAN, respectively.

The yields of each product are calculated on the basis of the amount of starting NP, and the selectivities for each DAN isomer are expressed based on the total amounts of the DAN isomers. The types of selectivities are described as follows, or stated otherwise. β,β-, α,β-, and α,α-selectivities are selectivities for β,β-, α,β-, and α,α-DAN among the DAN isomers, respectively. 2,6- and 2,7-selectivities are selectivities for 2,6- and 2,7-DAN among the DAN isomers, respectively.

The catalytic activities based on the yield of alkylates were described in Figs. S1–S4 in supplementary data.

2.3. Estimation of equilibrium mixtures of DIPN isomers

2,6-DIPN was contacted with FAU at 300 °C until no change of the composition of DIPN isomers occurred. Typical results are given in Table 2.

3. Results and discussion

3.1. The isopropylation

The influences of reaction temperature on the yields of the isopropylnaphtahlenes in the isopropylation are shown in Fig. 1 over MOR and FAU, and in Fig. 2 over BEA and CON. These zeolites have the similar features for the formation of isopropylnaphthalene (IPN), diisopropylnapthalene (DIPN), triisopropylnaphthalene (TriIPN), and tetraisopropylnaphthalene (TetraIPN) isomers. Particularly, IPN was the principal products in the lower temperatures, and reached the maximum at around 200 °C for all zeolites. The yield of IPN, then, decreased with the increase in the reaction temperature accompanying the formation of higher isopropylnaphthalenes, such as TriIPN and TetraIPN. The maximum yield of DIPN at 250 °C depends on the types of zeolites: BEA ≥ FAU ≥ MOR > CON. These results show that the isopropylation over these zeolites proceeds stepwise by the consecutive reaction mechanism although the catalytic activities depend on the properties of zeolites, such as channel structure, pore entrances, acidity, *etc.*

The influences of reaction temperature on the selectivities for DIPN isomers in the isopropylation were shown in Fig. 3 over MOR and FAU, and in Fig. 4 over BEA and CON. These zeolites have different features against the β,β-selectivities. The isopropylation over MOR gave selectivities for β,β-DIPN over 80–85% in the range of 150–300 °C, and the selectivities for α,β-DIPN (1,6-, 1,7-, and 1,3-) and α,α-DIPN (1,4- and 1,5-) were 10–20% and 0–5%, respectively. This means that MOR can exclude the bulky isomers by the steric restriction in the

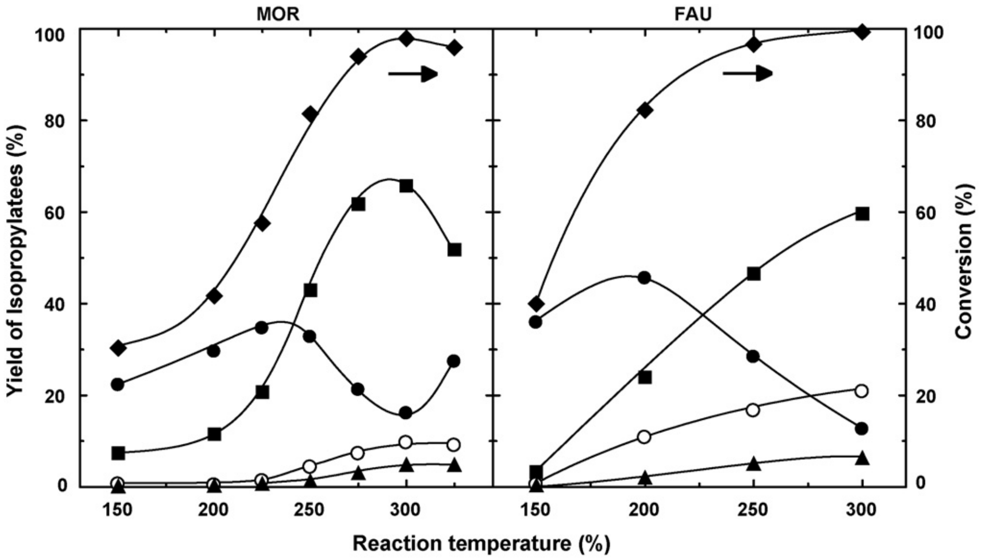

Fig. 1. The influences of reaction temperature on the yield of the isopropylates in the isopropylation of NP over MOR and FAU. Reaction conditions: NP, 50 mmol; catalyst, 0.25 g; temperature, 150–300 °C; propene pressure, 0.8 MPa; period, 4 h. Legends—(◆) conversion; yield: (●) IPN, (■) DIPN, (▲) TriIPN and (○) TetraIPN.

