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The isopropylation of biphenyl over H-mordenite - Roles of 3- and 4-isopropylbiphenyls

Chokkalingam Anand*, Tomonori Sugimura, Kenichi Komura**, Yoshihiro Kubota**, Jong-Ho Kim***, Gon Seo***, Ajayan Vinu*,†, and Yoshihiro Sugi*,**,†**

*The Australian Institute of Bioengineering and Nanotechnology,
The University of Queensland, Brisbane, 4072 QLD, Australia
**Department of Materials Science and Technology, Faculty of Engineering, Gifu University, Gifu 501-1193, Japan
***School of Applied Chemical Engineering, Chonnam National University, Gwangju 500-757, Korea
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Abstract−The isopropylation of biphenyl (BP) and 3- and 4-isopropylbiphenyls (3- and 4-IPBPs) was examined over H-mordenites (MOR) to elucidate the mechanism of shape-selective formation of 4,4′-diisopropylbiphenyl (4,4′-DIPB). The isopropylation of BP occurred predominantly to form 4-isopropylbiphenyl (4-IPBP) from BP and 4,4′-DIPB from 4-IPBP. However, 3-IPBP, a minor isomer from BP, cannot participate effectively in the formation of 3,4′-DIPB due to steric restriction of its isopropyl moiety with MOR channels. Selective formation of 4,4′-DIPB was observed at low to moderate temperatures: 225-275 °C. However, the selectivities for 4,4′-DIPB were decreased at high temperatures, 300-350 °C under propene pressure, 0.8 MPa, by the isomerization of 4,4′-DIPB at external acid sites. The isomerization of 4,4′-DIPB occurred under low propene pressure even at 250 °C. The roles of 3- and 4-IPBPs in the formation of DIPB isomers were examined in the isopropylation of their mixtures. 4-IPBP was consumed much faster than 3-IPBP in all cases examined. 4-IPBP was an exclusive precursor to DIPB isomers, particularly 4,4′-DIPB. 4,4′-DIPB was also found as a predominant isomer in encapsulated products at all conditions examined. These results show that 4-IPBP can preferentially establish active transition state with propene and acid site in MOR channels, resulting in selective formation of 4,4′-DIPB. It is concluded that the isopropylation of BP over MOR occurs through reactant selectivity mechanism and restricted transition state mechanism, but not through product selectivity mechanism.

Key words: MOR, Isopropylation, Biphenyl, 4,4′-Diisopropylbiphenyl, 4- and 3-Isopropylbiphenyls, Shape-selective Catalysis

INTRODUCTION

Shape-selective catalysis over zeolites occurs by differentiating the shape and size of reactants, products, and/or reaction intermediates according to sterically restricted environment of the pore structures of zeolites [1,2], and it is the most promising way to synthesize symmetrically substituted polynuclear aromatics. H-Mordenite (MOR), particularly after dealumination, has been proposed as an effective catalyst for shape-selective isopropylation of biphenyl (BP) to 4,4′-diisopropylbiphenyl (4,4′-DIPB) [3-13].

We have been interested in why and how shape-selective catalysis occurs in the isopropylation of BP over MOR [3-9]. The isopropylation of BP proceeds by two consecutive reactions: IPBP isomers from BP and DIPB isomers from IPBP isomers. Shape-selective catalysis in MOR channels afforded the least bulky isomers, 4-IPBP from BP and 4,4′-DIPB from 4-IPBP.

We have proposed that two types of mechanism, originally proposed by Csicsery [1], operate in these catalyses [3-9]. The first mechanism is a restricted transition state mechanism; it works in the first step of the isopropylation of BP to 4-isopropybiphenyl (4-IPBP), and in the second step of 4-IPBP to 4,4′-DIPB. Second mechanism is a reactant selectivity mechanism; it works to select 4-IPBP as a preferential precursor of 4,4′-DIPB in the second step. 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 examine the isopropylation of BP, particularly focusing on the roles of 3- and 4-IPBPs by starting from BP and mixtures of 3- and 4-IPBPs, and discuss their roles in the isopropylation of BP.

EXPERIMENTAL

1. Catalysts and Chemicals

H-Mordenites (MOR, SiO_2/Al_2O_3=128, 206, 220) were obtained from Tosoh Corporation, Tokyo, Japan, and calcined at 500-550 °C in an air stream just before use. BP, 4- and 3-IPBPs, and 4,4′-DIPB were purchased from Tokyo Kasei Kogyo Co., Ltd., Tokyo, Japan. 3-IPBP was a obtained as a mixture of 4-IPBP (3- : 4-=78 : 22). These reagents were used without further purification.

2. Isopropylation

The isopropylation was carried out in a 100-ml SUS-316 autoclave under propene pressure. Typical conditions are: 100 mmol of 3- and 4-IPBP mixture, 1 g of MOR, 0.8 MPa of propene pressure, 250 °C of temperature, and 4 h of operating period. An autoclave containing BP and MOR was purged with nitrogen before heating. After reaching reaction temperature, propene was introduced to the autoclave, and started the reaction with agitation. The pressure kept constant throughout the reaction. After cooling the autoclave, the catalysts were filtered off after the release of propene, and bulk prod-

†To whom correspondence should be addressed.
E-mail: ysugi@gifu-u.ac.jp, a.vinu@uq.edu.au
This article is dedicated to Prof. Gon Seo on the occasion of his retirement from Chonnam National University.

ucts were diluted with toluene. The products were analyzed by a Shimadzu gas chromatograph GC-14A or GC-18A equipped with an FID detector by using an Ultra-1 capillary column (25 m×0.2 mm; film thickness: 25 μm; Agilent Technologies Co. Ltd., MA, U.S.A.), and identified by a Shimadzu gas chromatograph-mass spectrometer GC-MS 5000 using the same column.

The analysis of encapsulated products in the catalyst used for the reaction was carried out as follows. The catalyst was filtered off, washed well with 200 ml of acetone, and dried at 110 °C for 12 h. A 50 mg of resulting catalyst was carefully dissolved using a 1 ml of aqueous hydrofluoric acid (47%) at room temperature. This solution was basified with solid potassium carbonate, and organic layer was extracted three times with 20 ml of dichloromethane. After removal of the solvent *in vacuo*, the residue was dissolved in 0.5 ml of toluene. GC analysis was done according to the same procedure for bulk products.

