© 2008 The Chemical Society of Japan Bull. Chem. Soc. Jpn. Vol. 81, No. 7, 897–905 (2008)

The Alkylation of Naphthalene over One-Dimensional Twelve-Membered Ring Zeolites. The Influence of Zeolite Structure and Alkylating Agent on the Selectivity for Dialkylnaphthalenes

Yoshihiro Sugi,* Hiroyoshi Maekawa, Hiroaki Naiki, Kenichi Komura, and Yoshihiro Kubota[†]

Department of Materials Science and Technology, Faculty of Engineering, Gifu University, Gifu 501-1193

Received September 25, 2007; E-mail: ysugi@gifu-u.ac.jp

Alkylation, i.e., isopropylation, *s*-butylation, and *t*-butylation, of naphthalene (NP) was examined over one-dimensional twelve-membered (12-MR) zeolites: H-mordenite (MOR), SSZ-24 (AFI), SSZ-55 (ATS), and SSZ-42 (IFR) in order to elucidate how zeolite structure and alkylating agent play roles in the shape-selective catalysis. The β,β-selectivities (for β,β-dialkylnaphthalene (2,6- and 2,7-dialkylnaphthalenes, β,β-DAN)) and the 2,6-selectivities (for 2,6-DAN) were varied with the types of zeolite and of alkylating agent. MOR and AFI gave high β,β-selectivities by using alkylating agents, propene, 1-butene, and 2-methylpropene. However, the β,β-selectivities were changed over ATS and IFR at 250 °C: 40% for the isopropylation, 80% for the *s*-butylation, and almost 100% for the *t*-butylation. The 2,6-selectivities in the isopropylation were as high as 60% over MOR and 50% over AFI at 250 °C; however, they were less than 20% over ATS and IFR. The selectivities increased by using bulky alkylating agents over these one-dimensional zeolites: selective formation of 2,6-DAN occurred in the *s*-butylation and *t*-butylation. The different features among zeolites are explained by the zeolite channel and the bulkiness of alkylating agent. MOR and AFI with straight channels gave smaller reaction spaces than ATS and IFR with corrugated channels. Bulky alkylating agent also enhances the discrimination of the isomers, particularly between 2,6- and 2,7-DAN. The β,β- and 2,6-selectivities are synergetically governed by the zeolite channel and the bulkiness of alkylating agents.

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.[1–8] Only molecules of which dimensions are less than pore size of the zeolite can enter, and react at internal catalytic sites. Bulky molecules, which can not be accommodated in zeolite channels, are excluded, and only molecules, which can diffuse through the channels, appear in the products, thus resulting in the formation of the least bulky isomers. In these catalyses, the selectivities for the least bulky isomers are determined by the discrimination of the isomers at the transition states in the channels: this is so called "restricted transition-state selectivity."[1] There are also possibilities to operate "reactant selectivity" by the discrimination of bulky reactants to enter the zeolites and "products selectivity" by preferential diffusion of the least bulky products from zeolite channels.[1]

The appearance of the shape-selectivity is highly influenced by the structure of zeolites, bulkiness of reagents, etc. If the zeolite channels are large enough to accommodate reactants and/or products isomers, or if reactants and products isomers are smaller than the zeolite channels, the catalysis does not operate under "restricted transition-state selectivity" because the formation of the transition states from bulky isomers is also allowed. In these cases, the catalyses operate under kinetic control due to the reactivity of each position at low temperatures, and under thermodynamic control due to the stability of the products at higher temperatures.[1–3] These features indicate that the exclusion of bulky molecules from the channels is a key factor for the shape-selective catalysis by zeolites, and that they depend on the type of zeolite and of alkylating agent.

The isopropylation of polynuclear hydrocarbons, such as naphthalene (NP) and biphenyl (BP) is a typical acid-catalyzed reaction for demonstrating the shape-selective nature of zeolite.[4–25] Selective formation of the least bulky 2,6-diisopropylnaphthalene (2,6-DIPN) and 4,4′-diisopropylbiphenyl (4,4′-DIPB) should be facilitated in the isopropylation of NP and BP if steric environments of catalytic sites are properly restricted. In a previous paper, we described that 2,6-DIPN was selectively produced from NP over dealuminated H-mordenite (MOR).[9] Catalytically active sites in MOR channels effectively exclude the transition states of bulky DIPN isomers, thus resulting in selective formation of the least bulky 2,6-DIPN. On the other hand, some large pore zeolites, such as Y-, β-, and L-zeolites, give mixtures of DIPN isomers, and the selectivities for 2,6-DIPN over these zeolites are much lower than those over MOR.[16–20] These results are due to non-selective reactions in large reaction spaces in the channels. However, there are several reports of shape-selective formation of 2,6-di-*t*-butylnaphthalene (2,6-DTBN) occurring if 2-methyl-2-propanol or 2-methylpropene is used as alkylating agent.[21–25] These results prompted us to study how zeolite structure, such as dimensionality, pore-entrance, and channel, is related to the catalysis, and how the bulkiness of alkylating agents influences transition states.

[†] Present address: Department of Materials Science and Engineering, Graduate School of Engineering, Yokohama National University, Yokohama 240-8501

doi:10.1246/bcsj.81.897

Table 1. Properties of Zeolites

Zeolite	FTC	Pore entrance /nm	Structure of channel	Cage (MR)[a]	SiO_2/Al_2O_3	Surface area /$m^2\,g^{-1}$	External surface area /$m^2\,g^{-1}$[b]	Pore volume /$mL\,g^{-1}$	NH_3-TPD peak temp /°C	Acid amount /$mmol\,g^{-1}$
Mordenite	MOR	0.67 × 0.72	Straight with 8-MR side-pocket	—	128	460	35	0.16	389	0.20
SSZ-24	AFI	0.72 × 0.72	Straight	—	202	414	5.4	0.16	274	0.11
SSZ-55	ATS	0.65 × 0.75	Corrugated	20	160	478	18	0.19	299	0.12
SSZ-42	IFR	0.62 × 0.72	Corrugated	24	280	518	11	0.20	255	0.08

a) The member of the cages of the zeolites is the maximum size of oxygen rings estimated from data in the reference.[26]
b) Calculated by *t*-plot of N_2 adsorption.