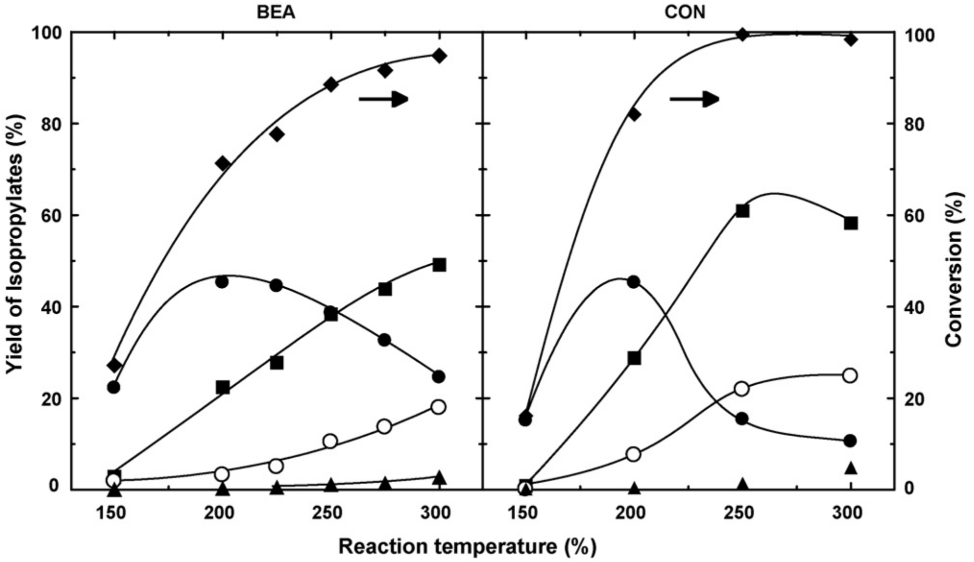

Fig. 2. The influences of reaction temperature on the yield of the isopropylates in the isopropylation of NP over BEA and CON. Reaction conditions: NP, 50 mmol; catalyst, 0.25 g. Other conditions and legend: see Fig. 1.

channels, thus resulting in the predominant formation of β,β-DIPN. On the other hand, FAU, BEA, and CON had quite different features from MOR in the isopropylation as shown in Figs. 3 and 4. α,α- and α,β-DIPN were the principal products at lower reaction temperatures over FAU, and their selectivities decreased at higher temperatures accompanying the increase in the β,β-selectivities. The formation of α,β- and α,α-DIPN was also predominant over BEA and CON at lower temperatures; however, the selectivities for these isomers over the zeolites were lower than those for FAU—BEA: 45% for α,β-DIPN and 30% for α,α-DIPN and CON: 50% for α,β-DIPN and 25% for α,α-DIPN at 150 °C. The selectivities for α,β- and α,α-DIPN over BEA and CON decreased with the increase in those for β,β-DIPN at higher temperatures. These results indicate that the channels of these zeolites are too large for the shape-selective formation of β,β-DIPN. The predominant formation of α,α- and α,β-DIPN at lower temperatures means that the isopropylation is controlled by the kinetic factors, *i.e.*, the nucleophilic attack of isopropyl carbenium ion to electron-rich α-carbon of NP leads to the predominant formation of α,α- and α,β-DIPN. However, the thermodynamic control operates in the isopropylation with the increase in the temperatures, thus resulting in the increase in the formation of the stable β,β-DIPN and the decrease in the formation of α,α- and α,β-DIPN.

Corresponding to these features on the β,β-selectivities, these zeolites had the different features on the 2,6-selectivities in the isopropylation as shown in Figs. 3 and 4. The selectivities for 2,6- and 2,7-DIPN were around 60% and 20% over MOR at the moderate temperatures below 275 °C, respectively. These results mean that MOR can differentiate 2,6-DIPN from its isomers, particularly from β,β-DIPN, by the steric restriction in the channels. On the other hand, the selectivities for 2,6-DIPN

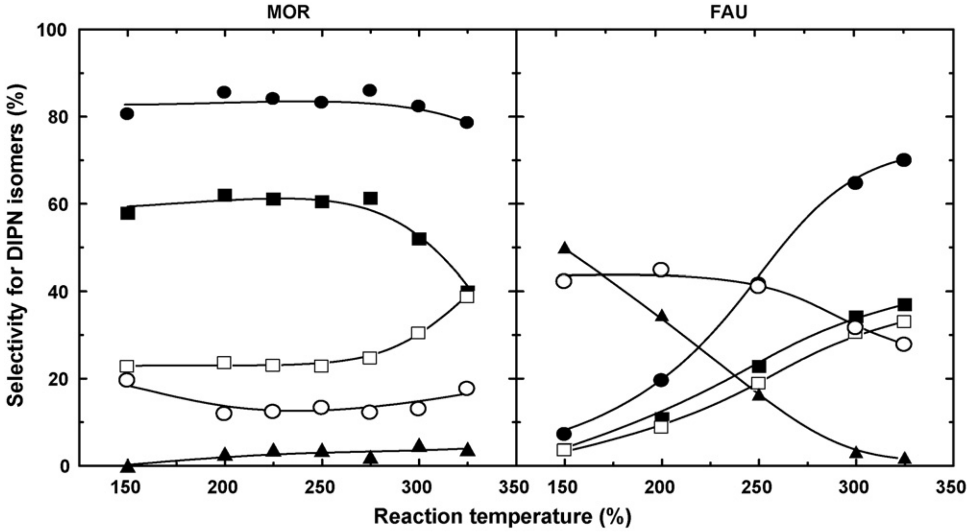

Fig. 3. The influences of reaction temperature on the selectivity for DIPN isomers the isopropylation of NP over MOR and FAU. Reaction conditions: see in Fig. 1. Legends: (●) β,β-DIPN; (○) α,β-DIPN; (▲) α,α-DIPN; (■) 2,6-DIPN; (□) 2,7-DIPN.