The yield of each product was calculated on the basis of the amount of starting BP and 3- and 4-IPBPs, where the GC sensitivities were normalized by their carbon numbers. The selectivities for each IPBP and DIPB isomer were calculated based on total amounts of IPBP and DIPB isomers, respectively. The composition of the bulk and encapsulated products was expressed on the mole basis of all products for the isopropylation of the mixtures of 3- and 4-IPBPs.

RESULTS AND DISCUSSION

1. The Isopropylation of BP

Fig. 1 shows a reaction profile of the isopropylation of BP based on BP conversion over MOR (SiO_2/Al_2O_3=220) at 250 °C under a propene pressure of 0.8 MPa. The isopropylation gave 4,4′- and 3,4′-DIPB as principal DIPB isomers, particularly the least bulky isomers 4,4′-DIPB, throughout the reaction. The formation of 4-IPBP was predominant in early stages, maximized at around 40-60% of BP conversion, and then decreased in later stages. However, the formation of 3-IPBP increased spontaneously with the conversion. These results show that the formation of 4,4′-DIPB occurred with the consumption of 4-IPBP and the accumulation of 3-IPBP. The selectivities for 4,4′-DIPB were almost constant during the reaction. The selectivities for 4-IPBP also remained constant at early stages: 4-IPBP steadily formed from BP and consumed by the formation of 4,4′-DIPB. However, they decreased rapidly at later stages, probably due to the consumption of 4-IPBP. Highly selective formation of 4,4′-DIPB shows that the isopropylation proceeds by a consecutive mechanism: BP to 4-IPBP in the first step, and 4-IPBP to 4,4′-DIPB in the second step. The selectivity for 4,4′-DIPB was around 80-85% during the catalysis; however, the selectivity for 4-IPBP was around 70% in the early stage of the catalysis. These differences are due to isopropyl moiety in 4-IPBP. The isopropyl moiety enhances the formation of the least bulky 4,4′-DIPB in the second step.

These results indicate that the isopropylation of BP over MOR at a moderate temperature and a propene pressure occurs by shape-selective catalysis to yield predominantly the least bulky isomers, 4-IPBP among IPBP isomers, and 4,4′-DIPB among DIPB isomers. The predominant formation of 4-IPBP was due to bulkiness for transition states by restricted transition state mechanism, because 4-IPBP has the smallest restriction among IPBP isomers with MOR channels. The difference in reactivities between 3- and 4-IPBP shows the selection of 4-IPBP among IPBP isomers for the formation of DIPB isomers by reactant selectivity mechanism. The selective formation of 4,4′-DIPB was enhanced by the steric restriction of isopropyl moiety of 4-IPBP with MOR channels by restricted transition state mechanism.

Figs. 2, 3, and 4 show the influences of reaction temperature on the isopropylation of BP over MOR (SiO_2/Al_2O_3=206). The catalytic activity, *i.e.*, BP conversion, was increased with increase in reaction temperatures (Fig. 2). The formation of IPBP isomers decreased

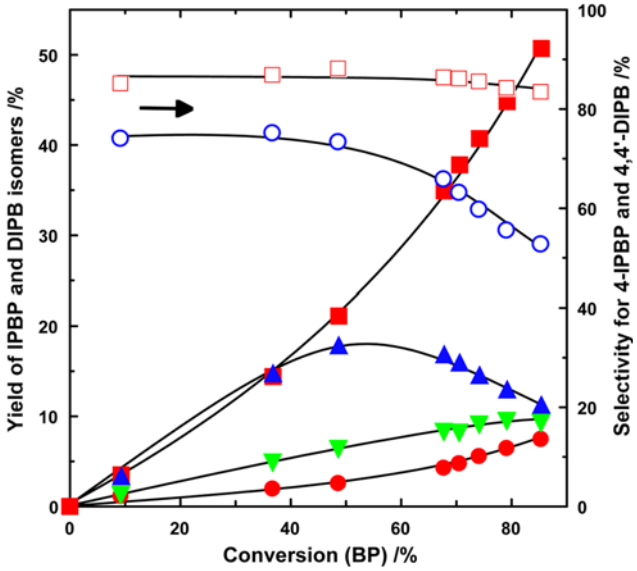


Fig. 1. Profiles of the isopropylation of BP over MOR. Reaction conditions: BP, 400 mmol; MOR (SiO_2/Al_2O_3=220), 2 g; temperature, 250 °C; propene pressure, 0.8 MPa. Legend: Yield; ■: 4,4′-DIPB; ●: 3,4′-DIPB; ▲: 4-IPBP; ▼: 3-IPBP; Selectivities: □: 4,4′-DIPB; ○: 4-IPBP.

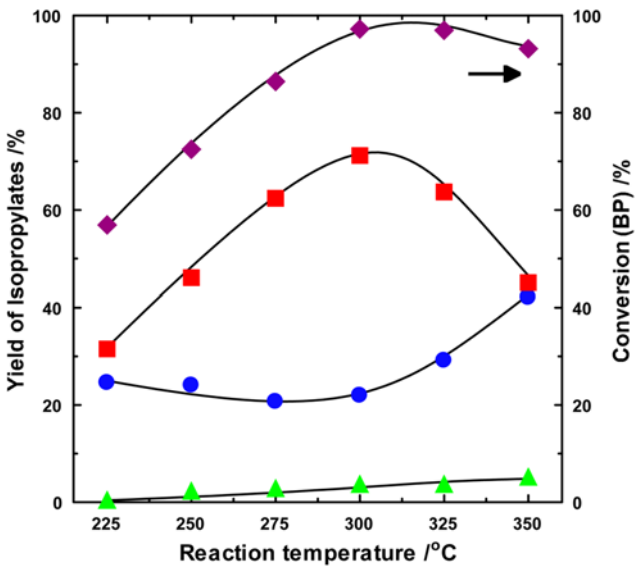


Fig. 2. The influence of reaction temperature on the catalytic activity in the isopropylation of BP. Reaction conditions: BP, 200 mmol; MOR (SiO_2/Al_2O_3=206), 1 g; temperature: 225-350 °C; propene pressure, 0.8 MPa; period, 4 h. Legend: (a) ●: IPBP; ■: DIPB; ▲: TIPB; ◆: Conversion (BP).

