Journal of Molecular Catalysis A: Chemical 304 (2009) 22–27

Contents lists available at ScienceDirect

Journal of Molecular Catalysis A: Chemical

journal homepage: www.elsevier.com/locate/molcata

The isomerization of 4,4′-diisopropylbiphenyl at external acid sites of H-mordenite during the isopropylation of biphenyl

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ARTICLE INFO

Article history:
Received 29 February 2008
Received in revised form 13 January 2009
Accepted 14 January 2009
Available online 21 January 2009

Keywords:
H-mordenite
External acid sites
Biphenyl
Isopropylation
Isomerization
4,4′-Diisopropylbiphenyl

ABSTRACT

The roles of internal and external acid sites of a dealuminated H-mordenite (MOR; $SiO_2/Al_2O_3 = 128$) on the selectivity for 4,4′-DIPB in the isopropylation of biphenyl (BP) are examined by changing catalyst amount. The isopropylation of BP gave high selectivity for 4,4′-DIPB at such a low temperature as 200 °C even by using large amounts of the catalyst; however, the decrease in the selectivity for 4,4′-DIPB, which accompanies the increase in the selectivity for 3,4′- and 3,3′-DIPB, occurred at such a high temperature as 300 °C, and started at lower temperatures with increasing catalyst amount. However, 4,4′-DIPB was highly selective in encapsulated products under all the conditions. These results indicate that shape-selective catalysis occurs inside MOR channels irrespective of reaction conditions, such as catalyst amount and/or reaction temperature, and that the decrease in the selectivity for 4,4′-DIPB is due to the isomerization of 4,4′-DIPB to thermodynamically stable 3,4′- and 3,3′-DIPB at external acid sites.

1. Introduction

Several researchers have attention to shape-selective catalysis for the alkylation of polynuclear aromatics such as the isopropylation of biphenyl (BP) [1–6] and naphthalene (NP) [1,7–14]. We found that a highly selective synthesis of 4,4′-diisopropylbiphenyl (4,4′-DIPB) are achieved in the isopropylation of BP over H-mordenite [1–5]. Lee et al. also reported that dealuminated H-mordenite with a high SiO_2/Al_2O_3 ratio (∼2600) is very active for the isopropylation of BP to give selectively 4,4′-DIPB [6], because the dealumination not only reduces the number of acid sites, but also increases mesopore volume [6,15]. From these results, we proposed that the selectivity in zeolite catalysis is controlled by steric restriction of transition state composed of substrates and acid sites in sterically restricted zeolite channels [1–6].

Acid sites of zeolites exist mainly inside the pores, and some of them are on the external surface. The reactions on external surface are generally governed by kinetic and/or thermodynamic controls to produce non-regioselective mixtures of isomers, and their rates are more rapid than those inside the pores [16,17]. Several other reports described the decrease in the selectivity for the catalysis by the non-regioselective reactions and the isomerization of products at external acid sites over zeolites [18,19]. The deactivation of external acid sites is essential for highly shape-selective catalysis [12,20–23]. The study on the external acid sites is an important key for the elucidation of their roles in the catalysis.

In this paper, we study the influence of external acid sites on the isopropylation of BP over a dealuminated H-mordenite (MOR; $SiO_2/Al_2O_3 = 128$) by changing the catalyst amount to clarify the relation between shape-selective formation of 4,4′-DIPB at internal acid sites and the isomerization of 4,4′-DIPB at external acid sites.

2. Experimental

2.1. Catalysts

Dealuminated H-mordenite (MOR; $SiO_2/Al_2O_3 = 128$; TSZ-690HOA) was obtained from Tosoh Corporation, Tokyo, Japan, and calcined at 550 °C during 5 h just before use.

