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The alkylation of biphenyl over three-dimensional large pore zeolites: The influence of zeolite structure and alkylating agent on the selectivity for 4,4′-dialkylbiphenyl

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Abstract

Catalytic properties of three-dimensional zeolites, Y (FAU), Beta (BEA), and CIT-1 (CON) zeolites were examined in the alkylation, isopropylation, *sec*-butylation, and *tert*-butylation, of biphenyl (BP), and compared to those of H-mordenite (MOR). The selectivities for 4,4′-dialkylbiphenyl (4,4′-DABP) varied with the types of zeolite and of alkylating agent. FAU, BEA, and CON gave only low selectivities for 4,4′-diisopropylbiphenyl (4,4′-DIPB) in the isopropylation, and predominant isomers were bulky and thermodynamically unstable 2,*x*′-DIPB (2,2′-, 2,3′-, and 2,4′-) at lower temperatures, and bulky and thermodynamically stable 3,4′- and 3,3′-DIPB at higher temperatures: this is quite different from catalytic features over MOR, which gave 4,4′-DIPB with high selectivities at moderate temperatures. These results suggest that FAU, BEA, and CON have no shape-selective nature in the isopropylation, and that the reaction is principally controlled kinetically at lower temperatures, and thermodynamically at higher temperatures. The *sec*-butylation gave similar results to the isopropylation. Although the selectivities for 4,4′-di-*sec*-butylbiphenyl (4,4′-DSBB) were higher than those in the isopropylation, predominant isomers were 2,*x*′-DSBB (2,2′-, 2,3′-, and 2,4′-) at lower temperatures, and 3,4′- and 3,3′-DSBB at higher temperatures. The *tert*-butylation gave 4,4′-di-*tert*-butylbiphenyl (4,4′-DTBB) in moderate to high selectivities over all zeolites at moderate temperatures: the selectivity for 4,4′-DTBB was higher than 80% over BEA and CON; however, it still remained at 50% over FAU. FAU channels with super cages are too large for selective formation of 4,4′-DTBB.

From these results, it is concluded that the selectivity for 4,4′-DABP in the alkylation over MOR, FAU, BEA, and CON is determined by the exclusion of bulky isomers at their transition states, and that the exclusion is caused by the steric restriction at the transition states of bulky isomers by the zeolite channels.

Keywords: Three-dimensional zeolite; Y zeolite; Beta zeolite; CIT-1 zeolite; Alkylation; Biphenyl; 4,4′-Dialkylbiphenyl; Shape-selectivity

1. Introduction

Shape-selective catalyses by zeolites occur by differentiating reactants, products, and/or reaction intermediates according to their shape and size in sterically restricted environment of the zeolite [1–4]. Only molecules of which dimensions are less than the pore size of the zeolite can enter their channel, and react at internal catalytic sites. Bulky molecules are excluded from the channels, resulting in the formation of the slim isomers, and only molecules which can diffuse through the channels will appear in the products. On the other hand, if the spaces of zeolite channels are large enough to accommodate the reactant and/or the products, or if the reactants and the products are smaller than the spaces inside the channels, the reaction is controlled kinetically due to the reactivity of each position at lower temperatures, and to the thermodynamic stability of the products at higher temperatures [1–6]. These considerations indicate that the extent of the exclusion of bulky molecules

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from the channels is one of key factors for shape-selective catalysis by zeolites, and that it depends on the types of zeolite and of alkylating agent.

The isopropylation of biphenyl (BP) is a typical acid-catalyzed reaction for demonstrating shape-selective nature of zeolite [4–29]. Selective formation of the least bulky 4,4′-diisopropylbiphenyl (4,4′-DIPB) should be facilitated over zeolites if the catalytic sites are sterically restricted. In previous papers, we described that 4,4′-DIPB was selectively obtained from BP over dealuminated H-mordenite (MOR) [4,6–13]. The high selectivity for 4,4′-DIPB suggests that catalytically active sites in MOR channels effectively exclude the transition state of bulky isomers from the channels, resulting in selective formation of the least bulky 4,4′-DIPB. On the other hand, many of large pore zeolites, such as Y, Beta, and L zeolites, gave mixtures of DIPB isomers, and the selectivities for 4,4′-DIPB over these zeolites were much lower than those over MOR [5,6]: these results are due to the large reaction spaces in their channels. However, there have been several works that shape-selective formation of 4,4′-di-*tert*-butylbiphenyl (4,4′-DTBB) occurred if 2-methyl-2-propanol or 2-methylpropene was used as alkylating agent [16–19]. These results prompted us to study how zeolite structure, particularly, dimensionality, pore size, and channel structure, affects on the catalysis, and how bulkiness of alkylating agent influences transition states leading to shape-selective catalysis in zeolite channels.

In this paper, we describe the alkylation, *i.e.*, isopropylation, *sec*-butylation, and *tert*-butylation, of BP over some three-dimensional zeolites, Y (FTC: FAU; 12-12-12 channels with super cages), Beta (FTC: BEA; 12-12-12 channels), and CIT-1 (FTC: CON; 12-12-10 channels) [30] from points of view how zeolite structure and bulkiness of alkylating agents affect shape-selective catalysis in their channels. The discussion in the paper is based on the selectivity for dialkylbiphenyl (DABP) isomers.

2. Experimental

2.1. Zeolites

Beta and CIT-1 zeolites were synthesized according to the literatures [31,32]. Mordenite ($SiO_2/Al_2O_3 = 128$; TSZ-690HOA; Tosoh Corp., Tokyo, Japan) and Y zeolite ($SiO_2/Al_2O_3 = 30$; CBVZ720, Zeolyst CV, Groningen, The Netherlands) were obtained commercially. All zeolites were used as acidic form in the catalytic reactions.

The structures and properties of zeolites have been characterized by FE-SEM, XRD, ICP analysis, ^{27}Al and ^{29}Si MAS NMR, N_2 adsorption, and NH_3-TPD. Table 1 summarizes typical properties of the zeolites in this study. Some of results of the characterization of zeolites are also shown in Figs. S1–S5 in supplementary data. The abbreviation of the type of zeolite is expressed by framework type code (FTC) from the IZA Structure Commission [30].