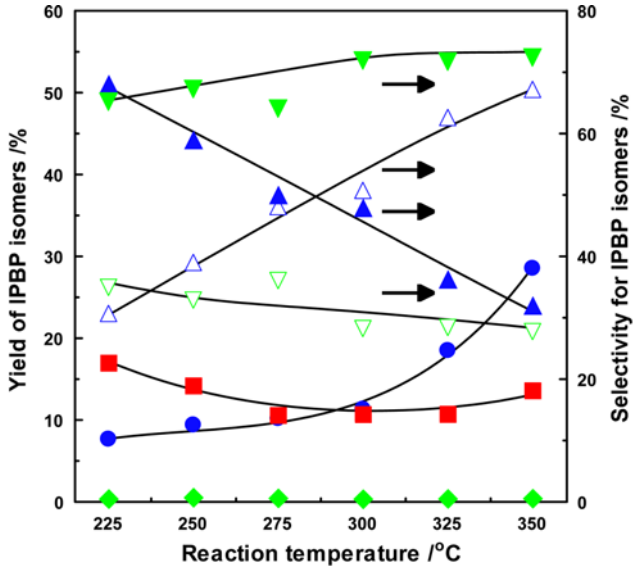


Fig. 3. The influence of reaction temperature on the yield and selectivity for IPBP isomers in the isopropylation of BP. Reaction conditions: see Fig. 2. Legends: ■: 4-IPBP; ●: 3-IPBP; ◆: 2-IPBP (Yields). ▲: 4-IPBP; △: 3-IPBP (Selectivity for bulk products); ▼: 4-IPBP; ▽: 3-IPBP (Selectivity for encapsulated products).

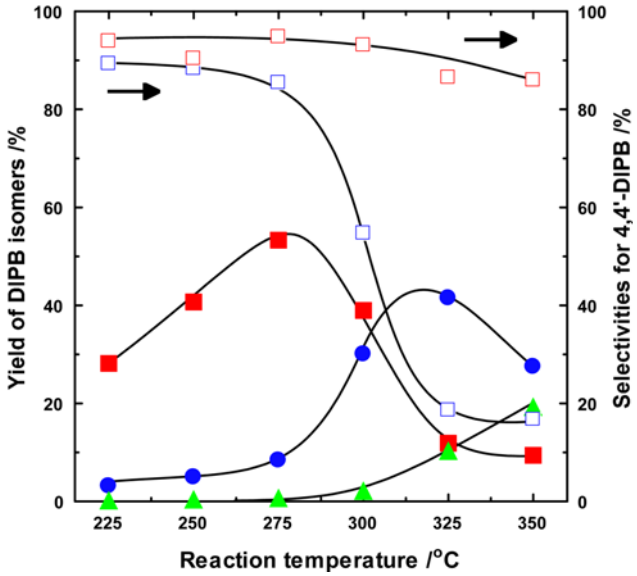


Fig. 4. The influencesof reaction temperature on the yield and selectivity for DIPB isomers in the isopropylation of BP. Reaction conditions: see Fig. 2. Legends: ■: 4,4′-DIPB; ●: 3,4′-DIPB; ▲: 3,3′-DIPB (Yield). □: 4,4′-DIPB (Selectivity for 4,4′-DIPB in bulk products); □: 4,4′-DIPB (Selectivity for 4,4′-DIPB in encapsulated products).

slightly with the increase in the temperatures, and increased rapidly above 300 °C. The yield of DIPB isomers also increased with increased temperature up to 300 °C; however, further increase in the temperature decreased the yield of DIPB isomers, accompanying the increased yield of IPBP isomers. The decrease in the yield of DIPB isomers at high temperatures was due to their de-alkylation. Further, the formation of triisopropylbiphenyls (TIPB) was increased with the increased temperature; however, remained in less than 5% yield.

Fig. 3 shows the influences of reaction temperature on the yield and selectivity for IPBP isomers in the isopropylation of BP. The yield of 4-IPBP was slightly decreased with the increase in the temperature: this is due to the steady formation and consumption by the formation of 4,4′-DIPB as discussed above. The yield of 3-IPBP increased spontaneously with the increase in the temperature, particularly above 300 °C; however, the yield of 4-IPBP was remained almost constant. This change of the yields were probably due to the de-alkylation of 4,4′-DIPB to IPBP isomers, particularly 3-IPBP, due to thermodynamic stability of these isomers. The formation of 2-IPBP was negligibly low at all temperatures.

The selectivities for 3- and 4-IPBP in bulk products were changed remarkably as shown in Fig. 3. The selectivities for 4-IPBP decreased spontaneously with the increased temperatures, accompanying the increase in those for 3-IPBP. However, the selectivities for 4- and 3-IPBP in encapsulated products remained almost constant with the increase in the temperature. These results indicate that shape-selective catalysis steadily occurred in the channels. The changes of the selectivities for 3- and 4-IPBP in bulk products were due to preferential consumption of 4-IPBP to 4,4′-DIPB at low and moderate temperatures, and due to the isomerization of 4-IPBP to more stable 3-IPBP at high temperatures.

Fig. 4 shows the influences of reaction temperature on the yield and selectivity for DIPB isomers in the isopropylation of BP. 4,4′-DIPB was the predominant isomer at low and moderate temperatures, and the yield reached a maximum at 275 °C. The further increase in temperature decreased the yield of 4,4′-DIPB with simultaneous increase in the yield of 3,4′-DIPB. The yield of 3,4′-DIPB was decreased with the increased temperatures at 325-350 °C, with the increase in the yield of 3,3′-DIPB. However, the selectivity for 4,4′-DIPB in encapsulated products remained high even at 350 °C. These results indicate that selective formation of 4,4′-DIPB occurred in the channels, and that 4,4′-DIPB isomerized to 3,4′- and 3,3′-DIPB at external acid sites, and not in the channels, probably due to no enough space for the isomerization in the channels. These results indicate that selective formation of 4,4′-DIPB occurred in the channels, and that 4,4′-DIPB isomerized to 3,4′- and 3,3′-DIPB at external acid sites, and not in the channels, probably due to no enough space for the isomerization in the channels. These discrepancies on the selectivity for 4,4′-DIPB between bulk and encapsulated products suggest that internal and external acid sites play different roles in the catalysis. Selective formation of 4,4′-DIPB occurs at internal acid sites due to steric restriction by the channels, and the prevention of non-selective catalyses, the isomerization and further isopropylation of 4,4′-DIPB at external acid sites, is important for selective formation of 4,4′-DIPB in the channels.