In this paper, we describe the alkylation, i.e., isopropylation, *s*-butylation, and *t*-butylation of NP, over one-dimensional 12-membered ring (12-MR) zeolites, H-mordenite and SSZ-24 with straight channels, and SSZ-55 and SSZ-42 with corrugated channels (20-MR cages for SSZ-55 and 24-MR cages for SSZ-42).[26–40] The discussion in the paper is based on the β,β-selectivity (selectivity for 2,6- and 2,7-dialkylnaphthalene (2,6- and 2,7-DAN)) and the 2,6-selectivity (selectivity for 2,6-DAN) in order to focus on key factors for controlling the catalysis in sterically restricted environments of zeolites. The abbreviations of zeolites are expressed by FTC from the IZA Structure Commission: MOR for Mordenite, AFI for SSZ-24, ATS for SSZ-55, and IFR for SSZ-42 unless otherwise stated.[26]

Experimental

Zeolites. AFI, ATS, and IFR were synthesized according to the literature.[27–39] MOR was obtained from Tosoh Corporation ($SiO_2/Al_2O_3 = 128$; TSZ-690HOA). All zeolites were used as H^+-form for the catalytic reactions. Table 1 shows typical properties of zeolites related to catalytic alkylation of NP. Other results on the characterization of the zeolites used in this work are shown in our previous paper.[41]

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 reaction period 4 h under propene pressure of 0.8 MPa (0.4 MPa for 1-butene in the *s*-butylation and for 2-methylpropene in the *t*-butylation). An autoclave containing NP and the catalyst was flushed with nitrogen before heating. After reaching reaction temperature, propene was introduced to the autoclave, and the reaction was started with agitation. The pressure was kept constant throughout the reaction. After cooling the autoclave, the catalyst was filtered off, and washed well with toluene. Liquid bulk products were analyzed by using a Shimadzu Gas Chromatograph GC-14A or GC-18A equipped with TC-17 (25 m × 0.25 mm; film thickness: 0.25 µm; Agilent Technologies) or HP-INNOWax (60 m × 0.25 mm; film thickness: 0.5 µm; Agilent Technologies) capillary columns. The products were also identified by using a Shimadzu Gas GC-MS 5000 Chromatograph-Mass Spectrometer equipped with the above columns.

The yields of alkylnaphthalene (AN) and dialkylnaphthalene (DAN) isomers each product are calculated on the basis of the amount of starting NP, and the selectivities for each DAN isomers are expressed based on total amounts of DAN isomers.

DAN isomers in the isopropylation, *s*-butylation, and *t*-butylation were defined as DIPN, DSBN, and DTBN, respectively. β,β-DAN is defined as a mixture of 2,6- and 2,7-DAN isomers, α,β-DAN as 1,3- 1,6-, and 1,7-DAN isomers, and α,α-DAN as 1,4- and 1,5-DAN isomers. The β,β-, α,β-, and α,α-selectivities are defined as the selectivities for β,β-, α,β-, and α,α-DAN among DAN isomers, respectively. The 2,6- and 2,7-selectivities are the selectivities for 2,6- and 2,7-DAN among DAN isomers, respectively.

The catalytic activities based on the yield of alkylated products were shown in Figures S1–S6 in the Supporting Information.

Results and Discussion

The Isopropylation. The isopropylation of NP over MOR, AFI, ATS, and IFR gave mixtures of isopropylnaphthalene (IPN), diisopropylnaphthalene (DIPN), triisopropylnaphthalene (TriIPN), and tetraisopropylnaphthalene (TetraIPN) isomers. The catalytic activities increased with reaction temperature; however, the conversion decreased at higher temperatures in some cases. The decrease in conversion was accompanied by the decrease in the yield of DIPN and the increase in the yield of IPN: this is due to de-alkylation of DIPN to IPN (see Figures S1 and S2 in Supporting Information).

The influences of reaction temperature on the selectivities for DIPN isomers in the isopropylation of NP are shown in Figure 1 over MOR and AFI, and in Figure 2 over ATS and IFR. The products consisted of mixtures of β,β-, α,β-, and α,α-DIPN isomers over these zeolites, and they were varied by the type of zeolite. The β,β-selectivities over MOR were almost constant in the range of 75–85% from 150 to 300 °C, and the α,β- and α,α-selectivities were totally less than 15–25%. On the other hand, the β,β-selectivities over ATS and IFR were much lower than those over MOR and AFI: α,β- and α,α-DIPN were principal products at low reaction temperatures, and they decreased with the increase in temperature accompanying the increase in the β,β-selectivities. These results indicate that MOR and AFI are shape-selective for the formation of β,β-DIPN; however, ATS and IFR are not.

These results suggest that mechanisms of the isopropylation are different among the zeolites. The differeces are due to the difference in the structure of the zeolites. The size of pore-entrance increases in the order: MOR < AFI ≈ ATS ≈ IFR, although differences are not significant.[26] They also have different types of channels: MOR and AFI have straight channels (pore-entrance: 0.67 nm × 0.72 nm for MOR and 0.72 nm × 0.72 nm for AFI). ATS and IFR have corrugated channels with 20-MR cages (pore-entrance: 0.65 nm × 0.75 nm) and with 24-MR cages (pore-entrance: 0.62 nm × 0.72 nm), respective-

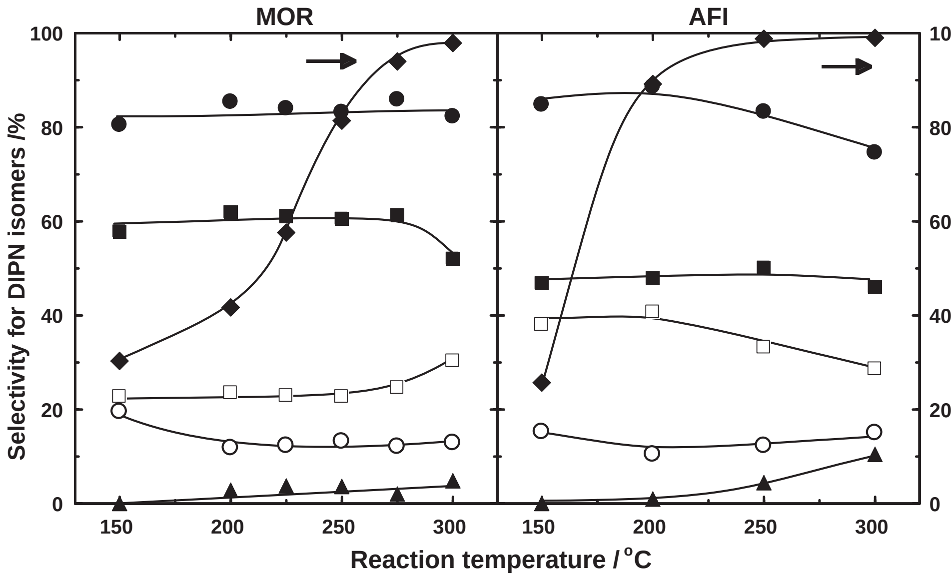

Figure 1. The influence of reaction temperature on the selectivity for DIPN isomers the isopropylation of NP over MOR and AFI. Reaction conditions: NP: 50 mmol; catalyst: 0.5 g; temperature: 150–350 °C; propene pressure: 0.8 MPa; period: 4 h. Legends: ■: 2,6-DIPN; □: 2,7-DIPN; ●: β,β-DIPN; ○: α,β-DIPN; ▲: α,α-DIPN.

