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The Alkylation of Biphenyl over Fourteen-Membered Ring Zeolites. The Influence of Zeolite Structure and Alkylating Agent on the Selectivity for 4,4′-Dialkylbiphenyl

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Alkylation, i.e. isopropylation, *s*-butylation, and *t*-butylation, of biphenyl (BP) was examined over fourteen-membered ring (14-MR) zeolites, CIT-5, UTD-1, and SSZ-53, in order to elucidate the relationships between structure of zeolites and bulkiness of alkylating agents on the shape-selective catalysis. CIT-5 zeolite (CFI) yielded 4,4′-diisopropylbiphenyl (4,4′-DIPB) in the level of 50–60% in the isopropylation in the range of 150–300 °C. 2,2′-, 2,3′-, and 2,4′-DIPB (2,*x*′-DIPB) isomers were obtained as the predominant DIPB isomers at lower temperatures, and the formation of 3,4′- and 3,3′-DIPB isomers increased with an increase in the temperature. However, the selectivities were in the level of 10–15% for UTD-1 (DON) and SSZ-53 (SFH) zeolites in the range of 150–350 °C. The *s*-butylation with 1-butene gave results similar to the isopropylation, although the selectivities for 4,4′-di-*s*-butylbiphenyl (4,4′-DSBB) were higher than those for 4,4′-DIPB at 250 °C: 80–85% for CFI, 40–50% for DON, and 30–40% for SFH. High selectivity for 4,4′-di-*t*-butylbiphenyl (4,4′-DTBB) was observed in the *t*-butylation at 250 °C: 95% for CFI, 90% for DON, and 80% for SFH. These differences are due to the spatial difference in their channels, and also due to bulkiness of alkylating agents, propene, 1-butene, and 2-methylpropene. The selectivity for 4,4′-dialkylbiphenyl (4,4′-DABP) was governed by the exclusion of the bulky DABP isomers at the transition state by steric restriction in the zeolite channels.

Shape-selective alkylation of polynuclear hydrocarbons is a promising way to manufacture advanced materials.[1–4] We have previously found that H-mordenite (MOR) was the excellent catalyst for the shape-selective isopropylation of biphenyl (BP) and concluded that shape-selective catalysis occurred by predominant formation of 4,4′-diisopropylbiphenyl (4,4′-DIPB), because of effective exclusion of bulky isomers from the channels at their transition states.[1–7]

Shape-selective catalysis over zeolites occur by differentiating the reactants, the products, and/or the reaction intermediates according to their shape and size in sterically restricted environments of the zeolite.[8–10] The reactant's fate and the product's formation probability inside the zeolite channels are determined by molecular size and configuration. Only molecules, of which dimensions are less than a critical size, can enter the pore and react at the internal catalytic sites, and the bulky molecules, which can not accommodate inside the channels, are thus excluded from the channels, resulting in the preferential formation of the least bulky isomers. Furthermore, only molecules that can diffuse through the channels will appear in the products. On the other hand, if reactants, products, and/or reaction intermediates are much smaller than the zeolite channels, the reaction is controlled kinetically due to the reactivity of each position of the reactant at low temperatures and to the thermodynamic stability of the products at higher temperatures. These considerations suggest that the extent of the exclusion by their zeolite channels is an important key factor in shape-selective catalysis, although it depends on the type of zeolite. From these points of view, it is interesting to elucidate how zeolite structures, particularly, dimensionality, pore-entrance, and channel, influence the catalysis and how shape-selective catalysis occurs in zeolites.

Many researchers have been interested in the synthesis of new type of zeolites.[11] Among them, one-dimensional fourteen-membered ring (14-MR) zeolites have been found in recent years.[12–16] Balkus et al. have synthesized UTD-1 zeolite (DON),[11] which has straight channels (pore-entrance: 0.74 nm × 0.95 nm) by using bis(pentamethylcyclopentadienyl)-cobalt(III) cation ($[^*Cp_2Co]^+$) as structure directing agent (SDA).[12,13] Wagner et al. have described the synthesis of CIT-5 zeolite (CFI),[11] which has slightly corrugated channels (16-MR cavity with pore-entrance: 0.72 nm × 0.75 nm), by using *N*(16)-methylsparteinium cation ($[MeSPA]^+$) as SDA.[14,15,17] More recently, Burton et al. have reported the synthesis of SSZ-53 zeolite (SFH),[11] which has largely corrugated one-dimensional channels (22-MR cavity with pore-entrance: 0.65 nm × 0.88 nm), by using [1-(4-fluorophenyl)cyclopentylmethyl]trimethylammonium cation ($[4\text{-FPCPMA}]^+$) as SDA.[16]

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Because UTD-1 and SFH-53 zeolites are obtained as their boron versions, the substitution of B^{3+} to Al^{3+} is necessary for solid acid catalysis. We are interested in catalytic properties of these zeolites, particularly in the alkylation of polynuclear aromatic hydrocarbons.

In this paper, we describe the alkylation, i.e., isopropylation, *s*-butylation, and *t*-butylation, of BP over one-dimensional 14-MR zeolites: CIT-5, UTD-1, and SSZ-53. We also discuss the influence of the selectivity for 4,4′-dialkylbiphenyl (4,4′-DABP) on the relation between zeolite structure and alkylating agent in order to elucidate where and how shape-selective catalysis occurs. The results of the 14-MR zeolites were compared to those of H-mordenite with straight channels of pore-entrance (0.67 nm × 0.72 nm), which is the most efficient catalyst for the isopropylation of BP.[1–7] We focus on the selectivities for DABP isomers to understand shape-selective catalysis in the alkylation by one-dimensional 14-MR zeolites. Types of zeolites in this paper were abbreviated by framework type code (FTC) by International Zeolite Association.[11]

Experimental

Zeolites. CIT-5 (CFI) zeolite was synthesized according to the literature.[17] UTD-1 (DON) and SSZ-53 (SFH) were also prepared from their borosilicates, [B]-UTD-1 and [B]-SSZ-53, respectively, according to the literature.[12,13,16] H-Mordenite (MOR; $SiO_2/Al_2O_3 = 128$; TSZ-690HOA) was obtained from Tosoh Corp., Tokyo. All zeolites were used as H-forms and calcined at 550 °C before use.

The Alkylation of BP. The alkylation of BP was carried out in a 100-mL SUS-316 autoclave. Typical reaction conditions of the isopropylation were: BP 7.71 g (50 mmol), catalyst 0.25 g, temperature 150–350 °C, and 4 h under a 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 BP and the catalyst was purged with nitrogen, and heated to reaction temperature. Propene was introduced to the autoclave, and the reaction was started with agitation. The pressure was maintained constant throughout the reaction. After cooling the autoclave to ambient temperature and careful release of excess propene, the catalyst was separated by the filtration, and the liquid products were subjected to the analyses by using a Gas Chromatograph GC14A or GC18A (Shimadzu Corp., Kyoto) equipped with an Ultra-1 capillary column (25 m × 0.2 mm; Agilent Technologies, Inc., MA, U.S.A.). The products were also identified by using a Shimadzu Gas Chromatograph-Mass Spectrometer GC-MS 5000.

Dialkylbiphenyl in the alkylation generally expresses as DABP in this study. DIPB, DSBB, and DTBB are dialkylbiphenyl isomers for isopropylation, *s*-butylation, and *t*-butylation, respectively.

