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The ethylation of biphenyl over H-mordenite: Reactivities of the intermediates in the catalysis

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Abstract

The ethylation of biphenyl (BP) with ethene was examined over dealuminated H-mordenite (MOR; $SiO_2/Al_2O_3 = 206$). The ethylation occurred non-shape-selectively, and gave a mixture of ethylbiphenyls (EBPs), diethylbiphenyls (DEBPs), and higher ethylates. The ethylation of BP to EBPs was yielded in the ratio, 2-EBP:3-EBP:4-EBP = 2:2:1 at the initial stages. The reaction occurs under kinetic control. The formation of 4,4′-DEBP was less selective than that of the other isomers; however, the combined selectivity for DEBPs with 4-ethyl groups was higher than 80% during the reaction. 4-EBP was consumed rapidly than the other EBPs in the ethylation of EBPs to DEBPs. Less bulky DEBPs, particularly, 4,4′-DEBP disappeared preferentially compared to the other DEBPs in the ethylation of EBPs to higher ethylates. These results show that the MOR channels are too large for the shape-selective formation of 4-EBP and 4,4′-DEBP by the "restricted transition state selectivity mechanism".

The reactivities of reaction intermediates in the ethylation of BP decreased in the order: 4,4′-DEBP > 4-EBP > BP ≫ 3-EBP ≫ 2-EBP. These three EBP isomers have quite different reactivities for the further ethylation: 4-EBP was preferentially consumed to yield DEBPs with 4-ethyl groups. 3-EBP partly participated in the ethylation to DEBPs, particularly, at high conversion; however, 2-EBP was not ethylated even at the high conversion. Further, 4,4′-DEBP was preferentially ethylated to higher ethylates because it is the most reactive among BP, EBPs, and DEBPs. These high reactivities of 4-EBP and 4,4′-DEBP among their isomers were due to the "reactant selectivity mechanism".

Molecular modeling of the diffusion of the products suggests that the MOR channels are too large for the selective formation of 4,4′-DEBP because all DEBPs can diffuse in the channels. The preferential disappearance of 4-EBP and 4,4′-DEBP is due to the difference of the diffusion in the channels among their isomers. These simulations are corresponding to the experimental results.

Keywords: Mordenite; Biphenyl; Ethylation; Shape-selective catalysis; 4-Ethylbiphenyl; 4,4′-Diethylbiphenyl

1. Introduction

Attempts to control product distribution in the alkylation of polynuclear aromatics by zeolites have attracted the attention of many researchers [1–14]. It is essential to understand what happens at acid sites on internal and external surfaces of zeolites in order to synthesize selectively the target isomer. We have found that the isopropylation of biphenyl (BP) over dealuminated H-mordenite (MOR) gave high yield with high selectivity for 4,4′-diisopropylbiphenyl (4,4′-DIPB) [1–7]. The high selectivity for 4,4′-DIPB was explained by the exclusion of bulky

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DIPBs at the transition state by the steric restriction in the channels [1–7].

Polynuclear aromatic hydrocarbons substituted symmetrically with ethyl groups are more versatile than those with isopropyl groups for the functionalization to advanced materials because the former has higher reactivities than the latter for the many reactions, such as oxidation, *etc*. However, it is difficult to obtain the slimmest isomer by the shape-selective ethylation compared to the isopropylation because the steric hindrance of ethyl moiety of BP inside the zeolite channels is less severe than that of the isopropyl moiety. Takeuchi et al. reported shortly on the ethylation of BP and NP over MOR [15–17]. We also published the preliminary works of the ethylation of BP over MOR [18,19]. In these works, the ethylation of BP and NP are non-selective for 4,4′-diethylbiphenyl (4,4′-DEBP) and 2,6-diethylnaphthalene (2,6-DEN), respectively. There have also been only a few works on the ethylation of BP and NP over other zeolites. ZSM-12, which has the smaller channels than MOR gave only low selectivity for 4,4′-DEBP and 2,6-DEN [15–17,20].

In order to establish the highly shape-selective synthesis of 4,4′-DEBP, it is very important to know how the ethylation of BP occurs over one-dimensional zeolites, and how the reaction intermediates play roles in the ethylation. In this work, we focus on the reactivities of the intermediate, i.e., ethylbiphenyls (EBPs) and diethylbiphenyls (DEBPs) in the ethylation of BP with ethene over MOR, and discuss how the catalysis occurs inside the MOR channels. Modeling of the fitting the products in the MOR channels are also discussed to compare with experimental results.

2. Experimental

2.1. Reagents

Dealuminated H-mordenite (MOR, $SiO_2/Al_2O_3 = 206$; TSZ-690HOA) was obtained from TOSOH Corporation, Tokyo, and calcined in an air stream at 450 °C before use. 3- and 4-EBPs, and 4,4′-DEBP were supplied from Shin-Nippon Steel Chemicals Co. Ltd., Tokyo. For the standards of the DEBPs for the analysis, 3,3′-, 3,4′-, 2,4′-, 3,4-, and 2,4-DEBPs were synthesized by the nickel catalyzed coupling of corresponding ethylphenyl magnesium bromide and bromoethylbenzene [21]. Some data in previous paper involve analytical errors of DEBP isomers [15].

2.2. The ethylation of BP

The ethylation of BP and its derivatives was carried out in a 100-ml SUS-316 autoclave. Typical reaction conditions for BP are: BP 200 mmol, catalyst 1 g, temperature 150–250 °C, and 4 h under ethene pressure of 0.8 MPa. An autoclave containing BP and the catalyst was purged with nitrogen, heated to reaction temperature, and ethene was introduced to the autoclave. The reaction was started with the agitation, and the pressure was maintained constant throughout the reaction. After cooling the autoclave to ambient temperature, excess of ethene was carefully released, and the catalyst was separated from organic products by filtration. The organic products were subjected to the analysis by using a Hewlett-Packard Model 5890 series II Gas Chromatograph or a Shimadzu Gas Chromatograph GC14A equipped with an Ultra-1 capillary column (25 m × 0.2 mm). The products were also identified with a Hewlett-Packard Model 5890 series II Gas Chromatograph equipped with a 5971A Mass Detector System or a Shimadzu Gas Chromatograph–Mass Spectrometer GC–MS 5000 using an Ultra-1 capillary column (25 m × 0.2 mm).

The yield of each product was calculated on the basis of the amounts of starting BP, and the selectivities for each EBP and DEBP isomers are expressed based on the total amounts of EBPs and DEBPs, respectively.

The analysis of the encapsulated products in the catalyst after the reaction was carried out as follows: MOR (50 mg) recovered from reaction, washed well with toluene, and dried at 100 °C overnight was placed in 3 ml of 48% aqueous hydrofluoric acid solution. Resulting suspension was stirred overnight at room temperature, and neutralized with potassium carbonate. Organic products were extracted three times with 20 ml of dichloromethane, and organic layer was dried over anhydrous sodium sulfate. After filtration of sodium sulfate and removal of solvent *in vacuo*, the residue was subjected to the analysis as in the bulk products. The selectivities for EBPs and DEBPs in the encapsulated products were defined in a similar manner as those in the bulk products. The encapsulated products were also expressed by the percentage of the composition of products in reaction mixtures, because it is difficult to analyze quantitatively with high reproducibility.

2.3. Modeling of BP, EBPs, and DEBPs inside the channels

Computational studies were carried out using Material Studio's (MS) supplied by Accelrys Inc., UK. All the structures of the organic molecules were completely optimized by using the density functional theory (DFT). As the exchange functional, Becke's hybrid exchange B3 was used as correlation functions, the Lee–Yang–Parr non-local functional (LYP). The basis set used to optimize the organic molecules were at the level of 6-311G* (d, p). The extents of the molecule in space were calculated for the generically favorable (optimized molecule) conformation and their sizes and shapes were analyzed. The dimensions of molecules in three-dimensional space were measured according to the procedure detailed elsewhere [22]. The three largest dimensions ($a \times b \times c$) of BP; 2-, 3-, 4-EBP, 2,4′-, 2,4-, 3,3′-, 3,4′-, and 4,4′-DEBP in mutually perpendicular directions are given in Table 2.