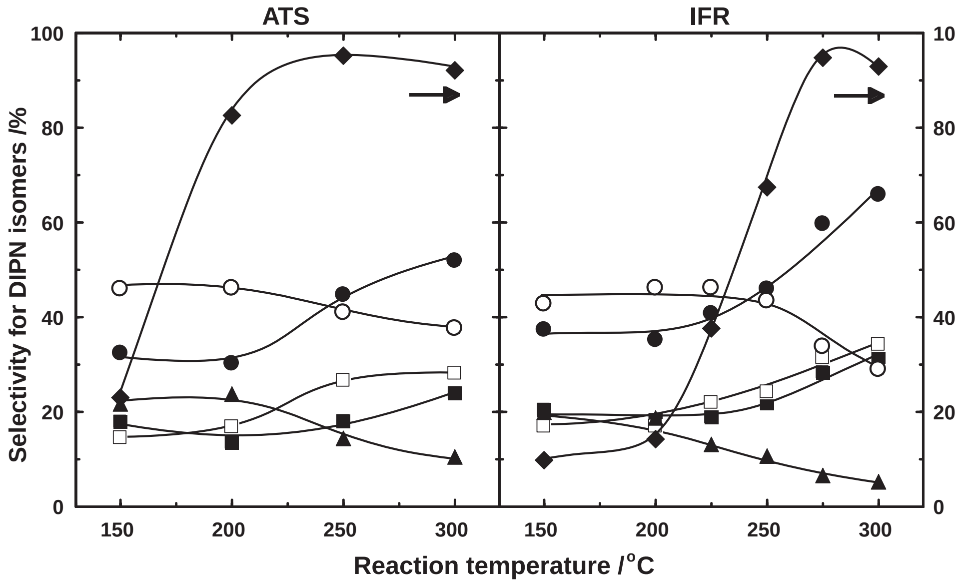

Figure 2. The influence of reaction temperature on the selectivity for DIPN isomers in the isopropylation of NP over ATS and IFR. Reaction conditions and legends: see Figure 1.

ly.[26,40] Thus, these differences in the zeolite structure cause the difference in reaction space in the order: MOR < AFI ≪ ATS ≪ IFR, and steric restriction with the channels decreased in the reversed order. The differences in reaction space and steric interaction in zeolite channels invoke the differences in the β,β-selectivities by using different type of zeolite. MOR and AFI channels are small enough to discriminate less bulky β,β-DIPN from the other bulky isomers, resulting in selective formation of β,β-DIPN. On the other hand, the isopropylation over ATS and IFR is principally operated by kinetic and/or thermodynamic controls: these zeolites cannot prevent the formation of bulky α,β- and α,α-DIPN isomers because their channels are too large for selective formation of β,β-DIPN. Kinetic control is predominated at lower temperatures, i.e., a nucleophilic attack of isopropyl carbocation to the electron-rich α-carbon of NP leads to the predominant formation of α,α- and α,β-DIPN. Thermodynamic control also operates in the reaction at higher temperatures, thus resulting in the increase in the formation of thermodynamically stable β,β-DIPN and the decrease in the formation of less stable α,α- and α,β-DIPN.

The 2,6-selectivities in the isopropylation over MOR and AFI were also different from those over ATS and IFR (Figures 1 and 2). The 2,6-selectivities were around 60% over MOR in the range of 150–275 °C, and around 50% over AFI in the range of 150–300 °C. These results mean that more precise

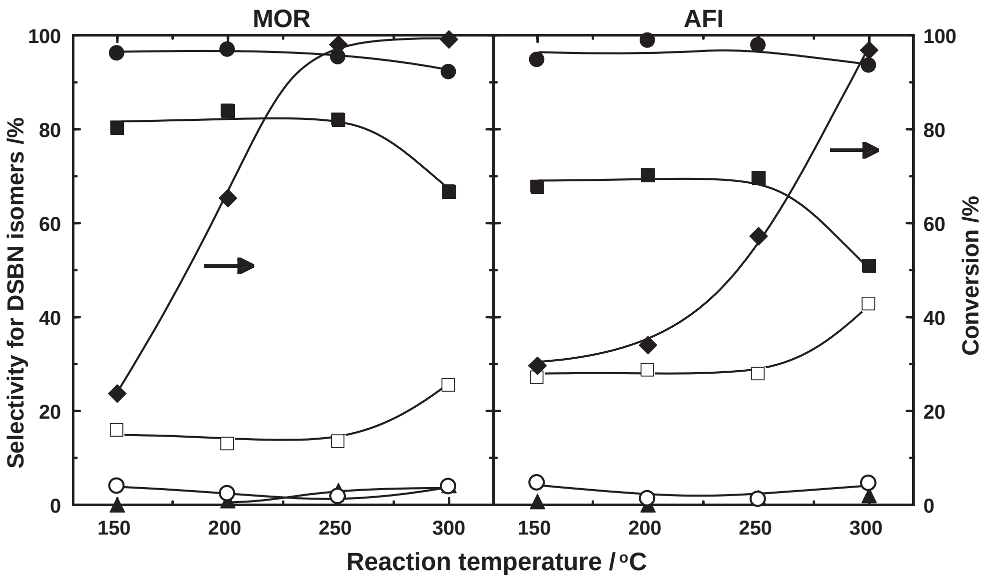

Figure 3. The influences of reaction temperature on the selectivity for DSBN isomers in the *s*-butylation of NP over MOR and AFI. Reaction conditions: BP: 50 mmol; catalyst: 0.25 g; temperature: 150–300 °C; 1-butene pressure: 0.5 MPa; period: 4 h. Legends: ◆: conversion; ■: 2,6-DSBN; □: 2,7-DSBN; ●: β,β-DSBN; ○: α,β-DSBN; ▲: α,α-DSBN.

discrimination of 2,6-DIPN from the other bulky isomers, particularly between 2,6- and 2,7-DIPN by zeolite channels is necessary for high 2,6-selectivities compared with the case of the β,β-selectivities. Straight channels of MOR can effectively discriminate 2,6- and 2,7-DIPN from the other isomers; however, AFI gave lower 2,6-selectivities than MOR although high β,β-selectivities were observed over these zeolites. The differences in these zeolites mean that the discrimination of 2,6- and 2,7-DIPN by AFI channels is looser than that by MOR channels, because AFI has slightly larger channels than MOR. On the other hand, the 2,6-selectivities over ATS and IFR were varied with reaction temperature: 15% at 150 °C to 25% at 300 °C over ATS and 20% at 150 °C to 35% at 300 °C over IFR: these low 2,6-selectivities reflect low β,β-selectivities as discussed in previous section. These results mean that corrugated channels of ATS and IFR cannot highly discriminate 2,6-, 2,7-, and other DIPN isomers. Moreover, the 2,6-selectivities over ATS and IFR at higher reaction temperatures accompanied the decrease in α,β- and α,α-DIPN. These results indicate that the isopropylation over ATS and IFR operates under kinetic control at low temperatures and/or under thermodynamic control at higher temperatures as discussed above for the β,β-selectivities.