We consider that non-selective catalyses are prevented by the propene adsorbed on external acid sites. The propene strongly adsorbed on external acid sites disturbs the access of BP, IPBP, and DIPB isomers to the acid sites, and prevents non-selective reactions, particularly at the low and moderate temperatures. However, vacant external acid sites, no propene adsorbed, appear at higher temperatures, and 4,4′-DIPB can adsorb on these sites. Resultant 4,4′-DIPB adsorbed on the sites easily isomerizes to 3,4′- and 3,3′-

DIPB. On the other hand, the propene adsorbed in the channels cannot disturb the access of BP and IPBP isomers to the acid sites because of steric limitation of channels, resulting in shape-selective formation of 4,4′-DIPB in the channels.

It is important to know the effect of propene pressure on the catalysis for the clarification of roles of propene the acid sites. Fig. 5 shows the influences of propene pressure on the formation of IPBP, DIPB, and TIPB isomers based on BP conversion over MOR (SiO_2/Al_2O_3=220) at 250 °C. BP conversion reached more than 80% within 800 min, and the yields of the products are on the same plot under all pressures. The results indicate that the isopropylation of BP proceeded by successive addition of propene: BP to IPBP isomers, and IPBP isomers to DIPB isomers, and the change of product distribution shown below occurs after the formation of DIPB isomers in the channels.

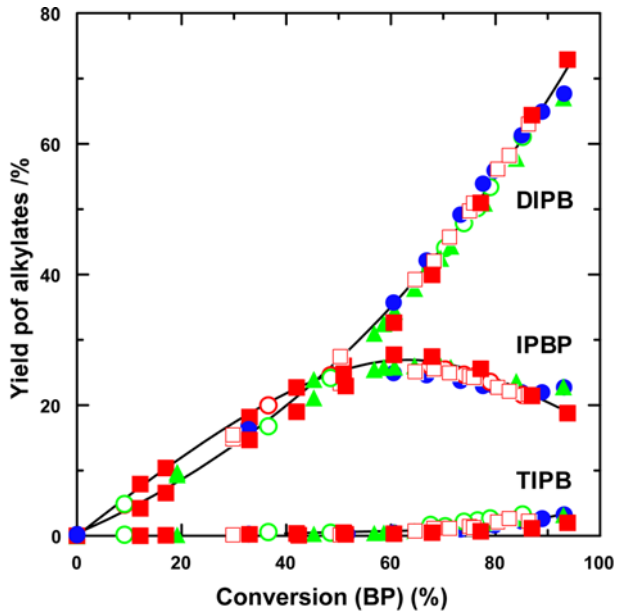


Fig. 5. The influence of propene pressure on the yield of isopropylates in the isopropylation of BP based on the BP conversion. Reaction conditions: BP, 400 mmol; MOR (SiO_2/Al_2O_3 =220), 2 g; temperature: 250 °C; propene pressure, 0.1-0.8 MPa; period, 4 h. Legend: ■: 0.1 MPa; ●: 0.2 MPa; ▲: 0.3 MPa; □: 0.6 MPa; ○: 0.8 MPa.

Fig. 6 shows the influences of propene pressure on the yield of IPBP isomers based on BP conversion. There was no significant influence of the propene pressure on the yield of IPBP isomers. The formation of 4-IPBP was more selective than that of 3-IPBP under these conditions. The yield of 4-IPBP reached a maximum at 50-60% conversion under all pressures, and decreased with further reaction. However, the yield of 3-IPBP increased spontaneously although saturated at higher conversions. The selectivity for 4-IPBP decreased with the increase in the conversion at all pressures. However, 2-IPBP was formed less than 1% under all pressures. These results indicate that 4-IPBP was selectively formed from BP, and that 4-IPBP works as a preferential precursor for the formation of DIPB isomers without the participation of 3-IPBP. It is interesting that the isomerization of 4-IPBP did not occur significantly even under low propene pressures although 4,4′-DIPB isomerized extensively as discussed below.

Fig. 7 shows the influence of propene pressure on the yields of 4,4′- and 3,4′-DIPB and the selectivity for 4,4′-DIPB based on the yield of DIPB isomers. The yield of 4,4′-DIPB increased with the yield of DIPB isomers under pressures higher than 0.3 MPa. However, the yield of 4,4′-DIPB deviated downwards under lower pressures as 0.1 and 0.2 MPa with upwards deviation of the yield of 3,4′-DIPB. Particularly, the yield of 4,4′-DIPB decreased after reaching a maximum at 60% of DIPB isomers under 0.1 MPa. The deviations of the formation of 4,4′-DIPB under low pressures accompanied

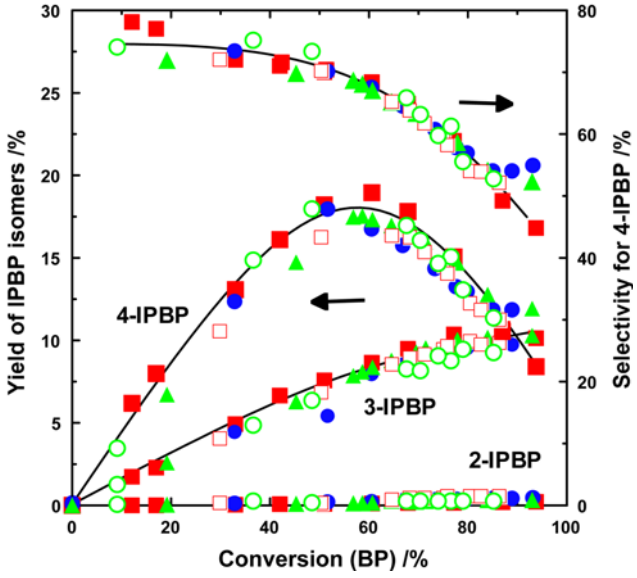


Fig. 6. The influence of propene pressure on the yield and selectivity for IPBP isomers in the isopropylation of BP based on the BP conversion. Reaction conditions: see Fig. 5. Legend: see Fig. 5.

