1160 *Bull. Chem. Soc. Jpn.*, ***78***, *1160–1166 (2005)*

The Transethylation of Biphenyl with Diethylbenzenes over H-Y Zeolite

Qiu Jun, Kenichi Komura, Yoshihiro Kubota,[†] and Yoshihiro Sugi*

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

Received November 9, 2004; E-mail: sugi@apchem.gifu-u.ac.jp

The liquid-phase transethylation of biphenyl (BP) with diethylbenzenes (DEBZ; *o*-:*m*-:*p*- = 5:66:29) was investigated by the use of zeolites, Y (FAU), Beta (BEA), mordenite (MOR), and ZSM-12 (MTW). Because H-Y (H-FAU(11) with $SiO_2/Al_2O_3 = 11$) was the most active among them, and we chose H-FAU(11) as a standard catalyst, and studied reaction parameters. Both the catalytic activity and the selectivity for 4,4′-diethylbiphenyl (4,4′-DEBP) were influenced by the reaction conditions. The selective formation of 4,4′-DEBP was observed at low temperatures; however, the selectivity for 4,4′-DEBP decreased with the temperature. The selectivity for 4,4′-DEBP in bulk products were lower than the case of encapsulated products. These results show that the catalysis occurred principally inside pores: 4,4′-DEBP was formed by the transethylation of BP and DEBZ inside the pores of H-Y zeolite. The resultant 4,4′-DEBP was easily isomerized to thermodynamically stable isomers, 3,4′- and 3,3′-DEBPs even at lower temperatures because the most acid sites of H-Y zeolite are inside large pores, and they are strong enough for the isomerization of 4,4′-DEBP. The shape-selective formation of 4,4′-DEBP at lower temperatures is due to the rapid diffusion of the least bulky isomer from the H-Y pores. DEBPs were polyethylated to polyethylbiphenyls (PEBPs), and deethylated to ethylbiphenyls (EBPs) by transethylation with DEBZ inside the pores.

Polynuclear aromatics, such as naphthalene and biphenyl, are valuable components in coal tar or in liquefied coal for chemical use. It is important to develop the utilization of these aromatics for advanced materials, such as liquid crystals, heat-resistant and liquid-crystalline polymers. We have described that the selective formation of 4,4′-diisopropylbiphenyl (4,4′-DIPB) in the isopropylation of biphenyl (BP) with propene over H-mordenite (H-MOR);[1,2] however, the formation of 4,4′-diethylbiphenyl (4,4′-DEBP) was not observed in the ethylation of BP with ethene over H-MOR.[3–6] Recently, Takeuchi and his co-workers found the selective formation of 4,4′-DEBP by the transethylation of BP with polyethylbenzenes over zeolite catalysts.[7,8] They described that the selective formation of 4,4′-DEBP is due to the catalysis under kinetic control conditions. Shape-selective trans-alkylation using zeolites are important industrial processes, such as in the manufacturing of *p*-xylene, *p*-cymene, and *p*-*t*-butyltoluene.[9–11]

We have been interested why 4,4′-DEBP is formed selectively in the transethylation with polyethylbenzenes over zeolites, because the mechanism for the selective formation of 4,4′-DEBP is still unclear. To understand what happens in zeolite pores, it is important to compare the products in bulk and encapsulated products, because the encapsulated products are the fingerprints of the catalysis. In the present work, we examined the transethylation of BP with diethylbenzene (DEBZ) over zeolites, and compared the distribution of bulk and encapsulated products.

Experimental

Materials. H-Y zeolite (H-FAU(11); HSZ-350HUA; $SiO_2/Al_2O_3 = 11$) and H-mordenite (H-MOR(20); Tosoh TSZ-640HOA; $SiO_2/Al_2O_3 = 20$) were supplied from Tosoh Corporation, Tokyo, Japan. Dealuminated Y zeolite (H-FAU(30), Zeolyst CBV720; $SiO_2/Al_2O_3 = 30$) and H-Beta (H-BEA(25); Zeolyst CP814B-25; $SiO_2/Al_2O_3 = 25$) were gifted from Zeolyst International, Conshohochen, PA, USA as H^+ or NH_4^+ forms. ZSM-12 (H-MTW, $SiO_2/Al_2O_3 = 100$) was synthesized according to previous papers.[12] All samples were calcined at 500 °C for 8 h in a flow of dry air before use. BP was obtained from Tokyo Kasei Kogyo Co., Ltd, and used without further purification. DEBZ (*o*-:*m*-:*p*- = 5:66:29; average ethyl number in benzene ring = 2.014) was gifted from Nippon Steel Chem. Co., Ltd.