Qualitative optimized structure fitting of BP, EBPs, and DEBPs inside the MOR channel is studied by molecular graphics (MG) and compared the dimensions of the molecules with pore diameter. The zeolite lattice is generated from crystallographic data reported in the literatures [23]. Further, the chemical interactions between the zeolite (host) and the organic molecules (guests) were studied using energy minimization calculations to understand the adsorption sites and diffusion characteristics of BP, EBPs, and DEBPs. For the generation of the three-

Table 1
Crystal characteristics and the dimensions of the simulation boxes for MOR

Symmetry	Orthorhombic
Unit-cell composition	$(SiO_2)_{48}$
a (nm)	1.8094
b (nm)	2.0516
c (nm)	0.7524
Pore diameter (nm)	0.65 × 0.70
Number of unit-cells in simulation box	2 × 2 × 8

dimensional zeolites model MS builder is used. The simulation box contained the zeolite generated from its crystal structure and the actual dimensions of the simulation is 2 unit × 2 unit × 8 unit (Table 1). The detailed methodology is reported elsewhere [22]. The size of the simulation boxes were chosen in such a way that the symmetry along the channel direction is taken care of and the box is just large enough in the other two directions to take care of the non-bonded interactions, which took a cut-off distance of 0.95 nm. The diffusion energy profiles symmetrically repeat themselves in each unit-cell, indicating the validity of the simulation box size, potential parameters, and energy minimization calculation procedures. The calculations were performed following well established forced diffusion procedures.

The force field energy minimization calculations were done with the Discover program, using consistent valence force field (CVFF) by Hagler et al. [24], and the parameters were obtained from the reports of Dauber-Osguthorpe et al. [25].

For the calculation of the diffusion of BP, EBPs, and DEBPs in the MOR channels, the molecules were forced to diffuse in regular steps of 0.2 nm along the diffusion path within the channel. At each point, a strong harmonic potential was used to constrain the molecule to lie at a fixed distance from the initial position while the energetically favorable conformation and orientation of the molecule were derived by varying the internal degrees of freedom as well as non-bonding interaction of the molecule with the zeolite framework. The interaction energy at each point was calculated using the following equation:

$$\text{interaction energy} = E_{\text{zeolite:molecule complex}} - (E_{\text{zeolite}} + E_{\text{molecule}}) \quad (1)$$

Thus, the diffusion energy profile is a graph showing the variation of interaction energy between a single molecule and the zeolite framework as the molecule diffuses within the zeolite channels. The difference in energy between the most favorable and most unfavorable sites in the diffusion energy profile gives the diffusion energy barrier for self-diffusivity. During these calculations of the interaction energy, the atoms in the zeolite lattice were fixed at their crystallographically determined geometries, whereas the guest molecules were flexible. The influence of the presence of more molecules on the diffusivity (mutual effect) and the influence of temperature are not considered in this work. In view of these approximations, suitable care was taken to interpret the results.

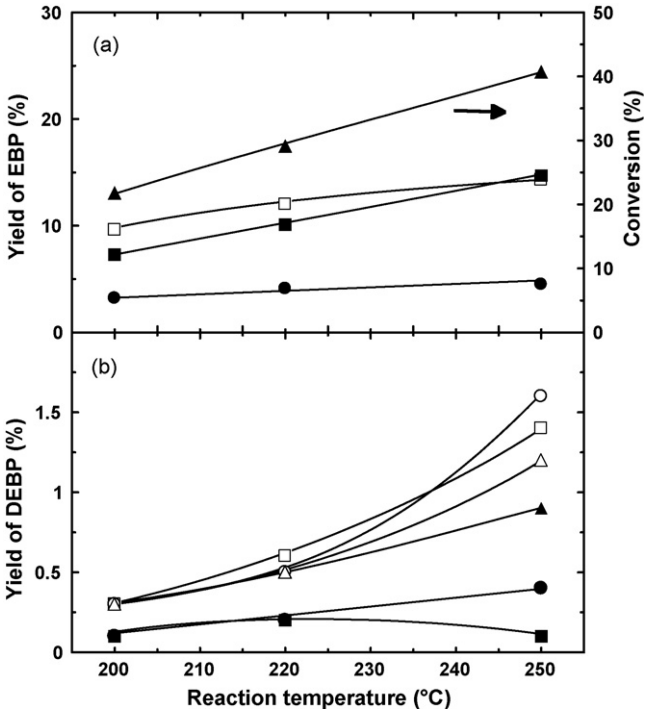


Fig. 1. The influence of reaction temperature on the yield of EBPs and DEBPs in the ethylation of BP. (a) Yield of EBPs. (b) Yield of DEBPs. Reaction conditions: BP, 3.08 g (200 mmol); MOR, 1 g; ethene pressure, 0.8 MPa; period, 0.5 h. Legends: EBPs: (▲) Conversion; (●) 4-; (■) 3-; (□) 2-. DEBPs: (■) 4,4′-; (□) 3,4′-; (●) 3,3′-; (◯) 3,4′-; (▲) 2,4′-; (△) 2,4-.

3. Results and discussion

3.1. Influence of reaction temperature on the ethylation of BP

Fig. 1 shows the influence of reaction temperature on the yield of EBPs and DEBPs in the ethylation of BP. The data were taken in early stages of the reaction. The yields of 2- and 3-EBPs increased with the increase in the temperature, but 4-EBP was obtained only in low yield at all temperatures (Fig. 1a). These results mean that the ethylation of BP is not shape-selective for the formation of the least bulky 4-EBP.

The formation of DEBPs from BP was varied with the temperature: the yields of 2,4-, 3,4-, 2,4′-, and 3,4′-DEBPs increased with the increase in the reaction temperature (Fig. 1b). However, 4,4′-DEBP behaved quite differently from the other isomers: the yield of 4,4′-DEBP was very low compared to the other isomers. It increased with conversion, and reached maximum at 40–60%. Further increase in the conversion accompanied the decrease in the yield. These results show that 4,4′-DEBP has higher reactivity for the further ethylation than the other isomers, and that 4,4′-DEBP is the principal precursor of higher ethylates. These features of the formation of EBPs and DEBPs in the ethylation of BP were quite different from those of the isopropylation [1–7]. Similar non-shape-selective ethylation was described in the literature over ZSM-12, silica–alumina and HY [15–17].

The results discussed above show that the selectivities of the products are caused by the difference of the reactivity of EBPs

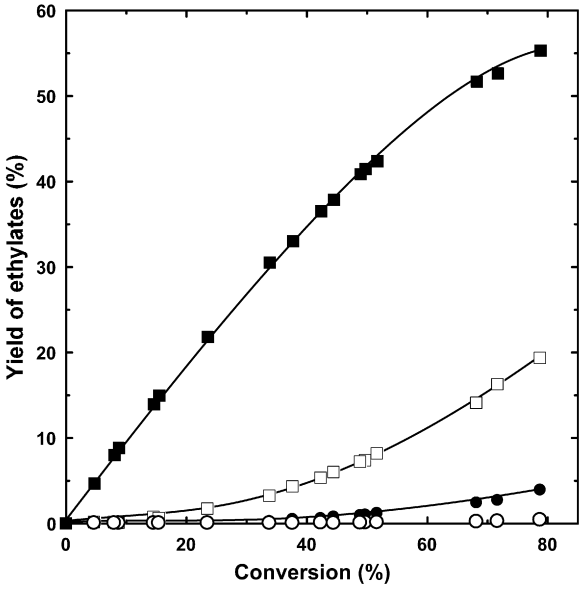


Fig. 2. The influence of the conversion on the yield of ethylates in the ethylation of BP. Reaction conditions: BP, 3.08 g (200 mmol); MOR, 1 g; ethene pressure, 0.8 MPa; temperature, 220 °C. Legends: (■) EBPs; (□) DEBPs; (●) TriEBPs; (◯) TetraEBPs.

and DEBPs in the ethylation of BP over MOR. We chose 220 °C as the reaction temperature for the further research.