2.2. Isopropylation of BP

The isopropylation of BP was carried out in a 100-ml SUS-316 autoclave using propene as an alkylating reagent. Standard conditions for the isopropylation were: 200 mmol (30.8 g) of BP, 0.05–5 g of MOR, 200–300 °C of temperature, 0.8 MPa of propene pressure, and 4 h of reaction period. The autoclave was purged

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doi:10.1016/j.molcata.2009.01.018

with nitrogen, and then heated to reaction temperature. Propene was supplied to the autoclave and kept at constant pressure throughout the reaction. The products were analyzed by gas chromatography using a Shimadzu GC-14A Gas Chromatograph (Ultra-1 capillary, 30 m × 0.2 mm, film thickness: 0.25 μm, Agilent Technologies), and identified by GC-Mass using a Shimadzu GC-MS5000 Gas Chromatograph–Mass Spectrometer by using the same column.

The yield of every product was calculated on the basis of BP used for the reaction; i.e. the selectivity for isomers of isopropylbiphenyl (IPBP) and diisopropylbiphenyl (DIPB) is expressed as a percentage of each IPBP and DIPB isomers among total IPBP and DIPB isomers for the isopropylation of BP, respectively.

Analysis of encapsulated products in the catalyst used for the reaction was typically carried out as follows. The catalyst, separated from organic products by filtration, was washed well with 200 mL of acetone, and dried at 110 °C for 12 h. A 50 mg sample of the resulting catalyst was carefully dissolved in 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 again dissolved in toluene (5 mL), and subjected to analysis by gas chromatography according to the same procedure as the analysis for bulk products. The selectivity for DIPB isomers of encapsulated products was calculated on the basis of product distribution, because it was difficult to analyze quantitatively the amounts of encapsulated products.

The isomerization of 4,4′-DIPB was carried in similar manner as the isopropylation of BP. The selectivity for DIPB isomers was calculated in the same manner as in the isopropylation of BP.

3. Results and discussion

3.1. The influence of catalyst amount on the isopropylation of BP

We previously found that the selective formation of 4,4′-DIPB occurs at low and moderate temperatures in the isopropylation of BP over H-mordenites, and that the selectivity for 4,4′-DIPB decreases at higher reaction temperatures. However, the selectivity for 4,4′-DIPB in encapsulated products remains high even at higher temperatures such as at 300 and 325 °C [1–5]. We proposed that the decrease is due to the isomerization of 4,4′-DIPB once formed in MOR channels [1–3,5]. The isomerization is due to the difference in thermodynamic stability among the isomers: 3,4′- and 3,3′-DIPB are more stable than 4,4′-DIPB [24]. The external surfaces bear active sites for the isomerization although they are much smaller than the internal surface. The number of the external acid sites is proportional to the external surface area, which can be changed by the catalyst amount. We examined to elucidate the role of external surface in the isomerization of 4,4′-DIPB during the isopropylation of BP by changing catalyst amount. The catalyst amount is expressed by BP/MOR (mmol/g) unless otherwise stated.

The influence of BP/MOR ratio on the isopropylation of BP over MOR at the reaction temperature: 200, 250, and 300 °C is shown in Fig. 1. Fig. 1a–c shows the influence of BP/MOR ratio on the conversion and the yield of isopropylates in bulk products. The conversion of BP was increased with the increase in catalyst amount (the decrease in BP/MOR ratio) at the all temperatures. Principal products are IPBP isomers for high BP/MOR ratios; however, the formation of DIPB was enhanced with the decrease in the ratio, accompanying the decrease of the yield of IPBP isomers at 200 and 250 °C. However, catalytic activities, particularly, the formation of