2.2. The alkylation of BP

The alkylation of BP was carried out in a 100-ml SUS-316 autoclave under the pressure of propene, 1-butene, or 2-methylpropene. Typical conditions of the isopropylation were: BP 7.71 g (50 mmol), catalyst 0.25 g, reaction temperature 150–250 °C, and 4 h of operating period under 0.8 MPa of propene pressure (0.4 MPa for 1-butene in the *sec*-butylation and for 2-methylpropene in the *tert*-butylation). An autoclave containing BP and the catalyst was purged with nitrogen before heating. After reaching the reaction temperature, propene was introduced into the autoclave, the reaction was started with agitation, and the pressure maintained constant throughout the reaction. After cooling the autoclave, the catalyst was filtered off, and washed well with toluene. Combined liquid bulk products were diluted with toluene, and subjected to analysis by using a gas chromatograph GC-14A (Shimadzu Corp., Kyoto, Japan) equipped with an Ultra-1 capillary column (25 mm × 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 using the Ultra-1 capillary column as shown above.

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

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

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 tempearture (°C)	Acid amount (mmol/g)	Note
Mordenite	MOR	2	12-8	0.65 × 0.70 (0 0 1)[a] 0.34 × 0.48 (0 1 0)	128	460	0.16	389	0.20	Side pocket (8MR:0.26 × 0.57)
Y	FAU	3	12-12-12	0.74 × 0.74 (1 1 1)	30	810	0.29	254	0.18	Super cage
Beta	BEA	3	12-12-12	0.66 × 0.77 (1 0 0) 0.56 × 0.56 (0 0 1)	111	660	0.28	304	0.18	
CIT-1	CON	3	12-12-10	0.64 × 0.70 (0 0 1) 0.59 × 0.70 (1 0 0) 0.45 × 0.51 (0 1 0)	40	538	0.22	303	0.23	

[a] Plane index.

The catalytic activities based on the yield of alkylates were described in Figs. S6–S9 of supplementary data.

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

3. Results and discussion

3.1. The isopropylation

The influences of reaction temperature on the yield of the isopropylates in the isopropylation of BP are shown in Fig. 1 over MOR and FAU and in Fig. 2 over BEA and CON. Quite different catalytic properties were observed over these zeolites. The yield of diisopropylbiphenyl (DIPB) isomers increased with an increase in reaction temperature over MOR, and that of isopropylbiphenyl (IPBP) isomers was almost constant even at high temperatures. However, further isopropylation to triisopropylbiphenyl (TriIPB) isomers occurred only in small amounts. On the other hand, the yield of DIPB isomers over FAU increased with increasing the temperature, accompanied by a decrease in the yield of IPBP isomers, and the yield of TriIPB isomers also increased at higher temperatures. A small amount of tetraisopropylbiphenyl (TetraIPB) isomers was also observed at higher temperatures. BEA gave IPBP isomers as predominant products even at 300 °C, although the formation of DIPB and TriIPB isomers increased with reaction temperature. Similar catalytic features to BEA were observed in the isopropylation over CON although the catalytic activity was much lower thanBEA in spite of the low SiO_2/Al_2O_3 ratio.

The isopropylation of BP over zeolites is considered to occur by a consecutive mechanism inside their channels [4,7–13,20–29]. The differences between the zeolites are due to their structures: MOR has a two-dimensional pore system with straight 12-MR and zigzag 8-MR channels (side pocket) [30]. FAU has a three-dimensional pore system with super cages (diameter: 1.3 nm) connected with 12-MR pore-entrances (diameter: 0.74 nm) [30]. BEA and CON also have three-dimensional pore systems with 12-12-12 and 12-12-10 channels, respectively [30]. They also have large spaces at the crossing of the channels although they have no super cages as in FAU. Large reaction spaces of FAU inside super cages allow the formation of IPBP, DIPB, and higher isopropylates. However, MOR, BEA, and CON afford reaction spaces for the formation of IPBP and DIPB isomers, although they do not allow the formation of higher isopropylates.

The influences of reaction temperature on the selectivity for DIPB isomers in the isopropylation of BP are shown in Fig. 3 over MOR and FAU and in Fig. 4 over BEA and CON. These zeolites have quite different features regarding the selectivity for DIPB isomers. MOR is a typical zeolite for shape-selective catalysis in the isopropylation of BP [4,7–14]. The selectivities for 4,4′-DIPB were higher than 90% in bulk products over MOR at low to moderate temperatures up to 275 °C; however, they decreased to 30% at 300 °C. The selectivities for 4,4′-DIPB in both bulk and encapsulated products over FAU were less than 10% in the range of 150–300 °C. Predominant products were 2,*x*′-DIPB (2,2′- 2,3′-, and 2,4′-) at lower temperatures. However, their selectivities decreased with an increase in the temperature, accompanied by the formation of thermodynamically more stable 3,4′-, 3,3′-, and 4,4′-DIPB, particularly, 3,4′-DIPB. The selectivities for 4,4′-DIPB over

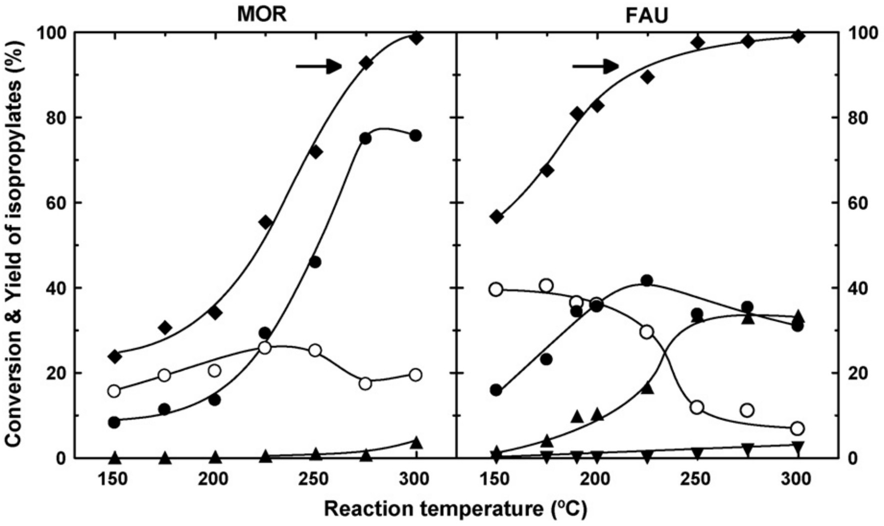

Fig. 1. The influences of reaction temperature on the yield of the isopropylates in the isopropylation of BP over MOR and FAU. Reaction conditions, BP: 100 mmol (MOR), 50 mmol (FAU); catalyst: 0.5 g (MOR), 0.25 g (FAU); temperature: 150–350 °C; propene pressure: 0.8 MPa; period: 4 h. Legends: (◆) conversion, yield of isopropylates (○) IPBP; (●) DIPB; (▲) TriIPB; (▼) TetraIPB.