Catalysis. The reaction was carried out in a 100 mL SUS-316 autoclave. The typical procedures were as follows: H-FAU(11) (0.5 g), BP (1.54 g; 10 mmol) and DEBZ (13.347 g, 99.5 mmol) were placed in an autoclave, and flushed twice with nitrogen. The autoclave was then heated at the requisite temperature for 6 h with magnetic stirring. After stopping the reaction, the autoclave was cooled to room temperature. The catalyst was separated from liquid products by filtration, and washed well with 100 mL of toluene. An aliquot (1.5 mL) of the products was analyzed by Shimadzu-14A gas chromatograph equipped with an Ultra-1 capillary column (12 m × 0.3 mm). The products were identified by GC-MS (Shimadzu GCMS-5000 with HP capillary column (12 m × 0.3 mm). The DEBPs were also identified according to previous papers.[4,5]

The conversion of BP was calculated on the basis of BP consumed for the reaction, and the selectivity for each isomer of ethylbiphenyls (EBPs) and diethylbiphenyls (DEBPs) expressed as the percentages of each EBP and DEBP isomers among total EBP and DEBP isomers for the transethylation of BP:

$$\text{Selectivity for a DEBP (EBP) isomer (\%)} = \frac{\text{Each DEBP (EBP) isomer (mol)}}{\text{DEBP (EBP) isomers (mol)}} \times 100, \qquad (1)$$

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

Published on the web June 6, 2005; DOI 10.1246/bcsj.78.1160

Table 1. Estimation of Equilibrium Mixture of DEBP Isomers

Period /h	DEBP composition/%				
	3,3′-	3,4′-	4,4′-	3,5-	others
10	35	37	14	0.2	14
20	38	38	13	1.6	8.9
30	38	39	12	1.6	8.6
40	39	38	11	1.5	9.4
50	39	38	11	3.1	10

Reaction conditions: 4,4′-DEBP, 10 mmol; H-FAU(11), 0.5 g; reaction temperature, 200 °C.

An analysis of encapsulated products was carried out as follows: after the catalyst was dried at 105 °C for 12 h, a 250 mg sample of the catalyst was carefully dissolved in 0.75 mL of aqueous hydrofluoric acid at room temperature. The resulting solution was neutralized with solid K_2CO_3, and then extracted three times with chloroform (20 mL). The combined organic layer was dried with anhydrous Na_2SO_4, and the solvent was removed in vacuo. The residue was dissolved in 1.5 mL of toluene and analyzed by GC, as described above.

The isomerization of 4,4′-DEBP over H-FAU(11) was also carried out in the presence of DEBZ, and a work-up was done by the same procedures as those for transethylation.

Estimation of Equilibrium Mixtures of DEBP Isomers. 4,4′-DEBP was contacted with H-FAU at 200 °C for a long period until no change of the composition of DEBP occurred. Typical results are given in Table 1.

Results and Discussion

Types of Zeolites. Figure 1 summarizes the influences of the type of zeolites on the transethylation of BP with DEBZ. The activity of the transethylation was changed by the types of zeolites and by the SiO_2/Al_2O_3 ratio. H-Y zeolite (H-FAU(11)) had only high activity for the reactions. However, H-Y zeolite with low Al_2O_3 content (H-FAU(30)) and H-BEA(25) had only low activities, and H-MOR(20) and H-MTW(100) had no activities under our conditions. These results show that the pore structure and acid amount of the zeolites influenced the activity of the transethylation. The H-Y zeolite with a high acid amount and with a pore structure to allow the transition states of BP and DEBZ is essential for the transethylation. The low activity of H-BEA(25), which contains the highest amount of Al_2O_3 obtained by conventional synthesis, is due to the lower acidity and the narrow space at the crossing of the three-dimensional pore system to allow the transition state of the transethylation. From these results, we chose H-FAU(11) for the standard catalyst to elucidate the key factor in the catalysis.

Takeuchi and his co-workers found higher selectivity for 4,4′-DEBP than ours under the corresponding reaction conditions.[7] One of the reasons for the lower selectivity is the difference between the alkylating agent of polyethylbenzene for their case and the diethylbenzenes for our case.

Influence of Reaction Temperature. Figure 2a summarizes the influences of reaction temperature on the selectivity for ethylated products. The formation of EBPs was predominant at lower temperatures; however, the EBPs were converted to DEBP with an increase of temperature, and then, DEBPs were further ethylated to PEBPs at higher temperatures.

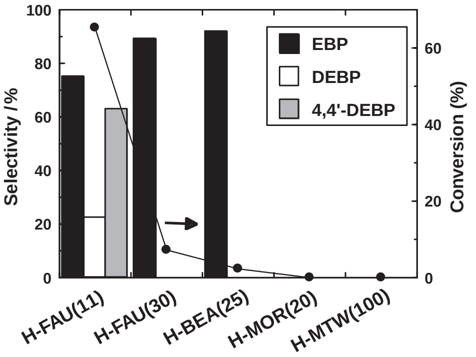


Fig. 1. Effects of type of zeolites on the transethylation of BP. Reaction conditions: BP, 10 mmol; DEBZ, 100 mmol; catalyst, 0.5 g; reaction temperature, 160 °C; period, 6 h. Legends: EBPs (■); DEBPs (□); Selectivity for 4,4′-DEBP (▨); Conversion (●).