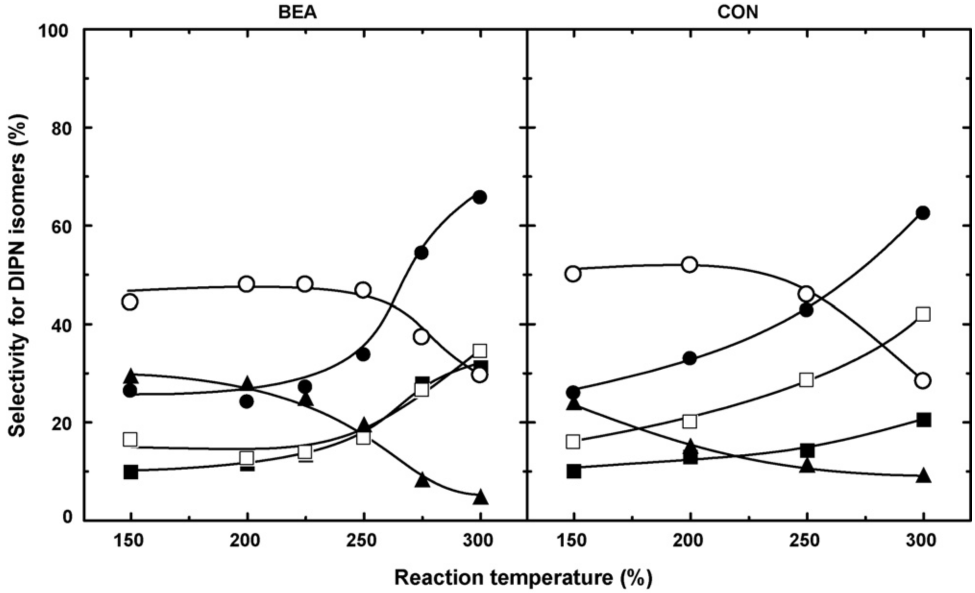

Fig. 4. The influences of reaction temperature on the selectivity for DIPN isomers in the isopropylation of NP over BEA and CON. Reaction conditions: see in Fig. 2. Legends: see Fig. 3.

over FAU, BEA, and CON were much lower than those over MOR at low to moderate temperatures, because the predominant isomers were α,α- and α,β-DIPN. 2,6- and 2,7-DIPN were simultaneously obtained in relatively similar amounts over these zeolites. Both of the selectivities for 2,6- and 2,7-DIPN were less than 10% over FAU at 150 °C, and as low as 10–20% over BEA in the temperatures at 150–250 °C. The selectivities over CON were also much lower than those for MOR, although the selectivities for 2,7-DIPN were slightly higher than those for 2,6-DIPN. However, the selectivities for 2,6- and 2,7-DIPN increased with increasing the temperatures—2,6-DIPN: 34% for FAU, 31% for BEA, and 21% for CON; 2,7-DIPN: 30% for FAU, 34% for BEA, and 42% for CON at 300 °C. These results indicate that the channels over these zeolites are too large for the shape-selective formation of 2,6-DIPN. The isopropylation over these zeolites operates under kinetic control at lower temperatures, and the participation of thermodynamic control increases with the increase in temperature as discussed above.

The characteristic features over FAU, BEA, and CON were simultaneous formation of 2,6- and 2,7-DIPN, particularly at higher temperatures. They are quite different from those over MOR because their channels are too large for the shape-selective catalysis. These catalyses operated under thermodynamic control, resulting in the simultaneous formation of 2,6- and 2,7-DIPN. The products composition under thermo-

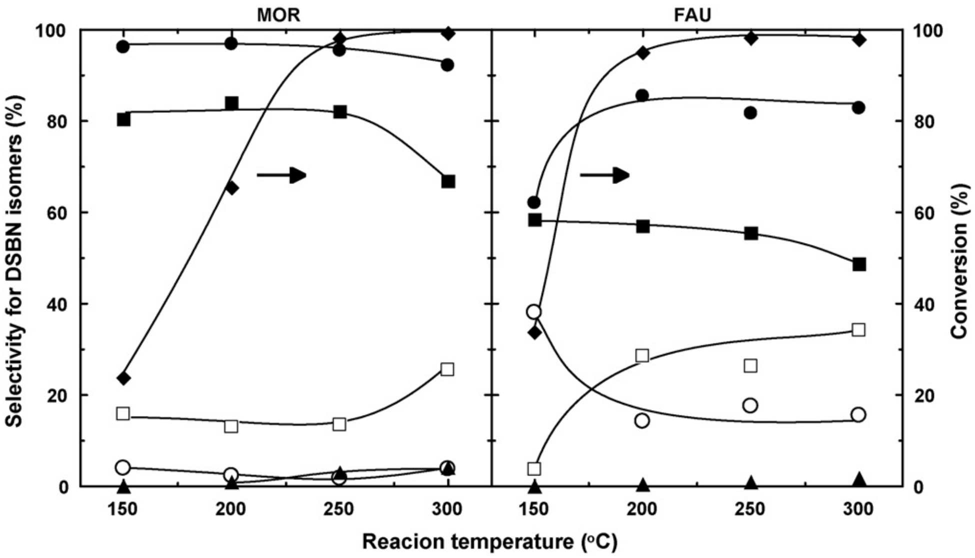

Fig. 5. The influences of reaction temperature on the selectivity for DSBN isomers in the *sec*-butylation of NP over MOR and FAU. Reaction conditions: NP, 50 mmol; catalyst, 0.25 g; temperature, 150–300 °C; 1-butene pressure, 0.5 MPa; period, 4 h. Legends—(◆) conversion; selectivity: (●) β,β-DSBN; (○) α,β-DSBN; (▲) α,α-DSBN; (■) 2,6-DSBN; (□) 2,7-DSBN.