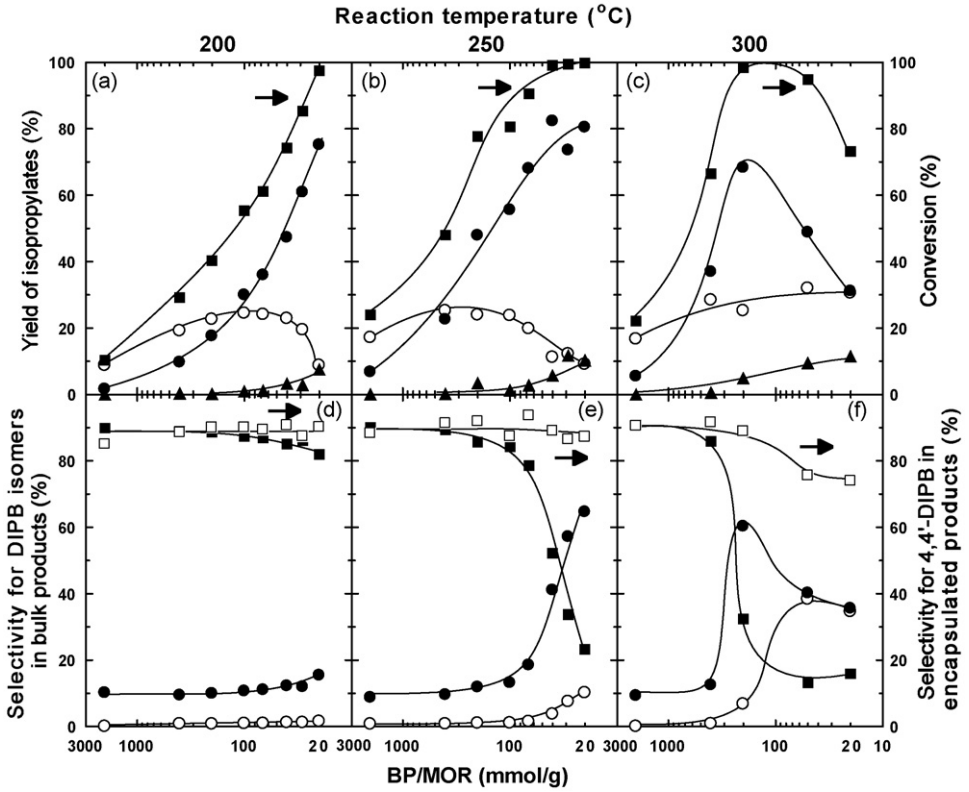

Fig. 1. The influence of catalyst amount on the isopropylation of BP at the reaction temperature: 200, 250, and 300 °C. (a)–(c) Conversion and yield of isopropylates in bulk products. (d)–(f) Selectivity for DIPB isomers in bulk and encapsulated products. Reaction conditions: BP, 100 mmol; MOR, 0.05–5 g (BP/MOR = 20–2000); temperature, 200, 250, and 300 °C; propene pressure: 0.8 MPa; period, 4 h. Legends: (a)–(c) ■: Conversion; ●: DIPB isomers; ○: IPBP isomers; ▲: TriIPB isomers. (d)–(f) ■: 4,4′-DIPB (bulk);●: 3,4′-DIPB (bulk); ○: 3,3′-DIPB (bulk); □: 4,4′-DIPB (encapsulated).

DIPB isomers, at 300 °C, were enhanced in relatively higher BP/MOR ratios (200–3000), and they decreased significantly for the ratio of 20–100 although the yield of IPBP isomers only increased gradually for all the BP/MOR ratios. The rapid decrease in catalytic activities is due to the de-alkylation and/or transalkylation of DIPB isomers, resulting in the decrease in the conversion of BP and the yield of DIPB isomers. The formation of triisopropylbiphenyl (TriIPB) isomers increased with the decrease in BP/MOR ratio at 200–300 °C.

