The roles of 3- and 4-isopropylbiphenyls in the isopropylation of biphenyl over a H-mordenite

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The isopropylation of mixtures of 3- and 4-isopropylbiphenyls (3- and 4-IPBPs) was examined over a dealuminated H-mordenite (HM) to elucidate the role of 3- and 4-IPBPs in the isopropylation of biphenyl (BP). 4-IPBP was consumed much faster than 3-IPBP in all cases. 4-IPBP was an exclusive precursor to diisopropylbiphenyls (DIPBs), particularly 4,4′-DIPB, and 4,4′-DIPB was found in encapsulated products during the reaction. These results show that 4-IPBP can allow establishment of an active complex with propylene and acid site in HM pores, whereas 3-IPBP cannot. It is concluded that the isopropylation of BP over HM occurs through a *reactant selectivity mechanism*, and through a *restricted transition state mechanism*, but not through a *product selectivity mechanism*.

KEY WORDS: 3- and 4-IPBS; isopropylation; biphenyl; H-mordenite

1. Introduction

Shape-selective catalysis over zeolites occurs by differentiating reactants, products, and/or reaction intermediates according to their shape and size in sterically restricted environments of their pore structures [1,2], and it is the most promising way to synthesize the symmetrically substituted polynuclear aromatics. H-mordenite (HM), paticularly after dealumination is the effective catalyst for shape-selective isopropylation of biphenyl (BP) to 4,4′-diisopropylbiphenyl (4,4′-DIPB) [3–10]. We have been interested in why and how shape-selective catalysis occurs, and proposed that two types of mechanisms, originally proposed by Csicsery [1], operate in this catalytic reaction [3,5]. The first mechanism is the *restricted transition state mechanism*; it works in the first step of the alkylation of BP to isopropylbiphenyls (IPBPs), and in the second stage of 4-IPBP to 4,4′-DIPB. The second mechanism is the *reactant selectivity mechanism*; it works on the second step of the alkylation of IPBP to DIPB to choose 4-IPBP as only a precursor of 4,4′-DIPB. However, roles of intermediate products, particularly 3- and 4-IPBPs were still unclear because they were observed only in low amounts during the reaction. In this paper, we describe the isopropylation of mixtures of 3- and 4-IPBPs over a dealuminated H-mordenite, and discuss their roles in the isopropylation of BP.

2. Experimental

The dealuminated HM ($SiO_2/Al_2O_3 = 128$) was obtained from TOSOH Corp., Tokyo, Japan, and calcined in air at 450 °C prior to the reaction. BP, 3-IPBP, 4-IPBP, and 4,4′-DIPB were obtained from Tokyo Kasei Kogyo Ltd. The isopropylation was carried out in a 100 ml stainless-steel autoclave in the presence of propylene. A standard set of reaction conditions is included: an equimolar mixture of 3- and 4-IPBPs 100 mmol, HM 1 g, propylene pressure 0.8 MPa and reaction temperature 250 °C. Product composition was determined by a Shimadzu gas chromatograph model GC-14A equipped with a capillary column of Ultra-1 from HP, as previously described [4,5]. Encapsulated products in catalysts recovered from the reaction were also analyzed by GC after the destruction of HM used for the reaction by aqueous hydrofluoric acid solution.

3. Results and discussion

The isopropylation of biphenyl over dealuminated HM at a moderate temperature and a propylene pressure occurs shape-selectively to yield predominantly the least bulky isomers, 4-IPBP among IPBP isomers (IPBPs), and 4,4′-DIPB among DIPB isomers (DIPBs) [3–5]. Diisopropylbiphenyls (DIPBs), particularly 4,4′-DIPB, were produced with the consumption of 4-IPBP and the accumulation of 2- and 3-IPBPs, and the selectivity for 4,4′-DIPB was almost constant during the reaction. However, roles of the intermediates, 3- and 4-IPBPs, are still unclear because their yields are too small to analyze their roles. It is important to elucidate the relative reactivity of 3- and 4-IPBPs, and the selectivity of DIPBs from them. For these purposes, we examined the isopropylation of an equimolar mixture of 3- and 4-IPBPs at 250 °C under 0.8 MPa of propylene. Figure 1 shows composition of bulk and encapsulated products during the reaction. The initial rate for the isopropylation of IPBPs was very