The 2,6-selectivities decreased slightly at higher temperatures in the isopropylation of NP over MOR; however, the β,β-selectivities were almost kept constant. These results indicate that the decrease in the selectivities is due to the isomerization of 2,6-DIPN to 2,7-DIPN at external acid sites as discussed in the isomerization of 4,4′-DIPB in the isopropylation of BP.[4–9]

The *s*-Butylation. The influence of reaction temperature on the *s*-butylation of NP over MOR, AFI, ATS, and IFR was examined in order to understand the influence of bulkiness of alkylating agent on the alkylation. These zeolites gave mixtures of *s*-butylnaphthalene (SBN), di-*s*-butylnaphthalene (DSBN), and tri-*s*-butylnaphthalene (TSBN) isomers. Catalytic activities were observed in the similar levels as in the isopropylation although the formation of higher *s*-butylnaphthalenes, such as TSBN isomers, decreased (see Figures S3 and S4 in Supporting Information).

The influences of reaction temperature on the selectivities for DSBN isomers in the *s*-butylation are shown in Figure 3 over MOR and AFI, and in Figure 4 over ATS and IFR. The products principally consisted of β,β- and α,β-DSBN over all zeolites, and the formation of α,α-DSBN was negligible. The β,β-selectivities over MOR and AFI were higher than 90–95% in the range of 150–300 °C. On the other hand, the β,β-selectivities over ATS and IFR were 65% and 70%, respectively, at 150 °C, and they gradually increased with reaction temperature. The increase in the β,β-selectivities was accompanied by the decrease in the α,β-selectivities. These results mean that the channels of ATS and IFR are small enough to exclude the formation of some of the bulky α,α- and α,β-DSBN isomers, resulting in the higher β,β-selectivities. However, the operation of kinetic control is still dominant particularly at low temperatures, resulting in the formation of α,β-DSBN, and thermodynamic control is also operated at higher temperatures, resulting in the formation of β,β-DSBN.

The 2,6-selectivities in the *s*-butylation were also around 70–80% over MOR and AFI at low and moderate temperatures. However, ATS and IFR gave lower 2,6-selectivities: 55% over ATS and 45–55% over IFR in the range of 150–300 °C. These results mean that these zeolites can discriminate 2,6-DSBN from the other DSBN isomers by steric restriction with their channels. MOR and AFI effectively discriminated 2,6-DSBN and the other isomers; however, the *s*-butylation over ATS and IFR accompanied the formation of α,β-DSBN, particularly at low temperatures. These results indicate that ATS and IFR channels cannot prevent effectively the formation of α,β-DSBN because they are too large for shape-selective catalysis, and that kinetic and/or thermodynamic controls still operate in the *s*-butylation over these zeolites.

The 2,6-selectivities were enhanced over all zeolites com-

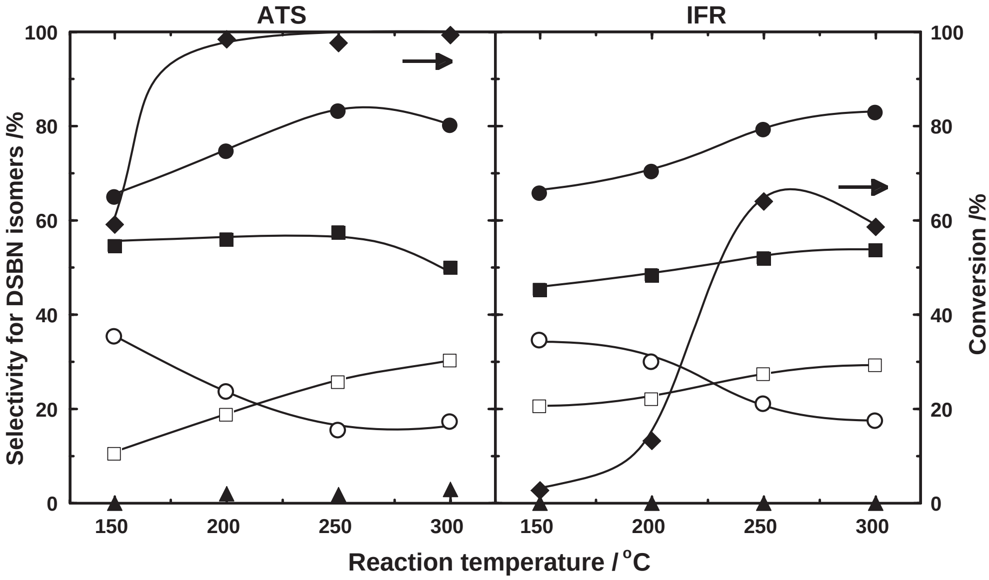

Figure 4. The influences of reaction temperature on the selectivity for DSBN isomers in the *s*-butylation of NP over ATS and IFR. Reaction conditions: NP: 25 mmol; catalyst: 0.125 g. Other conditions and legends: see Figure 3.

pared to those in the isopropylation. The higher 2,6-selectivities in the *s*-butylation are invoked by the difference in the bulkiness of isopropyl and *s*-butyl moieties in the products. The differences in the interaction of 2,6-DSBN with the channels enhanced much the discrimination from the other bulky isomers compared to those of 2,6-DIPN. Although effective molecular diameters of DSBN isomers are almost the same as those of DIPN isomers, the replacement of isopropyl moieties by *s*-butyl ones invokes much differences in the bulkiness of 2,6-DSBN and the other isomers by the interaction with the channels, resulting in the increase in the selectivities for 2,6-DSBN. The similar influence of isopropyl and *s*-butyl moieties of the products were observed in the β,β-selectivities.

The decrease in the 2,6-selectivities occurred in the *s*-butylation over MOR and AFI at 300 °C as in the isopropylation; however, the β,β-selectivities kept almost unchanged. These results indicate that the decrease in the selectivities is due to the isomerization of 2,6-DSBN to 2,7-DSBN at external acid sites as discussed in the isomerization of 4,4′-dialkylbiphenyl (4,4′-DABP) in the alkylation of BP.[4–8,41,42]

The *t*-Butylation. The steric restriction among DAN isomers by zeolite channels is enhanced by the bulkiness of alkylating agents as discussed in the isopropylation and *s*-butylation. It is interesting to understand the influence of bulky alkylating agent, 2-methylpropene on the selectivities for DTBN isomers. The *t*-butylation gave *t*-butylnaphthalene (TBN) and di-*t*-butylnaphthalene (DTBN), and small amounts of tri-*t*-butylnaphthalene (TTBN) isomers. However, catalytic activities in the *t*-butylation were lower than those in the isopropylation and *s*-butylation although they increased with temperature (see Figures S5 and S6 in Supporting Information).

The β,β-selectivities were higher than 95% in the range of 150–300 °C as shown in Figure 5 over MOR and AFI, and in Figure 6 over ATS and IFR. The formation of β,β-DTBN was exclusive over all zeolites, and α,α- and α,β-DTBN were negligible in the products. These results mean that the channels of these zeolites are small enough for the discrimination of β,β-DTBN from the other isomers.