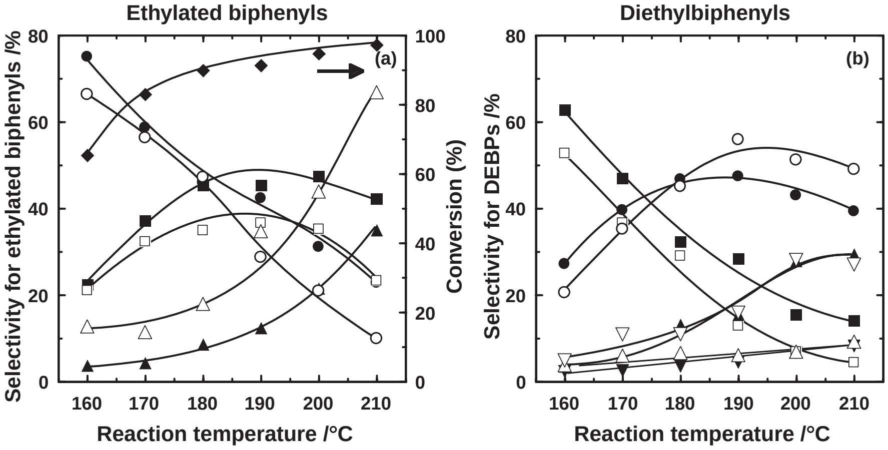


Fig. 2. Effects of reaction temperature on the transethylation of BP. Reaction conditions: BP, 10 mmol; DEBZ, 100 mmol; H-FAU(11), 0.5 g; period, 6 h. Legends: (a) bulk products: EBP (●); DEBP (■); PEBP (▲); Conversion (◆). Encapsulated products: EBP (○); DEBP (□); PEBP (△); (b) bulk products: 4,4′- (■); 3,4′- (●); 3,3′- (▲); 3,5- (▼); encapsulated products: 4,4′- (□); 3,4′- (○); 3,3′- (△); 3,5- (▽).

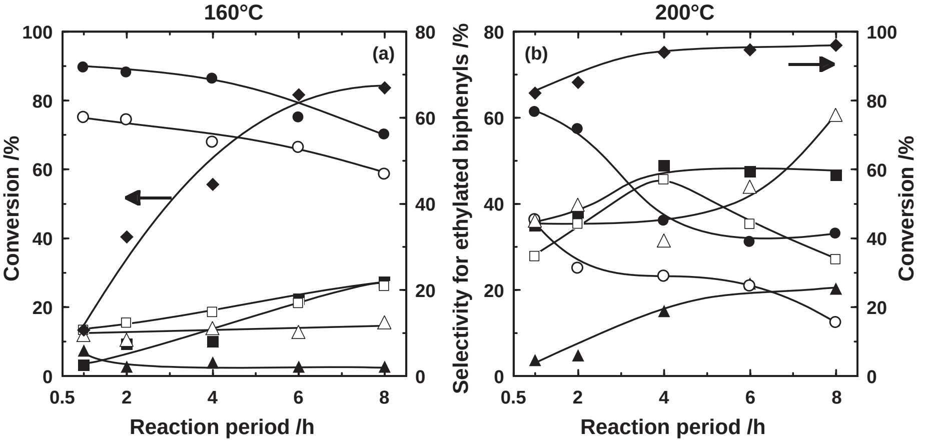


Fig. 3. Effects of reaction time on the transethylation of BP. Reaction conditions: BP, 10 mmol; DEBZ, 100 mmol; H-FAU(11) 0.5 g; temperature, 160 and 200 °C. Legends: bulk products: EBP (●); DEBP (■); PEBP (▲); Conversion (◆). Encapsulated products: EBP (○); DEBP (□); PEBP (△).

The formation of polyethylbiphenyls (PEBPs) in encapsulated products was extensive as compared to the bulk products. PEBPs increased with the temperatures. The accumulation of PEBPs inside the pores was due to low diffusion because of their steric bulkiness. These results show the polyethylation occurred much more significantly in the encapsulated products, and that the catalytic active sites are inside the pores.