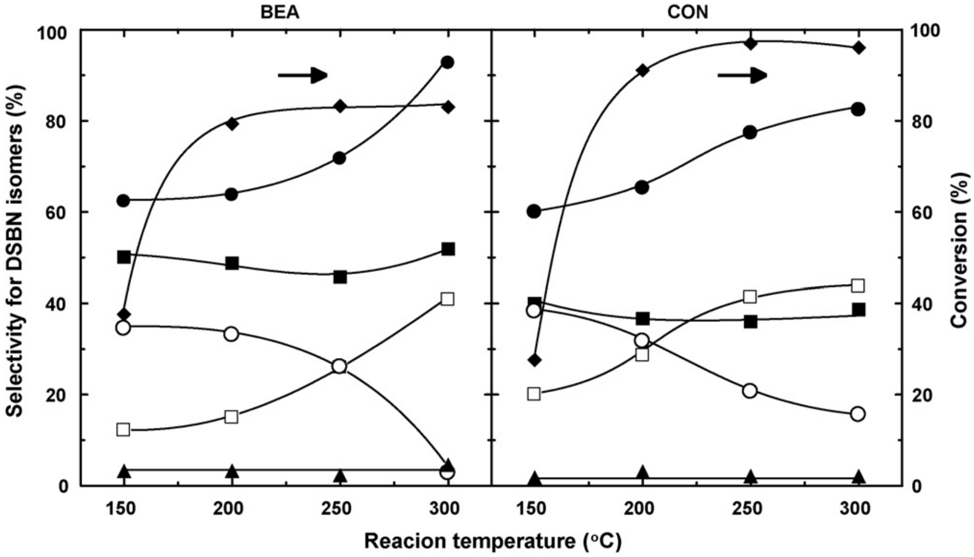

Fig. 6. The influences of reaction temperature on the selectivity for DSBN isomers in the *sec*-butylation of NP over BEA and CON. (a) BEA. (b) CON. Reaction conditions—NP: 25 mmol (BEA), 10 mmol (CON); catalyst: 0.125 g (BEA), 0.1 g (CON). Other conditions and legends: see Fig. 5.

dynamic control is are related to the equilibrium of the isomers. The equilibrium mixtures at 300 °C involve predominantly β,β-DIPN among DIPN isomers, and 2,6- and 2,7-DIPN are almost in equal amounts at the equilibrium (Table 2). These results also support contribution of thermodynamic control in the catalyses.

The selectivities for 2,6-DIPN decreased over MOR at higher temperatures were accompanied by the increase in those for 2,7-DIPN. This is due to the isomerization of 2,6-DIPN to 2,7-DIPN at the external acid sites as discussed in the isomerization of 4,4′-DIPB in the isopropylation of BP [5–8].

3.2. The sec-butylation

The influence of reaction temperature on the *sec*-butylation of NP over MOR, FAU, BEA, and CON was examined in order to know the influence of bulkiness of alkylating agent on the catalysis. The principal products were *sec*-butylnaphthalene (SBN), di-*sec*-butylnaphthalene (DSBN) and tri-*sec*-butylnaphthalene (TSBN) isomers. DSBN isomers increased with increasing temperatures, and saturated at around 200–250 °C. TSBN isomers were obtained in 20% over FAU and CON, and less than 10% over MOR and BEA: they increased with increasing the temperature (see Figs. S1 and S2 in supplementary data).

The influences of reaction temperature on the selectivities for DSBN isomers are shown in Fig. 5 over MOR and FAU, and in Fig. 6 over BEA and CON. The features in the *sec*-butylation were similar to those in the isopropylation, although the β,β-selectivities were higher than those in the isopropylation. The selectivities for β,β-DSBN over MOR were higher than 95% in the range of 150–300 °C, and the formation of α,α- and α,β-DSBN was only in small amounts. However, FAU, BEA, and CON gave 60% selectivities for β,β-DSBN at low temperatures as 150 °C. The selectivities for β,β-DSBN increased with increasing the temperature, and reached around 80% at 300 °C, accompanied by the decrease in the selectivities for α,β-DSBN. However, the formation of α,α-DSBN was negligible for all zeolites. The differences in the β,β-selectivities for DIPN and DSBN over these zeolites are due to the larger steric interaction in the transition states of bulky α,β- and α,α-DSBN compared to those of corresponding DIPN isomers. Further, the increase in β,β-selectivities in the *sec*-butylation at higher temperatures also involves the contribution of thermodynamic control as discussed in the isopropylation.

These zeolites also have different features in the 2,6-selectivities as shown in Figs. 5 and 6. The selectivities for 2,6- and 2,7-DSBN were around 80% and 15% over MOR at low to moderate temperatures, respectively. On the other hand, FAU, BEA, and CON gave lower 2,6-selectivities than MOR: the selectivities for 2,6-DSBN were 50–60% over FAU, around 50% over BEA, and around 40% over CON in the range of 150–300 °C, respectively. These results in the *sec*-butylation are very similar to those in the isopropylation. The selectivities for 2,6-DSBN in the *sec*-butylation were higher than those for 2,6-DIPN in the isopropylation because of the severer steric restriction of DSBN with 2-butyl moieties in the zeolite channels compared to those of isopropyl moieties. The increases in the selectivities for 2,6-DSBN over FAU, BEA, and CON, particularly at lower temperatures, were also due to more severe exclusion of bulky isomers by the increase in the steric restriction in the channels. This means the shape-selective catalysis partly operated in the *sec*-butylation over these zeolites because the replacement of isopropyl moieties with *sec*-butyl moieties effectively differentiates 2,6-DSBN from its isomers in the channels. Further, the increase in 2,6- and 2,7-selectivities at higher temperatures also involves the contribution of thermodynamic control as discussed in the isopropylation.