Figures 5 and 6 also show the influence of temperature on the 2,6-selectivities in the *t*-butylation. The 2,6-selectivities were also 95% over MOR, 90% over AFI, and 90% over ATS in the *t*-butylation at low and moderate temperatures below 250 °C. Over these zeolites, the shape-selective formation of 2,6-DTBN occurred in the channels, even in large ATS channels. On the other hand, the 2,6-selectivities over IFR were around 55% although the β,β-selectivities were higher than 95%. These results indicate that high β,β-selectivities do not mean always high 2,6-selectivities, and that the discrimination of 2,6-DTBN from its bulkier isomers is requested to fit precisely the transition state with the channels. The lower 2,6-selectivities over IFR mean that the channels are less able to recognize the difference between 2,6- and 2,7-DTBN than the other zeolites.

The decrease in the 2,6-selectivities occurred in the *t*-butylation over MOR, AFI, and ATS at 300 °C; however, the β,β-selectivities were almost kept constant. These results indicate the decrease in selectivities is due to the isomerization of 2,6-DTBN to 2,7-DTBN at external acid sites as discussed in the isomerization of 4,4′-DABP in the alkylation of BP.[4–8,41,42]

Shape-Selective Catalysis of the Zeolites in the Alkylation of NP. Catalytic performances of zeolites for shape-selective catalysis are generally influenced by many factors.[1,2] Some typical factors on zeolites are pore-entrance, channels, and physical properties, such as crystal size, morphology, density, and distribution of active species, which are also influenced by preparation and post-synthesis methods. Reaction conditions, such as temperature, pressure, period, and catalyst amount, also influence the catalytic performance. Among the factors, the structures of pore-entrance and channel are the most important for controlling shape-selectivity of the catalysis.

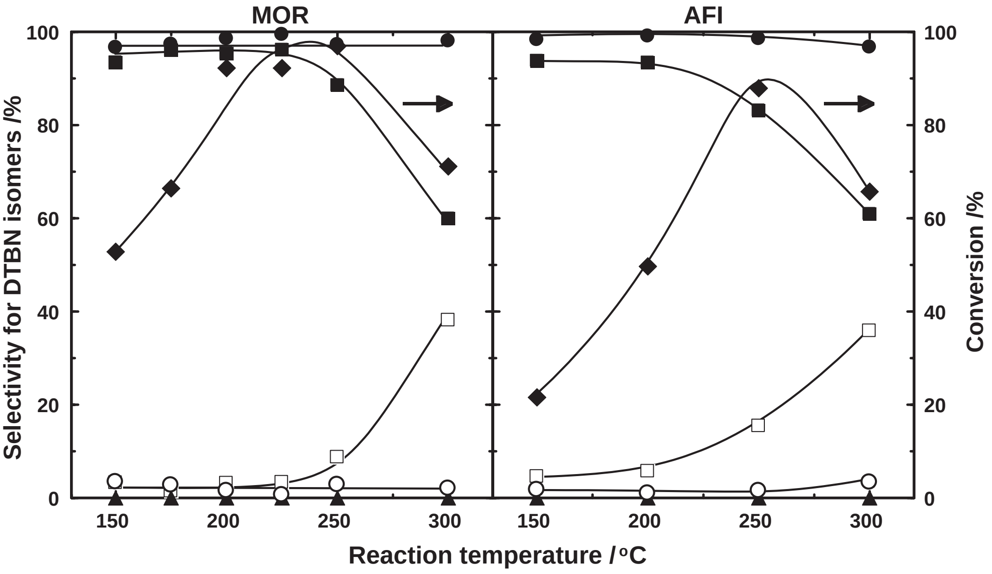

Figure 5. The influence of reaction temperature on the selectivity for DTBN isomers in the *t*-butylation of NP over MOR and AFI. Reaction conditions: BP: 50 mmol (MOR), 25 mmol (AFI); catalyst: 0.25 g (MOR); 0.125 g (AFI); temperature: 150–300 °C; 2-methylpropene pressure: 0.5 MPa; period: 4 h. Legends: ◆: conversion; ■: 2,6-DTBN; □: 2,7-DTBN; ●: β,β-DTBN; ○: α,β-DTBN; ▲: α,α-DTBN.

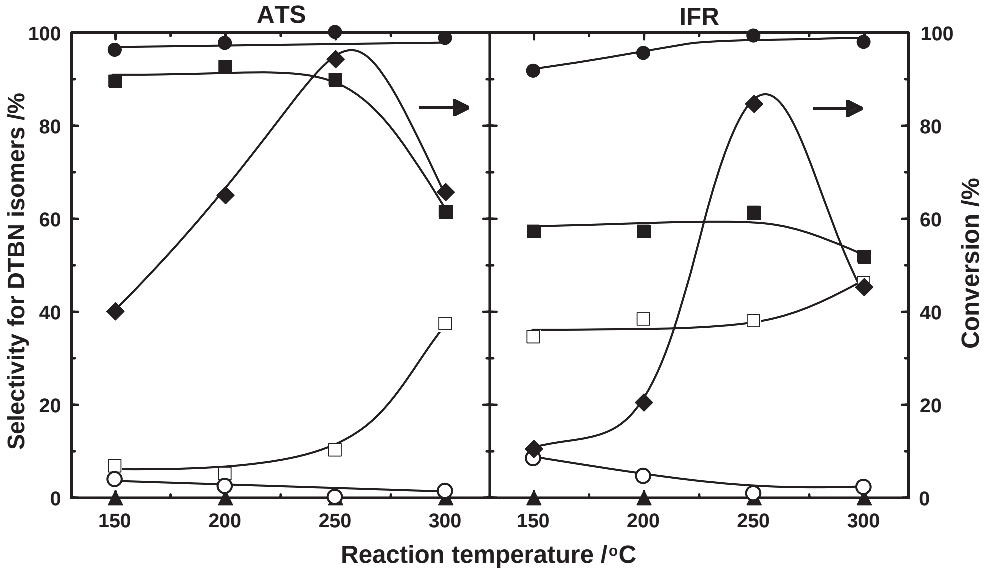

Figure 6. The influence of reaction temperature on the selectivity for DTBN isomers in the *t*-butylation of NP over ATS and IFR. Reaction conditions: NP: 25 mmol; catalyst: 0.125 g. Other conditions and legends: see Figure 5.

Two types of selectivities for DAN isomers appear in the alkylation of NP: β,β-selectivities and 2,6-selectivities. The β,β-selectivities are due to discrimination of less bulky β,β-DAN from bulkier α,α- and α,β-DAN by zeolite channels because sizes of DAN isomers decreased in the order: α,α-DAN > α,β-DAN > β,β-DAN. The α,α- and α,β-selectivities are an index for the bulky isomers formed principally under kinetic control. The appearance of high β,β-selectivities also occurs under thermodynamic control, which work particularly at higher temperatures under sterically less restricted reaction environments: the 2,7-DAN/2,6-DAN ratio should approach unity in the selectivities because of thermodynamic equilibrium.[45] The 2,6-selectivities are due to the discrimination of the least bulkier 2,6-DAN from the other DAN isomers, particularly from 2,7-DAN by steric restriction with zeolite channels.[4,5,9,11,14,25,43,44] If the channels are small enough to exclude bulky isomers by steric restriction in the channels, shape-selective catalysis occurs to yield the less bulky 2,6-DAN isomers. However, shape-selective catalysis will not occur if the channels are large enough for formation of transition states for bulkier isomers.

