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Effects of SiO_2/Al_2O_3 ratio of H-mordenite on encapsulated products inside the pores in shape-selective isopropylation of biphenyl

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The effects of SiO_2/Al_2O_3 ratio of H-mordenite on the selectivity of encapsulated products in the pores and of bulk products were investigated in the isopropylation of biphenyl. The selectivity of 4,4′-diisopropylbiphenyl (4,4′-DIPB) of bulk products was varied with SiO_2/Al_2O_3 ratio. Highly dealuminated H-mordenite gave a selectivity higher than 80%, whereas the selectivity was low for H-mordenite with SiO_2/Al_2O_3 ratio of 10–20. On the other hand, the selectivity of 4,4′-DIPB in encapsulated DIPB isomers was higher than 85% for all H-mordenites regardless of SiO_2/Al_2O_3 ratio. These results show that all H-mordenites catalyze the isopropylation of biphenyl with high shape-selectivity inside the pore. The low selectivity of 4,4′-DIPB in bulk products for H-mordenites with low SiO_2/Al_2O_3 ratio was not due to a lack of shape-selectivity of the H-mordenites, but to non-regioselective isopropylation at the external acid sites. Non-regioselective catalysis over H-mordenite with low SiO_2/Al_2O_3 ratio could be induced by choking pores by coke deposition.

Keywords: isopropylation, biphenyl, H-mordenite, SiO_2/Al_2O_3 ratio, encapsulated products, coke deposition

1. Introduction

Polynuclear aromatics such as biphenyl and naphthalene have attracted the attention of many researchers as key components of advanced materials such as heat-resistant and liquid crystalline polymers. The shape-selective alkylation using zeolite is a promising way for manufacturing symmetrically polynuclear aromatics [1]. H-mordenite has been found to be the most effective catalyst for the shape-selective isopropylation of biphenyl [2–5], and naphthalene with propylene and propanol-2 [6,7]. Particularly, highly dealuminated H-mordenite gave high catalytic activity and high selectivity of 4,4′-DIPB, while catalytic performances were low for the H-mordenite with low SiO_2/Al_2O_3 ratio [2–4]. It is still unclear where the reaction occurs because the selectivity of 4,4′-DIPB is changed much by many factors such as reaction conditions and the nature of the catalyst. In this paper, we describe the effect of SiO_2/Al_2O_3 ratio on encapsulated products inside the pores and on bulk products in the isopropylation of biphenyl, and discuss the mechanism of shape-selective alkylation over H-mordenite.

2. Experimental

H-mordenites (SiO_2/Al_2O_3 = 10, 15, 20, 25, 30, 73, 110 and 206) were supplied from Tosoh Corporation, Tokyo, Japan, and calcined at 550°C in an air stream just before use. Biphenyl and 4,4-DIBP were purchased from Tokyo Kasei Kogyo Co., Ltd., Tokyo, Japan, and 4-IPBP from Aldrich Chemical Ind. Co., Inc., Milwaukee, WI, USA. These reagents were used without further purification. The isopropylation of biphenyl was carried out in a 100 ml SUS-316 autoclave under propylene pressure. The autoclave containing biphenyl and H-mordenite was purged in air with nitrogen before heating. After reaching reaction temperature, propylene was introduced to the autoclave and the pressure was kept constant throughout the reaction. After cooling the autoclave, the bulk products were collected by using toluene as a solvent. The products were analyzed by a Hewlett-Packard 5890 II gas chromatograph equipped with an Ultra-1 capillary column (25 m×0.3 mm) and identified by a Hewlett-Packard 5978 gas chromatograph with mass selective detector. The yield of each product was calculated on the basis of consumed biphenyl, and the selectivities of each DIPB and isopropylbiphenyl (IPBP) isomers are expressed as:

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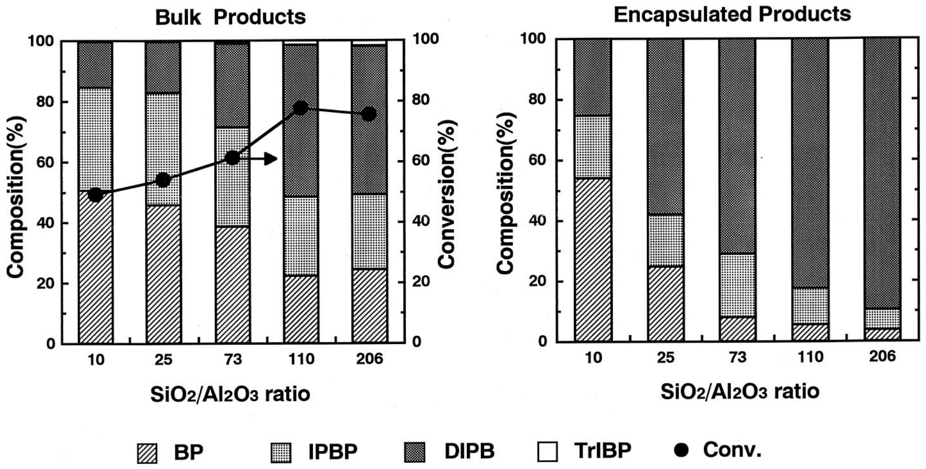