The decrease in the selectivity for 2,6-DSBN occurred in the *sec*-butylation over MOR at 300 °C accompanying the increase in that for 2,7-DSBN. This is due to the isomerization of 2,6-DSBN to 2,7-DSBN similarly to the isomerization of 2,6-DIPN in the isopropylation.

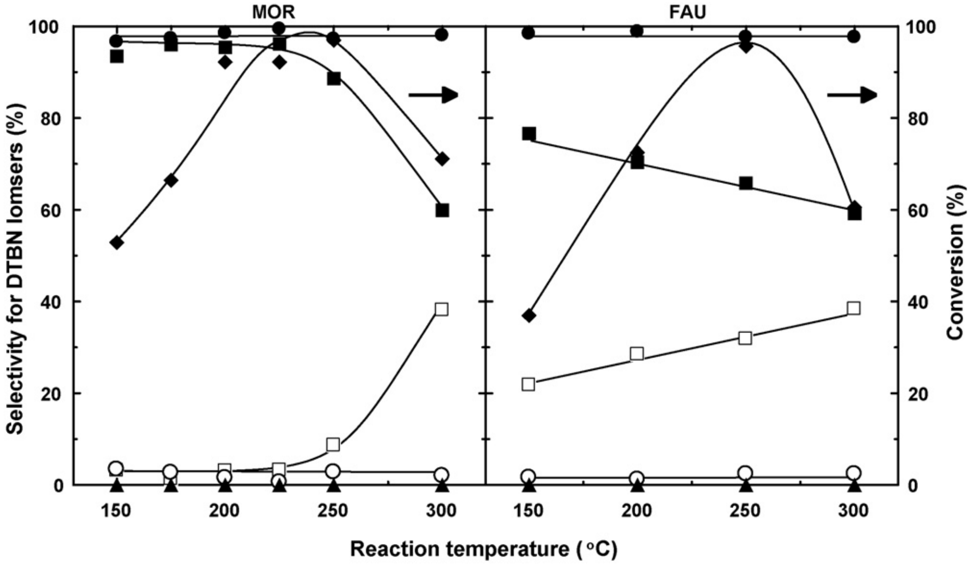

Fig. 7. The influences of reaction temperature on the selectivity for DTBN isomers in the *tert*-butylation of NP over MOR and FAU. Reaction conditions—NP: 50 mmol (MOR), 25 mmol (FAU); catalyst: 0.25 g (MOR), 0.125 g (FAU); temperature, 150–300 °C; 2-methylpropene pressure, 0.5 MPa; period, 4 h. Legends—(◆) conversion; selectivity: (●) β,β-DTBN; (○) α,β-DTBN; (▲) α,α-DTBN; (■) 2,6-DTBN, (□) 2,7-DTBN.

3.3. The tert-butylation

The steric restriction of DAN isomers by zeolite channels is enhanced by the bulkiness of alkylating agents as discussed in previous section. It is interesting to elucidate the influences of the bulky alkylating agent, 2-methylpropene, on the selectivities for di-*tert*-butylnaphthalene (DTBN) isomers in the alkylation of NP. The *tert*-butylation gave *tert*-butylnaphthalene (TBN) and DTBN isomers as principal products. The yields of DTBN were maximized at 200–250 °C, and decreased with further increase in temperatures (see Figs. S3 and S4 in supplementary data). However, tri-*tert*-butylnaphthalene (TTBN) isomers were negligible in the products.

The selectivities for β,β-DTBN were higher than 95% as shown in Fig. 7 over MOR and FAU, and in Fig. 8 over BEA and CON. These results mean that the zeolites have the small channels enough for the differentiation of β,β-DTBN from their isomers. However, these zeolites have quite different features on the selectivities for 2,6- and 2,7-DTBN. The formation of 2,6-DTBN was highly selective over MOR at low to moderate temperatures. This is due to the effective differentiation of 2,6- and 2,7-DTBN in MOR channels. On the other hand, FAU, BEA, and CON gave considerably lower selectivities for 2,6-DTBN than MOR because of the extensive formation of 2,7-DTBN. They decreased in the order: FAU > BEA ≥ CON at 150 °C. The selectivities for 2,6-DTBN over FAU were around 80% at 150 °C; however, they gradually decreased with the reaction temperatures, and reached 60% at 300 °C. The decrease in the selectivities for 2,6-DTBN accompanied the increase in those for 2,7-DTBN: 25% at 150 °C to 40% at 300 °C. The selectivities for 2,6-DTBN over BEA also decreased from 60% at 150–200 °C to 50% at 250–300 °C. The selectivities for 2,6-DTBN over CON were kept around 50% even at high temperatures as 300 °C. These results show that the channels of FAU, BEA, and CON cannot differentiate 2,6- and 2,7-DTBN although they are highly shape-selective for the formation of β,β-DTBN.

The decrease in the selectivities for 2,6-DTBN occurred in the *tert*-butylation of NP over MOR at 300 °C accompanying the increase in those for 2,7-DTBN. This is due to the isomerization of 2,6-DTBN to 2,7-DTBN similarly to the isomerization of 2,6-DIPN in the isopropylation and of 2,6-DSBN in the *sec*-butylation.

3.4. Shape-selective catalysis in the alkylation of NP

The shape-selectivities of the zeolites in the alkylation of NP are the selectivities for the less bulky DAN isomers among their isomers, and determined by the differentiation of the least bulky isomers from their 10 isomers by the steric restriction in the zeolite channels [5]. If the channels are small enough to exclude the bulky isomers by the steric limitation of transition states in the channels, the shape selective catalysis occurs to yield the less bulky isomers. However, the shape-selective catalysis will not happen if the channels are large enough for the formation of the transition states for the bulkier isomers in the channels. These considerations mean that the steric differentiation of transition states of the products by the restriction in the channels is essential for the shape-selective catalysis. The key factors are the structure of zeolite channels and bulkiness of alkylating agents as we proposed in the alkylation of BP [4–9,30–32].