Yields of each product were calculated on the basis of the amount of starting BP, and selectivities for each alkylbiphenyl (ABP) and dialkylbiphenyl (DABP) isomers were expressed based on the total amounts of ABP and DABP isomers, respectively.

$$\text{Selectivity for a DABP (ABP) isomer (\%)} = \frac{\text{Each DABP (ABP) isomer (mol)}}{\text{DABP (ABP) isomers (mol)}} \times 100. \quad (1)$$

The catalytic activities based on the yield of alkylates were described in Figs. S1–S6 of Supporting Information. The zeolites in this study show low activities in some cases such as at low temperatures, or in the *t*-butylation. In these cases, the analysis for DIPB isomers was carried out at high sensitivities by duplicate analyses.

Analysis of the encapsulated products in the catalyst used for the reaction was carried out as follows. The catalyst was separated by the filtration, washed well with acetone (200 mL), and dried at 110 °C for 12 h. Resultant catalyst (50 mg) was carefully dissolved in 3 mL of aqueous hydrofluoric acid (47%) at room temperature. This solution was neutralized with solid potassium carbonate, and organic layer was extracted three times with dichloromethane (20 mL). After removal of the solvent in vacuo, the residue was dissolved again in a toluene (5 mL), and subjected to GC and GC-MS analyses according to the same procedure as the analysis for bulk products.

The selectivities for ABP and DABP isomers in encapsulated products were defined in a similar manner as those in the bulk products. The encapsulated products were also expressed by the composition of reaction mixtures, because it is difficult to analyze quantitatively with high reproducibility.

The Characterization of Catalysts. The crystal structure of zeolites was determined by using powder X-ray diffraction on a Shimadzu XRD-6000 diffractometer with Cu $K\alpha$ radiation ($\lambda = 1.5418$ Å). Elemental analysis of zeolites was performed by using inductive coupled plasma atomic emission spectroscopy on a JICP-PS-1000 UV spectrometer (Teledyne Leeman Labs, Inc., NH, U.S.A.). Crystal size and morphology of the zeolites were determined on an S-4300 FE-SEM microscope (Hitachi Corp., Tokyo). Nitrogen adsorption on the zeolite was measured on a Belsorp 28SA apparatus (Bel Japan, Inc., Osaka). The adsorption of *o*-xylene was performed by a gravimetric method with a vapor pressure (0.48 kPa) using a highly sensitive quartz microbalance at 120 °C after evacuation at 550 °C. Ammonia temperature-programmed desorption (NH_3-TPD) from the zeolite was measured using a TPD-66 apparatus (Bel Japan); the catalyst was evacuated at 400 °C for 1 h, and ammonia was adsorbed at 100 °C followed by further evacuation for 1 h. Then, the sample was heated from 100 to 710 °C at a rate of 10 °C min^{-1} in a helium flow. The ^{11}B, ^{27}Al, and ^{29}Si NMR spectra of zeolites were recorded at room temperature under magic angle spinning (MAS) by using 7.0 mm diameter zirconia rotors spinning at 4 kHz on an Inova 400 spectrometer (Varian Corp., MA, U.S.A.).

Results and Discussion

Properties of Zeolites. Typical physicochemical properties of the zeolites, MOR, CFI, DON, and SFH used for the catalysis are shown in Table 1. These properties well agreed to those in the literature.[13,16,17]

Figure 1 shows the XRD patterns of calcined CFI, DON, and SFH. Figure 2 shows typical SEM images of the as-synthesized samples. XRD patterns and SEM images of these zeolites well agreed with those in the literature.[13,16,17] The substitution of B^{3+} in [B]-UTD-1 and [B]-SSZ-53 with Al^{3+} was carried out by using 1 M $Al(NO_3)_3$ aqueous solution (1 M = 1 mol dm^{-3}) at 80 °C according to the literature.[13,16] XRD patterns after repeating the substitution three times were almost the same as original calcined samples. These observations suggest that the structure does not collapse during calcination, acid treatment, and substitution of B^{3+} with Al^{3+}.

^{27}Al MAS NMR spectra of calcined CFI, DON, and SFH, are shown in Fig. 3. A peak assigned to tetrahedral Al^{3+} species, which is incorporated to zeolite framework, was observed at around 50 ppm for all zeolites. CFI had only tetrahedral

Table 1. Properties of Zeolites

Zeolite	FTC	MR	Channel structure	Pore entrance /nm^2	SiO_2/Al_2O_3	Surface area /m^2 g^{-1}	External surface area /m^2 g^{-1} a)	Pore volume /mL g^{-1}	NH_3 peak temperature /°C	Acid amount /mmol g^{-1}
Mordenite	MOR	12	Straight with 8-MR side pocket	0.67 × 0.72	128	460	35	0.16	389	0.20
CIT-5	CFI	14	Slightly corrugated	0.72 × 0.75	160	339	38	0.14	294	0.13
UTD-1	DON	14	Straight	0.70 × 0.95	200	403	15	0.16	288	0.12
SSZ-53	SFH	14	Largely corrugated	0.65 × 0.88	64	385	83	0.11	316	0.26

a) Calculated from *t*-plot of N_2 adsorption.

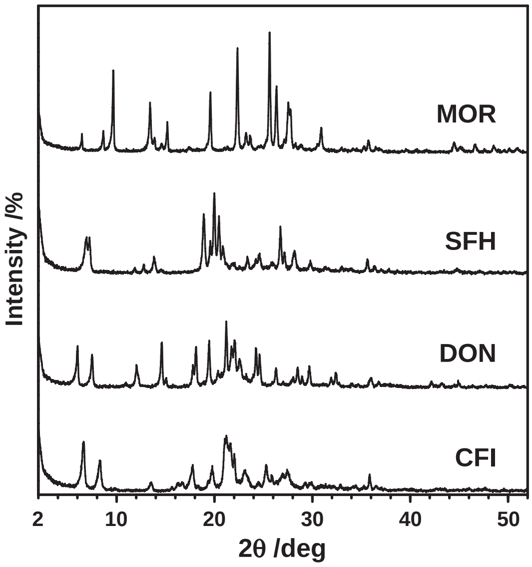


Fig. 1. XRD patterns of 14-MR zeolites (calcined) used as catalysts.

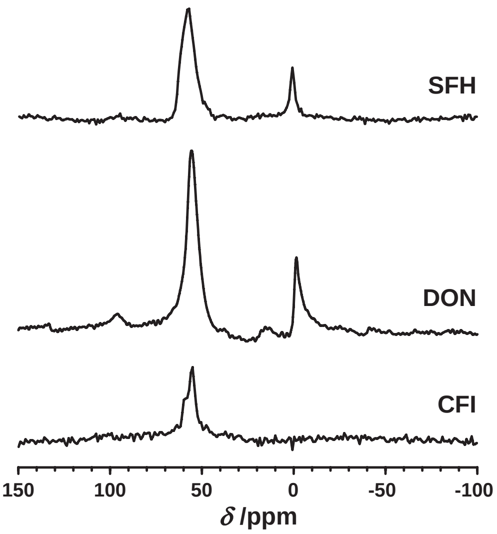
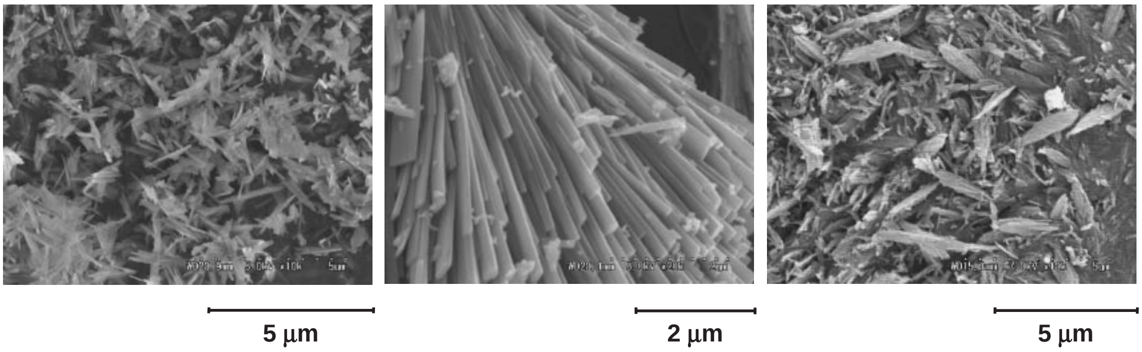


Fig. 3. ^{27}Al MAS NMR of 14-MR zeolites used as catalysts.