Figure 2b shows the influences of the reaction temperature on the distribution of DEBPs in bulk and encapsulated products. The selectivity for 4,4′-DEBP was as high as 63% at 160 °C for the bulk products, although the conversion of BP was low (65%). These results show that 4,4′-DEBP was the initial product by the transethylation, and that the decrease of the selectivity for 4,4′-DEBP was due to the subsequent isomerization, as proposed by Takeuchi and his co-workers.[7] The increase of the temperature enhanced the catalytic activity, but the selectivity for 4,4′-DEBP was decreased with an increase of 3,3′-DEBP. The selectivity for 4,4′-DEBP was as low as 11% at 210 °C. The selectivity for 3,4′-DEBP gradually increased with the increase of temperature and reached the maximum (46%) at 180 °C. However, then, the selectivity for 3,4′-DEBP decreased with an increase of 3,3′-DEBP at higher temperatures. The changes reflect the equilibrium of DEBPs,[7,8] as shown in Table 1. The 4,4′-DEBP was isomerized to 3,4′-DEBP, and then 3,4′-DEBP to 3,3′-DEBP with an increase of the temperature. Other minor isomers, 2,4′- and 2,4-DEBPs, were obtained in trace amounts at all reaction temperatures (∼2%). The less formation of these isomers is due to the steric hindrance at the 2-positions of BP in the transethylation with DEBZ. Similar changes of the selectivity for 4- and 3-EBPs were observed upon an increase of the reaction temperatures. The highest selectivity for 4,4′-DEBP in this study was lower than the case of Takeuchi and his co-workers:[8] their highest values were around 90%; however, it is difficult to understand the differences because alkylating agents, zeolites, and reaction conditions are different from them. For these reasons, we only discuss the trend of the results in this paper.

The selectivity for 4,4′-DEBP in encapsulated products was also decreased with an increase of the reaction temperature accompanying an increase of thermodynamically stable isomers, 3,4′- and 3,3′-DEBPs, and was lower than the case of bulk products at all temperatures from 160 to 210 °C. These results show that the isomerization of 4,4′-DEBP occurred principally inside the pores, even at 160 °C, although 4,4′-DEBP was formed selectively from BP and DEBZ.

Influence of Reaction Period. Similar features of products by changing the period were observed to the change of products by temperature, as shown in Fig. 3. The conversion of BP was increased with the reaction period, and reached to 95% within 8 h. The selectivity for EBPs gradually decreased with an increase of DEBPs and PEBPs. Similar changes of EBPs, DEBPs, and PEBPs were found in encapsulated products; however, the selectivity for EBPs in encapsulated products was lower than the case of bulk products. On the contrary, the selectivity for DEBPs and PEBPs in encapsulated products was higher than in the case of bulk products. Similar changes of the products were observed in bulk and encapsulated products at 200 °C: the formation of EBPs occurred in bulk products at the initial stages, and EBPs decreased with the period; however, the selectivity for DEBPs and PEBPs was increased with the decrease of EBPs. The decrease of EBPs was also observed in encapsulated products with an increase of DEBPs and PEBPs. At the later stages, DEBPs were also decreased with a substantial increase of PEBPs. These results show that the catalytic active sites are principally inside the pores, because the selectivity for PEBPs in encapsulated products was higher than the bulk products.

Figure 4 shows the influences of the reaction period on the selectivity for DEBPs in the transethylation of BP at 160 and 200 °C. The selective formation of 4,4′-DEBP was observed at an early stage of reaction within 1 h at 160 °C. The selectivity for 3,4′-DEBP increased with the reaction time, and the selectivity for 4,4′-DEBP gradually decreased. However, the selectivity for 4,4′-DEBP was as high as 40% in the initial stages at 200 °C, and decreased rapidly with the period. On the contrary, the selectivities for 3,3′- and 3,4′-DEBPs increased with a prolonged reaction period. It is considered that the isomerization of 4,4′-DEBP proceeds rapidly compared with the transethylation to yield 4,4′-DEBP from a steric constraint to form the transition state inside pores. These results indicate

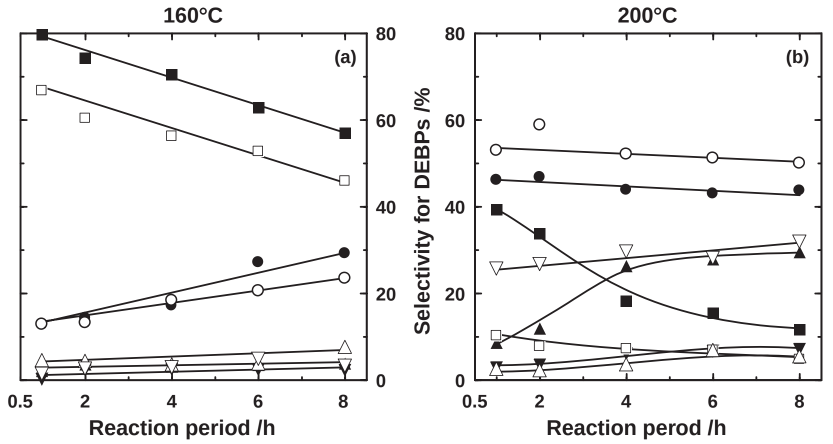


Fig. 4. Effects of reaction time on the selectivity for DEBPs in the transethylation of BP. Reaction conditions: see in Fig. 3. Legends: bulk products: 4,4′- (■); 3,4′- (●); 3,3′- (▲); 3,5- (▼). Encapsulated products: 4,4′- (□); 3,4′- (○); 3,3′- (△); 3,5- (▽).

