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Effects of reaction temperature on the isopropylation of biphenyl over H-mordenite

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The effects of reaction temperature on the selectivity for bulk products and for encapsulated products in the pores were investigated in the isopropylation of biphenyl over a highly dealuminated H-mordenite under 0.8 MPa of propylene. The selectivity for 4,4′-diisopropylbiphenyl (4,4′-DIPB) in bulk products was changed with the increase of reaction temperature: it decreased with increasing that for thermodynamically stable 3,3′- and 3,4′-DIPB. However, the selectivity for 4,4′-DIPB in encapsulated products was as high as 85–90% between 200 and 350 °C. These results show that H-mordenite catalyzes the isopropylation of biphenyl inside the pore with high shape selectivity at these temperatures, and that the decrease of the selectivity for 4,4′-DIPB in the bulk products is due to its isomerization to 3,3′- and 3,4′-DIPB on external acid sites.

Keywords: H-mordenite, isopropylation, biphenyl, 4,4′-DIPB, isomerization, encapsulated products

1. Introduction

H-mordenite has been found to be the most potential catalyst for shape-selective isopropylation of biphenyl with propylene and propanol-2 [1–8]. Especially, highly dealuminated H-mordenites gave high catalytic activity and high selectivity for 4,4′-DIPB. However, the selectivity decreased with increasing reaction temperature [4,5]. The decrease of the selectivity was ascribed to the isomerization of 4,4′-DIPB to thermodynamically stable 3,4′-DIPB [5]. It is still unclear where the isomerization occurs, because the selectivity for 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 effects of reaction temperature on bulk products and on encapsulated products inside the pores in the isopropylation of biphenyl over a dealuminated H-mordenite and discuss the mechanism of shape-selective alkylation.

2. Experimental

H-mordenite ($SiO_2/Al_2O_3 = 206$) was supplied from Tosoh Corp., 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-isopropylbiphenyl (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 0.8 MPa of propylene. Typical reaction and analytical procedures are as follows. Air in the autoclave containing biphenyl and H-mordenite was purged with nitrogen before heating. After reaching reaction temperature, propylene (0.8 MPa) was introduced to the autoclave, and the pressure 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 Shimadzu 14A gas chromatograph equipped with an Ultra-1 capillary column (25 m × 0.3 mm) and identified by a Shimadzu GCMS QP5000 gas chromatograph–mass spectrometer using the same column as described above. The yield of each product was calculated on the basis of consumed biphenyl and the selectivities for each DIPB and IPBP isomers, respectively.

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 an air atmosphere during 12 h. The resulting catalyst was destroyed by 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 in 5 ml of toluene and 10 mg of naphthalene was added as an internal standard. The GC analysis was done similar to the case of bulk products.

3. Results and discussion

The isopropylation of biphenyl with propylene over H-mordenites yielded mixtures of IPBP, DIPB, and triisopropylbiphenyls (TrIPB) [1–8]. Figure 1 shows the effect of reaction temperature on the compositions of bulk products and of encapsulated products in the pores. IPBP and DIPB

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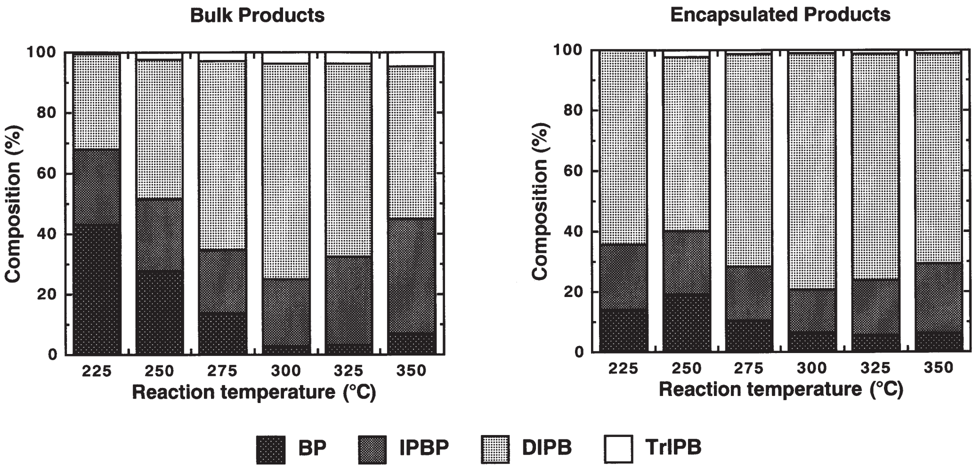