There are two types of the shape-selectivities in the alkylation of NP: β,β-, α,β-, and α,α-selectivities and 2,6- and 2,7-selectivities. The β,β-, α,β-, and α,α-selectivities appear by the differentiation of the less bulky β,β-DAN (2,6- and 2,7-DAN) and bulkier α,α-DAN (1,4- and 1,5-) and α,β-DAN (1,3-, 1,6-, and 1,7-DAN) because the sizes of DAN isomers decreased in the order: α,α-DAN > α,β-DAN > β,β-DAN. The β,β-selectivities are indexes for the less bulky DAN

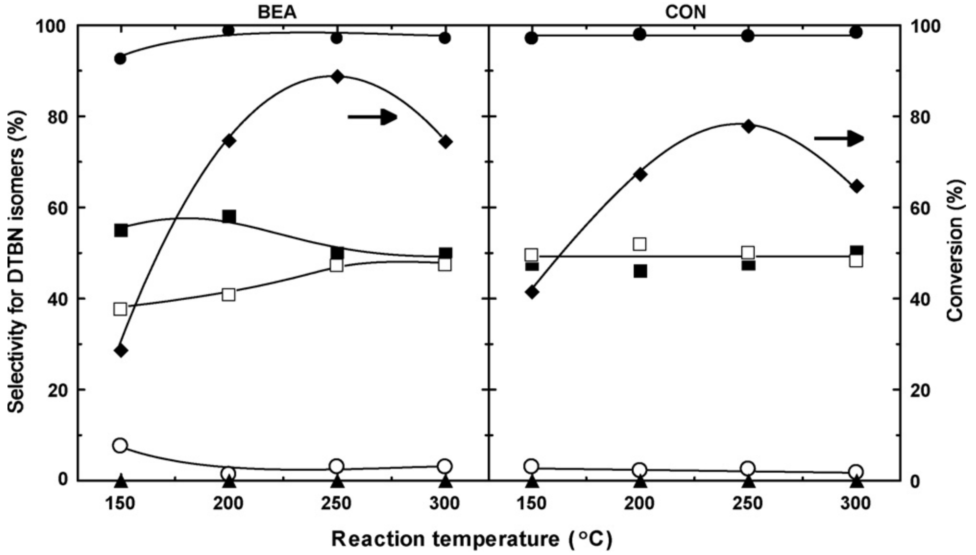

Fig. 8. The influences of reaction temperature on the selectivity for DTBN isomers in the *tert*-butylation of NP over BEA and CON. Reaction conditions—NP: 25 mmol (BEA), 50 mmol (CON); catalyst: 0.125 g (BEA), 0.25 g (CON). Other conditions and legends: see Fig. 7.

isomers for shape-selective catalysis and also for stable isomers under thermodynamic control. The latter selectivities work particularly at higher temperatures in sterically less restricted reaction environments, because β,β-DAN is thermodynamically more stable than α,β- and α,α-DAN. The β,β-selectivities should also increase with the bulkiness of alkylating agent because of the difference in size of β,β-DAN and the other isomers. The α,α- and α,β-selectivities for DAN isomers are indexes for the bulky isomers under kinetic control because the nucleophilic attack of alkyl carbenium ion to electron-rich α-carbon of NP leads to the predominant formation of α,α- and α,β-DAN. The 2,6- and 2,7-selectivities appears by the differentiation of the least bulky 2,6-DAN from the DAN isomers. Particularly, it is important to differentiate 2,6-DAN and 2,7-DAN because 2,7-DAN is slightly bulky than 2,6-DAN. The precise fitting of the transition states with the channels is an important key factor for differentiating two isomers.

The differences in zeolites, particularly, pore and channel structures are also influenced on the shape-selective nature in the alkylation. MOR has the 12-MR straight channels with 8-MR side pockets: pore-entrance of 0.67 nm × 0.72 nm. FAU has three-dimensional channels (12 × 12 × 12-MR) with super cages which afford large reaction space. BEA and CON have three-dimensional pore systems: 12 × 12 × 12-MR and 12 × 12 × 10-MR channels, respectively, which have large reaction spaces at the crossing of the channels. Thus, the reaction space in the channels increased in the order: MOR ≪ BEA ≈ CON ≪ FAU. This order means that the steric restriction in the catalysis decreased in the order: MOR ≫ BEA ≈ CON ≥ FAU.

Fig. 9 shows the β,β-, α,β-, and α,α-selectivities in the alkykation of NP over MOR, FAU, BEA, and CON at 250 °C. They are considered to be typical selectivities for zeolites because the isomerization of DAN isomers are not significantly under the reaction conditions at 250 °C. These zeolites have quite different features on β,β-selectivities. The high β,β-selectivities were observed in all alkylations over MOR: the MOR channels can exclude effectively the formation of bulky isomers, α,α- and α,β-DAN even in the isopropylation. On the other hand, the β,β-selectivities over FAU, BEA, and CON