The size of pore-entrance increases in the order: MOR < AFI ≈ ATS ≈ IFR, although the differences are not significant. However, their channel structures are different by the

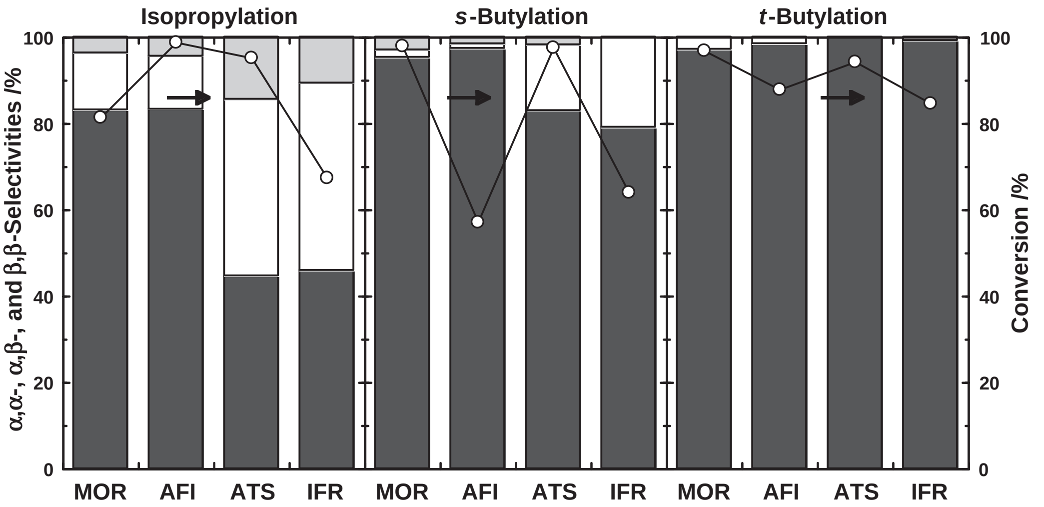

Figure 7. The selectivities for DAN isomers in the alkylation of NP over the zeolites. Reaction conditions: temperature: 250 °C. Other conditions: see Figures 1–6. Selectivities: ■: β,β-DAN; □: α,β-DAN; ▨: α,α-DAN; ○: conversion.

type of zeolite: straight channels for MOR and AFI and corrugated channels with 20-MR cage for ATS and with 24-MR cage for IFR. These differences suggest that reaction space in zeolite channels is in the order: MOR $<$ AFI $\ll$ ATS $<$ IFR, and steric interaction in the catalysis decreases in the reversed order: MOR $>$ AFI $\gg$ ATS $>$ IFR (see Figure S7 in Supporting Information).

Figure 7 shows the influence of the β,β-, α,β-, and α,α-selectivities on the zeolite and of the alkylating agent in the alkylation of NP at 250 °C. These selectivities are typical selectivities for DAN isomers over these zeolites because DAN isomers are not significantly isomerized under the reaction conditions at 250 °C.

The β,β-selectivities highly depend on the types of zeolite and of the alkylating agent. MOR and AFI were shape-selective for the isopropylation, *s*-butylation, and *t*-butylation. The β,β-selectivities over ATS and IFR are as low as 40% for the isopropylation, and they increased to around 80% in the *s*-butylation and *t*-butylation. These results indicate that the selectivities for DAN isomers are determined by synergetic effects of the types of zeolite and of alkylating agent. However, the β,β-selectivities increased with increasing reaction temperature in the isopropylation over ATS and IFR as shown in Figure 2. These results indicate that the catalysis operates under kinetic control at lower temperatures and by thermodynamic control at higher temperatures because the ATS and IFR channels are too large for selective formation of β,β-DIPN. Bulky alkylating agent enhances the β,β-selectivities even for ATS and IFR in the *s*-butylation and *t*-butylation. Particularly, the replacement of isopropyl moieties with bulky *s*-butyl and *t*-butyl ones invokes the differences in the bulkiness of β,β-DAN from the other bulky α,α- and α,β-DAN isomers, and also increases steric interaction of the DAN isomers in the channels, resulting in the increase in the β,β-selectivities. Particularly, the difference of the bulkiness between β,β- and α,β-DSBN in the *s*-butylation enhances the discrimination of the least bulky isomers in the zeolite channels although effective molecular diameters of β,β-DSBN are almost the same as that of β,β-DIPN. Thus, α,α- and α,β-DAN are effectively excluded from the channels by the increase in the bulkiness of alkylating agents in the order: isopropylation $<$ *s*-butylation $<$ *t*-butylation. From these synergetic effects of the types of zeolite and of alkylating agent, the β,β-selectivities increased with increasing the bulkiness of alkylating agent even over the zeolites with larger reaction spaces, such as ATS and IFR in the *t*-butylation.

Figure 8 shows the influence of the 2,6-selectivities on the types of zeolite and of the alkylating agent for the alkylation at 250 °C. The 2,6-selectivities reflect more precise fitting steric restriction with the channels than the β,β-selectivities. They were influenced by the type of the channels, and enhanced with the increase in the bulkiness of alkylating agents. MOR and AFI were selective for the formation of 2,6-DIPN even in the isopropylation, and the selectivities increased further with the increase in the bulkiness of alkylating agents. ATS and IFR, which have larger channels than MOR and AFI, also enhanced the 2,6-selectivities with the increase in the bulkiness of alkylating agents. However, IFR channels are too large for the high discrimination of 2,6- and 2,7-DTBN. These results indicate that fitting the least bulky 2,6-DAN at transition state in the channels are the most important key factor for shape-selective catalysis.