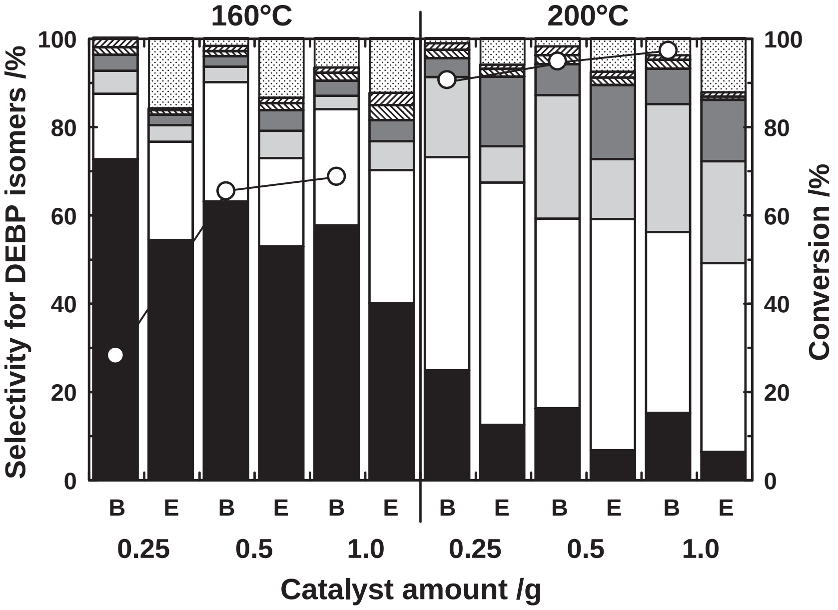


Fig. 5. Effects of catalyst amounts on the transethylation of BP. Reaction conditions: BP, 10 mmol; DEBZ, 100 mmol; period, 6 h. B: Bulk products; E: Encapsulated products. Legends: 4,4′- (■); 3,4′- (□); 3,3′- (░); 3,5- (▓); 2,4- (▧); 2,4′- (▨); others (▒); Conversion (○).

that 4,4′-DEBP was easily isomerized to thermodynamically stable 3,4′-DEBP within a short period at high temperatures; however, the isomerization of 4,4′-DEBP was slow at low temperatures. Similar results were obtained by Takeuchi and his co-workers.[7]

The selectivity for 4,4′-DEBP in both bulk and encapsulated products was decreased with an increase of the reaction period. The decrease of the selectivity for 4,4′-DEBP accompanied the increase of thermodynamically stable isomers, 3,4′- and 3,3′-DEBPs. The selectivity for 4,4′-DEBP in encapsulated products was lower than that in bulk products during the reaction at both 160 and 200 °C. These results show that the isomerization of 4,4′-DEBP occurred principally inside the pores, even at 160 °C after the formation of 4,4′-DEBP from BP and DEBZ. The reaction should be carried out at lower temperatures and for a short reaction period to achieve high selectivity for 4,4′-DIPB.

Influence of the Amount of Catalyst and the Ratio of DEBZ and BP. It is important to know the effects of the contact of catalysts with the reactant and the product in the transethylation of BP. We examined the effects of the catalyst amount and the ratio of DEBZ and BP on the distribution of DEBPs in the transethylation of BP at 160 and 200 °C. Figure 5 shows the effects of the catalyst amounts. The conversion and the distribution of DEBPs were increased with the amount of catalyst at both temperatures. A high selectivity for 4,4′-DEBP was achieved in the level of 60–65% at 160 °C; a small amount of catalyst enhanced the formation of 4,4′-DEBP with high selectivity. However, such a high selectivity for 4,4′-DEBP was not achieved even with a small amount of catalyst at a high temperature of 200 °C.