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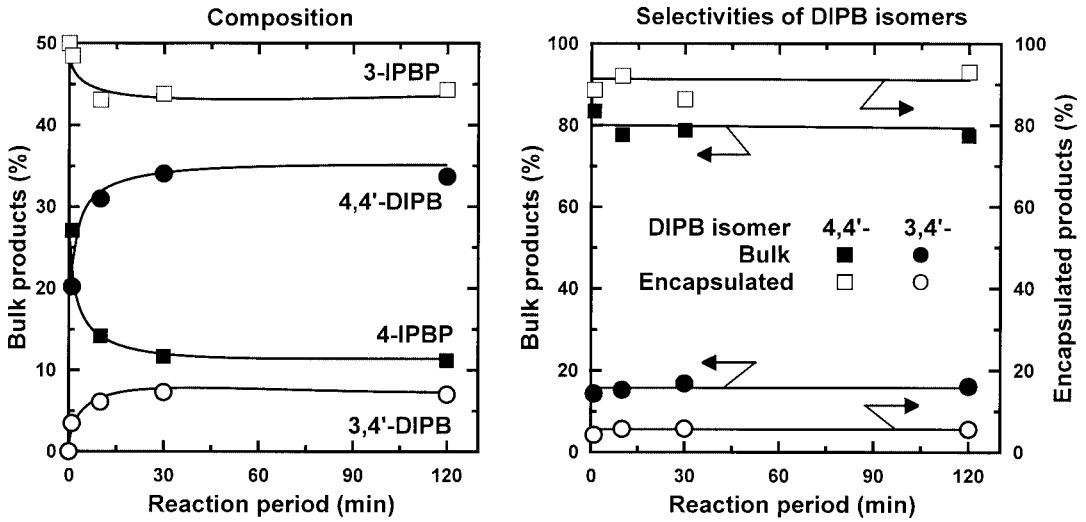
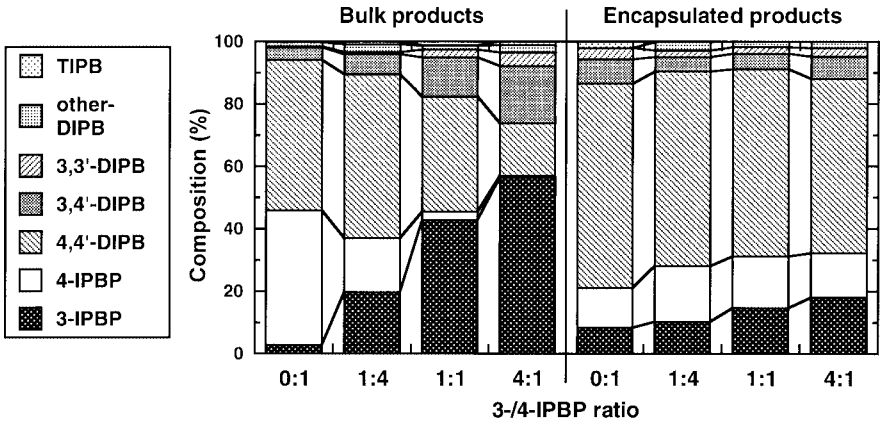


Figure 1. The isopropylation of an equimolar mixture of 3- and 4-IPBPs. Reaction conditions: 3- and 4-IPBPs (1 : 1) 100 mmol (total), HM(128) 1 g, propylene 0.8 MPa, temperature 250 °C.

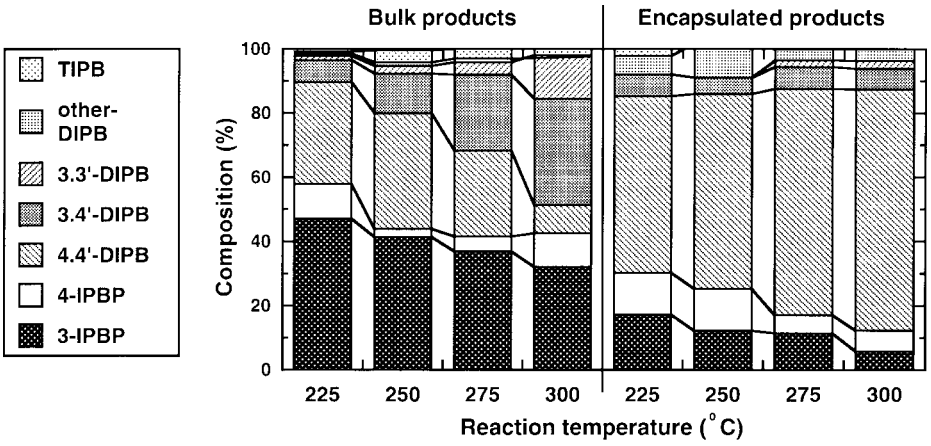


3-IPBP conversion(%)	--	1.5	12.1	26.5	--	--	--	--
4-IPBP conversion(%)	56.9	78.4	85.0	98.8	--	--	--	--
4,4'-DIPB selectivity(%)	85.2	84.6	72.9	40.2	85.2	86.9	87.1	82.4