The influence of BP/MOR ratio on the selectivity for DIPB isomers in the isopropylation is shown in Fig. 1d–f. The selectivities were influenced with the change of BP/MOR ratio at all reaction temperatures. The selectivity for 4,4′-DIPB at 200 °C was as high as 80–90% in the range of the BP/MOR ratio of 20–3000. However, rapid decrease in the selectivity for 4,4′-DIPB occurred at 250 and 300 °C with the decrease in the ratios (the increase in catalyst amount) although the selectivity is as high as 85–90% at BP/MOR above 800 for the all temperatures. The decrease in the selectivity for 4,4′-DIPB started at lower BP/MOR ratio with the increase in reaction temperature: 67 at 300 °C and 200 at 250 °C, accompanying the increase in those for 3,4′-DIPB under these conditions. Further, the selectivity for 3,3′-DIPB rapidly increased with the decrease in the ratio: 20–200 at 300 °C, accompanying the decrease in the selectivity for 3,4′-DIPB.

Features of the selectivity for 4,4′-DIPB in encapsulated products are quite different from those of bulk products. The selectivities for 4,4′-DIPB in encapsulated products were as high as 85–90% for all the BP/MOR ratios at 200 and 250 °C. They also remained higher than 75% at the ratios: BP/MOR = 20 and 50 even at 300 °C. These results mean that the formation of 4,4′-DIPB occurred inside MOR channels even at the low BP/MOR ratios such as 20, and that the isomerization of 4,4′-DIPB occurred at external acid sites.

Fig. 2 shows the influence of the catalyst amount (4,4′-DIPB/MOR ratio) on the isomerization of 4,4′-DIPB at 250 °C under 0.8 MPa of propene pressure. 4,4′-DIPB rapidly disappeared by the isomerization to 3,4′- and 3,3′-DIPB with the increase in catalyst amount (the low 4,4′-DIPB/MOR ratios) as shown in Fig. 2a; however, further isopropylation to TriIPB isomers or de-alkylation to IPBP isomers were not significant. The selectivity for 4,4′-DIPB was decreased corresponding to the increase in catalyst amount; however, the selectivity for 4,4′-DIPB in encapsulated products remains almost constant in the level of 90–95%. Theses results mean that the decrease in the selectivity for 4,4′-DIPB occurs at external acid sites as discussed on the isopropylation of BP.

Fig. 3 shows the influence of reaction temperature on the isopropylation of BP at the BP/MOR ratio: 50, 200, and 800. Fig. 3a–c shows the influence of reaction temperature on the conversion and yield of isopropylates in bulk products. Catalytic activities increased at all the ratios with the increase in reaction temperature. The yield of DIPB isomers was significantly increased with increasing the temperature, even at the higher ratios such as BP/MOR = 800. On the other hand, the yield of DIPB isomers was maximized at around 250–275 °C in the case of the lower ratios such as BP/MOR = 50, and, then, decreased with further increase in the reaction temperature, accompanying the decrease at 225–300 °C and the increase above 300 °C in the yield of IPBP isomers. The decrease of DIPB isomers at higher temperatures for BP/MOR = 50 is due to the de-alkylation of DIPB isomers. The formation of TriIPB isomers was not significant except the conditions at low BP/MOR and/or high temperatures because MOR channels are too small for the further isopropylation of DIPB isomers.

Selective formation of 4,4′-DIPB was observed in bulk products for all the BP/MOR ratios at low and moderate temperatures as shown in Fig. 3d–f. These results indicate that MOR channel has a highly shape-selective nature in the isopropylation of BP. However, the selectivity for 4,4′-DIPB was decreased at higher temperatures for all the BP/MOR ratios, accompanying the formation of 3,4′- and 3,3′-DIPB. The decrease in the selectivity for 4,4′-DIPB started at lower temperatures with the decrease in the BP/MOR ratio: 225–250 °C at 50, 275 °C at 200, and 300 °C at 800, accompanying the increase in the selectivity for 3,4′-DIPB, and 3,3′-DIPB appeared at higher temperatures around 300 °C. Particularly, the formation of 3,4′-DIPB occurred first at around 250 °C for BP/MOR = 50, and maximized at 275 °C. 3,3′-DIPB appeared by further increase in reaction temperatures above 300 °C, accompanying the decrease in the selectivity for 3,4′-DIPB.