Figure 1. Effect of reaction temperature on bulk and encapsulated products in the isopropylation of biphenyl. Reaction conditions: biphenyl 200 mmole; H-mordenite 1 g; propylene 0.8 MPa; period 4 h.

isomers increased with reaction temperatures in bulk products. The percentages of biphenyl in encapsulated products were much lower than that in bulk products, and DIPB isomers were dominant in encapsulated products at all temperatures. The formation of TrIPB isomers enhanced at high temperature in bulk products, although only small amounts of TrIPB isomers were observed in encapsulated products under all catalytic conditions. These results show that the isopropylation of biphenyl proceeds rapidly inside the pores to yield IPBP and DIPB, but not TrIPB. Low selectivity for TrIPB in encapsulated products was due to steric restriction of the pores against the isopropylation of DIPB. No conformation of DIPB isomers, especially 4,4′-DIPB, to form TrIPB should be allowed in the pores. TrIPB isomers in bulk products at higher temperature probably form on external acid sites. At higher temperature than 300 °C, the increase of yields of IPBP isomers was observed with the compensation of DIPB isomers in bulk and encapsulated products. This means that the dealkylation occurs at high temperatures during the isopropylation under high propylene pressures, and that it occurs on both internal and external acid sites.

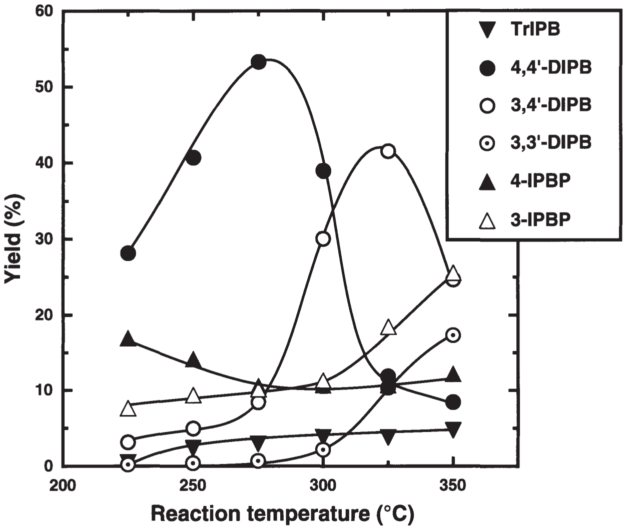

Figure 2. Effect of reaction temperature on the yield of IPBP and DIPB isomers in bulk products. The reaction conditions are the same as in figure 1.

Figure 2 shows the effects of reaction temperature on the yield of DIPB and IPBP isomers in the isopropylation of biphenyl. The yield of 4,4′-DIPB increased with the temperature and reached the maximum at 250 °C. However, it decreased with the increase of the yield of 3,4′-DIPB at temperatures higher than 275 °C. Moreover, further isomerization of 3,4′-DIPB to 3,3′-DIPB occurred above 300 °C. These changes are due to the isomerization of 4,4′-DIPB to thermodynamically stable isomers, 3,3′- and 3,4′-DIPB [9]. The yield of 3-IPBP also increased with the decrease of the yield of DIPB isomers especially above 300 °C, whereas the yield of 4-IPBP decreased with increasing reaction temperatures. These results suggest that dealkylation of DIPB isomers is also controlled by thermodynamic stability. Figure 3 shows the effects of reaction temperature on the selectivity for 3,3′-, 3,4′- and 4,4′-DIPB in the isopropylation of biphenyl. The features of encapsulated products are quite different from those of bulk products. The selectivity for 4,4′-DIPB was higher than 80% at all temperatures, even at 350 °C. Similar tendencies were observed for the formation of 3- and 4-IPBP. On the other hand, the selectivity for these DIPB isomers in bulk products varied with reaction temperature. The changes of the selectivities corresponded well to the yield of 3,4′-DIPB and 4,4′-DIPB, as discussed above. The selective formation of 4,4′-DIPB was observed at the temperature below 275 °C, whereas the selectivity for 4,4′-DIPB decreased with the increase of the temperature. The decrease in the selectivity for 4,4′-DIPB was compensated with the increase in that for 3,3′- and 3,4′-DIPB. The results show that shape-selective isopropylation occurs inside the pores of H-mordenite even at such a temperatures as high as 350 °C, and that low selectivities for 4,4′-DIPB in the bulk products at high temperatures are due to the isomerization on external acid sites and not to the lack of shape selectivity inside the pores.