CFI DON SFH

Fig. 2. SEM images of 14-MR zeolites (as-synthesized) used for the catalysis.

Al^{3+} species; however, a peak assigned to octahedral Al^{3+} species, which is not incorporated in the framework, also appeared at around 0 ppm upon the substitution of B^{3+} in the frameworks of [B]-UTD-1 and [B]-SSZ-53 with Al^{3+}. These tetrahedral Al^{3+} species work as Brønsted acidic sites related to the catalytic activity in the solid acid catalysis. Substitution of B^{3+} with Al^{3+} was also confirmed using the ^{11}B and ^{29}Si MAS NMR spectra.

The N_2 adsorption of CFI, DON, and SFH showed a typical type-I isotherm (Figure not shown). Specific surface area and pore volume were 340–400 m^2 g^{-1} and 0.11–0.16 mL g^{-1}, respectively. These results indicate that CFI, DON, and SFH

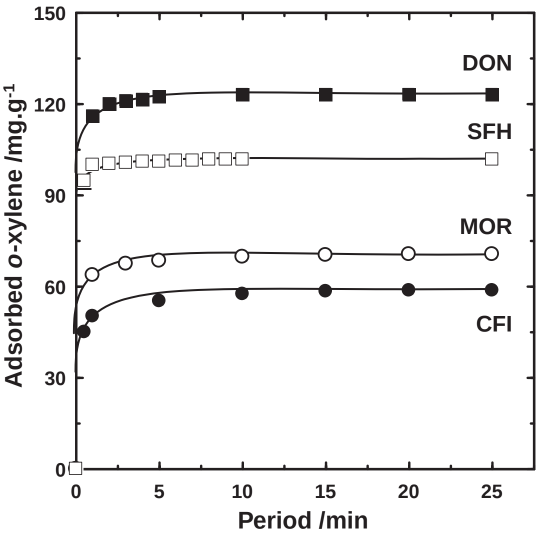


Fig. 4. *o*-Xylene adsorption on zeolites used as catalysts.

have typical microporous natures. External surface areas calculated from *t*-plot of N_2 adsorption were 38, 15, and 83 $m^2\,g^{-1}$ for CFI, DON, and SFH, respectively. SFH has higher external surface area compared to the other two zeolites.

Figure 4 shows the adsorption of *o*-xylene on CFI, DON, and SFH. The adsorption was saturated in short period on all zeolites. It means that their channels are large enough for the diffusion of *o*-xylene in them. DON and SFH adsorbed a larger amount of *o*-xylene than CFI did; however, the amount of *o*-xylene adsorbed on CFI was smaller than those of the MOR. These differences in N_2 and *o*-xylene adsorption are due to the difference in their topologies, and should reflect on the catalysis.

TPD profiles of CFI, DON, and SFH are shown in Fig. 5. They had *l*- and *h*-peaks in the range of 150–200 and 290–320 °C, respectively. *l*-Peak is due to physical adsorption of NH_3, and *h*-peak is assigned to Brønsted acidity, which is related to acidic sites in acid catalysis. All zeolites have similar level of acid strength judging from peak temperature of *h*-peak, and acid amounts, calculated from area of deconvoluted *h*-peak, correspond to the SiO_2/Al_2O_3 ratio (see Table 1). These zeolites have weaker acidities than MOR; however, their acidities are strong enough for acid catalysis.

The Isopropylation. Figure 6 shows the influence of reaction temperature on the isopropylation over MOR and CFI. The activities increased with an increase in the temperature for all zeolites. The high selectivity for 4,4′-DIPB, which is the least bulky isomer among the diisopropylbiphenyl (DIPB) isomers, was 85–90% over MOR at moderate temperatures below 250 °C as described in previous papers,[3–7] and 50–60% over CFI up to 300 °C. These results show that the shape-selective catalyses occur inside MOR and CFI channels and that bulky DIPB isomers are excluded from the channels by the steric restriction, resulting in the high selectivity for 4,4′-DIPB. The differences in the selectivity for 4,4′-DIPB over MOR and CFI are due to the difference in the reaction space inside the channels, because CFI channels are larger than MOR channels.

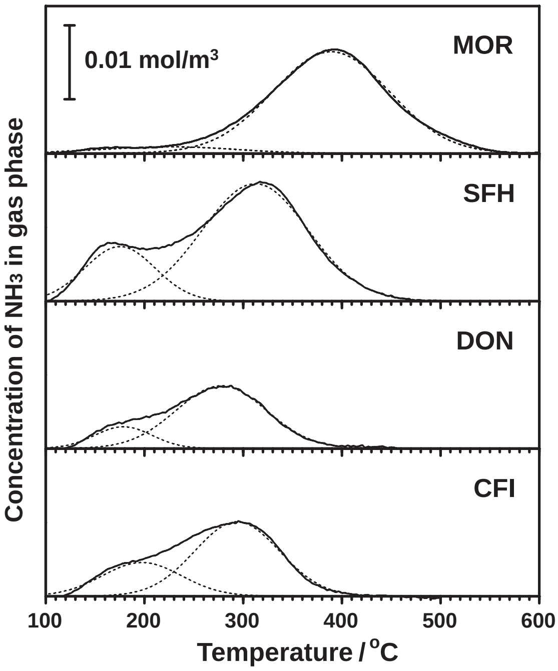


Fig. 5. NH_3-TPD profiles of zeolites used as catalysts. *l*- and *h*-Peaks by the deconvolution are plotted as dotted lines.

Figure 6 also shows the selectivities for 4,4′-DIPB in the encapsulated products over MOR and CFI in the isopropylation. The selectivity for 4,4′-DIPB in the encapsulated products over MOR maintained high even at high temperatures as 350 °C. However, the selectivities for 4,4′-DIPB in bulk products were as high as 85–90% at low and moderate temperatures below 250 °C; however, they decreased to 10% with an increase in the temperature to 350 °C These results indicate that the decrease in the selectivity over MOR is due to the isomerization of 4,4′-DIPB to thermodynamically stable 3,4′-DIPB.[18] The isomerization of 4,4′-DIPB over MOR occurred at external acid sites as previously discussed.[3–7] On the other hand, the selectivities for 4,4′-DIPB in bulk products over CFI was also in the similar level of those in encapsulated products at low and moderate temperatures. However, they decreased gradually to around 30% with a further increase in the reaction temperature to 350 °C. These differences in the selectivities indicate that the isomerization of 4,4′-DIPB proceeds at both external and internal acid sites. These results over CFI show that its channels are also large enough for the isomerization of 4,4′-DIPB at the higher temperatures, even if they are small enough for the predominant formation of 4,4′-DIPB in the isopropylation of BP. However, there is another possibility that the decrease in steric restriction by the CFI channels cause the decease in the selectivity for 4,4′-DIPB at high temperatures. The isomerization of 4,4′-DIPB inside the channels has also been observed in the isopropylation over SSZ-24[19] and MAPO-5 (M: Mg and Zn) with AFI topology.[20]