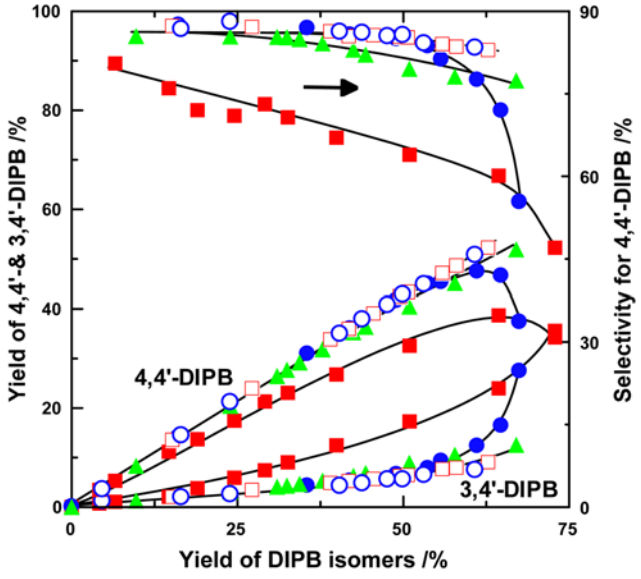


Fig. 7. The influence of propene pressure on the yield of 3,4′- and 4,4′-DIPB and selectivity for 4,4′-DIPB in the isopropylation of BP based on the BP conversion. Reaction conditions: see Fig. 5. Legend: See Fig. 5.

the decrease in the selectivities for 4,4′-DIPB. These deviations occurred after the formation of DIPB isomers including 4,4′-, 3,4′-, and 3,3′-DIPB because their combined yields were on the same lines as shown in Fig. 5 even under low pressures. These results indicate that the decreased yields of 4,4′-DIPB formed in the channels occurred by the isomerization of 4,4′-DIPB at external acid sites vacant for adsorption of propene under low pressure, and that adsorbed propene on the acid sites probably prevents non-selective catalysis, isomerization of 4,4′-DIPB and further isopropylation of 4,4′-DIPB, under high pressure.

These features in the isopropylation of BP shown in Figs. 1-7 indicate that 3- and 4-IPBPs work as the key intermediates during the catalysis. However, their yields during the catalysis are in too small amounts for understanding their roles in the catalysis. We were interested in the isopropylation of enhanced amounts of 3- and 4-IPBPs to clarify their roles in the isopropylation of BP. Therefore, we examined the isopropylation of mixtures of 3- and 4-IPBPs.

2. The Isopropylation of 3- and 4-IPBPs

Fig. 8 shows the influence of reaction period on the isopropylation of an equimolar mixture of 3- and 4-IPBPs over MOR (SiO_2/Al_2O_3=128) at 250 °C under 0.8 MPa of propene pressure. 4-IPBP was much more reactive than 3-IPBP. 70% of 4-IPBP was con-

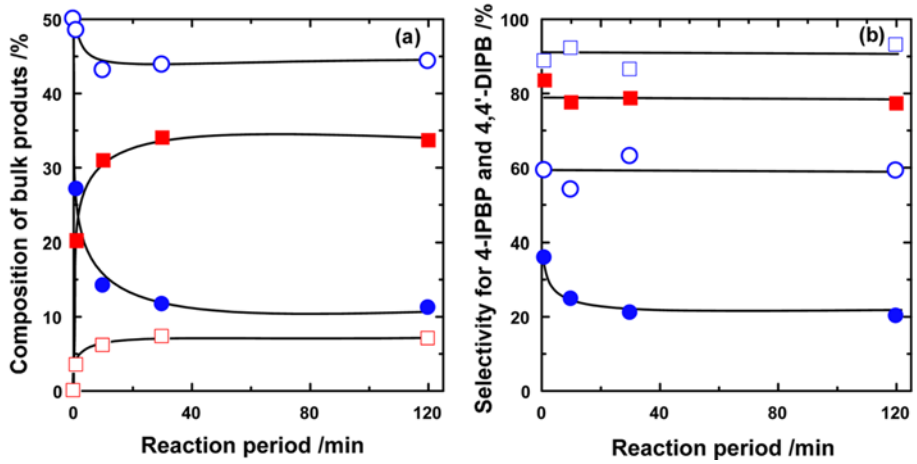


Fig. 8. The influence of reaction period on the isopropylation of an equimolar mixture of 3- and 4-IPBPs. (a) Composition of bulk products. (b) Selectivities for 4-IPBP and 4,4′-DIPB in bulk and encapsulated products. Reaction conditions: 3- and 4-IPBPs (1 : 1), 100 mmol (total); MOR (SiO_2/Al_2O_3=128), 1 g; propene, 0.8 MPa; temperature 250 °C. Legend: bulk products: ●: 4-IPBP; ○: 3-IPBP; ■: 4,4′-DIPB; □: 3,4′-DIPB. Selectivities for 4-IPBP and 4,4′-DIPB: ■: 4,4′-DIPB (bulk); □: 4,4′-DIPB (encapsulated); ●: 4-IPBP (bulk), ○: 4-IPBP (encapsulated).