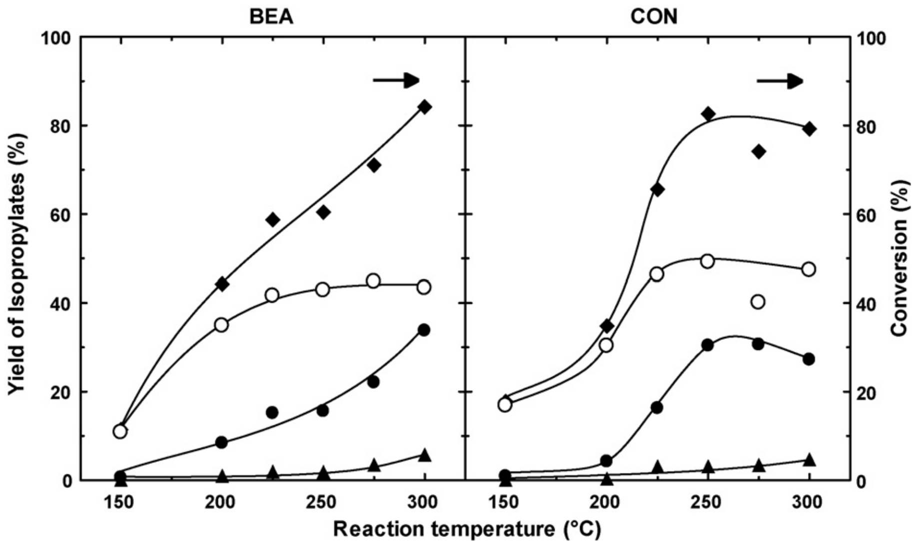

Fig. 2. The influences of reaction temperature on the yield of the isopropylates in the isopropylation of BP over BEA and CON. Reaction conditions, BP: 50 mmol; catalyst: 0.25 g. Other conditions and legend: see Fig. 1.

BEA and CON were much lower than those over MOR, although they were higher than those over FAU: 40% at 150 °C to 30% at 300 °C for BEA and 20–25% in the range of 150–300 °C for CON. The selectivities for 4,4′-DIPB in encapsulated products over BEA and CON were also much lower than those over MOR, although they were higher than those for FAU. The formation of 2,*x*′-DIPB over BEA and CON was also predominant at low temperatures, and decreased with the temperature, accompanied by an increase in the yield of 3,4′-DIPB although the selectivities are much lower than that over FAU.

These differences in the selectivities for DIPB isomers are due to differences in steric restriction at their transition states of the isomers by zeolite channels. 4-IPBP formed predominantly from BP is preferentially isopropylated to DIPB isomers because it can enter much rapidly in MOR channels compared to bulky 2- and 3-IPBP isomers [4,7–13]. MOR channels can also exclude the transition states to form bulky DIPB isomers, resulting in the selective formation of 4,4′-DIPB as discussed in previous papers [4,7–13]. However, three-dimensional zeolites, FAU, BEA, and CON, cannot exclude bulky DIPB isomers at their transition states inside their channels: these zeolites can allow the all DIPB isomers including bulky isomers such as 2,*x*′-, 3,3′-, and 3,4′-DIPB. The reactions over these zeolites are controlled kinetically to give 2,*x*′-DIPB preferentially at low temperatures due to the attack at electron-rich 2-position, and thermodynamic control is also operated to yield predominantly 3,4′- and 3,3′-DIPB at higher temperatures. These results of

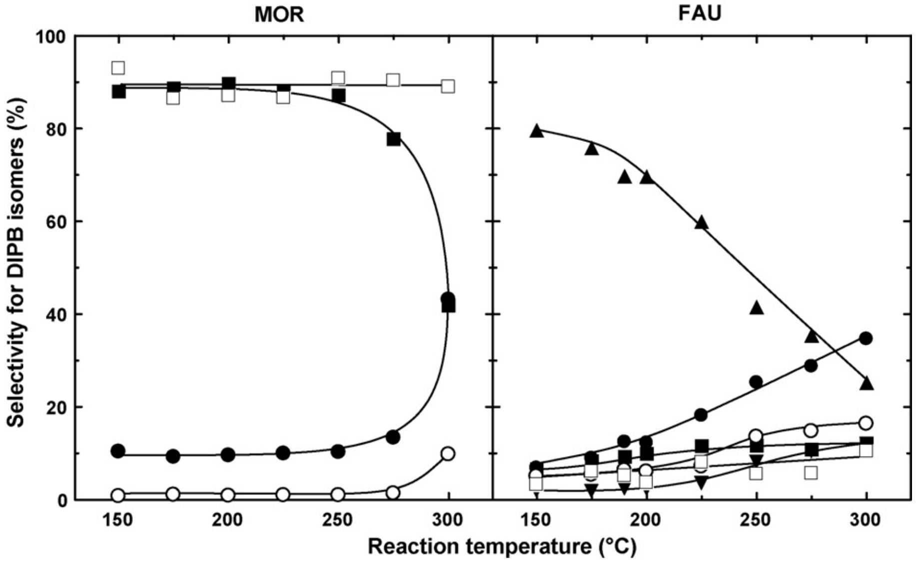

Fig. 3. The influences of reaction temperature on the selectivity for DIPB isomers in the isopropylation of BP over MOR and FAU. Reaction conditions, see Fig. 1. Legends: selectivity for bulk products: (■) 4,4′-DIPB; (●) 3,4′-DIPB; (○) 3,3′-DIPB; (▲) 2,*x*′-DIPB; (▼) 3,5-DIPB; selectivity for encapsulated products: (□) 4,4′-DIPB.