The features of the β,β- and 2,6-selectivities over one-dimensional 12-MR zeolites, MOR, AFI, ATS, and IFR, in this work are different from those over one-dimensional 14-MR zeolites, CFI, DON, and SFH and over three-dimensional zeolites, FAU, BEA, and CON in our previous papers.[25,44]

The β,β-selectivities over CFI were around 60% at 250 °C in the isopropylation; however, DON and SFH gave much lower β,β-selectivities. The β,β-selectivities were much improved in the *s*-butylation, particularly over CFI up to 90%; however, those over DON and SFH still remained at 60–65%. Further, the β,β-selectivities were almost 100% in the *t*-butylation over all 14-MR zeolites. The β,β-selectivities also increased with the increase in bulkiness of alkylating agent over FAU, BEA, and CON.[25] These differences in the β,β-selectivities are due to synergytic effects of zeolite channels and bulkiness of alkylating agents as discussed in previous sections. The pre-

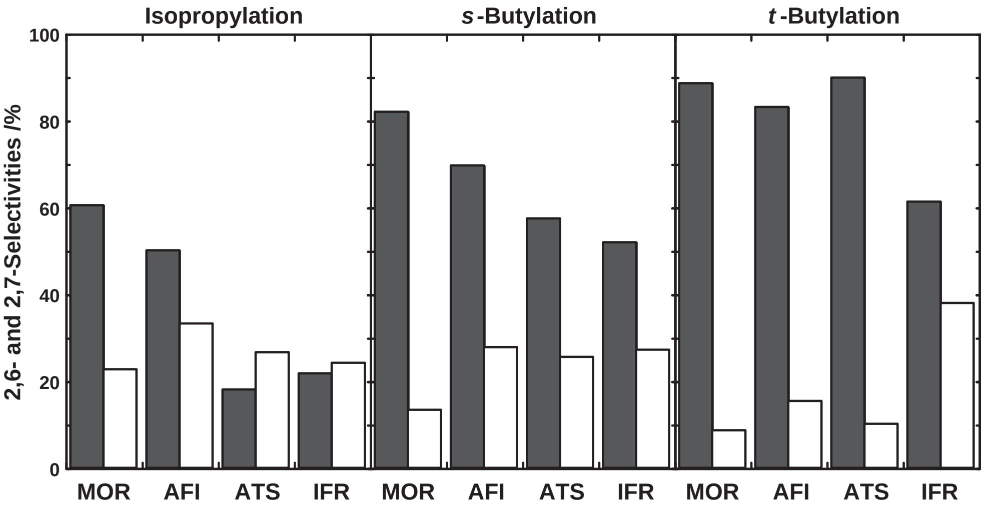

Figure 8. The 2,6- and 2,7-selectivities in the alkylation of NP over the zeolites. Reaction conditions: see Figure 7. Legends: ■: 2,6-DAN; □: 2,7-DAN.

cise fitting of β,β-DAN at the transition state in the channels is essential for the high β,β-selectivities. The low β,β-selectivities are due to large reaction space enough to allow the formation of bulky isomers by kinetic and/or thermodynamic controls.

The 2,6-selectivities are also related to the types of zeolite and alkylating agent. Among 14-MR zeolites, CFI gave the highest 2,6-selectivities in the isopropylation, *s*-butylation, and *t*-butylation: 45%, 65%, and 89%, respectively. The 2,6-selectivities over DON and SFH depended on the bulkiness of alkylating agent: they were less than 10% in the isopropylation, improved up to 50–60% in the *s*-butylation, and to around 90% in the *t*-butylation. On the other hand, the 2,6-selectivities was not significantly improved by changing the bulkiness of alkylating agent over FAU, BEA, and CON. Particularly, the no selective formation of 2,6-DTBN was observed even in the *t*-butylation although β,β-DTBN was highly selectively formed over these zeolites: these features are different from those over one-dimensional 12- and 14-MR zeolites. These results mean that the channels of FAU, BEA, and CON are too large for the discrimination of 2,6- and 2,7-DAN although they can recognize the differences in β,β-DAN and the other isomers.

From the results on the various zeolites in previous and current works,[25,44] it is concluded that β,β-DAN can be discriminated from the bulky isomers even over the zeolites with large reaction spaces in the channels if bulky alkylating agent are used, and that the 2,6-selectivities appear by the discrimination of small differences in steric interaction among DAN isomers with zeolite channels.

In our previous papers, we found that the increase in the selectivities for 4,4′-DABP (4,4′-selectivities) with the increase in the bulkiness of alkylating agent in the alkylation of BP over the zeolites.[41–43] The high 4,4′-selectivities are originated from the discrimination of 4,4′-DABP from the other isomers, particularly 3,4′-DABP, at their transition states. However, the difference in the bulkiness between 2,6- and 2,7-DAN was much small compared to the difference between 4,4′- and 3,4′-DABP in the alkylation of BP.

The results discussed on the alkylation of NP and BP over zeolites indicate that the β,β- and 2,6-selectivities for NP and the 4,4′-selectivities for BP are synergetically governed by the types of zeolite channels and of the bulkiness of alkylating agents.

Conclusion

The selectivities for dialkylnaphthalene (DAN) isomers in the alkylation, i.e., isopropylation, *s*-butylation, and *t*-butylation, of naphthalene (NP) were studied over one-dimensional 12-MR zeolites, mordenite (MOR), SSZ-24 (AFI), SSZ-55 (ATS), and SSZ-42 (IFR) in order to understand the mechanism of shape-selective catalysis. Two types of the selectivities: the β,β- and 2,6-selectivities were observed in the alkylation of NP, which were influenced by the types of zeolite and alkylating agent.

The β,β-selectivities, which are due to the discrimination of β,β-diisopropylnaphthalene (β,β-DIPN (2,6- and 2,7-DIPN)) from their other isomers, were higher than 90% in the isopropylation over MOR; however, those over AFI, ATS, and IFR were much lower than those over MOR: the predominant isomers over ATS and IFR were bulky and less stable α,β-DIPN (1,3-, 1,5-, and 1,7-DIPN) and α,α-DIPN (1,4- and 1,5-DIPN) at low temperatures, and the formation of stable β,β-DIPN increased with increasing temperature. The β,β-selectivities in the *s*-butylation were higher than 95% over MOR and AFI; however, they increased slightly with the increase in reaction temperature over ATS and IFR. The exclusive formation of β,β-di-*t*-butylnaphthalenes (β,β-DTBN) were observed in the *t*-butylation over all zeolites. These results suggest the increase in the bulkiness of alkylating agents enhances the steric restriction even on the zeolites with large reaction space, resulting in enhancing the β,β-selectivities.

The 2,6-selectivities, which are due to discrimination of 2,6-DAN from the other isomers, increased by using bulky alkylating agents. They are higher than 60% in the isopropylation over MOR at moderate temperature below 275 °C. Selective formation of 2,6-DAN was observed in the *s*-butylation and *t*-butylation over these one-dimensional zeolites.

The different features among zeolites are explained by the zeolite channel and the bulkiness of alkylating agent. MOR and AFI with straight channels gave smaller reaction spaces than ATS and IFR with corrugated channels. The bulkiness of alkylating agent also enhances discrimination of isomers, particularly, between 2,6- and 2,7-DAN. The 2,6- and β,β-selectivities are synergetically governed by the types of zeolite and of the bulkiness of alkylating agent.

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

A part of this work was financially supported by Grant-in-Aids for Scientific Research (B) Nos. 16310056 and 19310060, the Japan Society for the Promotion of Science (JSPS).

Supporting Information

Figures S1–S6: The influence of reaction temperature on the yield of alkylated products in the alkylation of NP. Figure S7: Models of pore entrances and channels of MOR, AFI, ATS, and IFR topologies. This material is available free of charge on the Web at: http://www.csj.jp/journals/bcsj/.