The selectivity for 4,4′-DIPB was less than 20% among DIPB isomers in the isopropylation of BP over DON and SFH, as shown in Fig. 7. Over these zeolites, the predominant DIPB isomers were the bulky and thermodynamically unstable 2,2′-, 2,3′-, and 2,4′-DIPB (2,*x*′-DIPB) isomers at lower temperatures, and the yield of thermodynamically stable 3,4′-, 3,3′-, and 4,4′-DIPB isomers increased with an increase in the tem-

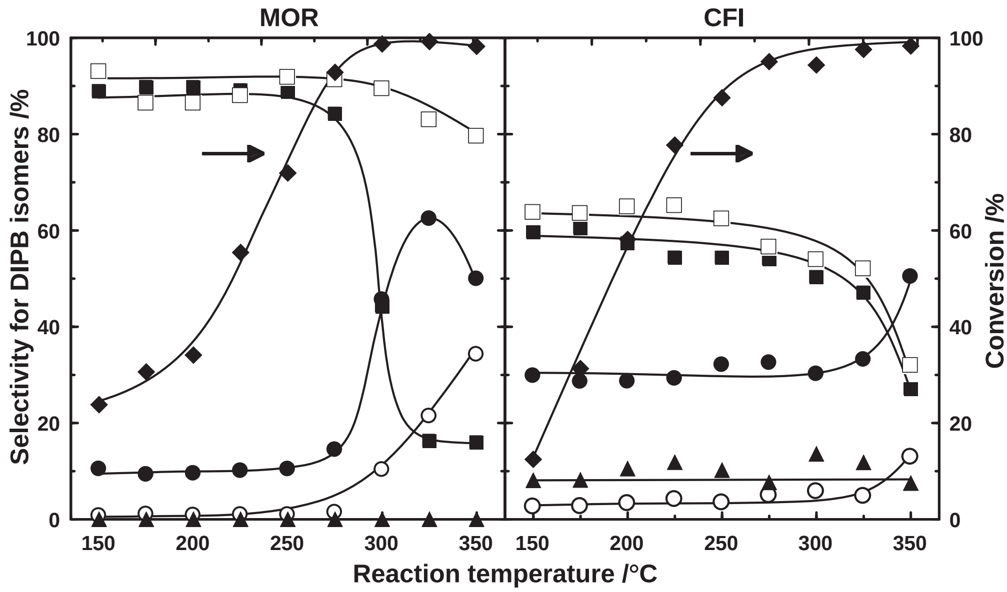


Fig. 6. The influence of reaction temperature on the isopropylation of BP over MOR and CFI zeolites. Reaction conditions: for MOR: BP, 30.84 g (200 mmol), catalyst, 1.0 g; for CFI: BP, 7.71 g (50 mmol); catalyst, 0.25 g; temperature, 150–350 °C; propene pressure, 0.8 MPa; period, 4 h. Legends: Bulk products. ■: 4,4′-DIPB; ●: 3,4′-DIPB; ○: 3,3′-DIPB; ▲: 2,x'-DIPB; ◆: conversion. Encapsulated products. □: 4,4′-DIPB.

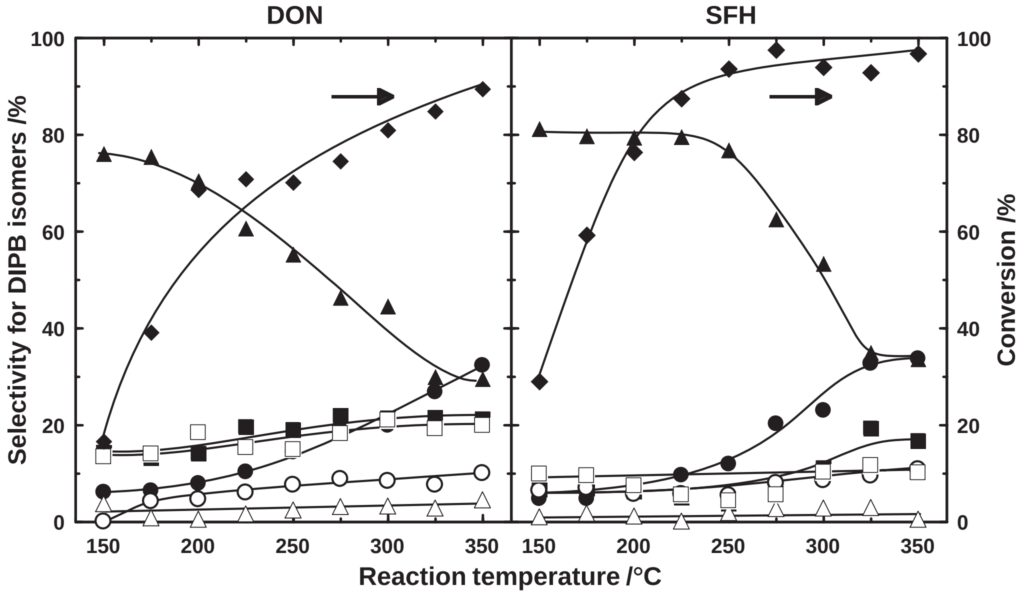


Fig. 7. The influence of reaction temperature on the isopropylation of BP over DON and SFH zeolites. Reaction conditions: for DON: BP, 7.71 g (50 mmol); catalyst, 0.25 g; for SFH: BP, 3.86 g (25 mmol); catalyst, 0.125 g; temperature, 150–350 °C; propene pressure, 0.8 MPa; period, 4 h. Legends: see Fig. 6.

perature. These results mean that the isopropylation over DON and SFH is principally controlled kinetically at lower temperatures and thermodynamically controlled at high temperatures. The 2- and 4-positions of BP moieties are preferentially attacked by the alkylating agent under kinetic control, resulting in the predominant formation of 2,x'-DIPB. The selectivity for 2,x'-DIPB decreased with an increase in the temperature under thermodynamic control accompanied by an increase in the selectivity for 3,4′-DIPB. These results indicate that SFH and DON channels are too large to form 4,4′-DIPB shape-selectively.

The selectivities for 4,4′-DIPB in both bulk and encapsulated products over DON and SFH were around 10–20% in the range of 150–300 °C, as shown in Fig. 7. These results suggest that the shape-selective formation of 4,4′-DIPB did not occur inside the channels of these zeolites. DON and SFH have the large reaction spaces inside their channels, thus allowing the formation of bulky DIPB isomers in the isopropylation of BP.