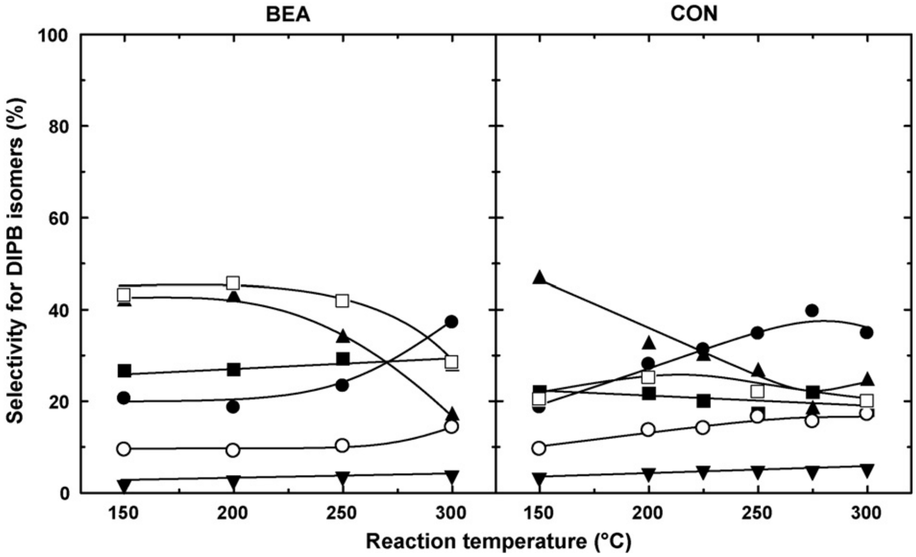

Fig. 4. The influences of reaction temperature on the selectivity for DIPB isomers in the isopropylation of BP over BEA and CON. Reaction conditions, see Fig. 2. Legends: see Fig. 3.

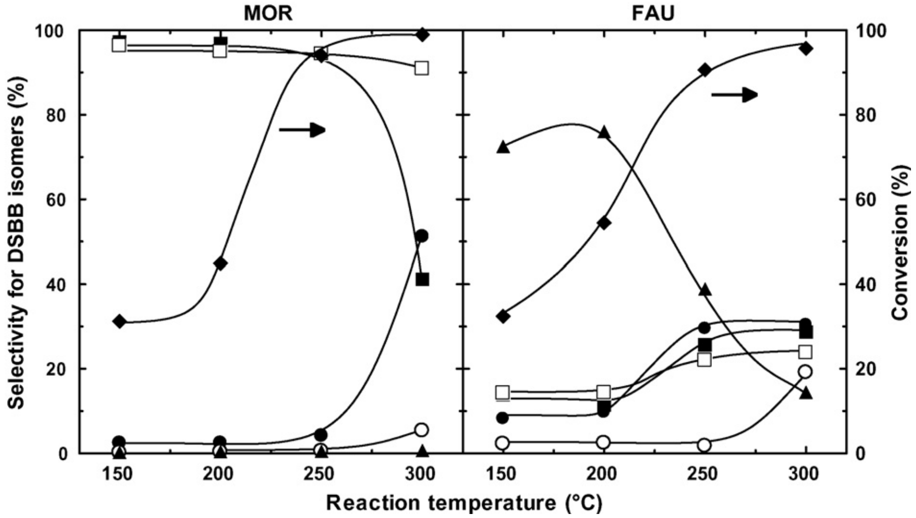

Fig. 5. The influences of reaction temperature on the selectivity for DSBB isomers in the *sec*-butylation of BP over MOR and FAU. Reaction conditions, BP: 50 mmol; catalyst: 0.25 g; temperature: 150–300 °C; 1-butene pressure: 0.5 MPa; period: 4 h. Legends: (◆) conversion; selectivity for bulk products: (■) 4,4′-DSBB; (●) 3,4′-DSBB; (○) 3,3′-DSBB; (▲) 2,x'-DIPB; (▼) 3,5-DIPB; selectivity for encapsulated products: (□) 4,4′-DSBB.

three-dimensional zeolites in the isopropylation suggest that FAU, BEA, and CON have too large reaction spaces for the selective formation of 4,4′-DIPB.

The decrease in the selectivities for 4,4′-DIPB in bulk products occurred over MOR at high temperatures as 300 °C. However, the selectivity for 4,4′-DIPB in encapsulated DIPB isomers kept high even at 300 °C. The decrease in the selectivities for 4,4′-DIPB is due to the isomerization to thermodynamically stable 3,4′- and 3,3′-DIPB,[2] and the isomerization occurs at external acid sites, but not inside MOR channels, because the reaction space in MOR is much smaller than that in FAU, BEA, and CON.

3.2. The sec-butylation

The *sec*-butylation of BP over three-dimensional zeolites was examined in order to know the influence of bulkiness of alkylating agent. Similar catalytic activity in the *sec*-butylation was observed as in the isopropylation: the products were principally *sec*-butylbiphenyl (SBBP) and di-*sec*-butylbiphenyl (DSBB) isomers with a small amount of tri-*sec*-butylbiphenyl (TSBB) isomers (see Figs. S6 and S7 in supplementary data).

The influences of reaction temperature on the selectivity for di-*sec*-butylbiphenyl (DSBB) isomers in the *sec*-butylation of BP are shown in Fig. 5 over MOR and FAU and in Fig. 6 over BEA and CON. These features in the *sec*-butylation were similar to those in the isopropylation, although the selectivities for DSBB isomers over these zeolites were higher than those in the isopropylation. MOR gave the highest selectivity for 4,4′-

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[2] Equilibrium composition of DIPB isomers at 300 °C: 3,4′- (33%), 3,3′- (37%), 4,4′- (9%), 3,5-DIPB (17%), and others (4%) [5].