Figure 1. Effect of the SiO_2/Al_2O_3 ratio of H-mordenite on the composition of bulk and encapsulated products in the isopropylation of biphenyl. Reaction conditions: biphenyl, 200 mmol; H-mordenite, 1 g; temperature, 250°C; period, 4 h.

$$\text{selectivity of DIPB (IPBP) isomers (\%)} = \frac{\text{yield of each DIPB (IPBP) isomer (mmol)}}{\text{yield of DIPB (IPBP) isomers (mmol)}} \times 100$$

The analysis of products encapsulated in the catalyst after the reaction was carried out as follows. The catalyst was filtered off, washed well with 200 ml of acetone, and dried at 110°C under air atmosphere during 12 h. The resulting catalyst was dissolved by using 3 ml of aqueous hydrofluoric acid (47%) at room temperature. This solution was neutralized with solid potassium carbonate, and the organic layer was extracted three times with 20 ml of dichloromethane. After removal of the solvent in vacuo, the residue was dissolved again in 5 ml of toluene and 10 mg of naphthalene added as an internal standard. The GC analysis was done similar to that of the bulk products.

Thermogravimetric analysis (TG) of H-mordenites after the reaction was carried out with the temperature programmed rate of 10°C/min in an air stream by TG-DTA 2000 (MAC Science Co. Ltd., Tokyo, Japan). The weight loss due to adsorbed water was corrected by blank measurement of the corresponding H-mordenite before the reaction.

3. Results and discussion

The isopropylation of biphenyl with propylene over H-mordenites yielded mixtures of IPBP, DIPB, and triisopropylbiphenyls (TrIPB) [2–4]. Figure 1 shows the effect of SiO_2/Al_2O_3 ratio on the compositions of bulk products and of encapsulated products in the pores. In the bulk products, the percentage of IPBP and DIPB isomers increased with the SiO_2/Al_2O_3 ratio. A small amount of TrIPB was also observed over all catalysts. On the other hand, the percentages of BP in encapsulated products were much lower than those in bulk products except in the case of HM(10)[1]. The DIPB isomers were dominant in the encapsulated products, especially with the highly dealuminated H-mordenite, whereas TrIPB isomers were not observed in the encapsulated products with all catalysts. These results show that the isopropylation of BP proceeds rapidly to yield IPBP and DIPB, but not TrIPB. The absence of TrIPB in the encapsulated products was due to the steric restriction of the pores against the isopropylation of DIPB. No configuration of DIPB isomers, especially 4,4′-DIPB, to form TrIPB should be allowed in the pores. The low percentages of IPBP and DIPB over H-mordenites with low SiO_2/Al_2O_3 ratio are due to deactivation by severe coke deposition inside the pores (see below).

Figure 2 shows the effects of SiO_2/Al_2O_3 ratio on the selectivities of 4,4′- and 3,4′-DIPB in the DIPB isomers. In bulk products, the selectivity of 4,4′-DIPB increased with the SiO_2/Al_2O_3 ratio, whereas that of 3,4′-DIPB was low and almost constant for all catalysts. The shape-selective formation of 4,4′-DIPB was observed for dealuminated H-mordenites, particularly for HM(206). However, the selectivity of 4,4′-DIPB with HM(10) was low and other DIPB isomers were obtained in high amounts. The features of encapsulated products are quite different from those of bulk products. The selectivities of 4,4′-DIPB were higher than 85% with all H-mordenites, even with HM(10). The results show that the shape-selective isopropylation occurs inside the pores of all H-mordenites. Therefore, low selectivity of 4,4′-DIPB in the bulk products for HM(10) is not due to the lack of shape-selectivity of the pores, but to the non-selective alkylation on the external acid sites still active in spite of coke deposition.

The high selectivities of 4,4′-DIPB both in bulk and

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[1] The number in parentheses shows the SiO_2/Al_2O_3 ratio of H-mordenites.

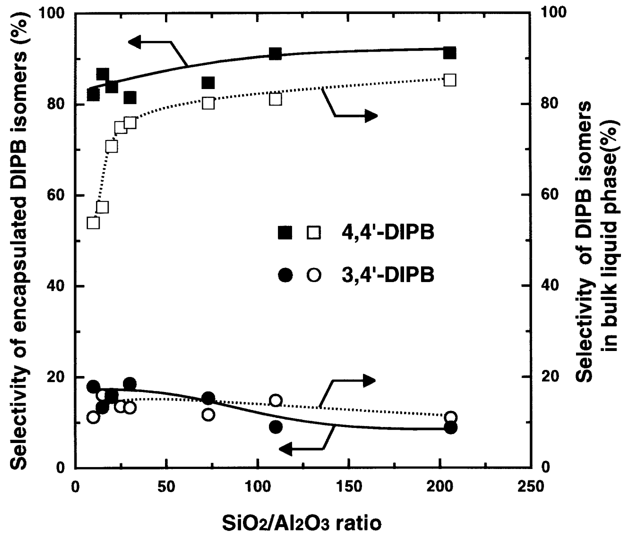

Figure 2. Effect of the SiO_2/Al_2O_3 ratio of H-mordenite on the selectivity of 4,4′- and 3,4′-DIPB in bulk and encapsulated products. Reaction conditions: see figure 1.

encapsulated products for dealuminated H-mordenite show that the isopropylation occurs principally inside the pores, and that the external acid sites do not act as principal catalytic sites. As we described previously, high propylene pressure is essential for the selective formation of 4,4′-DIPB [4]. The highly shape-selective catalysis for the formation of 4-IPBP and 4,4′-DIPB is ascribed to steric restriction of the transition states at microporous environments of the pores of H-mordenite to produce the narrowest products.