Figure 2. Effects of initial 3-/4-IPBP ratio on the isopropylation of the mixture of 3- and 4-IPBP. Reaction conditions: 3- and 4-IPBPs 100 mmol (total), HM(128) 1 g, temperature 250 °C, propylene 0.8 MPa, period 4 h.

high. The 4-IPBP isomer was much more reactive than 3-IPBP. Although 70% of 4-IPBP was consumed in the initial 10 min, only 7% of 3-IPBP was consumed during the same period. The results mean that there is an about ten times difference between these two isomers in their initial reaction rate. After initial rapid reaction over fresh catalysts, the isopropylation slowed down, and proceeded gradually with reaction period. The selectivity for 4,4′-DIPB in both bulk and encapsulated products was high and constant during the reaction. The selectivity for 4,4′-DIPB in encapsulated products was higher than that for bulk products; the difference is due to the isopropylation of 3-IPBP at acid sites on the external surface. These results show that the isopropylation of BP occurs by a consecutive mechanism inside HM pores: BP is isopropylated to IPBPs with selective formation of 4-IPBP, and 4-IPBP yields 4,4′-DIPB regioselectively in the second reaction step. Some of 3-IPBP should participate in the isopropylation, whereas its principal reaction sites should be at the external surface of HM.

Figure 2 summarizes the effect of initial 3-/4-IPBP ratio on their isopropylation. The selectivity of bulk products was changed significantly with the ratio of both isomers. When the isopropylation started from a mixture with initial 3-/4-IPBP ratio of 1 : 4, 4-IPBP was consumed preferentially to form 4,4′-DIPB, whereas the conversion of 3-IPBP was very low. However, the conversion of 3-IPBP and the yield of 3,4′-DIPB increased with the increase of the amount of 3-IPBP in the reactant mixture. It means that 3-IPBP isomers could participate in the isopropylation after the amount of 4-IPBP decreased. Product composition of encapsulated products was also shown in figure 2. The encapsulated DIPB isomer was exclusively 4,4′-DIPB for all initial 3-/4-IPBP



3-IPBP conversion(%)	10.7	17.4	27.0	42.5	--	--	--	--
4-IPBP conversion(%)	78.3	94.9	90.8	90.8	--	--	--	--
4,4'-DIPB selectivity(%)	78.2	69.4	48.4	15.8	81.5	79.2	85.0	84.8

Figure 3. Effects of reaction temperature on the isopropylation of an equimolar mixture of 3- and 4-IPBPs. Reaction conditions: 3- and 4-IPBPs (1 : 1) 100 mmol, HM(128) 1 g, temperature 225–325 °C, propylene 0.8 MPa, period 4 h.