Figure 5 also shows a comparison of the distribution of

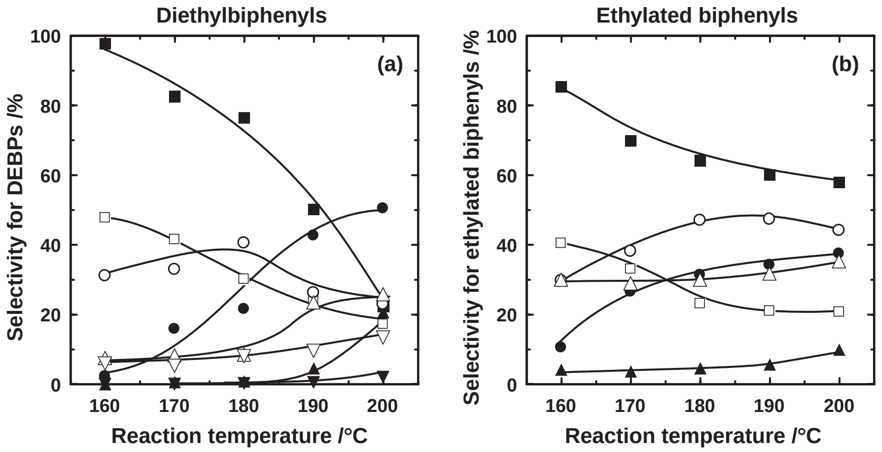


Fig. 6. Effects of reaction temperature on the composition of DEBPs in the isomerization of 4,4′-DEBP. Reaction conditions: 4,4′-DEBP, 5 mmol; DEBZ 50 mmol; H-FAU(11), 0.25 g; period, 4 h. Legends: (a) bulk products: DEBP (■); EBP (●); PEBP (▲); encapsulated products: DEBP (□); EBP (○); PEBP (△). (b) bulk products: 4,4′- (■); 3,4′- (●); 3,3′- (▲); 3,5- (▼); encapsulated products: 4,4′- (□); 3,4′- (○); 3,3′- (△); 3,5- (▽).

DEBPs in both bulk and encapsulated products. The distribution of DEBPs in bulk and encapsulated products at 160 °C had a similar tendency, although the selectivity for 4,4′-DEBP in encapsulated products was slightly lower than that in bulk products. However, the products distribution at 200 °C was almost in equilibrium for both bulk and encapsulated DEBPs.

Similarly, the effects of the ratio of DEBZ and BP on the distribution of DEBPs were examined in the transethylation of BP (*Figure not shown*). The increase of DEBZ enhanced the formation of DEBPs at 160 °C along with an increase of the selectivity for 4,4′-DEBP. However, the selective formation of 4,4′-DEBP was not observed by using a higher amount of DEBZ at higher temperatures. The distributions of DEBPs in bulk and encapsulated products at 160 °C showed a similar tendency, although the selectivity for 4,4′-DEBP in encapsulated products was a slightly lower than that for the bulk products. However, the products distribution at 200 °C was almost in equilibrium for both of bulk and encapsulated DEBPs.

These results on the amount of catalyst and the ratio of DEBZ and BP show that these factors are not the principal key for the selective formation of 4,4′-DEBP.

Isomerization of 4,4′-DEBP. Figure 6a summarizes the effects of the temperature on the isomerization of 4,4′-DEBP in the presence of DEBZ. The selectivity for 4,4′-DEBP decreased with reaction temperature in the bulk products, as shown in Fig. 6a, and 3,4′- and 3,3′-DEBPs increased along with a decrease of 4,4′-DEBP. However, the selectivity for 4,4′-DEBP in encapsulated products was 50%, even at 160 °C, because of extensive isomerization to 3,4′-DEBP. 3,4′-DEBP succesively isomerized to 3,3′-DEBP with increasing the temperature at 180 and 200 °C. A substantial amount of 3,5-DEBP was also observed in encapsulated products, probably due to low diffusion of the bulky isomer.

Figure 6b shows the deethylation and polyethylation of BP during the isomerization of 4,4′-DEBP. The deethylation to yield EBPs increased in bulk products with increasing the temperature, and PEBPs, including tri- and tetraethylbiphenyls, did not appear extensively. However, extensive deethylation and polyethylation occurred in encapsulated products, even at 160 °C. As discussed above, these reactions accompanied the isomerization of 4,4′-DEBP in both bulk and encapsulated products, particularly, at higher temperatures. These extensive reactions inside the pores show that the active sites for the catalysis, including the transethylation of BP and isomerization, deethylation, and polyethylation of 4,4′-DEBP and its ethylates, were principally inside the pores of H-Y zeolite.

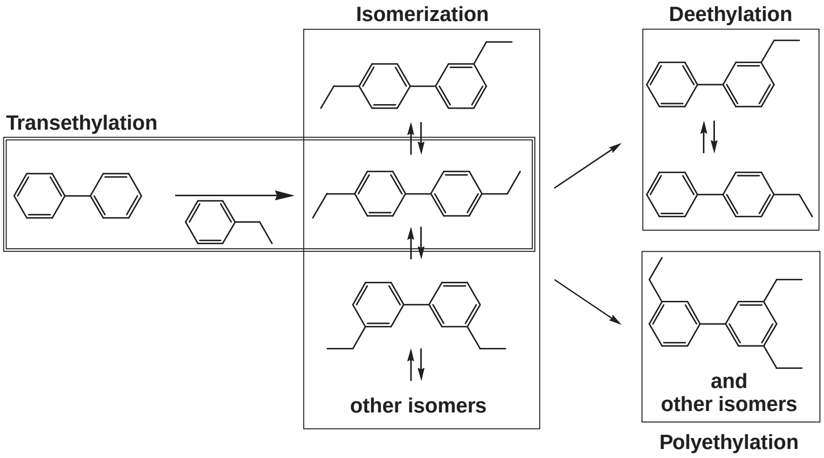
Mechanistic Aspects of the Transethylation. The transethylation of BP with DEBZ catalyzed by H-FAU(11) led to the selective formation of 4,4′-DEBP at lower temperatures, whereas an increase of reaction temperature decreased the formation of 4,4′-DEBP with increasing 3,4′- and 3,3′-DEBPs. These results are quite different from the ethylation of BP over H-Y with ethene as an alkylating agent; the formation of 4,4′-DEBP was very little.