3.2. The influence of the conversion on the ethylation of BP

The ethylation of BP over MOR was examined at 220 °C under 0.8 MPa of ethene in order to elucidate how the ethylation of BP proceeds. Fig. 2 shows influence of the conversion on the yield of ethylates in the ethylation of BP. EBPs were principal products in the initial stages, and DEBPs increased gradually with increasing the conversion. The small amounts of higher ethylates, triethylbiphenyls (TriEBPs) and tetraethylbiphenyls (TetraEBPs), were also observed at high conversion.

Fig. 3 shows the profile of the ethylation of BP against the conversion of BP. The selectivities for EBPs were nearly in the ratio: 4-EBP:3-EBP:2-EBP = 1:2:2 at an early stage of the reaction (Fig. 3a). These results mean that the reaction is non-shape-selective for the formation of the least bulky 4-EBP, and occurs under kinetic control because MOR channels are too loose for the selective formation of 4-EBP. The high selectivity for 2-EBP suggests that the nucleophilic attack of ethyl carbenium ion to 2-positions is predominated over other positions due to their high electron densities.

The three EBP isomers behave differently for the further ethylation at higher conversion of BP. The yield of 4-EBP reached maximum at 40–50% of the conversion, and decreased with the further conversion. The yield of 3-EBP increased at the early and middle stages; however, it was saturated at the late stage. On the other hand, the yield of 2-EBP increased monotonously during the reaction even at the high conversion. These results suggest that these three isomers have different reactivities for the further ethylation to DEBPs in the order: 4-EBP ≫ 3-EBP ≫ 2-EBP. These differences depend on their bulkiness: the least bulky 4-

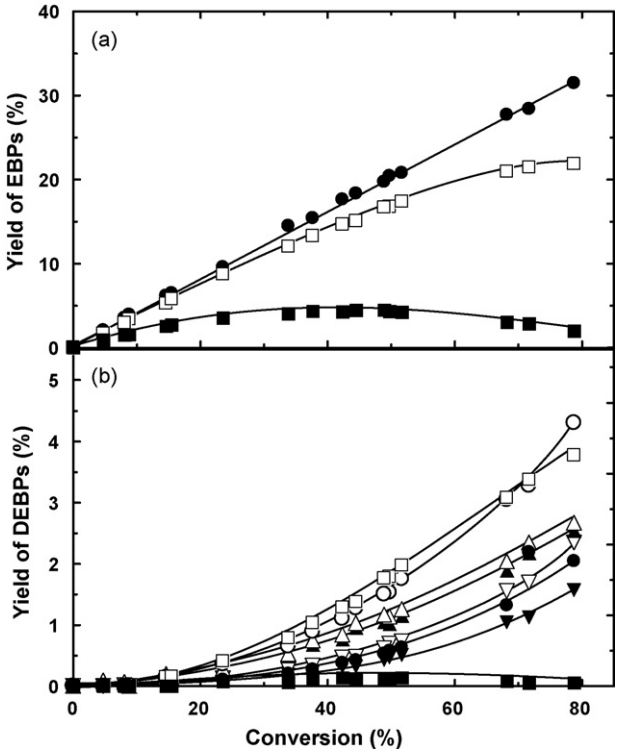


Fig. 3. The influence of the conversion on the yield of EBPs and DEBPs in the ethylation of BP. (a) Yield of EBPs. (b) Yield of DEBPs. *See* in Fig. 2. Legends: EBPs: (■) 4-; (□) 3-; (●) 2-. DEBPs: (■) 4,4′-; (□) 3,4′-; (◯) 3,4-; (△) 2,4-; (▲) 2,4′-; (●) 3,3′-; (▼) unidentified 1; (▽) unidentified 2.

EBP is consumed at the highest rate among three isomers. The ethylation of 3-EBP occurs, particularly, at the higher conversion although 3-EBP has is less reactive than 4-EBP. However, 2-EBP is not ethylated under the conditions.

The yields of DEBPs in the ethylation of BP against the conversion of BP are also shown in Fig. 3b. The ethylation of EBPs gave the mixtures of 2,4-, 3,4-, 3,4′-, 2,4′-, 3,3′-, and two unidentified DEBPs.[4] Their yields increased with increasing the conversion of BP. Among DEBP isomers, the yields of 3,4′- and 3,4-DEBPs were slightly higher than other DEBP isomers, and the almost same amount of 3,4′- and 3,4-DEBPs was formed during the reaction. Similar phenomena were observed for the formation of 2,4′- and 2,4-DEBPs. On the other hand, the yield of 4,4′-DEBP was much lower than the other isomers. The yield of 4,4′-DEBP increased in the initial stages, reached maximum at 40–60% of the conversion, and then, decreased at higher conversion. These results show that 4,4′-EBP has the highest reactivity among the DEBPs for the further ethylation, thus resulting in higher yields of higher ethylates, and that MOR channels cannot differentiate the attack to 2- and 2′-positions and 3- and 3′-positions for the formation of 2,4′- and 2,4-DEBPs from 4-EBP, and 3,4′- and 3,4-DEBPs from 3-EBP, respectively. The appearance of 3,3′-DEBP also shows that the participation of 3-EBP, and a part of 3,4′- and 3,4-DEBPs is also formed from 3-EBP.

[4] The structure of these isomers has not been identified yet. They may be two of 2,3-, 2,3′-, 2,5-, and 3,5-DEBPs.

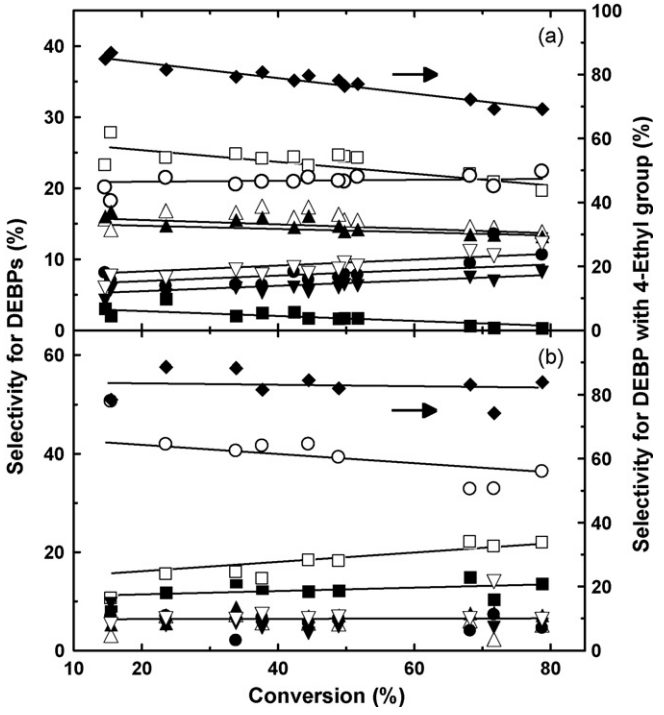


Fig. 4. The influence of the conversion on the selectivity for DEBPs of bulk and encapsulated products in the ethylation of BP. (a) Selectivity for DEBPs in bulk products. (b) Selectivity for DEBPs in encapsulated products. Reaction conditions: *see* Fig. 2. Legends: DEBPs: (■) 4,4'-; (□) 3,4'-; (◯) 3,4-; (△) 2,4-; (▲) 2,4'-; (●) 3,3'-; (▼) unidentified 1; (▽) unidentified 2; (⧫) DEBPs with 4-ethyl group.