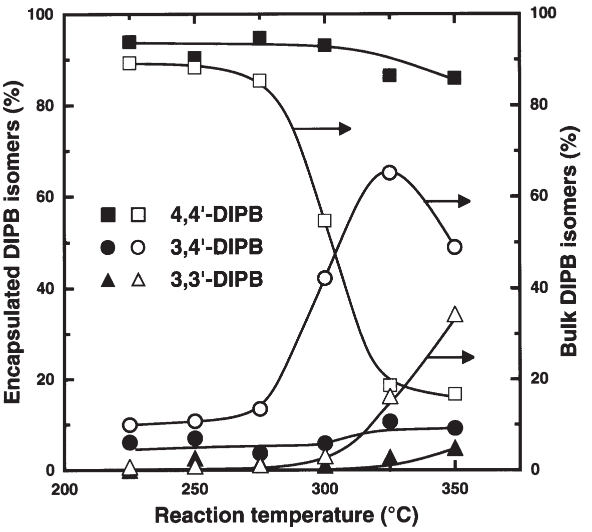

Figure 3. Effect of reaction temperature on the selectivity for DIPB isomers in bulk and encapsulated products. The reaction conditions are the same as in figure 1. Open marks: bulk products. Solid marks: encapsulated products.

Figure 4 summarizes the effects of reaction temperature on the yield of bulk and encapsulated products in the isomerization of 4,4′-DIPB under 0.8 MPa of propylene. At the temperatures higher than 275 °C, dealkylated IPBP isomers were increased significantly, with the decrease of DIPB isomers. On the other hand, small amounts of dealkylated products, biphenyl and IPBP, were observed in encapsulated products at all temperatures. These results show that no significant isopropylation of DIPB isomers occurs inside the pores even at a temperature as high as 350 °C, and that the dealkylation of 4,4′-DIPB occurs on both internal and external acid sites. A small amount of TrIPB was observed at all temperatures below 275 °C, and the yield increased with the temperature. However, the formation of TrIPB was scarcely observed inside the pores at all temperatures. This means that the isopropylation of 4,4′-DIPB prevents inside the pores.

Figure 5 shows the effect of reaction temperature on the selectivity for 3,3′-, 3,4′- and 4,4′-DIPB in the isomerization of 4,4′-DIPB under propylene pressure. As previously described, the isomerization was not extensive under high propylene pressures at moderate temperature such as 250 °C. However, the isomerization to 3,3′- and 3,4′-DIPB occurred extensively with some dealkylation reactions at higher temperatures. The yield of 3,3′-DIPB increased with the increase of the temperature. However, the selectivity for 4,4′-DIPB in encapsulated products was higher than 90% at all temperatures. These results support that the isomerization occurs on external acid sites as discussed above.

The high selectivities for 4,4′-DIPB both in bulk and encapsulated products at moderate temperatures show that the isopropylation occurs selectively inside the pores, and that external acid sites do not act as principal catalytic sites in the isopropylation of biphenyl. 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. The selectivity for 4,4′-DIPB in bulk products decreased with the increase of that for 3,4′-DIPB at higher temperatures, whereas the selectivity for 4,4′-DIPB was higher than 85% at all temperatures. These results show that the isopropylation of biphenyl to 4,4′-DIPB occurs inside the pores even at high temperatures, and that the formation of 3,4′-DIPB is to the isomerization of 4,4′-DIPB on external acid sites.