The results obtained in this study can be summarized as follows: the selectivity for 4,4′-DEBP in bulk and encapsulated products decreased with the reaction temperature, and the selectivity for 4,4′-DEBP in encapsulated products became lower than in bulk products during the reaction at every temperature. The decrease of the selectivity for 4,4′-DEBP accompanied an increase of the thermodynamically more stable isomers, 3,4′- and 3,3′-DEBPs. A similar change of the selectivities occurred in both bulk and encapsulated products by a long reaction period. It is considered that the active sites for the transethylation of BP with DEBZ, and the isomerization of 4,4′-DEBP are at internal and external acid sites.

From these discussions, we can propose two possible mechanisms in the transethylation of BP with DEBZ:

1. The formation of 4,4′-DEBP was occurred by shape-selective catalysis: the restriction of transition states composed of BP (4-EBP), DEBZ and acid sites inside the pores of H-Y zeolite leads to the selective formation of 4,4′-DEBP. This mechanism assumes that the H-Y pores including super cages are small enough for restricting the transition state to form other isomers, except for 4,4′-DEBP. The resultant 4,4′-DEBP was isomerized to thermodynamically stable DEBPs.

2. The selective formation of 4,4′-DEBP is due to the electronic effects under kinetically controlled conditions. The bul-



Scheme 1. Reaction paths for the transethylation of BP with DEBZ over H-Y zeolite.

ky alkylating agent, DEBZ, attacks electron-rich 4-positions preferentially because 2-positions are prevented by steric hindrance. The resultant 4,4′-DEBP was isomerized to thermodynamically stable DEBPs. However, an attack at the 3-position at higher temperatures possibly decreased the selectivity for 4,4′-DEBP. This mechanism was proposed by Takeuchi and his co-workers.[7]

We currently consider that the selective formation of 4,4′-DEBP occurred principally inside the pores of H-Y by mechanism **1**. The reasons are as follows. The acid sites of H-Y zeolite are almost inside the pores, and their pores, especially super cages, are large enough for the isomerization of 4,4′-DEBP formed by the transethylation to thermodynamically stable isomers, 3,4′- and 3,3′-DEBPs. The selectivity for 4,4′-DEBP was higher in bulk products than in encapsulated products at lower temperatures, such as 160 °C. These results suggest that the product-selectivity mechanism operates in shape-selective catalysis:[1,11,12] the least-bulky isomer, 4,4′-DEBP diffused out from the pores among the DEBPs. The diffusion of bulkier DEBPs, enhanced by increasing reaction temperatures and/or by prolonging the reaction period, resulted in a decrease of the selectivity for 4,4′-DEBP.

These conclusions were supported from results of the isomerization of 4,4′-DEBP:

1. Extensive isomerization was observed in encapsulated products, even at lower temperatures, although the selectivity for 4,4′-DEBP remained high in bulk products. The selectivity for 4,4′-DEBP in encapsulated products was lower than that in bulk products.
2. The extensive deethylation and polyethylation occurred much in encapsulated products compared with bulk products.

Takeuchi and his co-workers proposed mechanism **2** in a previous paper including amorphous silica-alumina.[7] We have no definitive exclusion of mechanism **2**; however, a comparison of the bulk and encapsulated products suggests that the principal transethylation of BP occurs at the internal acid sites for H-Y catalysts. A further investigation is necessary for a full understanding of the mechanism.

From these discussions, we propose a scheme for the catalysis, as shown in Scheme 1. The transethylation of BP with DEBZ yields 4,4′-DEBP inside the pores of H-Y zeolites. The 4,4′-DEBP diffuses out from the pores at low temperatures to achieve high selectivity for 4,4′-DEBP. The resultant 4,4′-DEBP is also possibly isomerized to thermodynamically stable isomers, even at low temperatures, because the pores of H-Y are large enough for isomerization, and H-Y zeolites have acid sites strong enough for isomerization. Deethylation and polyethylation also occurred inside the pores.