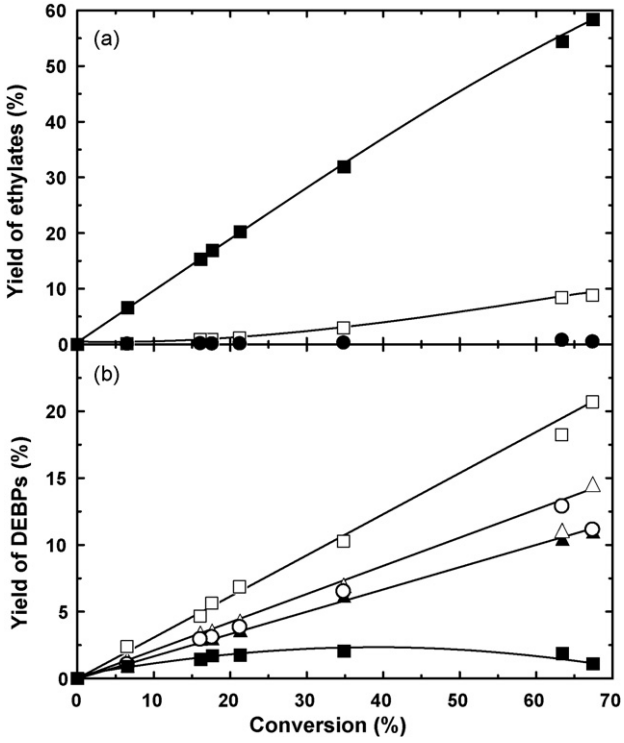


Fig. 5. The influence of conversion on the ethylation of 4-EBP. (a) Yield of ethylates. (b) Yield of DEBPs. Reaction conditions: 4-EBP, 1.54 g (100 mmol); MOR, 1 g; ethene pressure, 0.8 MPa; temperature, 220 °C. Legends: Ethylates: (■) DEBPs; (□) TriEBPs; (●) TetraEBPs. DEBPs: (▲) 2,4′-; (△) 2,4-; (□) 3,4′-; (◯) 3,4-; (■) 4,4′-.

Fig. 4 shows the selectivities for DEBP isomers of bulk and encapsulated products in the ethylation of BP. The selectivities were not so much influenced by the conversion; however, the relatively rapid decreases in the selectivities were observed for 3,4′- and 4,4′-DEBPs, which are the less bulkier DEBPs among the isomers (Fig. 4a). The selectivities for DEBPs in the encapsulated DEBPs were also not much changed during the reaction although the selectivity for the medium bulky 3,4′- and 3,4-DEBP was higher than the other isomers (Fig. 4b).

The combined selectivities of DEBPs with 4-ethyl groups, i.e., 2,4-, 3,4-, 3,4′-, 2,4′-, and 4,4′-DEBPs, maintained higher than 70–85% in bulk products and 80% for encapsulated products during the reaction (Fig. 4a and b). These results clearly show that DEBPs were yielded preferentially from 4-EBP although the selectivity for 4-EBP was the lowest among EBPs. Similarly, the decrease in the selectivity for 3,4′-DEBP was observed during the reaction: this means that 3-EBP also participates in the further ethylation.

The least bulky 4,4′-DEBP behaved quite differently from the other isomers. 4,4′-DEBP was consumed more rapidly than the other isomers, resulting in the formation of the higher ethylates (Figs. 3b, 4a and b). These features are quite similar to the behavior of 4-EBP. We examined the further research on the ethylation of EBPs and 4,4′-DEBP to clarify difference of the reactivity of the intermediates.

3.3. The ethylation of 3- and 4-EBPs

The ethylation of 4-EBP gave similar features to the ethylation of BP except no formation of 3,3′-DEBP as shown in Fig. 5. DEBPs with 4-ethyl groups were obtained with the formation of small amount of higher ethylates, TriEBPs and TetraEBPs (Fig. 5a). The yield of 2,4-, 3,4-, 3,4′-, and 2,4′-DEBPs increased with the conversion of 4-EBP (Fig. 5b). However, the yield of 4,4′-DEBP increased at lower conversion, and decreased with the increase in the conversion. These results show that 4,4′-DEBP was consumed rapidly than the other isomers. The features quite resemble the ethylation of BP to EBPs and DEBPs.

Fig. 6 shows the influence of the conversion in the ethylation of 3-EBP. DEBPs with 3-ethyl groups were obtained with small amount of the higher ethylates (Fig. 6a); however, the rate of the consumption of 3-EBP was slower than that of 4-EBP. The yields of 3,4′-, 3,3′-, and 3,4-DEBPs, and other unidentified three isomers[5] increased with increasing the conversion of 3-EBP (Fig. 6b). Particularly, 3,3′-DEBP increased monotonously against the conversion. However, the yield of 3,4′-DEBP was the lowest among the DEBPs, and saturated at higher conversion. These results mean that the least bulky 3,4′-DEBP among DEBPs with 3-ethyl group participate in the ethylation of 3-EBP

[5] The structure of these isomers has not been identified, yet. They may be three of 2,3-, 2,3′-, 2,5-, and 3,5-DEBPs. They were not observed in the ethylation of BP because of low reactivity of 3-EBP.

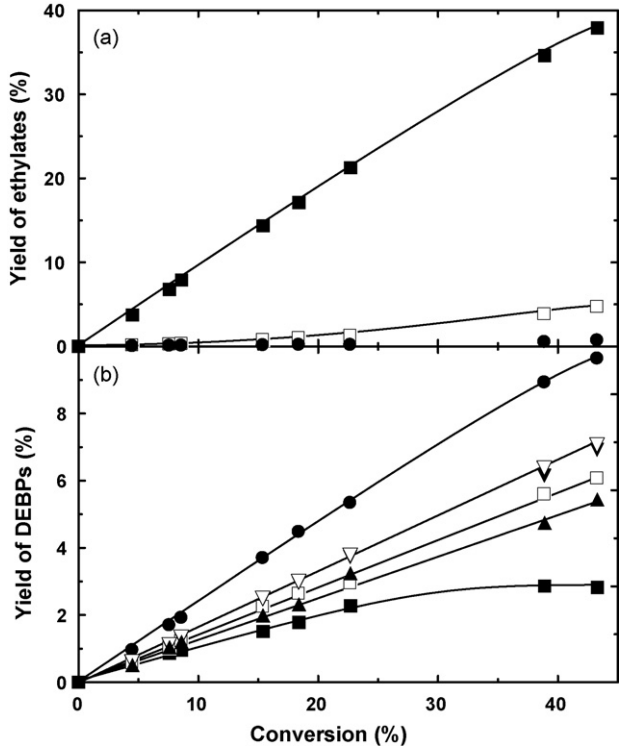


Fig. 6. The influence of the conversion on the ethylation of 3-EBP. (a) Yield of ethylates. (b) Yield of DEBPs. Reaction conditions: 3-EBP, 1.54 g (100 mmol); MOR, 1 g; ethene pressure, 0.8 MPa; temperature 220 °C. Legends: Ethylates: (■) DEBPs; (□) TriEBPs; (●) TetraEBPs. DEBPs: (■) 3,4′-; (□) 3,4-; (●) 3,3′-; (▼) unidentified 1; (▽) unidentified 2; (▲) unidentified 3.