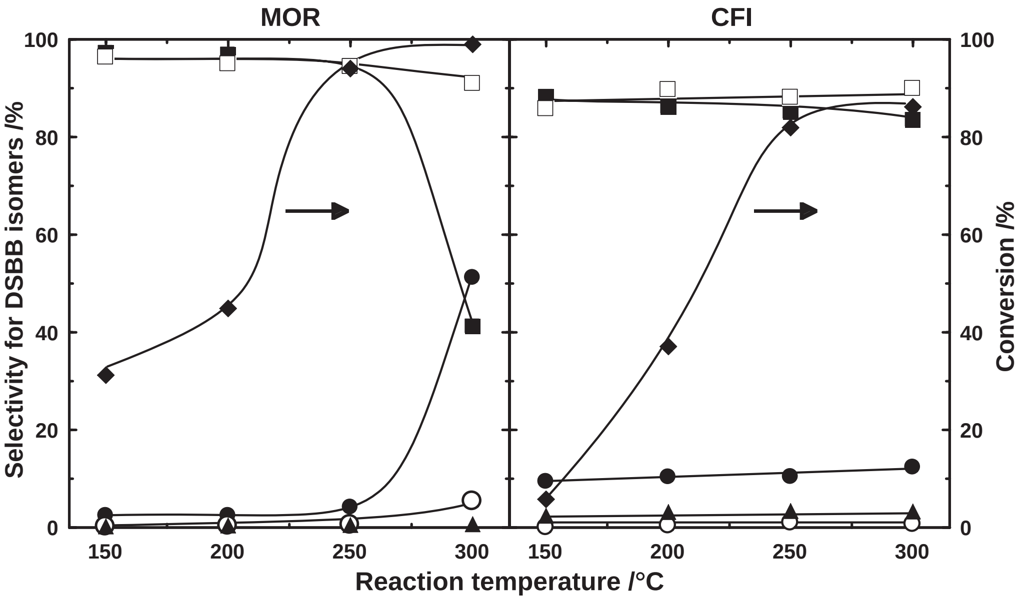


Fig. 8. The influence of reaction temperature on the *s*-butylation of BP over MOR and CFI zeolites. Reaction conditions: for MOR: BP, 7.71 g (50 mmol); catalyst, 0.25 g; for CFI: BP, 3.86 g (25 mmol); CFI, 0.125 g; temperature, 150–300 °C; 1-butene pressure, 0.5 MPa; period, 4 h. Legends: Bulk products. ■: 4,4′-DSBB; ●: 3,4′-DSBB; ○: 3,3′-DSBB; ▲: 2,*x*′-DSBB; ◆: conversion. Encapsulated products. □: 4,4′-DSBB.

SFH has larger external surface area compared to the other zeolites; however, currently, there is no evidence that external surface area influences the catalytic properties. Detailed studies are necessary for the clarification.

The *s*-Butylation. Figure 8 shows the influence of reaction temperature on the selectivity for 4,4′-di-*s*-butylbiphenyl (4,4′-DSBB) among di-*s*-butylbiphenyl (DSBB) isomers in the *s*-butylation over MOR and CFI. The selectivities for 4,4′-DSBB were higher than those for 4,4′-DIPB in the isopropylation, that is, the selectivity for 4,4′-DSBB was higher than 95% below 250 °C for MOR and 80% for CFI in the *s*-butylation in the range of 150–300 °C. The selective formation of 4,4′-DSBB over MOR and CFI indicates that the *s*-butylation occurs shape-selectively inside their channels similar to the isopropylation. The channels of MOR and CFI can discriminate more effectively 4,4′-DSBB than 4,4′-DIPB from corresponding isomers at their transition states, because the steric restriction of *s*-butylation by the channels is severer than that of isopropylation. The substitution with isopropyl and *s*-butyl groups invokes the difference in steric interaction at the transition states with the channels, although the effective molecular diameter of 3,4′-DSBB is almost the same as that of 3,4′-DIPB. 3,4′-DSBB and other bulky isomers are effectively excluded from the channels compared to 3,4′-DIPB and its bulky isomers.

Figure 8 also shows the selectivities for 4,4′-DSBB in the encapsulated products in the *s*-butylation over MOR and CFI. The selectivity in the encapsulated products over MOR was higher than 95% even at high temperatures; however, the selectivity in the bulk products decreased from around 90% at 250 °C to 40% at 300 °C. These results show that the decrease is due to the isomerization of 4,4′-DSBB to 3,4′-DSBB at the external acid sites as discussed in the isopropylation.[1–7] The selectivities for 4,4′-DIPB over CFI in bulk products were in the similar level of those for encapsulated products in the range of 150–300 °C, and no significant isomerization of 4,4′-DSBB occurred even at the temperature as high as 300 °C.

The influence of reaction temperature on the selectivity for DSBB isomers over DON and SFH is shown in Fig. 9. The selectivities for 2,2′-, 2,3′-, and 2,4′-DSBB (2,*x*′-DSBB) isomers decreased with an increase in the temperature from 50 to 20% for DON and from 62 to 25% for SFH in the ranges of 150–300 °C. The features of the *s*-butylation resemble those of the isopropylation over DON and SFH, although the selectivities for 2,*x*′-DSBB were lower than those in the isopropylation. However, they are quite different from those over CFI in the *s*-butylation. These results mean that the catalyses over DON and SFH are principally controlled kinetically at lower temperatures and thermodynamically at higher temperatures.

The selectivities for 4,4′-DSBB in both bulk and encapsulated products over DON and SFH were 40–50% for DON and 30–40% for SFH in the range of 150–300 °C, as shown in Fig. 9. The selectivities for 4,4′-DSBB should be much higher than those from equilibrium mixtures estimated from DIPB isomers.[19] These results suggest that DON and SFH channels have some shape-selective natures for the *s*-butylation. The channels can enhance the formation of 4,4′-DSBB with a decrease in bulky DIPB isomers, such as 2,*x*′-DSBB, because *s*-butyl substitution increases the steric restriction at the transition state of bulky isomers in their channels. However, kinetic control still contributes to the formation of 2,*x*′-DSBB at 250 °C, because these channels cannot effectively exclude the bulky isomers. The contribution of thermodynamic control increases with the increase in the temperature, resulting in the decrease in the selectivity for 2,*x*′-DSBB and the increase in the selectivity for 3,4′-DSBB. The selectivities for 4,4′-DSBB over DON were higher than those over SFH, and the selectivities for 2,*x*′-DSBB over SFH were higher than those over DON. The differences in the selectivities are due to the differ-

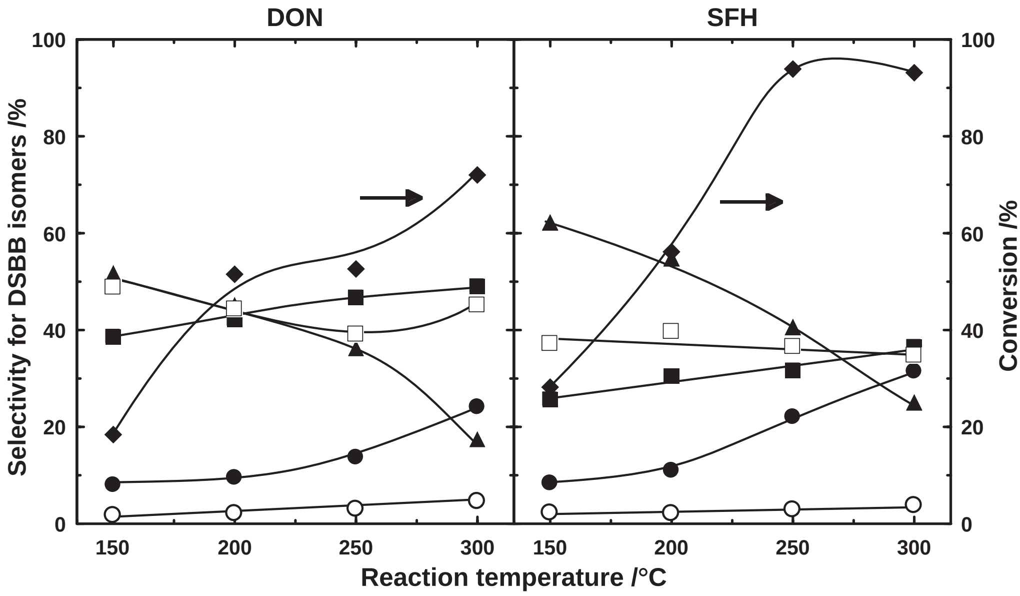


Fig. 9. The influence of reaction temperature on the *s*-butylation of BP over DON and SFH zeolites. Reaction conditions. for DON: BP, 3.86 g (25 mmol); catalyst, 0.125 g; for SFH: BP, 3.08 g (20 mmol); catalyst, 0.1 g; temperature, 150–300 °C; 1-butene pressure, 0.8 MPa; period, 4 h. Legends: see Fig. 8.