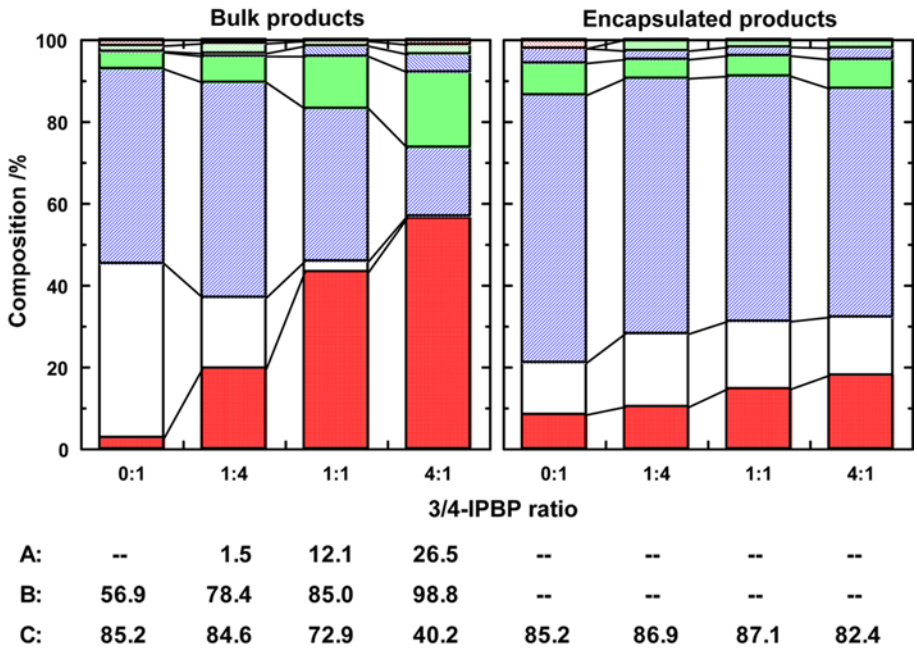


Fig. 9. The influence of initial 3-/4-IPBP ratio on the isopropylation of the mixture of 3- and 4-IPBPs. A: Conversion of 3-IPBP/%; B: Conversion of 4-IPBP/%; C: Selectivities for 4,4′-DIPB/%. Reaction conditions: 3- and 4-IPBPs, 100 mmol (total); MOR (SiO_2/Al_2O_3=128), 1 g; temperature, 250 °C; propene pressure, 0.8 MPa; period, 4 h. Legend: ■: 3-IPBP; □: 4-IPBP; ■: 4,4′-DIPB; ■: 3,4′-DIPB; ■: 3,3′-DIPB; ■: other DIPB isomers; ■: TIPB.

sumed in initial 10 min; however, only 7% of 3-IPBP was consumed during the period. The results mean that there is about a ten times difference in initial reactivity between these two isomers. After initial rapid reaction over fresh catalysts, the isopropylation slowed down gradually and saturated with reaction period.

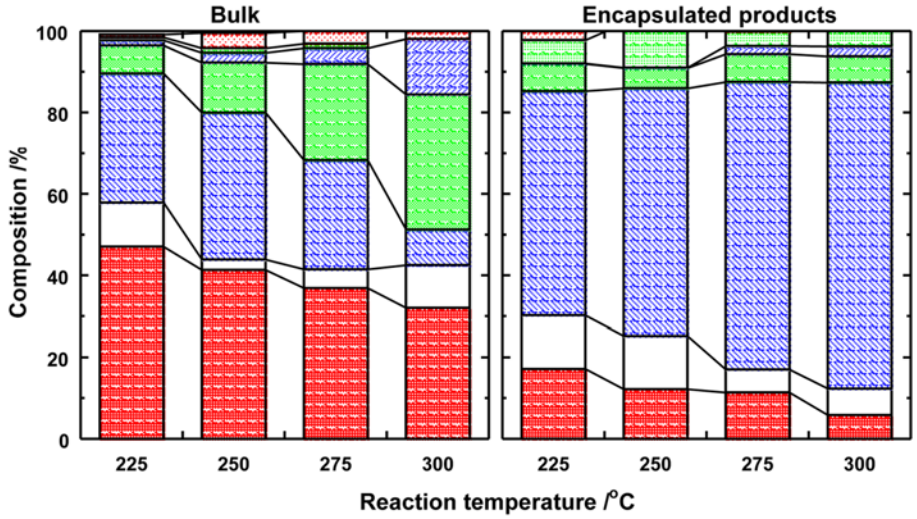
The selectivities for 4,4′-DIPB in both bulk and encapsulated products were high and constant during the reaction. The selectivities for 4-IPBP in encapsulated products were almost constant; however, the selectivities for 4-IPBP in bulk products decreased rapidly during the reaction. These results show that steady shape-selective catalysis occurred in the channels by a consecutive mechanism as suggested in previous section: 4-IPBP yields 4,4′-DIPB regio-selectively. However, 3-IPBP, a minor isomer in IPBP isomers, was not so reactive for the formation of DIPB because the selectivities for 4,4′-DIPB in encapsulated products were higher than those in bulk products. However, some of 3-IPBP participates in the isopropylation; however, its principal reaction sites should not be in the channels, but at external acid sites.

Fig. 9 summarizes the influences of ratios of 3- and 4-IPBPs on their isopropylation over MOR (SiO_2/Al_2O_3=128) at 250 °C under 0.8 MPa of propene. The conversions of 4-IPBP were much higher than those of 3-IPBP for all ratios. 4-IPBP afforded predominantly 4,4′-DIPB, even started from 3- and 4-IPBPs with the ratio of 1 : 4, while 3-IPBP was slowly consumed. The selectivities for 4,4′-DIPB of bulk products were decreased with increasing the ratio of 3-IPBP, resulting in the increase in the selectivities for 3,4′-DIPB. The conversion of 3-IPBP and the selectivities for 3,4′-DIPB increased with the increase in the ratio of 3-IPBP. Thus, 3,4′-DIPB was principally formed at external acid sites from 3-IPBP rich mixtures. These results mean that 3-IPBP participated in the isopropylation of BP after consuming of 4-IPBP at the late stages.

4,4′-DIPB was obtained as a predominant isomer in encapsulated products for all ratios of 3- and 4-IPBPs, and its selectivities were higher than 80% even from 3-IPBP rich mixtures. These high selectivities show that 4-IPBP works as an almost exclusive precursor for DIPB isomers, particularly 4,4′-DIPB, and that selective formation of 4,4′-DIPB occurs in the channels. 3-IPBP was found in considerable amount in encapsulated products, particularly, from 3-IPBP rich mixtures. However, the selectivities for 3,4′-DIPB were less than 10-18% in all encapsulated products. It means that the isopropylation of 3-IPBP does not occur effectively in the channels. The low reactivity of 3-IPBP is ascribed to the fact that MOR channels are too narrow to establish active transition states of 3,4′-DIPB due to its isopropyl moiety. These results of encapsulated products indicate that the formation of 3,4′-DIPB in bulk products from 3-IPBP rich mixtures occurs at external sites by the isopropylation of 3-IPBP in addition to minor formation of 3,4′-DIPB from 4-IPBP in the channels. Further, almost no isopropylation of 4,4′-DIPB to TIPB and higher products was observed in both bulk and encapsulated products for all mixtures under the conditions.