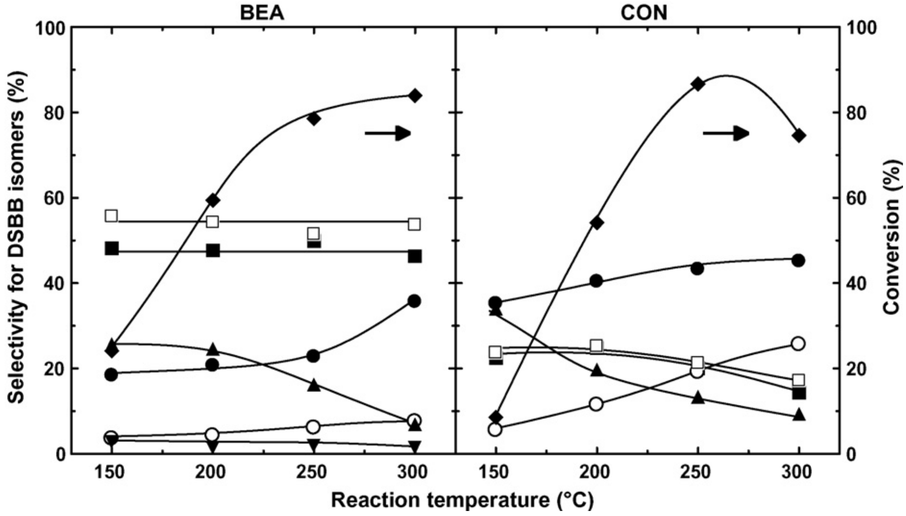

Fig. 6. The influences of reaction temperature on the selectivity for DSBB isomers in the *sec*-butylation of BP over BEA and CON. Reaction conditions, BP: 25 mmol (BEA), 50 mmol (CON); catalyst: 0.125 g (BEA), 0.25 g (CON). Other conditions and legends: see Fig. 5.

DSBB, resulting in highly shape-selective catalysis at low to moderate temperatures up to 250 °C. However, the selectivity decreased to 40% at 300 °C although the selectivity in encapsulated products remained high even at 300 °C. On the other hand, the selectivities for 4,4′-DSBB over FAU increased from 5% at 150 °C to 30% at 300 °C for bulk products and from 15% at 150 °C to 25% at 300 °C for encapsulated products. The formation of 2,*x*′-DSBB was predominant at lower temperatures; however, it decreased with an increase in the temperature, accompanied by an increase in the yield of thermodynamically stable 3,4′- and 3,3′-DSBB. BEA gave selectivities for 4,4′-DSBB at the level of around 50% from 150 °C to 300 °C in bulk and encapsulated products, and 2,*x*′- and 3,4′-DSBB were obtained as by-products. The selectivities for 2,*x*′-DSBB decreased with the increase in the temperature, accompanied by the increase in those for thermodynamically stable 3,4′-DSBB. These variations in the selectivity for 4,4′-DSBB mean that BEA has a shape-selective nature for the *sec*-butylation although bulkier isomers are not completely excluded. The effective molecular diameter of DSBB isomers is almost the same as that of DIPB isomers in the isopropylation. However, the differences in bulkiness of these two DSBB isomers at the interaction of the transition states with BEA channels are enhanced by the replacement of isopropyl groups with the *sec*-butyl groups in 3,4′- and 4,4′-DSBB, resulting in the improvement of shape-selectivities in the *sec*-butylation over BEA although BEA channels are still too large for selective formation of 4,4′-DSBB. CON gave the selectivities for 4,4′-DSBB at similar levels as those for 4,4′-DIPB in the isopropylation. CON channels are too small for selective formation of 4,4′-DSBB. These differences in the selectivities for 4,4′-DSBB over BEA and CON suggest that the reaction

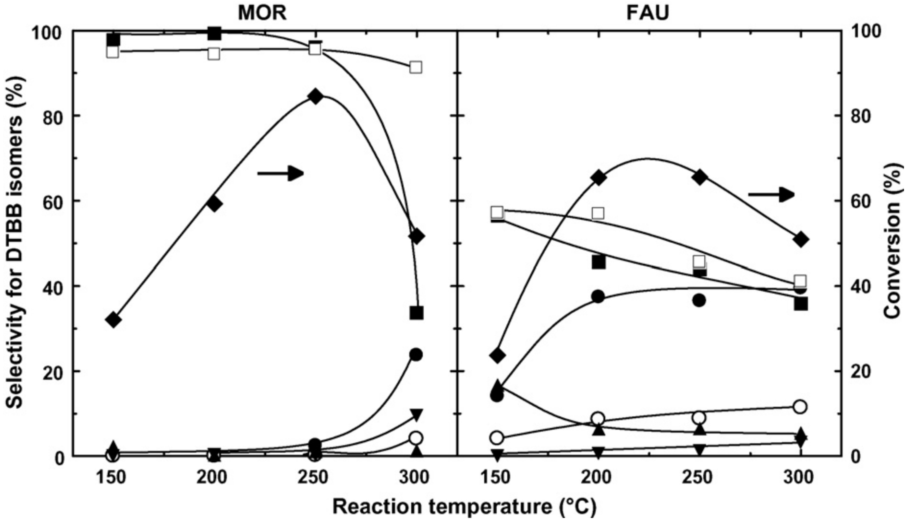

Fig. 7. The influences of reaction temperature on the selectivity for DTBB isomers in the *tert*-butylation of BP over MOR and FAU. Reaction conditions, BP: 50 mmol; catalyst: 0.25 g; temperature: 150–300 °C; 2-methylbutene pressure: 0.5 MPa; period: 4 h. Legends: (◆) conversion; selectivities for bulk products: (■) 4,4′-DTBB; (●) 3,4′-DTBB; (○) 3,3′-DTBB; (▲) 2,*x*′-DTBB; (▼) 3,5-DIPB; encapsulated products (□) 4,4′-DTBB.

space of CON is larger than that of BEA. These results of the *sec*-butylation over three-dimensional zeolites, FAU, BEA, and CON, indicate that they do not have reaction spaces to fit for the selective formation of 4,4′-DSBB.