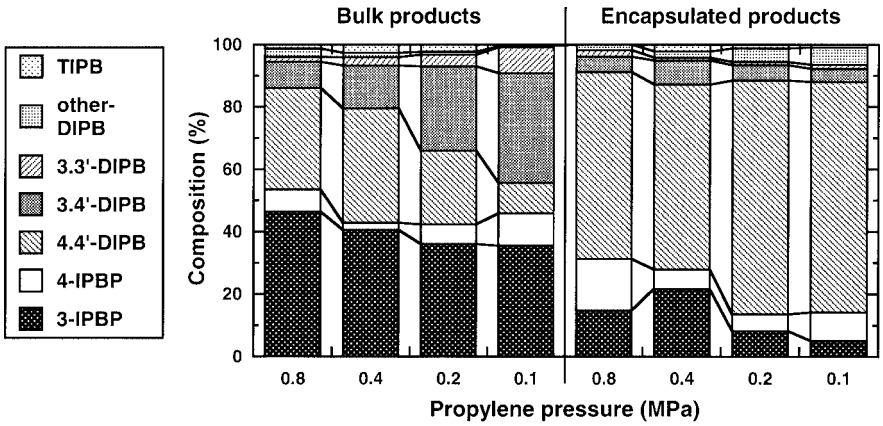
ratios, and their selectivities were *ca.* 80% even when the reaction started from initial 3-/4-IPBP ratio of *ca.* 4 : 1. These high selectivities in encapsulated products show that 4-IPBP was the exclusive precursor for 4,4′-DIPB and that selective formation of 4,4′-DIPB occurs inside the pore. 3-IPBP was found in considerable amount in encapsulated products, particularly when a mixture which contains 3-IPBP in the high ratio was used as substrate. However, the selectivity for 3,4′-DIPB was less than 10% in all encapsulated products. It means that the isopropylation of 3-IPBP does not occur significantly although 3-IPBP can enter HM pores. The low reactivity of 3-IPBP inside the pores is ascribed to the fact that the HM pore is too narrow to establish an active complex. Almost no further isopropylation of 4,4′-DIPB was observed in both bulk and encapsulated products in all mixtures. HM pores are too small to form polyisopropylbiphenyls (PIPBs), as discussed in previous papers [3–5].

Figure 3 shows the effect of reaction temperature on the isopropylation of an equimolar mixture of 3- and 4-IPBPs. The conversion of 3- and 4-IPBPs increased with the increase of temperature, and 4-IPBP was consumed much faster than 3-IPBP. 4,4′-DIPB was selectively formed at low to moderate temperatures; however, the selectivity of 4,4′-DIPB decreased with temperatures higher than 275 °C. The product composition of isopropylated BP derivatives inside pores was quite different from that of bulk products. The selectivity for 4,4′-DIPB was higher than 80% at all temperatures, even at such a high temperature as 300 °C. These results again show that the precursor of 4,4′-DIPB is 4-IPBP, and that 3-IPBP is not isopropylated effectively to DIPBs including 3,4′-DIPB, although 3-IPBP is found in considerable amounts in encapsulated products. These features are very similar to the isopropylation of BP [3,5]. The catalysis occurs inside HM pores to give 4,4′-DIPB shape-selectively at every temperature, whereas 4,4′-DIPB formed inside pores is isomerized at the external acid sites at higher temperatures.

Figure 4 summarizes the effect of propylene pressure on the isopropylation of an equimolar mixture of 3- and 4-IPBPs. The composition of bulk and encapsulated products shows similar features to the isopropylation of BP [3,4]; the selectivity for 4,4′-DIPB decreased with the decrease in propylene pressure, whereas the selectivity for 4,4′-DIPB in encapsulated product remained constant under every pressure, even under low pressure as 0.2 MPa. These results show that 4,4′-DIPB is formed exclusively from 4-IPBP under every pressure. The decrease of the selectivity under low pressure of propylene is due to the isomerization of 4,4′-DIPB to thermodynamically stable 3,4′-DIPB at the external acid sites [3,4].

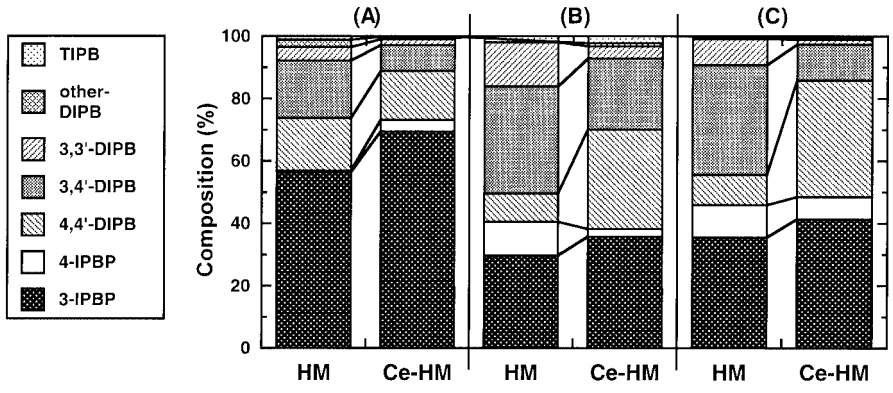
Figure 5 shows the effect of ceria-modification on the isopropylation of mixtures of 3- and 4-IPBPs. Ceria modification is an effective method to deactivate acid sites over external surface of HM [10]. The selectivity of 4,4′-DIPB increased from 47 to 68% in the isopropylation of initial 3-/4-IPBP ratio of 1 : 3. Similar improvement of the selectivity for 4,4′-DIPB was observed at high temperature and under low propylene pressure from an equimolar mixture of 3- and 4-IPBPs as shown in figure 5, and the selectivity of 3,3′- and 3,4′-DIPBs decreased significantly. The improvement resulted by the deactivation of external acid sites, as described in the previous paper [10].