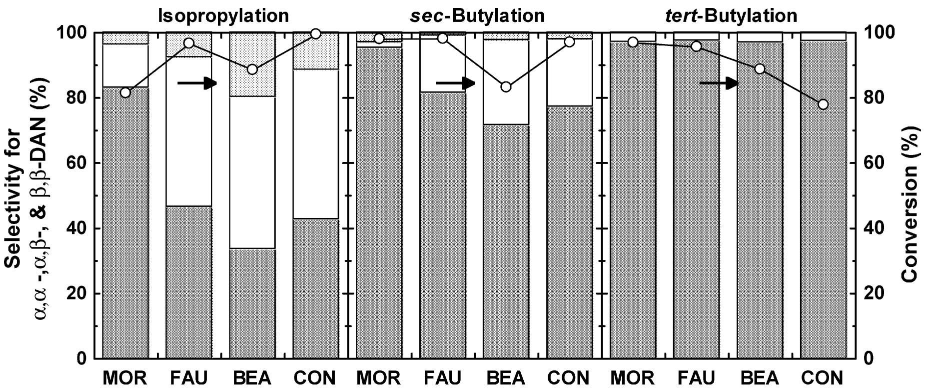

Fig. 9. The selectivity for DAN isomers in the alkylation of NP over the zeolites. Reaction conditions: temperature, 250 °C. Other conditions: see Figs. 1–8. Legends—selectivities: (▩) β,β-DAN (2,6- and 2,7-), (□) α,β-DAN (1,3-, 1,6-, and 1,7-) and (░) α,α-DAN (1,4- and 1,5-); (○) conversion.

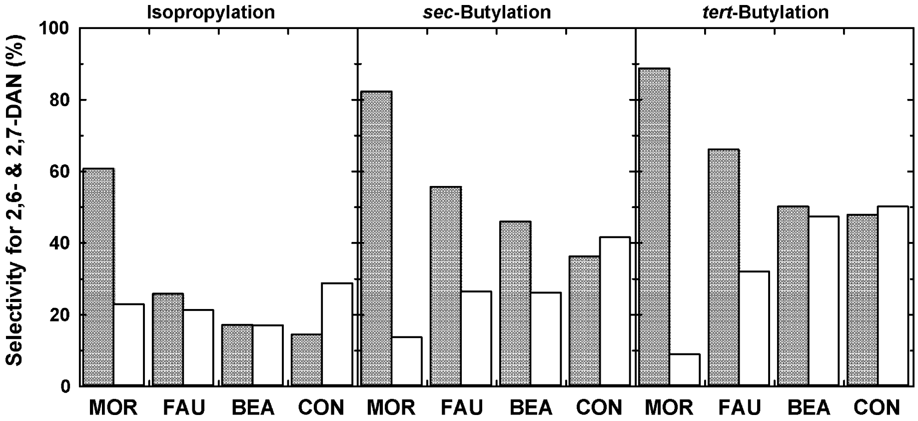

Fig. 10. The selectivity for 2,6- and 2,7-DAN in the alkylation of NP over the zeolites. Reaction conditions: see Fig. 9. Legends: (▨) 2,6-DAN; (☐) 2,7-DAN.

increased by the increase in bulkiness of alkylating agent in the order: isopropylation < *sec*-butylation < *tert*-butylation. These results indicate that the channels of FAU, BEA, and CON cannot prevent the formation of α,α- and α,β-DIPN, particularly, α,β-DIPN by their channels in the isopropylation. However, they can differentiate β,β-DAN from their isomers in the *sec*-butylation and *tert*-butylation, thus resulting, particularly in the complete selection of β,β-DTBN from their isomers in the *tert*-butylation over all zeolites. These results indicate that the β,β-selectivities are decided by the differentiation of β,β-DAN from their isomers due to the steric restriction occurred by structure of zeolite channels and bulkiness of alkylating agents. The kinetic and thermodynamic controls are co-operated in the catalysis if the steric restriction of channels is too loose for differentiating the DAN isomers.

The replacement of isopropyl group with bulky *sec*-butyl and *tert*-butyl groups invokes the differences in bulkiness of β,β-DAN from the other bulky α,α- and α,β-DAN, and also increases the steric interaction of the DAN isomers in the channels, resulting in the increase in the selectivities for β,β-DAN. Particularly, the difference of bulkiness between β,β- and α,β-DAN enhances the formation of the less bulky isomers in the zeolite channels. Thus, α,α- and α,β-DAN are effectively excluded from the channels by the use of bulky alkylating agents. From these synergetic effects of zeolite and alkylating agent, the β,β-selectivities increased with increasing the bulkiness of alkylating agent even over the zeolites with larger reaction spaces.

The 2,6- and 2,7-selectivities in the alkylation of NP over MOR, FAU, BEA, and CON at 250 °C are shown in Fig. 10. MOR gave high selectivity for 2,6-DIPN in the isopropylation, and the selectivities for 2,6-DAN increased in the *sec*-butylation and *tert*-butylation. These results mean that the differentiation of 2,6-DAN from their isomers, particularly from β,β-DAN, over MOR was enhanced by the increase in the bulkiness of alkylating agent. On the other hand, FAU, BEA, and CON gave quite different features on the 2,6- and 2,7-selectivities. The selectivities for 2,6- and 2,7-DIPN in the isopropylation over these zeolites were much lower than those over MOR. They were particularly lower at lower temperatures with the extensive formation of bulky and thermodynamically unstable α,α- and α,β-DIPN, and they increased simultaneously with the increase in temperatures, resulting in low selectivities for 2,6- and 2,7-DIPN as shown in Figs. 3 and 4. These results indicate that FAU, BEA, and CON are not shape-selective for the formation of 2,6- and 2,7-DIPN in the isopropylation. The 2,6-selectivities over these zeolites were much lower than those over MOR even in the *sec*-butylation and *tert*-butylation: the selectivities for 2,6-DSBN were 55% over FAU, 46% over BEA, and 36% over CON in the *sec*-butylation, and the selectivities for 2,6-DTBN were 66% over FAU, 50% over BEA, and 48% over CON in the *tert*-butylation, although they gave β,β-DAN with high selectivities. These simultaneous formations of 2,6- and 2,7-DAN over FAU, BEA, and CON, which is quite different from that over MOR, indicate that the channels of these zeolites cannot effectively differentiate these isomers although shape-selective nature appeared for the formation of β,β-DAN by using bulky alkylating agents.