A decrease in the selectivity for 4,4′-DSBB in bulk products occurred over MOR at high temperatures as 300 °C. However, the selectivity for 4,4′-DSBB in encapsulated DSBB isomers kept high even at 300 °C. These results indicate that the decrease in the selectivity for 4,4′-DSBB is due to the isomerization to thermodynamically stable 3,4′-DSBB: the isomerization occurs at external acid sites, but not inside the MOR channels similar to that in the isopropylation.

3.3. The tert-butylation

Steric restriction of dialkylbiphenyl (DABP) isomers by zeolite channels was enhanced by the bulkiness of alkylating agents as discussed in the previous section. It is interesting to know the influence of a bulky alkylating agent, 2-methylpropene, on the selectivity for DABP isomers in the alkylation of BP.

The catalytic activities of the zeolite in the *tert*-butylation were much lower than those in the isopropylation and *sec*-butylation. The predominant products were *tert*-butylbiphenyl (TBBP), and the yield of di-*tert*-butylbiphenyl (DTBB) was much lower than that in the isopropylation and the *sec*-butylation. Particularly, the activities of CON were low in spite of low SiO_2/Al_2O_3 ratio (see Figs. S8 and S9 in supplementary data).

The influences of reaction temperature on the selectivity for DTBB isomers in the *tert*-butylation of BP are shown in Fig. 7 over MOR and FAU and in Fig. 8 over BEA and CON. The selectivities for 4,4′-DTBB were much higher than those observed in the isopropylation and *sec*-butylation. Highly shape-selective catalysis to form 4,4′-DTBB occurred over MOR at moderate temperatures up to 250 °C, and the selectivity for 4,4′-DTBB in the bulk products decreased to 30% at 300 °C. However, the selectivity in the encapsulated products kept 90% selectivity for 4,4′-DTBB even at 300 °C. The selectivities for 4,4′-DTBB in bulk and encapsulated products in the *tert*-butylation over FAU were enhanced up to 55% at 150 °C. These results show that a shape-selective nature appeared in the *tert*-butylation over FAU although the formation of bulky and thermodynamically stable 3,4′-DTBB was accompanied. The selectivities for 4,4′-DTBB over BEA and CON were higher than 80% at low to moderate temperatures up to 250 °C, and they decreased to around 50% at 300 °C, although the selectivities in encapsulated products kept high even at 300 °C. Selective formation of 4,4′-DTBB over these zeolites means that BEA and CON can exclude effectively the bulkier isomers by their channels: the bulky alkylating agent prevents the formation of the transition state of bulky isomers by steric restriction even in the large channels of BEA and CON. Similar selective formation of 4,4′-DTBB was described in the literatures in the *tert*-butylation of BP over MOR, FAU, and BEA [16–19].

A decrease in the selectivities for 4,4′-DTBB was observed at higher temperatures over all zeolites. However, the selectivities for 4,4′-DTBB in encapsulated products kept high even at 300 °C over MOR, BEA, and CON. The results mean that the decrease in the selectivities for 4,4′-DIPB by the isomerization occur at external acid sites, and that the isomerization does not occur inside the channels. However, the selectivities for 4,4′-DTBB in bulk and encapsulated products decreased with increasing the temperature over FAU. FAU channels with super cages allow the isomerization of 4,4′-DTBB to 3,4′-DTBB even though they have a shape-selective nature.

These results of *tert*-butylation for three-dimensional zeolites suggest that the channels of FAU, BEA, and CON have some shape-selective natures, although their shape-selectivities are much lower than those over MOR. FAU channels are too large even for selective formation of 4,4′-DTBB.

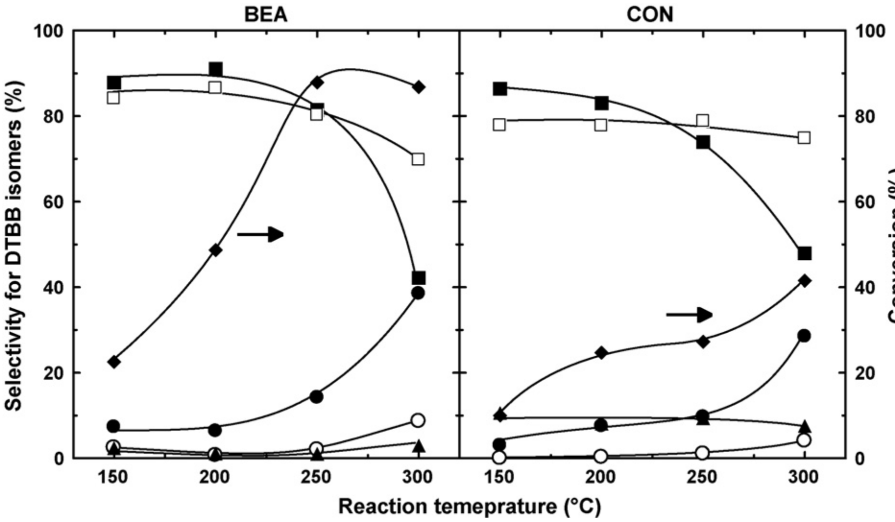

Fig. 8. The influences of reaction temperature on the selectivity for DTBB isomers in the *tert*-butylation of BP over BEA and CON. Reaction conditions, BP: 25 mmol (BEA), 50 mmol (CON); catalyst: 0.125 g (BEA), 0.25 g (CON). Other conditions and legends: see Fig. 7.

3.4. The influence of types of zeolite and alkylating agent

FAU has a three-dimensional pore system with super cages (diameter: 1.3 nm) connected with 12-MR pore-entrances (diameter: 0.74 nm). BEA and CON have three-dimensional pore systems with 12-12-12 and 12-12-10 channels, respectively. The latter two zeolites also have large reaction spaces at the crossing of the channels although they have no super cages as in FAU. These differences of the structures reflect the difference of reaction spaces in the order: FAU $\gg$ BEA $>$ CON $\gg$ MOR. Large reaction spaces of FAU inside super cages allow the formation of IPBP, DIPB, and bulky higher isopropylates, such as TriIPB and TetraIPB. However, MOR, BEA, and CON effectively yielded IPBP and DIPB isomers: they do not allow the formation of bulky TriIPB and higher isopropylates. These results show that the effectiveness for the exclusion of bulky isomers by zeolite channels is in the order: MOR $\gg$ BEA $>$ CON $\gg$ FAU. The differences in bulkiness of 4,4′-DABP and other isomers increase by the replacement of isopropyl groups with bulky *sec*-butyl and *tert*-butyl groups. They also enhance at the steric interaction of their transition states with the channels. These synergetic effects result in appearance of high shape-selectivities with increasing the bulkiness of alkylating agents in the order: isopropylation $<$ *sec*-butylation $\ll$ *tert*-butylation.