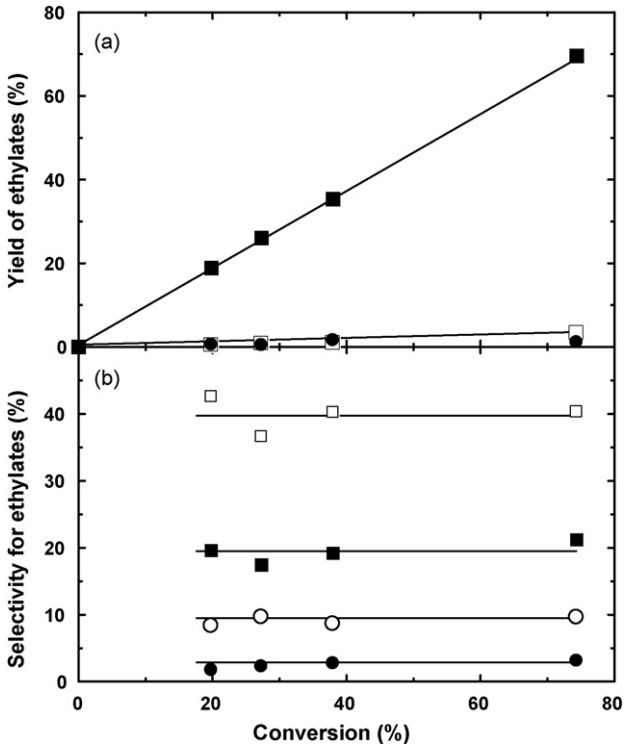


Fig. 7. The influence of the conversion on the ethylation of 4,4′-DEBP. (a) Yield of ethylates in bulk products. (b) Selectivity for DEBPs in the encapsulated products. Reaction conditions: 4,4′-DEBP, 3.30 g (100 mmol); MOR, 1 g; ethene pressure, 0.8 MPa; temperature, 220 °C. Legends: (■) TriEBPs; (□) TetraEBPs; (◯) PentaEBPs; (●) 3,4′-DEBP.

at higher conversion, and consumed preferentially among these isomers.

These results of the ethylation of 3- and 4-EBPs show that the ethylation of BP occurs principally through 4-EBP and 4,4′-DEBP although some of 3-EBP also participate in the further ethylation, particularly at higher conversion of BP.

3.4. The ethylation of 4,4′-DEBP

Fig. 7 shows the ethylation of 4,4′-DEBP. 4,4′-DEBP was ethylated rapidly, resulting in the formation of mixtures of higher ethylates (Fig. 7a). TriEBPs were predominantly formed in the bulk products accompanying small amounts of TetraEBPs and pentaethylbiphenyls (PentaEBPs). However, TetraEBPs and PentaEBPs were observed in considerably large amounts in addition to TriEBPs in the encapsulated products (Fig. 7b). The percentages of the composition of TetraEBPs and PentaEBPs in the encapsulated products were almost constant during the reaction. These results mean that 4,4′-DEBP was ethylated rapidly, and relatively less bulky TriEBPs were diffused out from the MOR channels; however, that the higher ethylates, particularly, TetraEBPs and PentaEBPs, cannot diffuse out easily from the MOR channels, resulting in their accumulation inside the channels. Their constant percentages of the composition suggests that 4,4′-DEBP consumed selectively for the formation of TriEBPs and its higher ethylates in the ethylation of BP over MOR.

3.5. Rates of the ethylation of BP, EBPs, and DEBPs

Fig. 8 shows the rates of the ethylation of BP, 3- and 4-EBPs, and 4,4′-DEBP. The rate of the ethylation of these intermediates was at the same level except that of 3-EBP. The ease of the reaction for BP, 4-EBP, and 4,4′-DEBP may be comparable regardless of the substitution with ethyl group. These results

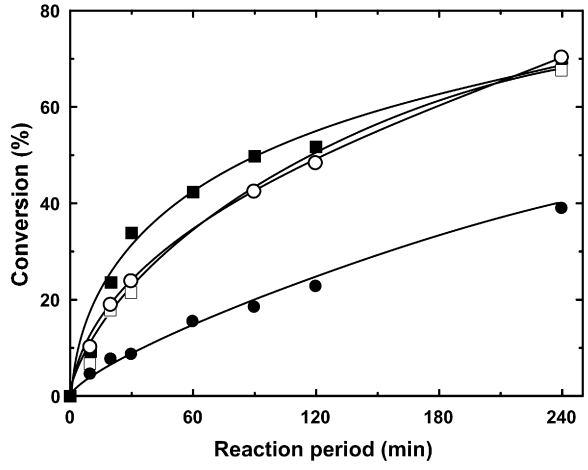


Fig. 8. Rate of the ethylation of BP, 3- and 4-EBPs, and 4,4′-DEBP. Reaction conditions: 100 mmol for 3- and 4-EBPs, and 4,4′-DEBP; 200 mmol for BP, catalyst: 1 g for 3- and 4-EBP and 4,4′-DEBP; 2 g for BP; ethene pressure, 0.8 MPa; temperature, 220 °C. Legends: (■) BP; (□) 4-EBP; (●) 3-EBP; (◯) 4-EBP.

show that the steric restriction of the transition state for the ethylation of BP and 4-EBP in the MOR channels is too loose for the shape-selective catalysis, and that the channels have space large enough for the further ethylation of 4,4′-DEBP.

3.6. Competitive ethylation of 3- and 4-EBPs

The competitive ethylation of 3- and 4-EBPs was examined to know the roles of these isomers in the ethylation of BP. Fig. 9 shows the ethylation of equimolar 3- and 4-EBPs against reaction period. 4-EBP disappeared rapidly; however, 3-EBP maintained almost constant during the reaction (Fig. 9a). The selectivity for DEBPs with 4-ethyl groups was higher than 90% in the bulk products during the reaction. These results show that 4-EBP was preferentially consumed from the mixture of 3- and 4-EBPs, and that the reactivity of 4-EBP was significantly higher than that of 3-EBP. 4-EBP was contained in higher amount than that of 3-EBP in the encapsulated products, and it decreased gradually during the reaction; however, the amount of 3-EBP was almost constant during the reaction. The selectivity for DEBPs with 4-ethyl groups in the encapsulated products also maintained higher than 80% during the reaction (Fig. 9b). These results showed that DEBPs were yielded principally from 4-EBP inside the channels. The considerably large amounts of higher ethylates, TriEBPs and TetraEBPs, were observed in the encapsulated products. These bulky higher ethylates are accumulated inside the MOR channels because of their slow diffusion.

Fig. 10 shows the ethylation of the mixtures of 3- and 4-EBPs with the different ratios: 20:80, 50:50, and 80:20. 4-EBP was consumed much rapidly compared to 3-EBP in all mixtures. DEBPs were predominant products in the bulk products, and the selectivity for 4,4′-DEBP was only in the range of 0.2–1.9%.