References

1 S. M. Csicsery, *Zeolites* **1984**, *4*, 202.

2 P. B. Venuto, *Microporous Mater.* **1994**, *2*, 297.

3 N. Y. Chen, W. E. Garwood, F. G. Dwyer, *Shape-selective Catalysis in Industrial Applications*, 2nd ed., Marcel Dekker, New York, **1996**.

4 Y. Sugi, M. Toba, *Catal. Today* **1994**, *19*, 187.

5 Y. Sugi, Y. Kubota, in *Catalysis*, ed. by J. J. Spivey, Specialist Periodical Report, Royal Soc. Chem., **1997**, Vol. 13, pp. 55–84.

6 Y. Sugi, *Korean J. Chem. Eng.* **2000**, *17*, 1.

7 Y. Sugi, Y. Kubota, T. Hanaoka, T. Matsuzaki, *Catal. Surv. Jpn.* **2001**, *5*, 43.

8 Y. Sugi, K. Komura, J.-H. Kim, *J. Korean Ind. Eng. Chem.* **2006**, *17*, 235.

9 J.-H. Kim, Y. Sugi, T. Matsuzaki, T. Hanaoka, Y. Kubota, X. Tu, M. Matsumoto, *Microporous Mater.* **1995**, *5*, 113.

10 A. Katayama, M. Toba, G. Takeuchi, F. Mizukami, S. Niwa, S. Mitamura, *J. Chem. Soc., Chem. Commun.* **1991**, 39.

11 C. Song, *C. R. Acad. Sci., Ser. IIc: Chim.* **2000**, *3*, 477.

12 P. Moreau, A. Finiels, P. Geneste, J. Solofo, *J. Catal.* **1992**, *136*, 487.

13 P. Moreau, C. He, Z. Liu, F. Fajula, *J. Mol. Catal. A: Chem.* **2001**, *168*, 105.

14 R. Brzozowski, W. Tęcza, *Appl. Catal., A* **1998**, *166*, 21.

15 M. G. Cutrufello, I. Ferino, R. Monaci, E. Rombi, V. Solinas, P. Magnoux, M. Guisnet, *Appl. Catal., A* **2003**, *241*, 91.

16 I. Ferino, R. Monaci, E. Rombi, V. Solinas, P. Magnoux, M. Guisnet, *Appl. Catal., A* **1999**, *183*, 303.

17 R. Anand, R. Maheswari, K. U. Gore, S. S. Khaire, V. R. Chumbhale, *Appl. Catal., A* **2003**, *249*, 265.

18 G. Kamalakar, S. J. Kulkarni, K. V. Raghavan, S. Unnikrishnan, A. B. Halgeri, *J. Mol. Catal. A: Chem.* **1999**, *149*, 283.

19 J. Wang, J.-N. Park, Y.-K. Park, C. W. Lee, *J. Catal.* **2003**, *220*, 265.

20 R. Brzozowski, A. Vinu, T. Mori, *Catal. Commun.* **2007**, *8*, 1681.

21 P. Moreau, A. Finiels, P. Geneste, J. Joffre, F. Moreau, J. Solofo, *Catal. Today* **1996**, *31*, 11.

22 E. Armengol, A. Corma, H. García, J. Primo, *Appl. Catal., A* **1997**, *149*, 411.

23 G. Kamalakar, M. Ramakrishna Prasad, S. J. Kulkarni, K. V. Raghavan, *Microporous Mesoporous Mater.* **2002**, *52*, 151.

24 R. P. Marathe, S. Mayadevi, S. A. Pardhy, S. M. Sabne, S. Sivasanker, *J. Mol. Catal. A: Chem.* **2002**, *181*, 201.

25 Y. Sugi, H. Maekawa, Y. Hasegawa, H. Naiki, K. Komura, Y. Kubota, *Catal. Today* **2008**, *132*, 27.

26 Intern. Zeolite Assoc. http://www.iza-structure.org/databases/.

27 S. I. Zones, U.S. Patent 4,665,110, **1987**.

28 S. I. Zones, Y. Nakagawa, *Microporous Mater.* **1994**, *2*, 557.

29 R. F. Lobo, M. E. Davis, *Microporous Mater.* **1994**, *3*, 61.

30 Y. Kubota, H. Maekawa, S. Miyata, T. Tatsumi, Y. Sugi, *Microporous Mesoporous Mater.* **2007**, *101*, 115.

31 C.-Y. Chen, S. I. Zones, U.S. Patent 6,468,501, **2002**.

32 S. A. Elomari, T. V. Harris, U.S. Patent, 6,475,463, **2002**.

33 S. A. Elomari, S. I. Zones, *Stud. Surf. Sci. Catal.* **2001**, *135*, 479.

34 M. G. Wu, M. W. Deem, S. A. Elomari, R. C. Medrud, S. I. Zones, T. Maesen, C. Kibby, C.-Y. Chen, I. Y. Chan, *J. Phys. Chem. B* **2002**, *106*, 264.

35 S. I. Stacy, U.S. Patent, 5,653,956, **1997**.

36 P. A. Barrett, M. A. Camblor, A. Corma, R. H. Jones, L. A. Villaescusa, *Chem. Mater.* **1997**, *9*, 1713.

37 C. Y. Chen, L. W. Finger, R. C. Medrud, P. A. Crozier, I. Y. Chan, T. V. Harris, S. I. Zones, *Chem. Commun.* **1997**, 1775.

38 C. Y. Chen, L. W. Finger, R. C. Medrud, C. L. Kibby, P. A. Crozier, I. Y. Chan, T. V. Harris, L. W. Beck, S. I. Zones, *Chem.—Eur. J.* **1998**, *4*, 1312.

39 C. Y. Chen, S. I. Zones, L. T. Yuen, T. V. Harris, S. A. Elomari, Proceedings of 12th International Zeolite Conference, **1999**, Vol. 3, p. 1945.

40 The member of the cages of the zeolites is the maximum size of oxygen rings estimated from the data in the reference.[26]

41 Y. Sugi, H. Maekawa, S. A. R. Mulla, A. Ito, C. Naitoh, K. Nakagawa, K. Komura, Y. Kubota, J.-H. Kim, G. Seo, *Bull. Chem. Soc. Jpn.* **2007**, *80*, 2232.

42 Y. Sugi, H. Maekawa, A. Ito, C. Ozawa, T. Shibata, A. Niimi, C. Asaoka, K. Komura, Y. Kubota, J.-Y. Lee, J.-H. Kim, G. Seo, *Bull. Chem. Soc. Jpn.* **2007**, *80*, 1418.

43 Y. Sugi, H. Maekawa, Y. Hasegawa, A. Ito, R. Asai, D. Yamamoto, K. Komura, Y. Kubota, J.-H. Kim, G. Seo, *Catal. Today* **2008**, *131*, 413.

44 Y. Sugi, H. Maekawa, H. Naiki, K. Komura, Y. Kubota, *Bull. Chem. Soc. Jpn.*, in press.

45 G. Takeuchi. H. Okazaki, T. Kito, Y. Sugi, T. Matsuzaki, *Sekiyu Gakkaishi* **1991**, *34*, 242.