The DABP isomers from the alkylation of BP are classified into three categories: 4,4′-DABP for the least bulky isomer by shape-selective catalysis, 3,*x*′-DABP (3,4′- and 3,3′-) for thermodynamically stable and bulky isomers formed principally under thermodynamic control, and 2,*x*′-DABP (2,2′-, 2,3′-, and 2,4′-) for the bulky and thermodynamically unstable isomers formed principally under kinetic control.

Fig. 9 shows the selectivities for 4,4′-, and 2,*x*′-DABP over MOR, FAU, BEA, and CON at 250 °C. The selectivities of DABP isomers were typical in relation to zeolite structure because further isomerization of DABP isomers was almost negligible over these zeolites at 250 °C. The selectivities for 4,4′-DABP depend on the types of zeolite and of alkylating agent. Particularly, the high selectivities were observed for the zeolites with small reaction space and by bulky alkylating agent. The selectivities were also influenced by reaction temperatures as discussed in the previous sections.

Shape-selective formation of 4,4′-DIPB was only observed over MOR among the zeolites in this study: the selectivities for 4,4′-DIPB are due to the prevention of the transition states of bulky DIPB isomers by steric restriction in the channels. Three-dimensional zeolites, FAU and BEA with 12-12-12 ring system and CON with 12-12-10 ring system gave much lower selectivities for 4,4′-DIPB, and the predominant DIPB isomers were bulky and thermodynamically unstable 2,*x*′-DIPB and bulky and stable 3,*x*′-DIPB. The reaction may occur at the acidic sites in 12-MR straight channels and crossings of BEA and CON channels; however, these reaction spaces inside the zeolites are too large to exclude the bulkier DIPB isomers. These results show that the isopropylation over three-dimensional zeolites is governed by kinetic and thermodynamic factors, and not by the steric restriction by the channels. Particularly, high selectivity for 2,*x*′-DIPB and high yield of higher isopropylates, such as TriIPB over FAU, suggest the loose steric constraints of FAU channels with bulky products in the isopropylation.

The features in the *sec*-butylation resembled those in the isopropylation, although the selectivities for 4,4′-DSBB were higher than those for 4,4′-DIPB. These results suggest that the formation of bulky isomers, such as 3,*x*′- and 2,*x*′-DSBB, in the *sec*-butylation is more hindered than that in the isopropylation because the replacement of isopropyl groups with *sec*-butyl groups increases the differences in bulkiness of the isomers and, resultantly, of the steric restriction inside the zeolite channels. The selectivities for 4,4′-DSBB in the *sec*-butylation over MOR were higher than that in the isopropylation. However, three-dimensional zeolites, FAU, BEA, and CON, also gave the low selectivities for 4,4′-DSBB in the *sec*-butylation. These reactions in their channels should be principally controlled by kinetic or thermodynamic factors depending on the temperatures. BEA gave the highest selectivity for 4,4′-DSBB among the three-dimensional zeolites: the steric restriction of transition states of bulky isomers by the channels may be

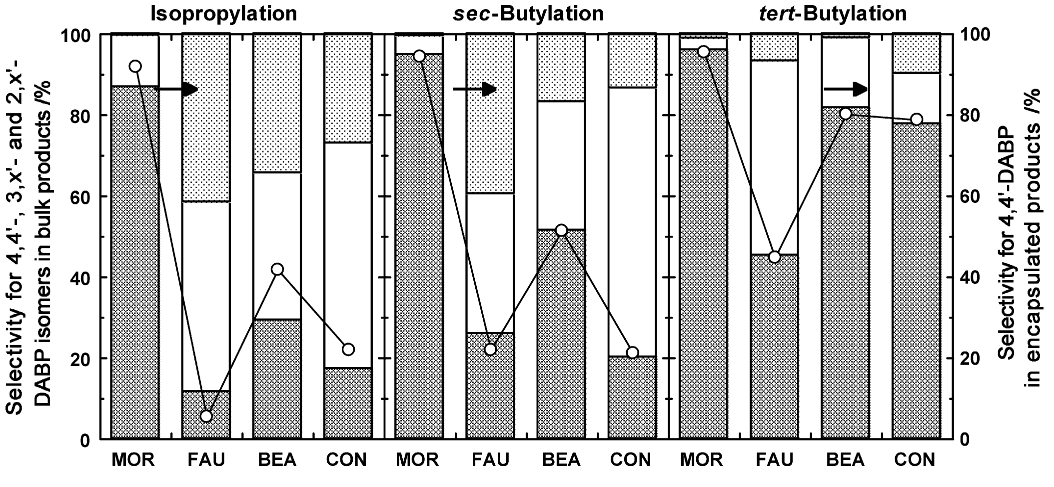

Fig. 9. The selectivities for DABP isomers in the alkylation of BP over the zeolites. Reaction conditions, temperature: 250 °C. Other conditions: see Figs. 1–8. Legends: bulk products: (▩) 4,4′-DABP; (□) 3,*x*′-DABP (3,4′- and 3,3′-); (▨): 2,*x*′-DABP (2,2′-, 2,3′-, and 2,4′-): encapsulated products: (○) 4,4′-DABP.

operated to some extents because *sec*-butyl group is effectively bulky in the channels.

The selectivity for 4,4′-DTBB was enhanced in the *tert*-butylation over all zeolites, although it depends on the type of zeolite. MOR gave high selectivities for 4,4′-DTBB (>95%). The selectivities for 4,4′-DTBB were at the level of 80% over BEA and CON although CON gave the higher selectivities for 2,*x*′-DTBB than BEA. The selectivity for 4,4′-DTBB over FAU remained at the level of 50%. These results suggest that the selectivities in the *tert*-butylation are due to reaction space inside the zeolite channels.