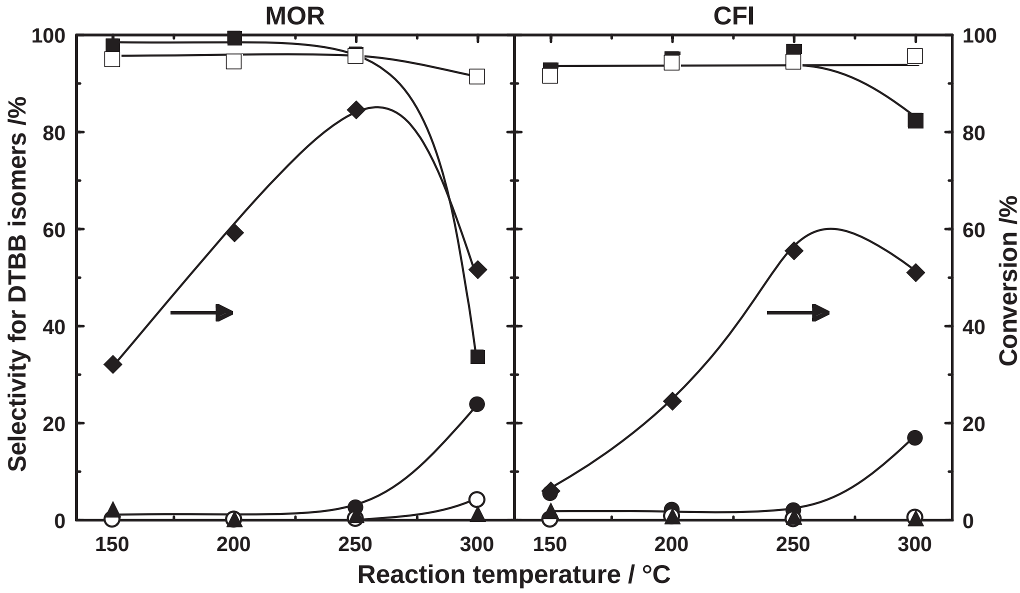


Fig. 10. The influence of reaction temperature on the *t*-butylation of BP over MOR and CFI zeolites. Reaction conditions: for MOR: BP, 7.71 g (50 mmol); catalyst, 0.25 g; for CFI: BP, 3.86 g (25 mmol); catalyst, 0.125 g; temperature: 150–300 °C; 2-methylpropene pressure, 0.5 MPa; period: 4 h. Legends. Bulk products: ■: 4,4′-DTBB; ●: 3,4′-DTBB; ○: 3,3′-DTBB; ▲: 2,*x*′-DTBB; ◆: conversion. Encapsulated products: □: 4,4′-DTBB.

ence in channel structures: straight channels for DON and corrugated channels for SFH.

The *t*-Butylation. The influence of reaction temperature on the selectivity for 4,4′-di-*t*-butylbiphenyl (4,4′-DTBB) among di-*t*-butylbiphenyl (DTBB) isomers is shown in Fig. 10 for MOR and CFI and in Fig. 11 for DON and SFH. The selective formation of 4,4′-DTBB was observed over these zeolites at low and moderate temperatures below 250 °C. The selectivities for 4,4′-DTBB were around 95% for MOR and CFI, 90% for DON, and 80% for SFH. These results indicate that the *t*-butylation occurs inside the channels of these zeolites, leading to the selective formation of the least bulky 4,4′-DTBB: this is due to severer exclusion of bulky isomers from bulky alkylating agent at the transition states in their channels. The lower selectivities for 4,4′-DTBB over DON and SFH compared to those over MOR and CFI were due to the differences in the reaction spaces inside their large channels. Particularly, corrugated SFH channels afford large reaction space for the catalysis, resulting in the lower selectivity of around 80%. The catalytic activities in the *t*-butylation were

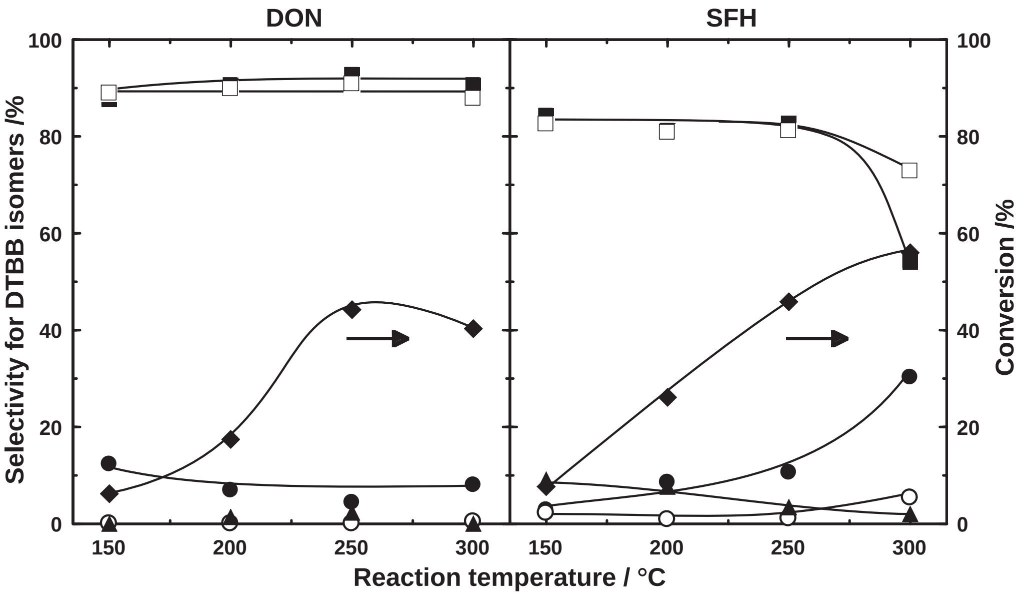


Fig. 11. The influence of reaction temperature on the *t*-butylation of BP over DON and SFH zeolites. Reaction conditions: BP, 3.86 g (25 mmol); catalyst, 0.125 g; temperature: 150–300 °C; 2-methylpropene pressure, 0.5 MPa; period: 4 h. Legends: see Fig. 10.

lower than those in the *s*-butylation and the *t*-butylation over the zeolites: this may be due to the lower diffusivity of bulky 4,4′-DTBB from their channels.

The selectivities for 4,4′-DTBB in the encapsulated products in the *t*-butylation are also shown in Fig. 10 for MOR and CFI and in Fig. 11 for DON and SFH. The selectivities for 4,4′-DTBB in the bulk products over MOR, CFI, and SFH were high at the temperatures below 250 °C, and they decreased significantly at 300 °C. However, the selectivities for 4,4′-DTBB in encapsulated products were around 95% for MOR, 90% for DON and CFI, and 80% for SFH in the range of 150–300 °C. These results indicate that the decreases in the selectivity for 4,4′-DTBB in the bulk products are due to the isomerization at the external acid sites of MOR, CFI, and SFH, as discussed in previous sections, because their channels are not large enough for the isomerization of 4,4′-DTBB. However, no decrease in the selectivity for 4,4′-DTBB in both bulk and encapsulated products occurred in the *t*-butylation over DON even at high temperatures, which may be due to the low density of external acid sites of DON. However, further investigation is necessary for the elucidation of the details.