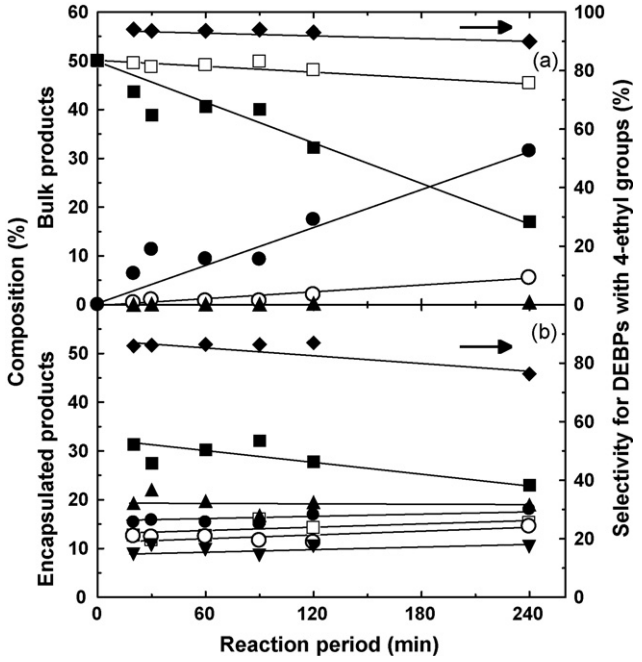
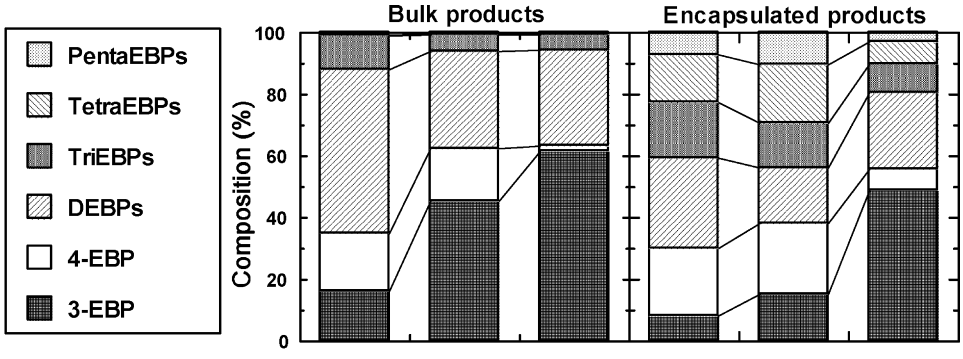


Fig. 9. Profiles of competitive ethylation of 3- and 4-EBPs. (a) Bulk products. (b) Encapsulated products. Reaction conditions: 3-EBP (50 mmol) and 4-EBP (50 mmol); MOR, 1 g; ethene pressure, 0.8 MPa; temperature, 220 °C. Legends: ((□) 4-EBP; (■) 3-EBP; (●) DEBPs; (◯) TriEBPs; (▲) TetraEBPs; (♦) DEBPs with 4-ethyl groups.

However, the selectivity for DEBPs with 4-ethyl group among DEBPs was higher than 90% from the mixture of 3- and 4-EBPs with the ratio of 20:80 and 50:50. The selectivity for 3,3′-DEBP, one of the products from 3-EBP, was less than 5%. However, 3,3′-DEBP, produced only from 3-EBP, appeared with the decrease in DEBPs with 4-ethyl group in the case of the mix-



	Bulk products			Encapsulated products		
	20:80	50:50	80:20	20:80	50:50	80:20
3-EBP Conv.(%)	18.9	9.2	23.0	--	--	--
4-EBP Conv.(%)	76.6	66.0	91.5	--	--	--
4,4'-DEBP Sel.(%)	1.5	1.9	0.2	1.1	2.3	0.8
DEBPs with 4-Et (%)	97.1	89.9	64.6	74.1	76.3	67.4
3,3'-DEBP Sel.(%)	1.7	4.6	15.6	3.3	10.7	15.0

Fig. 10. The influence of the ratio of 3- and 4-EBPs on their competitive ethylation. Reaction conditions: 3-/4-EBP (20/80, 50/50; 80/20) (total 100 mmol); MOR, 1 g; ethene pressure, 0.8 MPa; temperature, 220 °C.

ture in the ratio of 3- and 4-EBPs of 80:20. These results show that some of 3-EBP participated in the ethylation even though 4-EBP is much more reactive than 3-EBP. Similar behaviors were observed for 4,4′- and 3,3′-DEBPs in the encapsulated products. TriEBPs and TetraEBPs were also found in considerably high amounts in the encapsulated products: these higher ethylates were probably produced by the further ethylation of 4,4′-DEBP, and they are accumulated inside the channels because of their slow diffusion.

3.7. Competitive ethylation of BP, 4-EBP, and 4,4′-DEBP

Fig. 11 shows the competitive ethylation of BP, 4-EBP, and 4,4′-DEBP against the reaction period. 4-EBP was consumed faster than BP to yield DEBPs as one of principal products from a mixture of BP and 4-EBP (Fig. 11a). The selectivity for 4,4′-DEBP was around 10–20% at the initial stages; however, it decreased at the level of 3–5% at the late stages (not shown in figure). 4,4′-DEBP was consumed much faster than BP from the mixture of BP and 4,4′-DEBP, resulting in the formation of TriEBPs as principal products (Fig. 11b). 4,4′-DEBP was consumed much faster than 4-EBP from a mixture of 4-EBP and 4,4′-DEBP, and the higher ethylates were found even at the early stages of the reaction (Fig. 11c). In the competitive ethylation, the higher ethylates were accumulated inside the channels because of their slow diffusion.

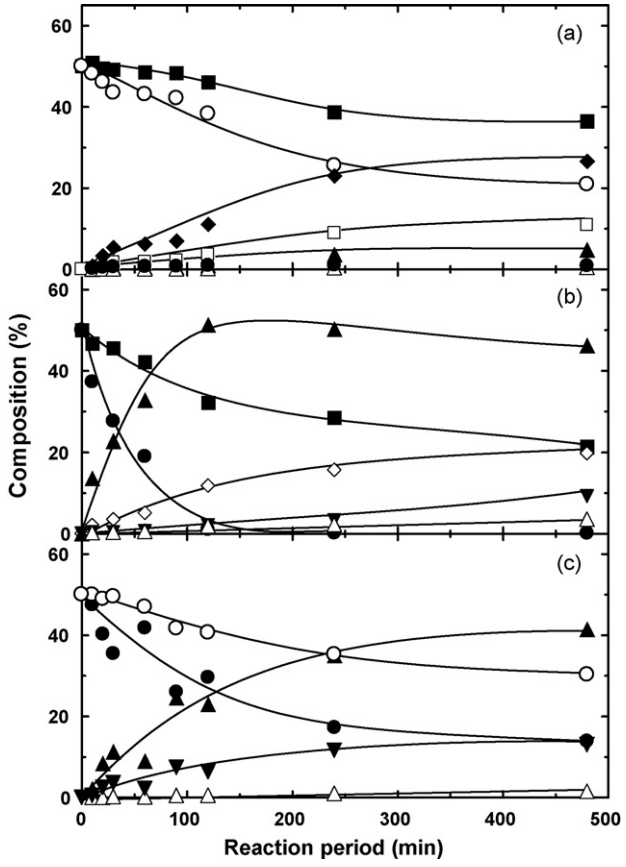


Fig. 11. Profiles of the competitive ethylation of BP, 4-EBP, and 4,4′-DEBP. (a) BP and 4-EBP. (b) BP and 4,4′-DEBP. (c) 4-EBP and 4,4′-DEBP. Reaction conditions: equal mole of mixture of BP/4-EBP, BP/4,4′-DEBP, and 4-EBP/4,4′-DEBP: 100 mmol (total); MOR, 1 g; ethene pressure, 0.8 MPa; temperature, 220 °C. Legends: (■) BP; (◯) 4-EBP; (●) 4,4′-DEBP; (□) 2- and 3-EBPs; (◊) EBPs; (♦) DEBPs; (▼) other-DEBPs; (▲) TriEBPs; (△) TetraEBPs.