The features of encapsulated products are quite different from those of bulk products in the isopropylation of BP, particularly by using large amounts of catalyst. The selectivity for 4,4′-DIPB in the isopropylation of BP was higher than 80% in encapsulated products at all the temperatures, irrespective of catalyst amounts, even for BP/MOR = 50. These results mean that the formation of 4,4′-DIPB occurred in MOR channels even at high temperatures such as 300

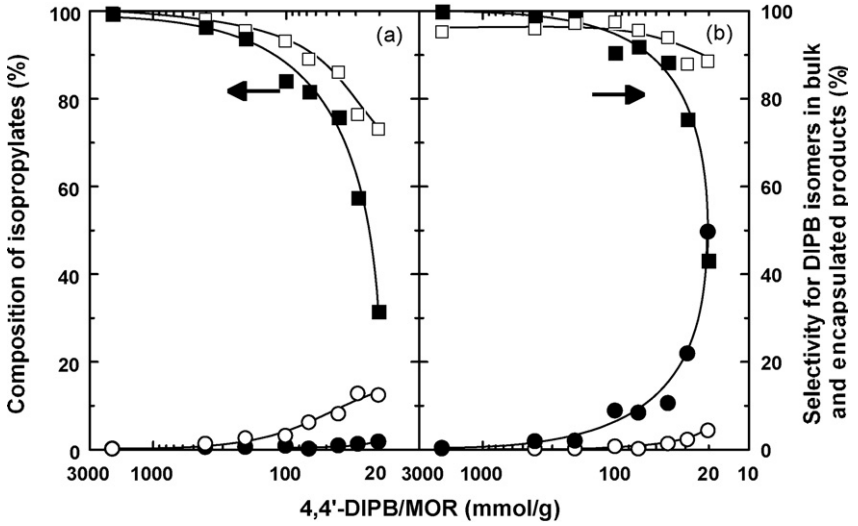

Fig. 2. The influence of catalyst amount on the isomerization of 4,4′-DIPB under propene pressure at 250 °C. (a) Conversion and yield of isopropylates. (b) Selectivity for DIPB isomers in bulk and encapsulated products. Reaction conditions: 4,4′-DIPB, 50 mmol; MOR, 0.025–2.5 g (4,4′-DIPB/MOR = 20–2000 mmol/4,4′-DIPB; temperature, 250 °C; propene pressure: 0.8 MPa; period, 4 h. Legends: (a) ■: 4,4′-DIPB; □: DIPB isomers except 4,4′-DIPB; ●:IPBP isomers; ○: TriIPB isomers. (b) ■: 4,4′-DIPB (bulk);●: 3,4′-DIPB (bulk); ○: 3,3′-DIPB (bulk); □: 4,4′-DIPB (encapsulated).