The Influence of Types of Zeolites and Bulkiness of Alkylating Agents. CFI, DON, and SFH have 14-MR pore-entrances with different channel structure: CFI has slightly corrugated one-dimensional channels with 16-MR cavity (pore-entrance: 0.72 nm × 0.75 nm),[11,14,15] DON has straight one-dimensional channels (pore-entrance: 0.74 nm × 0.95 nm),[11–13] and SFH has largely corrugated one-dimensional channels with 22-MR cavity (pore-entrance: 0.65 nm × 0.88 nm) (see also Figs. S7–S9 in Supporting Information).[11] The differences in the 14-MR zeolites indicate that the reaction space inside the channels increases in the order: CFI ≪ DON ≪ SFH, and that the size of pore-entrance increased in the order: CFI < SFH < DON. These comparisons suggest that the steric restriction with the channels decreases in the order: CFI ≫ DON > SFH. The differences in the steric restriction should reflect the difference in the exclusion of bulky DABP isomers from the channels in the alkylation.

Figure 12 shows the selectivity for DABP isomers in the alkylation, i.e., isopropylation, *s*-butylation, and *t*-butylation, of BP over CFI, DON, SFH, and MOR at 250 °C with the alkylating agents: propene, 1-butene, and 2-methylpropene. These selectivities of DABP isomers suggest typical selectivities by channels of the zeolites, because further isomerization of 4,4′-DABP was almost negligible in the alkylation at 250 °C over these zeolites.

The products in the alkylation of BP are classified to three categories: 4,4′-DABP for the least bulky isomer by the shape-selective catalysis, 3,*x*′-DABP (3,4′- and 3,3′-) for the thermodynamically stable and bulky isomers under thermodynamic control, and 2,*x*′-DABP (2,2′-, 2,3′-, and 2,4′-) for the bulky and thermodynamically unstable isomers under kinetic control. The selectivities for 4,4′-, 3,*x*′-, and 2,*x*′-DABP highly depended on type of zeolites and bulkiness of alkylating agents. Particularly, the selectivities for 4,4′-DABP decreased with an increase in the reaction spaces of zeolites, and increased with an increase in bulkiness of the alkylating agents. The selectivities for 3,*x*′- and 2,*x*′-DABP were also influenced by reaction temperatures in addition to type of zeolites and alkylating agents as discussed in the previous sections. The selectivities for 4,4′-DABP in encapsulated products were in similar level of those in bulk products at 250 °C, as shown in Fig. 12. These variations of the selectivities by the type of zeolites and alkylating agents indicate that the alkylation occurs inside the channels and that the selectivity for DABP isomers should reflect the differences in the steric restriction inside the channels.

The selective formation of 4,4′-DIPB in the isopropylation was observed only over CFI among the 14-MR zeolites. The selectivity for 4,4′-DIPB over CFI was as high as 54% at 250 °C; it is much lower than that over MOR. These results

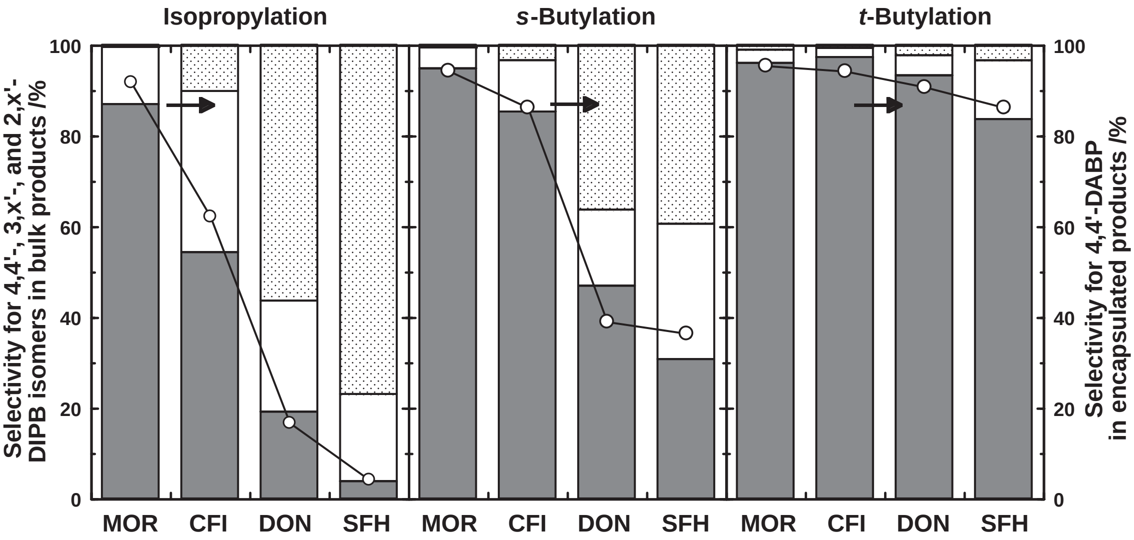


Fig. 12. The selectivity for DABP isomers in the alkylation of BP over the zeolites. Reaction condition: temperature: 250 °C. Other conditions: see Figs. 6–11. Legends: ■: 4,4′-DABP; □: 3,*x*′-DABP (3,4′-, 3,3′-, and 3,5-); ▨: 2,*x*′-DABP (2,2′-, 2,3′-, and 2,4′-); ○: 4,4′-DABP in encapsulated products.

mean that CFI channels can exclude the bulky DIPB isomers at the transition state, resulting in predominant formation of 4,4′-DIPB. However, steric restriction in CFI channels is less severe than that in MOR because CFI has larger reaction spaces than MOR. On the other hand, DON and SFH gave predominantly 2,*x*′-DIPB at low temperatures and 3,*x*′-DIPB at high temperatures; however, the selectivities for 4,4′-DIPB in both bulk and encapsulated products were 10–15% for DON and 4–6% for SFH. DON and SFH channels can allow bulky transition states, leading to predominant formation of the bulky DIPB isomers; the isopropylation over these zeolites can occur under kinetic control to form bulky 2,*x*′-DIPB at lower temperatures, as discussed in the previous section. The rapid decrease in the selectivities for 2,*x*′-DIPB and the increase in stable 3,*x*′-DIPB, particularly, 3,4′-DIPB, with an increase in the temperature, indicate the participation of thermodynamic control (see also Fig. 7).

The high selectivities for 4,4′-DSBB were observed in the *s*-butylation over MOR and CFI: 95% for MOR and 85% for CFI. These differences indicate that the steric restriction in the channels of two zeolites for the formation of 4,4′-DSBB is severer than that of 4,4′-DIPB. On the other hand, the formation of 2,*x*′-DSBB was dominant over DON and SFH at lower temperatures, and it decreased at higher temperatures (see also Fig. 9), meaning that kinetic and thermodynamic controls still contribute to the *s*-butylation. However, the selectivities for 4,4′-DSBB were 47% for DON and 32% for SFH at 250 °C, which are much higher than equilibrium composition of DSBB isomers estimated from DIPB isomers.[19] These results suggest that DON and SFH also have some shape-selective natures in the *s*-butylation. The channels can enhance the formation of 4,4′-DSBB with a decrease in the bulky DSBB isomers, such as 2,*x*′-DSBB, because *s*-butyl substitution increases the steric restriction at the transition state of the bulky isomers. The selectivities for 4,4′-DSBB over DON were higher than those over SFH, whereas the selectivities for 2,*x*′-DSBB over DON were lower than those over SFH. These differences in the selectivities are due to the difference in the structure: straight channels for DON and corrugated channels for SFH.