The prevention of the isomerization of 4,4′-DEBP is essential for the selective formation of 4,4′-DEBP in the transethylation of BP with DEBZ, because 4,4′-DEBP is easily isomerized inside H-Y pores. Some of the conditions for high selectivity for 4,4′-DEBP are low temperature, short reaction period, low catalyst amount, and high DEBZ/BP ratio.

The features of the transethylation of BP with DEBZ are quite different from the ethylation of BP with ethene over H-Y catalysts. The selectivity for 4,4′-DEBP was 5–10% in the ethylation of BP with ethane, even at temperatures of lower than 200 °C. The difference of the catalyses using H-Y zeolite is due to the difference of the mechanism. The pores of H-Y have no shape-selective character because they are too large to restrict the transition states for the bulkier DEBPs in the ethylation of BP with ethene. However, the pores of H-Y work as active sites for shape-selective catalysts in the transethylation of BP with DEBZ to form 4,4′-DEBP. 4,4′-DEBP is selectively yielded if the isomerization can be prevented.

Conclusion

H-Y zeolites (H-FAU(11)) were the most active in the transethylation of BP with diethylbenzene (DEBZ) among zeolites. The catalytic activity of H-FAU(11) was investigated under various reaction conditions. The selective formation of 4,4′-diethylbiphenyl (4,4′-DEBP) occurred at low temperatures, whereas the increase of temperature decreased the selectivity for 4,4′-DEBP. The product distribution in encapsulating products was lower than in bulk products, and the selectivities for 4,4′-DEBP also decreased with increasing reaction temperature. The results obtained from both bulk and encapsulated products suggest that principal catalytic reactions, including transethylation, isomerization, deethylation, and polyethylation, occurred inside pores of H-Y zeolite.

There are two possibilities for the formation of 4,4′-DEBP: (i) shape-selective catalysis inside H-Y pores and (ii) an electrophilic attack of bulky DEBZ to electron-rich 4-positions.

The shape-selective formation of 4,4′-DEBP prefers the former mechanism based on our results. The resultant 4,4′-DEBP was easily isomerized to thermodynamically stable isomers, 3,4′- and 3,3′-DEBPs, even at lower temperatures, because H-Y zeolite has large pores and strong enough acid sites for the isomerization of 4,4′-DEBP. The selective formation of 4,4′-DEBP at lower temperatures is due to a rapid diffusion of the least bulky isomer from the H-Y pores.

A further investigation concerning the selective formation of 4,4′-DEBP and an elucidation of the mechanism is now in progress.

A part of this work was financially supported by a Grant-in Aid for Scientific Research (B) 15350093 and 16310056, the Japan Society for the Promotion of Science (JSPS). The authors acknowledged to Nippon Steel Chem. Co., Ltd. for the gift of DEBZ.

References

1 Y. Sugi, Y. Kubota, T. Hanaoka, and T. Matsuzaki, *Catal. Surv. Jpn.*, **5**, 43 (2001).

2 Y. Sugi and Y. Kubota, "Catalysis," ed by J. J. Spivey, Royal Soc. Chem., London (1997), Vol. 13, a Specialist Periodical Report, Chap. 3, p. 55.

3 X. Tu, M. Matsumoto, T. Maeda, Y. Sugi, T. Matsuzaki, T. Hanaoka, Y. Kubota, and J.-H. Kim, *Microporous. Mater.*, **3**, 593 (1995).

4 M. Matsumoto, X. Tu, T. Matsuzaki, T. Hanaoka, Y. Kubota, Y. Sugi, J.-H. Kim, K. Nakajima, and K. Kunimori, *Stud. Surf. Sci. Catal.*, **105**, 1317 (1997).

5 K. Nakajima, T. Hanaoka, Y. Sugi, T. Matsuzaki, Y. Kubota, A. Igarashi, and K. Kunimori, "Shape Selective Catalysis—Chemicals Synthesis and Hydrocarbon Processing," ACS Symp. Ser. (1999), Vol. 738, p. 260.

6 Y. Sugi, S. Tawada, T. Sugimura, Y. Imada, Y. Kubota, T. Hanaoka, and T. Matsuzaki, *Stud. Surf. Sci. Catal.*, **135**, 4558 (2001). (CD-ROM: 28-P-09).

7 G. Takeuchi, Y. Shimoura, and T. Hara, *Appl. Catal., A: General*, **137**, 87 (1996).

8 G. Takeuchi, *Catal. Surv. Jpn.*, **2**, 77 (1998).

9 N. Y. Chen, W. E. Garwood, and F. G. Dwyer, "Shape Selective Catalysis in Industrial Applications," 2nd ed, revised and expanded, Marcel Dekker, New York (1996).

10 S. M. Csicsery, *Zeolites*, **4**, 202 (1984).

11 P. B. Venuto, *Microporous. Mater.*, **2**, 297 (1994).

12 E. J. Rosinski and M. K. Rubin, U.S. Patent 3 832 449 (1974).