Table 2
Kinetic dimensions and potential energies of BP, EBPs, and DEBPs

DEBP	Dimensions ($a \times b \times c$) (nm)	Potential energy (a.u.)
BP	0.52 × 0.52 × 1.08	−463.4228
2-EBP	0.54 × 0.70 × 1.02	−542.0695
3-EBP	0.58 × 0.72 × 1.02	−542.0743
4-EBP	0.52 × 0.52 × 1.20	−542.0743
2,4′-DEBP	0.51 × 0.71 × 1.02	−614.3379
2,4-DEBP	0.54 × 0.75 × 1.02	−615.0338
3,3′-DEBP	0.64 × 0.66 × 1.10	−615.0363
3,4′-DEBP	0.57 × 0.72 × 1.22	−615.0366
4,4′-DEBP	0.52 × 0.52 × 1.44	−615.0365

3.8. Molecular fitting and diffusion of BP, EBPs, and DEBPs in MOR channels

The shape-selectivity achieved by zeolites in catalytic conversion is governed by several factors, among which pore diameters of the zeolite as well as the size and the shape of the molecules. The diffusion of reactants, intermediate, and products also plays dominant roles. Molecular dimensions of BP, EBPs, and DEBPs are given in Table 2. Energetically favorable conformation shows that 4-EBP and 4,4′-DEBP are the least bulky among EBPs and DEBPs, respectively. The 3,4′- and 3,3′-DEBPs are bulkier than 4,4′-DEBP. Similarly, 2- and 3-EBPs are bulkier than 4-EBP. Their molecular diameters are less than pore-entrances of MOR (0.65 nm × 0.70 nm). These results indicate that all BP, EBPs, and DEBPs shown in Table 3 can diffuse through the MOR channels, and the diffusion of 4-EBP and 4,4′-DEBP is the easiest among their isomers.

In order to determine the influence of bulkiness of molecules in the MOR channels, BP; 2-, 3-, 4-EBPs; 2,4-, 2,4′-, 3,3′-, 3,4′-, and 4,4′-DEBPs were chosen as reactants and products in the ethylation. The dimension of zeolite, reactant, and products plays a crucial role in the ethylation of BP over the MOR channels. The zeolites with a pore diameter of 0.55–0.76 nm should be able to sieve BP, EBPs, and DEBPs, particularly, 3,4′-, 3,3′-, and 4,4′-DEBPs. The molecular graphics (MG) pictures of 3,4′-, 3,3′-, and 4,4′-DEBPs in the MOR channels are shown

Table 3
Diffusional energy barriers of DEBPs in MOR channels

Products	Diffusion energy barrier (kcal/mol)
BP	0.9
2-EBP	1.4
3-EBP	2.5
4-EBP	0.5
2,4′-DEBP	7.9
2,4-DEBP	13.0
3,3′-DEBP	3.7
3,4′-DEBP	3.8
4,4′-DEBP	2.1

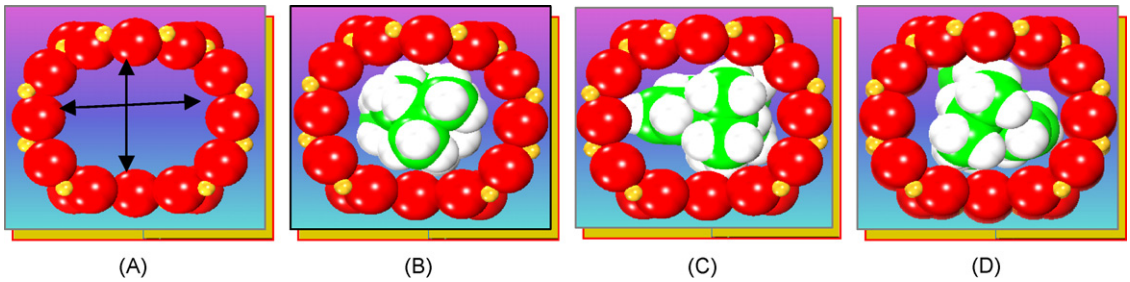


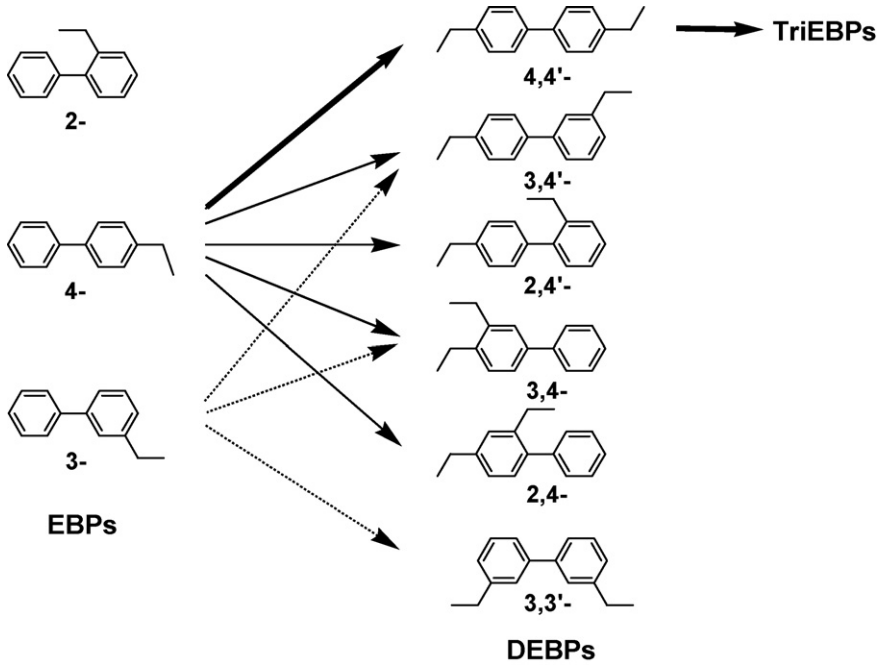
Fig. 12. The MG picture of the fitting of DEBPs (CPK model) in the MOR channels. (A) Pore geometry; (B) 4,4′-DEBP; (C) 3,4′-DEBP; (D) 3,3′-DEBP. White: hydrogen atom; green: carbon atom; red: oxygen atom; yellow: silicon atom. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

in Fig. 12. They indicate that these isomers can easily accommodate in the MOR channels. We conclude that MOR channels can allow the rapid diffusion of 3,3′-, 3,4′-, and 4,4′-DEBPs. The relative compression of MG in MOR, MTW and MFI channels are given in details elsewhere [20].

It is difficult to generalize experimentally the diffusion characteristics of EBPs inside the zeolite channels. However, it is relatively easy to calculate the diffusion energy profiles from the interaction energies and to know the relative rates of diffusion through the zeolite channels. The calculation of diffusion of BP, EBPs, 2-, 3-, and 4-EBP, and DEBPs, such as 2,4-, 2,4′-, 3,3′-, 3,4′-, and 4,4′-DEBPs, was carried out in the MOR channels. The molecules pass several maxima in the diffusion through a unit-cell. The diffusion energy barriers for BP, EBPs, and DEBPs are shown in Table 3. The MOR channels have not significant diffusion barriers for BP, EBPs and DEBPs except the DEBPs with 2-ethyl groups. 4-EBP has much lower barrier than 2- and 3-EBPs although 2-EBP diffuses slightly faster than 3-EBP in the simulation. 4,4′-DEBP diffuse much more rapidly than 3,3′-, 3,4′-, and other bulky isomers. The diffusion barriers of all EBPs in MOR channels are also much lower than those of DEBPs. These modeling results suggest that the MOR channels are still too large for the selective formation of 4,4-DEBP in the ethylation of BP, because BP, 4-EBP, and 4,4′-DEBP can diffuse easily in the MOR channels compared with the other isomers. These results correspond to the difference of reactivities between these BP derivatives. The simulation gave slightly higher barrier of 3-EBP compared to that of 2-EBP although the differences are small. These simulation results correspond to the low reactivities of 2- and 3-EBPs compared to that of 4-EBP; however, it is difficult to understand lower reactivity of 2-EBP compared to that of 3-EBP.