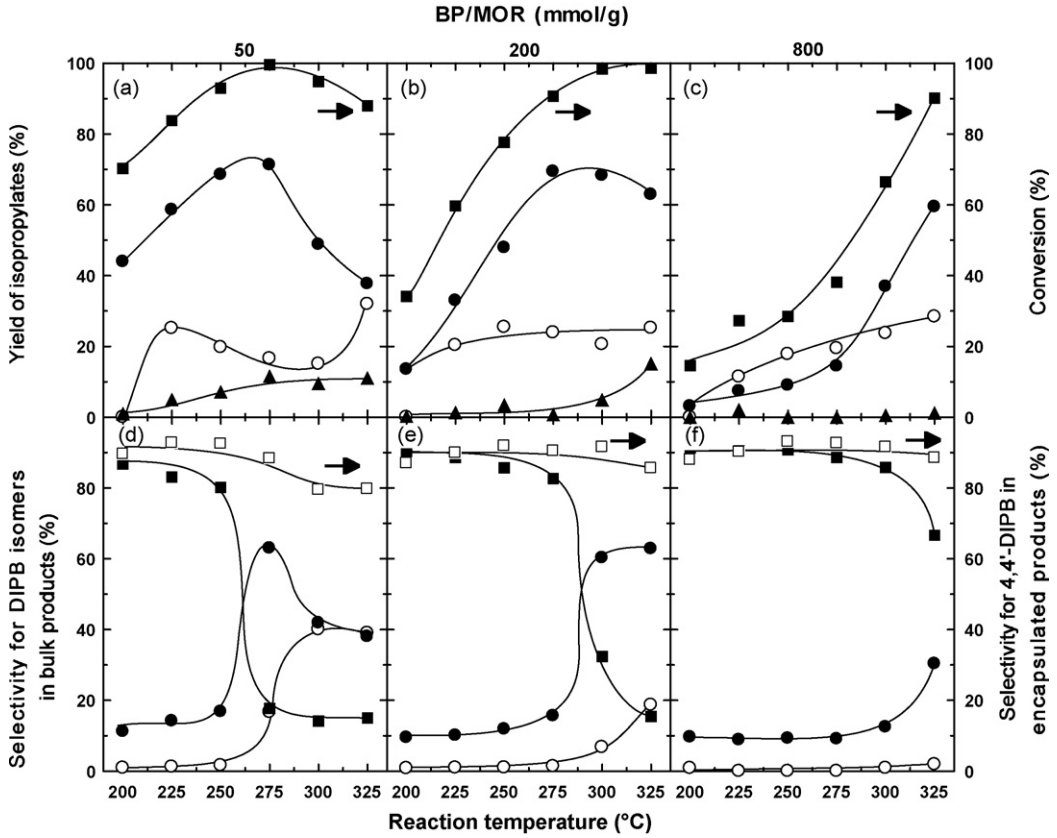

Fig. 3. The influence of reaction temperature on the isopropylation of BP at BP/MOR = 50, 200, and 800 mmol/g. (a)–(c) Conversion and yield of isopropylates in bulk products. (d)–(f) Selectivity for DIPB isomers in bulk and encapsulated products. Reaction conditions: BP: 100 mmol; MOR: 2, 0.5 and 0.125 g (BP/MOR = 50, 200, and 800 mmol/g); temperature: 200–325 °C; propene pressure: 0.8 MPa; period: 4 h. See legend in Fig. 1.

and 325 °C and at the low BP/MOR ratios such as 50 in the isopropylation of BP. However, the isomerization of 4,4′-DIPB occurs at the external acid sites, and not at the internal acid sites because of steric limitation inside the channels. The number of the external acid sites is proportional to the external surface area, which can be changed by the amount of MOR used. The increase in the external acid sites enhanced the isomerization of 4,4′-DIPB even at moderate temperatures such as 250 °C, and the decrease in catalyst amounts resulted in the decrease in the isomerization at any temperatures.

Fig. 4 shows the influence of reaction temperature on the isomerization of 4,4′-DIPB over MOR under 0.8 MPa of propene pressure at BP/MOR = 100. The decrease in 4,4′-DIPB occurred rapidly with the