The *t*-butylation of BP over the 14-MR zeolites gave high selectivities for 4,4′-DTBB: 95% for CFI, 90% for DON, and 80–85% for SFH in low and moderate temperatures. These results indicate that even the large channels of these 14-MR zeolites can discriminate 4,4′-DTBB from other bulky DTBB isomers if the alkylating agent is bulky 2-methyl-2-propene. The differences in the selectivity among zeolites are caused by the difference in channel structure as discussed above.

The selectivities for DABP isomers over a zeolite were influenced by the bulkiness of alkylation agents. The selective formation of 4,4′-DABP was observed in the alkylation, i.e. isopropylation, *s*-butylation, and *t*-butylation, of BP over small CFI and MOR channels. These high selectivities for the least bulky isomers are due to "restricted transition state selectivity."[1] However, the alkylation over DON and SFH was influenced by the types of alkylating agent: the selectivities for 4,4′-DIPB in the isopropylation were 20% for DON and 10% for SFH at 250 °C. However, the *s*-butylation gave higher selectivities for 4,4′-DSBB at 250 °C: 50% for DON and 35% for SFH. However, the selective formation of 4,4′-DTBB occurred over DON and SFH in the *t*-butylation. These results indicate that the channels of these zeolites are too large for the shape-selective isopropylation, that some shape-selective natures appear in the *s*-butylation, and that highly shape-selective catalysis occurs in the *t*-butylation. Kinetic control at low temperatures and thermodynamic control at high temperatures contribute to the isopropylation and also to the *s*-butylation, yielding 2,*x*′- and 3,*x*′-DABP as principal products. Effective exclusion of the bulky DTBB isomers during the *t*-butylation occurred even inside large DON and SFH channels, resulting in the selective formation of 4,4′-DTBB. However, the selectivities for 4,4′-DSBB and 4,4′-DTBB over SFH were slightly lower than those over DON. These differences are due to the differences in channel structure as discussed above. These results indicate that "product selectivity,"[1] in which the least bulky isomers predominantly diffuse out from the mixtures inside the channels, is not operated in these alkylations, because the selective formation of 4,4′-DABP was accompanied by their high selectivities in the encapsulated products. The isomerization of 4,4′-DABP inside the channels may not be rapid to establish or approach an equilibrium.

The isomerization of 4,4′-DABP occurred in some alkylations at high temperatures, such as 300–350 °C: isopropylation over MOR and CFI, *s*-butylation over MOR, and *t*-butylation over MOR, CFI, and SFH. In these cases, the selectivities for 4,4′-DABP in the encapsulated products remained high even at high temperatures, except in the isopropylation over CFI. The isomerization of 4,4′-DABP during the alkylation occurs at the external acid sites as discussed for the isopropylation of BP over MOR in previous papers.[1–7] These results show that the channels of these zeolites are too small for the isomerization of 4,4′-DABP. However, the isopropylation of BP over CFI has a different feature among the 14-MR zeolites: the selectivities for 4,4′-DIPB in both bulk and encapsulated products in the isopropylation over CFI gradually decreased with an increase in the temperature, and they decreased to around 30% at 350 °C. The channels of CFI are large enough for the isomerization of 4,4′-DIPB at both external and internal acid sites at high temperatures. However, there is another possibility that the decrease in the steric restriction by CFI channels causes a decrease in the selectivity for 4,4′-DIPB at high temperatures. No significant isomerization in the *s*-butylation and the *t*-butylation over DON. This is due to the weak acidity, and not due to the zeolite structure. However, further research on these aspects is necessary for full understanding.

We have found the shape-selective formation of 4,4′-DIPB in the isopropylation of BP over several one-dimensional 12-MR zeolites with straight channels: H-Mordenite (MOR),[1–7] ZSM-12 (FTC: MTW),[20] SSZ-24 (FTC: AFI),[21] MAPO-5 (FTC: AFI; M: Mg, Ca, Sr, Ba, and Zn),[22] SAPO-5 (FTC: AFI),[23] and SSZ-31.[24] The selectivity level for 4,4′-DIPB (60–90%) reflected the reaction space in the zeolite channels: MOR > SSZ-24, MAPO-5 (M: Mg, Ca, Sr, Ba, and Zn), and SAPO-5 ≈ SSZ-31 > ZSM-12. The highly selective formation of 4,4′-DABP has also been observed in the *s*-butylation and the *t*-butylation over these zeolites.[21–23] Particularly, 4,4′-DSBB and 4,4′-DTBB were selectively obtained over SSZ-24 and SSZ-31, which have the largest channels among 12-MR zeolites.

The selectivities for 4,4′-DIPB over the one-dimensional zeolites with corrugated channels, SSZ-55 (FTC; ATS),[25] SSZ-42 (FTC: IFR),[25] and MAPO-36 (FTC: ATS; M: Mg and Zn)[26,27] were around 20–40%. These zeolites have similar size of pore-entrance: 0.62 nm × 0.72 nm for IFR and 0.65 nm × 0.75 nm for ATS. Their reaction spaces inside the channels are much larger than the zeolites with straight channels listed above. The loose exclusion of the transition states of the bulky isomers by the channels resulted in the lower selectivity for 4,4′-DIPB. These differences in straight and corrugated zeolites indicate that the structure of channel and the size of pore-entrance are an important key factor for the shape-selective catalysis. However, the increase in bulkiness of alkylating agent enhanced the selectivity for 4,4′-DSBB and 4,4′-DTBB in the *s*-butylation and *t*-butylation, respectively, even over corrugated zeolites.[25] These results also support the above discussion that the shape-selectivity of zeolites is governed by the exclusion of bulky isomers at the transition states by steric restriction in the channels of the zeolites.

Conclusion

Alkylation, i.e., isopropylation, *s*-butylation, and *t*-butylation, of BP was examined over the 14-MR zeolites CFI, DON, and SFH. CFI yielded 4,4′-DIPB shape-selectively in the isopropylation. However, the predominant DIPB isomers were 2,*x*′-DIPB with 2-isopropyl group over DON and SFH, and the selectivities for 4,4′-DIPB were 10–15% in both bulk and encapsulated products. The selectivities for 4,4′-DSBB and 4,4′-DTBB were enhanced by using bulky alkylating agent, 1-butene, and 2-methylpropene, respectively. Particularly, 4,4′-DTBB was obtained selectively in the *t*-butylation over all zeolites.

These differences are due to the spatial difference inside their channels: CFI with slightly corrugated one-dimensional channels (16-MR cavity with a pore-entrance of 0.72 nm × 0.75 nm), DON with straight one-dimensional channels (pore-entrance = 0.74 nm × 0.95 nm), and SFH with largely corrugated one-dimensional channels (22-MR cavity with a pore-entrance of 0.65 nm × 0.88 nm). They are also due to bulkiness of alkylating agents: propene, 1-butene, and 2-methylpropene. The selectivity for 4,4′-DABP was governed by the exclusion of bulky isomers at transition states by the steric restriction inside their channels. The exclusion of bulky isomers from large channels occurs effectively if the transition states are large enough for the differentiation of the least bulky isomers from the isomers by using bulky alkylating agent, such as in the *t*-butylation over DON and SFH.

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Supporting Information

Figures S1–S6: The influences of yields of alkylates in the alkylation of BP. Figures S7–S9: Images of structure of CFI, DON, and SFH zeolites. This material is available free of charge on the Web at http://www.csj.jp/journals/bcsj/.

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