Fig. 10 shows the influences of reaction temperature on the isopropylation of an equimolar mixture of 3- and 4-IPBPs over MOR (SiO_2/Al_2O_3=128) under 0.8 MPa of propene pressure. The conversion of 3- and 4-IPBPs increased with the increase in the temperature, and 4-IPBP was consumed much faster than 3-IPBP. 4,4′-DIPB was formed selectively from 4-IPBP at low to moderate temperatures. The selectivities for 4,4′-DIPB decreased at the temperatures higher than 275 °C due to the isomerization of 4,4′-DIPB to 3,4′- and 3,3′-DIPB at external acid sites. However, some of 3,4′- and 3,3′-DIPB were possibly formed from 3-IPBP at external acid sites, particularly at high temperatures.

Encapsulated products had quite different features from bulk products. The selectivities for 4,4′-DIPB were higher than 80% at all temperatures, even at 300 °C. These results also indicate that 4-IPBP



A:	10.7	17.4	27.0	42.5	--	--	--	--
B:	78.3	94.9	90.8	90.8	--	--	--	--
C:	78.2	69.4	48.4	15.8	81.5	79.2	85.0	84.8

Fig. 10. The influence of reaction temperature on the isopropylation of an equimolar mixture of 3- and 4-IPBPs. A: Conversion of 3-IPBP/%; B: Conversion of 4-IPBP/%; C: Selectivities for 4,4′-DIPB/%. Reaction conditions: 3- and 4-IPBPs (1 : 1), 100 mmol; MOR (SiO_2/Al_2O_3=128), 1 g; temperature, 225-300 °C; propene, 0.8 MPa; period, 4 h. Legend: see Fig. 9.

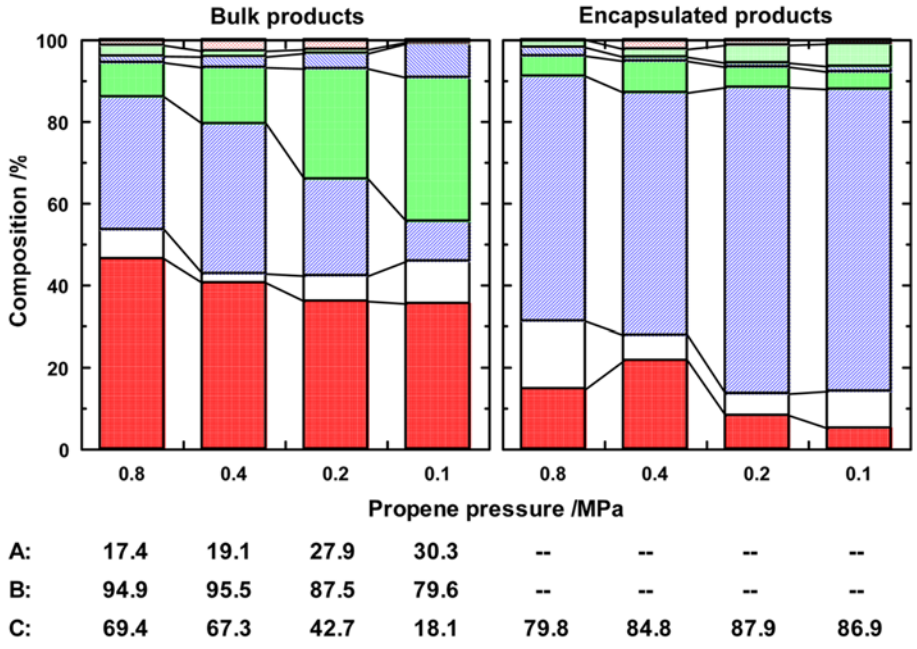


Fig. 11. The influence of propene pressure on the isopropylation of an equimolar mixture of 3- and 4-IPBPs. A: Conversion of 3-IPBP/%; B: Conversion of 4-IPBP/%; C: Selectivities for 4,4′-DIPB/%. Reaction conditions: 3- and 4-IPBPs (1 : 1), 100 mmol; MOR (SiO_2/Al_2O_3=128), 1 g; temperature, 250 °C; propene, 0.1-0.8 MPa; period, 4 h. Legend: see Fig. 9.

works as an almost exclusive precursor of 4,4′-DIPB, and that 3-IPBP does not participate effectively in the formation of DIPB isomers including 3,4′-DIPB, although 3-IPBP was found in considerable amounts in encapsulated products. Thus the isopropylation of 4-IPBP occurred in the channels, resulting in shape-selective formation of 4,4′-DIPB at all temperatures, and in the isomerization of 4,4′-DIPB at external acid sites at higher temperatures.

Fig. 11 shows the influences of propene pressure on the isopropylation of an equimolar mixture of 3- and 4-IPBPs over MOR (SiO_2/Al_2O_3=128) at 250 °C. Product composition of bulk products shows similar features to the isopropylation of BP as discussed in Figs. 5-7: the selectivity for 4,4′-DIPB decreased with the decrease in propene pressure due to the isomerization under low propene pressures. However, the selectivities for 4,4′-DIPB in encapsulated product remained constant under all pressures, even 0.2 MPa. These results show that 4,4′-DIPB was formed exclusively from 4-IPBP in the channels under all propene pressures, and that 4,4′-DIPB isomerized to 3,4′-DIPB at external acid sites under low propene pressures. The conversion of 3-IPBP increased at lower pressures, although those of 4-IPBP decreased. These differences suggest that the isopropylation of 3-IPBP occurred at vacant external acid sites, resulting in the non-selective catalysis.