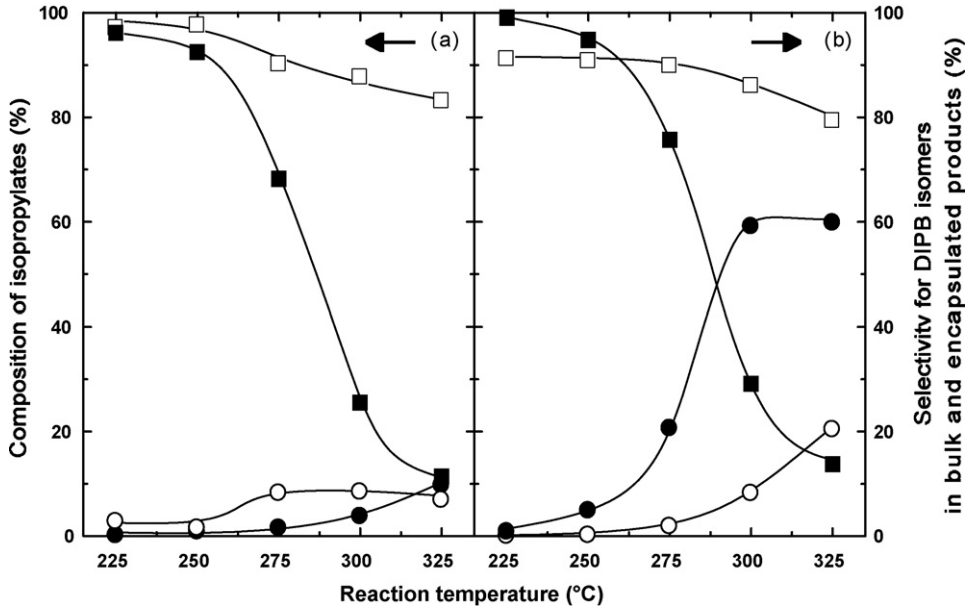

Fig. 4. The influence of reaction temperature on the isomerization of 4,4′-DIPB under propene at 4,4′-DIPB/MOR = 100. (a) Conversion and yield of isopropylates. (b) Selectivity for DIPB isomers in bulk and encapsulated products. Reaction conditions: 4,4′-DIPB: 100 mmol; MOR, 1 g; temperature, 225–325 °C; propene pressure: 0.8 MPa; period, 4 h. See legend in Fig. 2.

increase in the temperature as shown in Fig. 4a. However, the formation of IPBP and TriIPB isomers was increased much more slowly than the decrease of 4,4′-DIPB. These results mean the decrease in the selectivity for 4,4′-DIPB is due to the isomerization of 4,4′-DIPB to thermodynamically more stable 3,4′- and 3,3′-DIPB as shown in Fig. 4b. However, 4,4′-DIPB was almost only an isomer in encapsulated DIPB isomers in the isomerization of 4,4′-DIPB, even at high temperatures such as 300 °C. These results indicate that the shape-selective formation of 4,4′-DIPB in the isopropylation of BP occurs inside MOR channels even at such a high temperature as 300 °C, and that the decrease in the selectivity for 4,4′-DIPB in bulk products at high temperatures is due to the isomerization on external acid sites, and not to the lack of shape-selectivity inside the pores.

The results discussed above can be summarized as follows. The selective formation of 4,4′-DIPB occurs inside MOR channels at moderate BP/MOR ratios and temperatures, and is not influenced by the amount of external acid sites. However, 4,4′-DIPB, once released from the channels, isomerizes rapidly to 3,4′- and 3,3′-DIPB over the external acid sites, particularly in the presence of large amounts of catalyst and/or at higher temperatures.

3.2. Mechanistic aspects of the isomerization of 4,4′-DIPB during the isopropylation of BP

One of the most important points in the shape-selective alkylation of polynuclear hydrocarbons over zeolites is where and how the catalyses occur [1–4]. Shape-selective catalysis occurs at internal acid sites to yield preferentially the least bulky products [3–5]. It is important to clarify the role of internal and external acid sites, particularly, to elucidate the reason why external acid sites do not work for the alkylation. In general, external acid sites are more active than internal acid sites due to the difference of steric limitation of internal acid sites. If external acid sites work on the catalysis, non-regioselective alkylation should lower the selectivity for the least bulky isomers. From these reasons, deactivation of external acid sites is an important key for shape-selective catalysis inside the channels.

The change of catalyst amount and/or reaction temperature cause the discrepancies of the selectivity for 4,4′-DIPB in bulk and encapsulated products (Figs. 1 and 3). The selectivities for 4,4′-DIPB in encapsulated products were kept almost constant under all our conditions; however, they were significantly varied in bulk products by the changing the catalyst amount (BP/MOR = 20–2000) and/or the reaction temperatures (200–325 °C). High BP/MOR ratio and/or low temperature favor the selective formation of 4,4′-DIPB. However, the increase in catalyst amount and/or in reaction temperature cause the decrease in the selectivity for 4,4′-DIPB in bulk products, and finally, the extensive decrease occurred by using large catalyst amount and/or at high temperature.