Table 1 shows the isomerization of 4,4′-DIPB over HM(25) and HM(206) under 0.8 MPa of propylene pressure to examine the participation of external acid sites. The isomerization of 4,4′-DIPB was very slow with both catalysts, and 4,4′-DIPB was found as an exclusive encapsulated product inside the pores. We already showed that the isomerization of 4,4′-DIPB was prevented by preferential adsorption of propylene on the acid sites at high propylene pressure [4]. These results suggest that DIPB isomers were scarcely changed to other products during the reaction at the external acid sites, after they formed. Therefore, the low selectivity of 4,4′-DIPB with H-mordenite with low SiO_2/Al_2O_3 ratio is not due to the isomerization of 4,4′-DIPB, but to the non-selective alkylation at external acid sites as discussed above.

Table 1
The isomerization of 4,4′-DIPB under propylene pressure[a]

Catalyst	Bulk products	Encapsulated products
HM(25)	96	99
HM(206)	94	98

[a] Reaction conditions: 4,4′-DIPB, 100 mmol; H-mordenite, 1 g; propylene, 0.8 MPa; temperature, 250°C; period 4 h.

Figure 3 shows thermogravimetric (TG) profiles of the catalysts used for the isopropylation of biphenyl. The amounts of coke observed as a peak around 600°C decreased with the SiO_2/Al_2O_3 ratio of H-mordenite. Volatile organic compounds, which are ascribed to isopropylated biphenyls encapsulated in the pores discussed above, were also found at 300–350°C for dealuminated H-mordenite ($SiO_2/Al_2O_3 > 70$). These results are explained by preferential removal of strong acid sites by the dealumination of H-mordenite [8,9]. The coke deposition easily occurs on strong and dense acid sites by the dehydrogenation of alkylated aromatics [10–12]. It is considered that most of the volatile compounds in the pores of H-mordenites with low SiO_2/Al_2O_3 ratio were converted to coke deposits, and that major parts of acid sites in the pores could not act as catalytic active sites by blocking the pore entrance. Highly dealuminated H-mordenites such as HM(206) effectively catalyze shape-selective isopropylation of biphenyl without the inhibition by coke deposition.

4. Conclusion

The shape-selective formation of 4,4′-DIPB was observed in the isopropylation of biphenyl over dealuminated H-mordenites. The selectivity of 4,4′-DIPB changed with the SiO_2/Al_2O_3 ratio, and it was low for H-mordenites with low ratio. However, encapsulated products showed that the selectivities of 4,4′-DIPB inside the pores were higher than 85% for all H-mordenites regardless of the ratio. These results show that shape-selective catalysis occurs inside the pores for all H-mordenites,

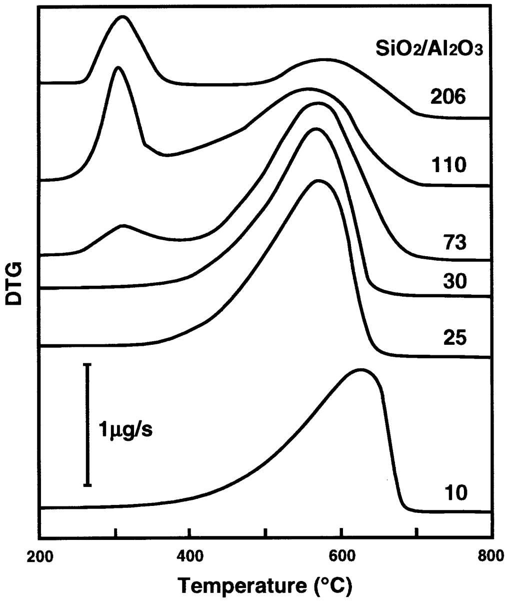

Figure 3. Thermogravimetric profiles of H-mordenite after the reaction under air atmosphere. TG conditions: H-mordenite, 10 mg; programmed rate, 10°C/min. Reaction conditions: see figure 1.

while non-regioselective alkylation at the external surface is predominant for H-mordenites with low SiO_2/Al_2O_3 ratio. This means that acid sites inside the pores do not always act as principal active sites for the alkylation. Particularly, on H-mordenites with low ratio, coke deposition occurs on these acid sites by the dehydrogenation of isopropylated biphenyls, and blocks the pores. However, highly dealuminated H-mordenites such as HM(206) effectively catalyze the shape-selective isopropylation without the inhibition by coke deposition.

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