We previously described similar discrepancies between bulk products and encapsulated products inside the pores [6]: the selectivity for 4,4′-DIPB in the bulk products decreased under low propylene pressure, whereas the selectivity for 4,4′-DIPB encapsulated inside the pores kept constant under all pressures. The decrease of the selectivity was ascribed to the isomerization of 4,4′-DIPB on external acid sites. We proposed that the preferential adsorption of propylene prevents the isomerization and the iso-

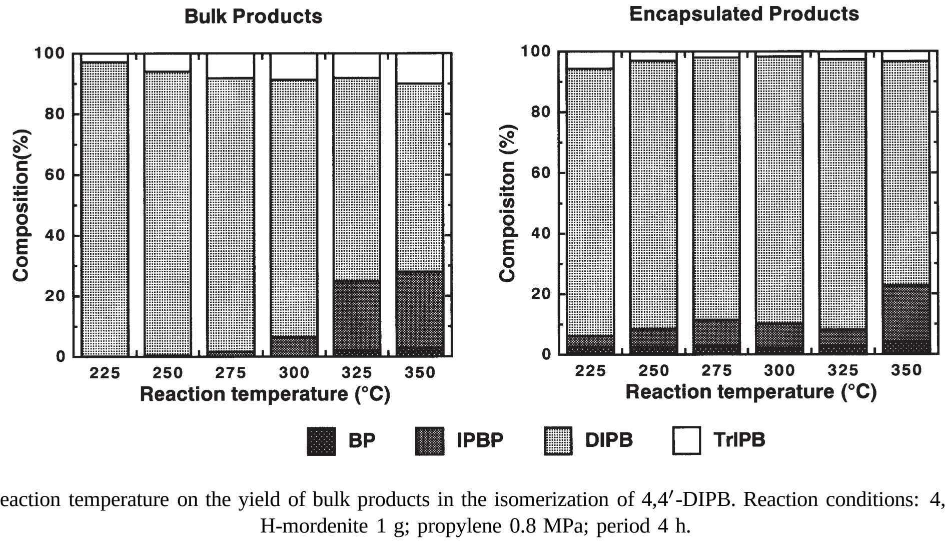

Figure 4. Effect of reaction temperature on the yield of bulk products in the isomerization of 4,4′-DIPB. Reaction conditions: 4,4′-DIPB 100 mmole; H-mordenite 1 g; propylene 0.8 MPa; period 4 h.

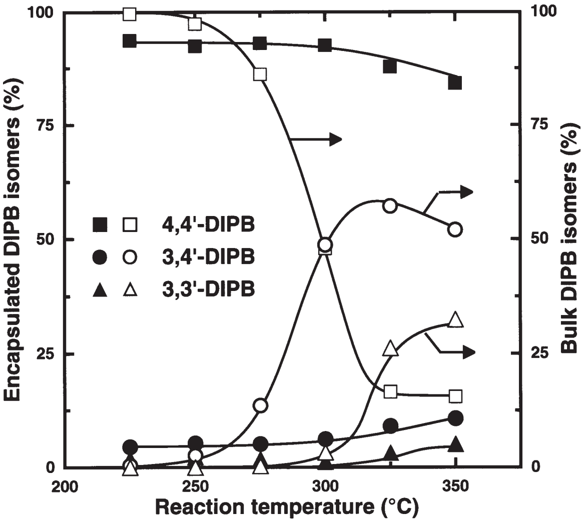

Figure 5. Effect of reaction temperature on the selectivity for DIPB isomers in bulk and encapsulated products in the isomerization of 4,4′-DIPB. The reaction conditions are the same as in figure 4. Open marks: bulk products. Solid marks: encapsulated products.

propylation of 4,4′-DIPB under high pressures [3,6]. The effects of discrepancy of bulk and encapsulated products on the reaction temperature were explained by similar effect of preferential adsorption of propylene. At moderate temperatures, high selectivity for 4,4′-DIPB shows that the isomerization was effectively prevented by preferential adsorption of propylene on external surfaces. However, the adsorption of propylene should not play a primary role in controlling the acid sites at high temperatures, and thus, the isomerization of 4,4′-DIPB occurs on external acid sites.

4. Conclusion

The effects of reaction temperature on the selectivity for encapsulated products in the pores and for bulk products were investigated in the isopropylation of biphenyl over a highly dealuminated H-mordenite. The selectivity for 4,4′-DIPB in bulk products was changed with the increase of reaction temperature: it decreased with increasing that for 3,3′- and 3,4′-DIPB. However, the selectivity for 4,4′-DIPB in encapsulated products was as high as 80–90% between 225 and 350 °C. These results show that all H-mordenites catalyze the isopropylation of biphenyl with high shape selectivity inside the pores even at high temperatures as 350 °C, and that the decrease of the selectivity for 4,4′-DIPB in the bulk products is due to its isomerization to 3,3′- and 3,4′-DIPB on external acid sites.

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