3.9. Reactivities of intermediates in the ethylation of BP in MOR channels

The results of the ethylation of BP and its intermediates for higher ethylates discussed above show that the reactivities decrease in the order: 4,4′-EBP > 4-EBP > BP ≫ 3-EBP ≫ 2-EBP. These results mean that the ethylation of BP to EBPs occurs under kinetic control. The MOR channels are too large to form the least bulky 4-EBP and 4,4′-DEBP by the “restricted



Scheme 1. The pathway of the ethylation of EBPs and DEBPs. Unidentified products are not shown.

transition state selectivity mechanism". However, these three EBP isomers have quite different reactivities in the ethylation: 4-EBP was preferentially consumed to yield DEBPs with 4-ethyl groups. 3-EBP partly participated in the ethylation to DEBPs, particularly, at high conversion; however, 2-EBP was not ethylated even at the high conversion. Further, 4,4′-DEBP disappeared preferentially among their isomers, resulting in the formation higher ethylates because it is the most reactive among the products from BP. These results indicate that 4-EBP and 4,4′-DEBP are principal intermediates of higher ethylates in the ethylation of BP as shown in Scheme 1. 3-EBP, second smallest isomer, also participates possibly in the formation of 3,3′-, 3,4′- and 2,3′-DEBP, particularly in the latter stages. These results indicate that these catalyses are governed by the "reactant selectivity mechanism".

Molecular modeling on the diffusion of products suggests that all EBPs and DEBPs in Table 2 can diffuse in the MOR channels, although BP, 4-EBP, and 4,4′-DEBP can diffuse most rapidly among DEBPs: the formation of 4,4′-DEBP is the most favorable from the aspects of the diffusion. The simulation results correspond well to the experimental results. They indicate that the MOR channels are too large for the selective formation of 4-EBP and 4,4′-DEBP. The rapid disappearance of 4-EBP and 4,4′-DEBP may be due to the difference of the diffusion in the channels among their isomers.

4. Conclusion

The ethylation of BP and its reaction intermediates was examined with ethene over MOR. The ethylation occurred non-shape-selectively, affording the mixture of EBPs, DEBPs, and TriEBPs. These results mean that the ethylation of BP to EBPs occurs under kinetic control. The least bulky 4-EBP and 4,4′-DEBP was much less selective than the other isomers in both bulk and encapsulated products. The steric restriction of the transition state in the ethylation of BP and 4-EBP inside the MOR channels is too loose for the shape-selective catalysis, and that the channels have the reaction space large enough for the further ethylation of 4,4′-DEBP.

The reactivities of reaction intermediates, ethylbiphenyls, decreased in the ethylation of BP in the order: 4,4′-EBP > 4-EBP > BP ≫ 3-EBP ≫ 2-EBP. The three EBP isomers have quite different reactivities for their ethylation: 4-EBP was preferentially consumed to yield DEBPs with 4-ethyl groups. 3-EBP partly participated in the ethylation to DEBPs, particularly, at high conversion; however, 2-EBP was not ethylated even at the high conversion. The least bulky 4-EBP and 4,4′-DEBP are principal intermediates of higher ethylates in the ethylation of BP because they are highly reactive than the other DEBPs.

Molecular modeling of the diffusion of the products suggests that the MOR channels are too large for the selective formation of 4,4′-DEBP because all DEBPs can diffuse in the channels. The preferential disappearance of 4-EBP and 4,4′-DEBP may be due to the difference of the diffusion in the channels among their isomers. These simulations correspond well to the experimental results.

The results obtained in this study indicate that the MOR channels are too large for the shape-selective ethylation of BP to EBPs by "restricted transition state selectivity mechanism", and that they are small enough for the differentiation of 4-EBP and 4,4′-DEBP from the other bulky isomers inside the MOR channels in the ethylation of EBPs to DEBPs by "reactant selectivity mechanism".

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References

[1] Y. Sugi, Y. Kubota, Catalysis, vol. 13, Specialist Periodical Reports, Royal Soc. Chem., 1997, pp. 55–84 (Chapter 3).
[2] Y. Sugi, Y. Kubota, T. Hanaoka, T. Matsuzaki, Catal. Surv. Jpn. 5 (2001) 43.
[3] Y. Sugi, K. Komura, J.-H. Kim, J. Korean Ind. Eng. Chem. 17 (2006) 235.
[4] T. Matsuzaki, Y. Sugi, T. Hanaoka, K. Takeuchi, T. Tokoro, G. Takeuchi, Chem. Express 4 (1989) 413.
[5] X. Tu, M. Matsumoto, T. Matsuzaki, T. Hanaoka, Y. Kubota, J.-H. Kim, Y. Sugi, Catal. Lett. 21 (1993) 71.
[6] Y. Sugi, T. Matsuzaki, T. Hanaoka, Y. Kubota, J.-H. Kim, X. Tu, M. Matsumoto, Catal. Lett. 26 (1994) 181.
[7] Y. Sugi, S. Tawada, T. Sugimura, Y. Kubota, T. Hanaoka, T. Matsuzaki, K. Nakajima, K. Kunimori, Appl. Catal. A: Gen. 189 (1999) 251.
[8] G.S. Lee, J.J. Maj, S.C. Rocke, J.M. Garces, Catal. Lett. 2 (1989) 243.
[9] T. Matsuda, E. Kikuchi, Appl. Catal. A: Gen. 123 (1995) 205.
[10] Katayama, M. Toba, G. Takeuchi, F. Mizukami, S. Niwa, S. Mitamura, J. Chem. Soc., Chem. Commun. (1991) 31.
[11] C. Song, A.D. Schmitz, Sekiyu Gakkaishi 42 (1999) 275 (and their previous papers).
[12] J.-H. Kim, Y. Sugi, T. Matsuzaki, T. Hanaoka, Y. Kubota, M. Matsumoto, X. Tu, Micropor. Mater. 5 (1995) 113.
[13] X. Tu, M. Matsumoto, T. Maeda, Y. Sugi, T. Matsuzaki, T. Hanaoka, Y. Kubota, Micropor. Mater. 3 (1995) 593.
[14] G. Takeuchi, H. Okazaki, K. Hiroshi, T. Kito, Y. Sugi, T. Matsuzaki, Sekiyu Gakkaishi 34 (1991) 242.
[15] G. Takeuchi, Y. Shimoura, T. Hara, Appl. Catal. A: Gen. 137 (1996) 87.
[16] G. Takeuchi, Y. Shimoura, T. Hara, Catal. Lett. 41 (1996) 195.
[17] G. Takeuchi, Y. Shimoura, Catal. Surv. Jpn. 2 (1998) 77.
[18] M. Matsumoto, X. Tu, T. Matsuzaki, T. Hanaoka, Y. Kubota, Y. Sugi, J.-H. Kim, K. Nakajima, K. Kunimori, Stud. Surf. Sci. Catal. 105 (1997) 1317.
[19] K. Nakajima, T. Hanaoka, Y. Sugi, T. Matsuzaki, Y. Kubota, A. Igarashi, K. Kunimori, ACS Symp. Ser. 738 (1999) 271.
[20] S.A.R. Mulla, S.B. Waghmode, S. Watanabe, H. Maekawa, K. Komura, Y. Kubota, Y. Sugi, J.-H. Kim, G. Seo, Bull. Chem. Soc. Jpn. 80 (2007) 215.
[21] K. Tamao, K. Sumitani, M. Kumada, J. Am. Chem. Soc. 94 (1972) 4374.
[22] S.B. Waghmode, P. Bharathi, S. Sivasanker, R. Vetrivel, Micropor. Mesopor. Mater. 38 (2000) 433.
[23] A. Alberti, P. Davoli, G. Vezzalini, Z. Kristallogr. 175 (1986) 249.
[24] A.T. Hagler, S. Lifson, P. Dauber, J. Am. Chem. Soc. 101 (1979) 5122.
[25] P. Dauber-Osguthorpe, V.A. Roberts, D.J. Osguthorpe, J. Wolff, M. Genest, A.T. Hagler, Proteins: Struct. Func. Genet. 4 (1988) 31.