An important key for the selective formation of 4,4′-DIPB is the deactivation of non-regioselective reactions such as the alkylation of BP and IPBP isomers and the isomerization of 4,4′-DIPB. The discrepancies on the selectivities for 4,4′-DIPB in bulk and encapsulated products suggest that internal and external acid sites play the different roles in the catalysis due to the difference of their steric environments. The selective formation of 4,4′-DIPB occurs at the internal acid sites: the transition state to the least bulky 4,4′-DIPB was established preferentially among the other isomers because of steric restriction by the MOR channels [1–5,10–13]. We have proposed non-regioselective reactions are deactivated by the propene adsorbed on external acid sites in the shape-selective isopropylation of BP [5,11]. The propene adsorbed inside the channels cannot disturb the access of BP and IPBP isomers to the acid sites because of the steric limitation of channels, resulting in the shape-selective formation of 4,4′-DIPB inside the MOR channels. On the other hand, propene strongly adsorbed on external acid sites disturbs the access of BP, IPBP, and DIPB isomers to the acid sites, and deactivates non-regioselective reactions, particularly, the isomerization of 4,4′-DIPB, particularly, by using small amounts of catalyst and/or at the low and moderate temperatures. However, vacant acid sites appear with the increase of surface area by the use of large amount of catalyst and/or at higher temperatures. 4,4′-DIPB and propene can adsorb competitively on these vacant external acid sites, and 4,4′-DIPB directly adsorbed on the external acid sites easily isomerizes to 3,4′- and 3,3′-DIPB. Similar isomerization supposed by the vacant acid sites were observed in the isopropylation of BP over MOR under low propene pressures [11]. The deactivation of external acids by the ceria modification is effective for the prevention of the isomerization of 4,4′-DIPB [22].

The phenomena shown in this work indicate that the formation of 4,4′-DIPB in the isopropylation of BP occurs in MOR channels even at higher temperatures, and that the acid sites for the isomerization of 4,4′-DIPB are on external surfaces, and not inside the channels.

4. Conclusion

The influence of external acid sites of a dealuminated H-mordenite (MOR; SiO_2/Al_2O_3 = 128) on the selectivity for 4,4′-DIPB was examined by changing catalyst amounts. Highly selective formation of 4,4′-DIPB occurred at such a low temperature as 200 °C even by using large amounts of catalysts. However, the selectivity for 4,4′-DIPB decreased by using large amounts of catalyst and/or at higher temperatures such as 300 °C accompanying the increase in the selectivity for 3,4′-DIPB. The decrease started at lower temperatures with increasing catalyst amount: BP/MOR = 200 at 300 °C and 67 at 250 °C. However, the selectivities for 4,4′-DIPB were highly selective in encapsulated products under all conditions.

Shape-selective formation of 4,4′-DIPB occurred at the acid sites inside the channels with restricted steric environment. It is also essential to deactivate non-regioselective reactions, particularly the isomerization of 4,4′-DIPB at external acid sites for highly shape-selective catalysis. Preferential propene adsorption on external acid sites may effectively retard the adsorption of BP and 4,4′-DIPB at low and moderate temperatures and/or by using small amounts of the catalyst, resulting in the deactivation of the isomerization of 4,4′-DIPB. Although the formation of 4,4′-DIPB occurs inside MOR channels at all conditions, competitive adsorption of propene and 4,4′-DIPB at vacant external acid sites leads to the isomerization of 4,4′-DIPB to 3,4′- and 3,3′-DIPB in the presence of large amounts of catalyst and/or at high temperatures.

Acknowledgement

A part of this work was financially supported by Grant-in Aids for Scientific Research (B) 16310056 and 19310030, the Japan Society for the Promotion of Science (JSPS).

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