The above discussion can be summarized as follows. The effectiveness for the exclusion of bulky isomers by zeolite channels is in the order: MOR $\gg$ BEA $>$ CON $\gg$ FAU. The selectivity for 4,4′-DABP increased with increasing bulkiness of alkylating agent in the order: isopropylation $<$ *sec*-butylation $\ll$ *tert*-butylation.

Fig. 9 also shows the selectivities for 4,4′-DABP in encapsulated products. The selectivities for 4,4′-DABP were at almost the same levels in bulk and encapsulated products. These results indicate that the alkylation over three-dimensional zeolites occurs inside the channels even in *tert*-butylation, and that the selectivity for 4,4′-DABP depends on the steric restriction of the transition state leading to bulky isomers by the channels as discussed in the previous sections.

The selectivity for 4,4′-DABP in bulk products decreased with increasing the temperature in the alkylation over some zeolites as shown in Figs. 3–8. In these cases, the selectivities for 4,4′-DABP in encapsulated products remained at the high level. These results suggest that the decrease in the selectivity for 4,4′-DABP is principally caused by the isomerization of 4,4′-DABP to more stable 3,4′-DABP at external acid sites, because the channels are too small for the isomerization of 4,4′-DABP to bulkier DABP isomers.

We have also found the shape-selective formation of 4,4′-DIPB in the isopropylation of BP over several one-dimensional 12-MR zeolites with straight channels: MOR [4–13,22], ZSM-12 (FTC: MTW) [20], SSZ-24 (FTC: AFI) [20–22], MAPO-5 (FTC: AFI; M: Mg, Ca, Sr, Ba, and Zn) [23], SAPO-5 (FTC: AFI) [24], and SSZ-31 [25] at levels of 60–90%. The level of the selectivity for 4,4′-DIPB reflects the width of the channel of the zeolites: MOR (pore-entrance: 0.65 nm × 0.70 nm) > SSZ-24, MAPO-5 (M: Mg, Ca, Sr, Ba, and Zn), and SAPO-5 (pore-entrance: 0.72 nm × 0.72 nm) ≈ SSZ-31 (pore entrance: 0.56 nm × 0.82 nm) > ZSM-12 (pore-entrance: 0.59 nm × 0.60 nm) [30]. The selectivities for 4,4′-DABP in *sec*-butylation and *tert*-butylation were also improved over these zeolites. Particularly, the *tert*-butylation occurred with high shape-selectivity over all zeolites [22].

The selectivities for 4,4′-DIPB over corrugated zeolites, SSZ-42 (FTC: IFR) [20,22,26], SSZ-55 (FTC: ATS) [20,22,26], and MAPO-36 (FTC: ATS; M: Mg, Zn) [27,28] were in the level of 20–40%. Their corrugated channels with pore-entrances around 0.60–0.75 nm offer large reaction spaces for the isopropylation of BP. They are too large to differentiate the transition states of DIPB isomers, resulting in lower selectivity for 4,4′-DIPB. However, the selectivities for 4,4′-DSBB in *sec*-butylation and for 4,4′-DTBB in *tert*-butylation over these zeolites were higher than those for 4,4′-DIPB in the isopropylation [22].

These results correspond well to the results of 14-MR zeolites [29]. The selectivity for 4,4′-DABP was also influenced by the types of zeolite and of alkylating agent over one-dimensional 14-MR zeolites: CFI with one-dimensional slightly corrugated channels (pore-entrance: 0.72 nm × 0.75 nm), DON with one-dimensiona1 straight channels (pore-entrance: 0.74 nm × 0.95 nm), and SFH with one-dimensional corrugated channels (pore-entrance: 0.65 nm × 0.88 nm) [30]. CFI is the only 14-MR zeolite that gave 4,4′-DABP selectively in all alkylations, isopropylation, *sec*-butylation, and *tert*-butylation, of BP. DON and SFH gave selectively 4,4′-DABP only in the *tert*-butylation. The extensive formation of 2,*x*′-DABP for the isopropylation and *sec*-butylation over DON and SFH means that the steric restriction of transition states of DABP isomers, derived from propene or 1-butene, with the channels is too loose to differentiate 4,4′-DABP from the other isomers resulting in the formation of bulky isomers. In these cases, the selectivities for 2,*x*′-DABP over SFH were higher than those over DON: SFH has larger reaction space than DON because of its corrugated channels. Shape-selective catalysis in the *tert*-butylation over all zeolites indicates that the steric restriction of transition states in the channels is large enough for selective formation of 4,4′-DTBB.

4. Conclusion

The alkylation, isopropylation, *sec*-butylation, and *tert*-butylation, of BP was examined 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 MOR. The selectivity for 4,4′-DABP varied with the types of zeolite and of alkylating agent. FAU, BEA, and CON gave only low selectivities for 4,4′-DIPB in the isopropylation, and principal isomers were bulky 2,*x*′-DIPB and bulky and thermodynamically stable 3,4′- and 3,3′-DIPB; however, MOR gave selectively 4,4′-DIPB. These results suggest that FAU, BEA, and CON have no shape-selective nature in the isopropylation, and that the selectivities for DIPB isomers are kinetically and/or thermodynamically controlled depending on the temperatures. The *sec*-butylation occurred in the similar levels to the isopropylation: the selectivities for 4,4′-DSBB in the *sec*-butylation were higher than those in the isopropylation over all zeolites although the selectivities was still low over BEA and CON. The selectivities for 4,4′-DTBB were enhanced in the *tert*-butylation over all zeolites: 80% over BEA and CON and 50% over FAU. FAU channels with super cages are too large even for shape-selective *tert*-butylation.

The decrease in the selectivity for 4,4′-DABP was observed in the alkylation over some zeolites at higher temperatures. The decrease is due to the isomerization of 4,4′-DABP, which was originally formed inside the channels of the zeolite, at external acid sites because the channels are not large enough for the isomerization of 4,4′-DABP to more stable 3,4′-DABP.

Further investigations of the influence of types of zeolite and of alkylating agent on shape-selective catalysis are in 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.2007.10.060.

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