3. Role of 3- and 4-IPBPs in the Isopropylation of BP

MOR channels work as efficient nano-sized reactor for the isopropylation of BP, leading to highly selective formation of 4,4′-DIPB. The catalysis occurs in consecutive reaction steps, selective formation of BP to 4-IPBP and 4-IPBP to 4,4′-DIPB. BP afforded 4-IPBP as a predominant isomer in the first step. 4-IPBP works as an almost exclusive precursor to DIPB isomers among IPBP isomers in the second step. The formation of 4,4′-DIPB occurred more selectively compared to the first step from BP to 4-IPBP. These results indicate that the isopropyl moiety of 4-IPBP enhances the formation of 4,4′-DIPB by its restriction with the channels, leading to the higher selectivity for 4,4′-DIPB from 4-IPBP compared to 4-IPBP from BP. However, 3-IPBP cannot establish effectively the transition state to 3,4′-DIPB by severe steric restriction of its isopropyl moiety with the channels. However, the roles of 3- and 4-IPBP still remain unclear from the results of the isopropylation of BP because they were observed only in low amounts.

Our findings in the isopropylation of mixtures of 3- and 4-IPBPs clearly indicate that 4-IPBP had much higher reactivity than 3-IPBP: the initial rate of 4-IPBP was ten times faster than that of 3-IPBP, resulting in selective formation of 4,4′-DIPB even from 3-IPBP rich mixtures. The occurrence of the formation of 4,4′-DIPB in the channels is clearly shown by high selectivities for 4,4′-DIPB in encapsulated products at all conditions, even at high temperatures, under low propene pressures, and/or starting from 3-IPBP rich mixtures. These results mean that only 4-IPBP can exclusively form an active transition state with propene and acid site in the channels, resulting in selective formation of 4,4′-DIPB. 3-IPBP was found in considerable amount in encapsulated products, particularly from the mixtures rich in 3-IPBP. However, the selectivity for 3,4′-DIPB was less than 10-18% in all encapsulated products. It means that 3-IPBP cannot establish effective transition state to DIPB isomers due to severe steric restriction of its isopropyl moiety with the channels. These features of the isopropylation of 3- and 4-IPBPs agree well with the features of the isopropylation of BP.

The selectivities for 4,4′-DIPB decreased at high temperatures and under low propene pressures in the isopropylation of mixtures of 3- and 4-IPBPs; however, the selectivity for 4,4′-DIPB in encapsulated products remained high at all conditions, including the products started from the 3-IPBP rich mixtures. The results clearly indicate that 4,4′-DIPB was formed in the channels, and that the decrease in the selectivities for 4,4′-DIPB, thus formed, is due to the

isomerization of 4,4′-DIPB to 3,4′- and 3,3′-DIPB at external acid sites. The isomerization of 4,4′-DIPB on external acid sites are disturbed by the adsorbed propene on them particularly at the low and moderate temperatures. However, vacant external acid sites, no propene adsorbed, appear at higher temperatures and/or under low propene pressures. 4,4′-DIPB, adsorbed on these sites, isomerized to 3,4′- and 3,3′-DIPB; the decrease in the selectivity for 4,4′-DIPB is not due to the decrease in the shape-selectivity of the channels.

Three types of mechanism of shape-selective catalyses, restricted transition state mechanism, reactant selectivity mechanism, and product selectivity mechanism, were proposed by Sciscsery [1] and modified by us [3,5]. They depend on whether the pore size limits the entrance of reactant molecules, the departure of product molecules, or the formation of certain transition states. Our findings in this work lead to the conclusion that both restricted transition state mechanism and reactant selectivity mechanism operate in the isopropylation of BP over MOR. The former mechanism works in the first step of the isopropylation: 4-IPBP is predominantly formed from BP with accompanying 3-IPBP as a minor product due to restricted transition state mechanism, because 4-IPBP has smaller transition state from BP. Both mechanisms work in the second step from IPBP isomers to DIPB isomers: 4-IPBP, the least bulky among IPBP isomers, works as a precursor to DIPB isomers by reactant selectivity mechanism, and yields 4,4′-DIPB in high selectivity by restricted transition state mechanism, because it forms the smallest transition state with propene and acid sites in the channels. On the other hand, product selectivity mechanism does not operate in the isopropylation of BP. If it operates, 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 least bulky products, 4-IPBP and/or 4,4′-DIPB, come out to the bulk products.

CONCLUSION

The isopropylation of biphenyl (BP) and 3- and 4-isopropylbiphenyls (3- and 4-IPBPs) was examined over H-mordenites (MOR) to elucidate the mechanism of shape-selective formation of 4,4′-diisopropylbiphenyl (4,4′-DIPB) in the isopropylation of BP. The isopropylation of BP proceeded predominantly to form 4-IPBP from BP and 4,4′-DIPB from 4-IPBP. However, 3-IPBP cannot participate effectively in the formation of 3,4′-DIPB due to steric restriction with MOR channels with its isopropyl moiety.

Selective formation of 4,4′-DIPB was observed at low to moderate temperatures, 225-275 °C. However, the selectivities for 4,4′-DIPB were decreased at high temperatures, 300-350 °C under propene pressure, 0.8 MPa, by the isomerization of 4,4′-DIPB at external acid sites. The isomerization of 4,4′-DIPB occurred under low propene pressure even at 250 °C.

4-IPBP had much higher reactivity than 3-IPBP in the isopropylation of mixtures of 3- and 4-IPBPs: the initial rate of 4-IPBP was ten times faster than that of 3-IPBP, resulting in selective formation of 4,4′-DIPB even 3-IPBP rich mixtures. These results mean that 4-IPBP can preferentially form an active transition state with propene and acid site in MOR channels, resulting in selective formation of 4,4′-DIPB. 3-IPBP cannot establish effective transition state of 3,4′-DIPB due to severe steric restriction of its isopropyl moiety with the channels although 3-IPBP was found in considerable amount in encapsulated products.

These shape-selective catalyses occur through restricted transition state mechanism and through reactant selectivity mechanism. On the other hand, product selectivity mechanism does not operate in the isopropylation of BP over MOR. Shape selective formation of 4,4′-DIPB occurred exclusively from 4-IPBP due to the selection of the smallest 4-IPBP among the isomers, and to the least bulky transition state from 4-IPBP in MOR channels.

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