In previous papers, we studied the alkylation of NP over one-dimensional 12-MR zeolites, SSZ-24 (AFI), SSZ-55 (ATS), and SSZ-42 (IFR) and 14-MR zeolites, CIT-5 (CFI), UTD-1 (DON), and SSZ-53 (SFH) [28,29]. The high β,β-selectivities in the isopropylation were observed over MOR, AFI, and CFI. On the other hand, ATS, IFR, DON, and SFH gave much lower β,β-selectivities. However, the increase in bulkiness of alkylating agent enhanced the β,β-selectivities over all zeolites with large channels including ATS, IFR, DON, and SFH, particularly, in the *tert*-butylation. These results indicate that β,β-DAN can be differentiated from their bulky isomers over the zeolites with large reaction spaces in the channels by using the bulky alkylating agents.

The high 2,6-selectivites in the isopropylation were observed over MOR, AFI, and CFI; however, ATS, IFR, DON, and SFH gave much lower selectivities for 2,6-DIPN. On the other hand, the increase in bulkiness of alkylating agent enhanced the 2,6-selectivities over all zeolites including ATS, IFR, DON, and SFH. The channels of these zeolites are too large for differentiating 2,6- and 2,7-DIPN in the isopropylation; however, they can differentiate 2,6- and 2,7-DAN in the *sec*-butylation and *tert*-butylation. The features are quite different from those of three-dimensional zeolites, FAU, BEA, and CON in this paper. These results indicate that FAU, BEA, and CON have much larger reaction spaces than the other zeolites, and that the shape-selective nature appeared by the synergetic effects of types of zeolites and alkylating agents.

We found that the increase in the selectivities for 4,4′-dialkylbiphenyl (4,4′-DABP) with the increase in bulkiness of alkylating agent over one-dimensional 12-MR zeolites, MOR, AFI, ATS, and IFR [30], one-dimensional 14-MR zeolites, CFI, DON, and SFH [31], and three dimensional zeolites, FAU, BEA, and CON [32]. The high selectivities of 4,4′-DABP are originated from differentiating 4,4′- and 3,4′-DABP at their transition states. However, the differentiation of 2,6- and 2,7-DAN was much severer than that of 4,4′- and 3,4′-DABP in the alkylation of BP because the differences in bulkiness of DAN isomers is much smaller than those of DABP isomers.

4. Conclusion

The selectivities for dialkylnaphthalene (DAN) isomers in the alkylation, *i.e.*, isopropylation, *sec*-butylation, and *tert*-butylation of naphthalene (NP) was studied to elucidate the mechanism of shape-selective catalysis over three-dimensional zeolites, Y (FAU), Beta (BEA), and CIT-1 (CON), and compared to that over mordenite (MOR) with 12-MR straight channels with 8-MR side pockets. Two types of the shape-selectivities, β,β- and 2,6-selectivities, appeared in the alkylation of NP. These selectivities varied by the types of zeolites and alkylating agents.

The β,β-selectivities, which are due to the differentiation of β,β-DAN from their isomers, were higher than 80% in the *sec*-butylation and *tert*-butylation over FAU, BEA, and CON; however, they did not appear in the isopropylation. However, the high β,β-selectivities appeared in the all akylations over MOR. These results mean that β,β-selectivities are controlled by the differentiation of β,β-DAN from their isomers due to the steric restriction at the transition state in their channels, and that the kinetic and thermodynamic controls work if the steric restriction is too loose for the differentiation of DAN isomers in the zeolite channels.

The 2,6-selectivities, which are due to the differentiation of 2,6-DAN from their isomers, particularly from β,β-DAN. MOR gave high 2,6-selectivities in the all alkylations, and the selectivities enhanced with the increase in the bulkiness of alkylating agent. However, FAU, BEA, and CON gave much lower 2,6-selectivities than MOR in the isopropylation, and principal isomers were bulky α,α-DIPN (1,4- and 1,5-) and α,β-DIPN (1,3-, 1,6-, and 1,7-) at lower temperatures, and thermodynamically stable β,β-DIPN (2,6- and 2,7-) at higher temperatures. The selectivities for 2,6-DAN in the *sec*-butylation and *tert*-butylation over FAU, BEA, and CON were much lower than those over MOR although the selectivities increased compared to the isopropylation.

From the results discussed in this paper, we can conclude that MOR can differentiate 2,6-DAN from β,β-DAN, even in the isopropylation, and that such a differentiation of 2,6-DAN from β,β-DAN does not operate in the *sec*-butylation and *tert*-butylation over FAU, BEA, and CON although highly shape-selective nature appeared for the formation of β,β-DAN. The channels of these zeolites with three-dimensional pore-system are too large to exclude 2,6-DAN from β,β-DAN at their transition state by the steric restriction in the channels even with bulky alkylating agents, 1-butene and 2-methylpropene.

Further investigation of the types of zeolites and alkylating agents on the shape-selective catalysis are under progress.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.cattod.2007.12.009.

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