The results of this work are in a good agreement with the features of the isopropylation of BP, in which 4,4′-DIPB was formed principally from 4-IPBP inside HM pores, and some of 3,4′-DIPB was formed from 3-IPBP at the external acid sites. The high reactivity of 4-IPBP, as compared to 3-IPBP, was due to the recognition of difference in bulkiness among IPBP isomers inside HM pores. These findings lead to the conclusion that both the *restricted transition state mechanism* and the *reactant selectivity mechanism* operate in



3-IPBP conversion(%)	17.4	19.1	27.9	30.3	--	--	--	--
4-IPBP conversion(%)	94.9	95.5	87.5	79.6	--	--	--	--
4,4'-DIPB selectivity(%)	69.4	67.3	42.7	18.1	79.8	84.8	87.9	86.9

Figure 4. Effects of propylene pressure on the isopropylation of an equimolar mixture of 3- and 4-IPBPs. Reaction conditions: 3- and 4-IPBPs (1 : 1) 100 mmol, HM(128) 1 g, temperature 250 °C, propylene 0.1–0.8 MPa, period 4 h.



3-IPBP conversion(%)	26.1	8.9	40.6	28.6	29.1	17.4
4-IPBP conversion(%)	97.8	84.0	78.4	95.0	79.2	85.7
4,4'-DIPB selectivity(%)	40.2	58.9	15.8	53.5	18.2	73.4

Figure 5. Effects of ceria modification of HM on the isopropylation of the mixture of 3- and 4-IPBPs. Reaction conditions: (A) 3- and 4-IPBPs (78 : 22) 100 mmol (total), HM(128) 1 g (as HM for Ce(30)HM(128)), temperature 250 °C, propylene 0.8 MPa, period 4 h. (B) 3- and 4-IPBPs (1 : 1) 100 mmol (total), HM(128) 1 g (as HM for Ce(30)HM(128)), temperature 300 °C, propylene 0.8 MPa, period 4 h. (C) 3- and 4-IPBPs (1 : 1) 100 mmol (total), HM(128) 1 g (as HM for Ce(30)HM(128)), temperature 250 °C, propylene 0.1 MPa, period 4 h.

this isopropylation reaction. The former mechanism works in the first step of the isopropylation: 4-IPBP is predominantly formed because it has the smallest transition state among IPBP isomers. Both mechanisms work in the second step from IPBPs to DIPBs; 4-IPBP becomes the precursor to DIPBs because it is the least bulky among IPBP isomers, yielding 4,4′-DIPB because it forms the smallest transition state with propylene and acid sites inside pores. On the other hand, the *product selectivity mechanism* does not operate in the isopropylation of BP. If it operated, the isomer compositions in encapsulated products should be in equilibrium, or at least the selectivity for 4,4′-DIPB in encapsulated products should be much lower than that in bulk products because only the less bulky products, 4-IPBP and/or 4,4′-DIPB come out to the bulk products.

4. Conclusion

The isopropylation of BP over HM occurs shape-selectively to yield 4,4′-DIPB. 3- and 4-IPBPs are considered to be key intermediates in the isopropylation. We examined the isopropylation of mixtures of 3- and 4-IPBPs over a dealuminated HM to elucidate their roles in the isopropylation of BP.

The initial rate of 4-IPBP was ten times faster than that of 3-IPBP. This is one of the major reasons for the shape-selective catalysis. 4-IPBP was almost exclusive precursor to DIPBs, particularly 4,4′-DIPB. 4,4′-DIPB was always found with high selectivity in encapsulated products. This is a second indication for shape-selective catalysis. Only 4-IPBP can form an active complex with propylene and acid

site in HM pores, whereas 3-IPBP cannot. These shape-selective reactions occur through the *restricted transition state mechanism* and through the *reactant selectivity mechanism*. On the other hand, the *product selectivity mechanism* does not operate in the isopropylation of BP over HM.

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