

Shape-selective alkylation of biphenyl catalyzed by H-[Al]-SSZ-31 zeolite

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Abstract

The isopropylation of biphenyl (BP) was examined over H-[Al]-SSZ-31 (SSZ-31) zeolites synthesized by hydrothermal synthesis (HTS) and dry-gel conversion (DGC). The synthetic method was found not to be the principal factor determining the shape-selective character of SSZ-31 zeolite, although the catalytic performance varied depending on the synthetic route employed. The least bulky isomers, 4-isopropylbiphenyl (4-IPBP) and 4,4'-diisopropylbiphenyl (4,4'-DIPB), were formed selectively over SSZ-31 synthesized by DGC and HTS. The selectivity for 4,4'-DIPB in the encapsulated products was higher than that in the bulk products over SSZ-31 by HTS; the isomerization of 4,4'-DIPB to the thermodynamically more stable 3,4'-DIPB occurred at external acid sites in the bulk products. This decrease in selectivity was not observed for SSZ-31 synthesized by DGC. The selectivity for 4,4'-DIPB in the bulk products decreased with increasing temperature above 275 °C, whereas, that for the encapsulated product increased. The reaction is considered primarily to occur inside the pores at all temperatures, in particular near the pore mouth, and at high temperatures, to increase the participation of deep acid sites away from the pore mouth due to increased diffusion of products. SSZ-31 was also found to be more selective in *s*- and *t*-butylations with 2-methylpropene and 1-butene than in isopropylation due to steric factors.

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1. Introduction

4,4'-Dialkylbiphenyls are promising precursors for biphenyl-4,4'-dicarboxylic acid, which is an intermediate for polyester fibers, engineering plastics, and liquid crystalline polymers for electronic and mechanical devices and films with high heat resistance and strength [1]. Traditional Friedel–Crafts, catalysts such as Lewis acids or silica/alumina are non-selective

and generally produce products with low *para*-selectivity. In contrast, zeolites, being microporous and crystalline, shape-selectively yield the least bulky *para*-isomers [2]. Medium-pore zeolites (10 MR) are well-known catalysts for the alkylation of mononuclear aromatics [2]. However, large-pore zeolites are more useful in the alkylation of bulky polynuclear aromatics. 4,4'-Diisopropylbiphenyl (4,4'-DIPB) and 2,6-diisopropyl-naphthalene (2,6-DIPN) have been selectively produced from biphenyl (BP) and naphthalene (NP), respectively, over dealuminated H-mordenite (HM) [3–10]. Other relevant findings are the

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shape-selectivity of SAPO-5 and CIT-5 for the isopropylation of BP [11,12], the selective production of 2,6-di-*t*-butylnaphthalene in the *t*-butylation of NP and BP by 2-methylpropanol due to steric factors over HY zeolite [13], and higher activity of HY zeolite compared to H β zeolite in the selective alkylation of BP with 2-methyl-2-propanol [14].

H-[Al]-SSZ-31 (SSZ-31) is a one-dimensional, high-silica large-pore zeolite with potential application as a catalyst in the alkylation of polynuclear aromatics using alkylating agents such as propene and butene. Zones et al. [15] first reported the synthesis of all silica SSZ-31 by a hydrothermal synthesis (HTS) method, and Lobo et al. [16] subsequently established the structure of SSZ-31. The structure is highly faulted with intergrowth of four different polymorphs, and is closely related to NCL-1 [17] and OU-1 [18]. The borosilicate version of SSZ-31 has been synthesized using a number of structure-directing agents (SDA), with subsequent conversion to the aluminum version by postsynthesis modification [15,19,20]. We have described the direct synthesis of SSZ-31 by a dry-gel conversion (DGC) method on small and large scales [21,22], and the hydrothermal synthesis of SSZ-31 zeolite with relatively low SiO₂/Al₂O₃ ratio using a [Al]-BEA precursor [23].

We previously described a preliminary report on the isopropylation of BP over SSZ-31 [24]. In this paper, the catalytic performances of SSZ-31 synthesized by DGC and HTS methods for the isopropylation of BP is discussed. The effects of bulkiness of the alkylating agent on the alkylation of BP over SSZ-31 zeolite are also investigated.

2. Experimental

2.1. Synthesis of [Al]-SSZ-31

2.1.1. Synthesis of [Al]-SSZ-31 by dry-gel conversion (DGC)

The zeolite was synthesized by DGC using reported procedures [21,22]. A typical synthesis procedure was as follows. A solution containing 33 g (8 mmol) of 1,1,1,8,8,8-hexaethyl-1,8-diazaoctane dihydroxide (R²⁺(OH⁻)₂, 0.242 mmol/g) was added to 0.42 g (3.36 mmol) of 32 wt.% aqueous NaOH solution, followed by the addition of 6.01 g (40 mmol)

of colloidal silica (Snowtex 40, Nissan Chemical Co.). The mixture was stirred for ca. 15 min, then 0.048 g (0.104 mmol) of aluminum sulfate dissolved in warm water (8.88 g) was added while stirring. The resulting gel was then stirred for ca. 1 h at room temperature. The final gel had the composition SiO₂-0.2 R²⁺(OH⁻)₂-0.084NaOH-0.0035Al₂O₃-61H₂O. The gel was then dried at 80 °C to complete dryness, weighed, accurately halved, and transferred into Teflon cups. The cups were placed in autoclaves containing water (0.2 g water per gram of gel). The autoclaves were heated at 150 °C for 48 h and then 175 °C for 12 h in a convection oven. They were then quenched with cold water, and the product obtained was filtered, washed with distilled water, and dried overnight to give as-synthesized SSZ-31.

2.1.2. Synthesis of [Al]-SSZ-31 by hydrothermal synthesis (HTS)

The zeolite was synthesized by the HTS method using a [Al]-BEA (BEA) precursor according to the procedure described recently by the present authors [23]. BEA was synthesized by HTS [25] and DGC [26]. A typical procedure for synthesis of SSZ-31 was as follows. A 7.79 g (2.0 mmol) aqueous solution of R²⁺(OH⁻)₂ (0.257 mmol/g) was added to 0.105 g (0.84 mmol) of 32% aqueous NaOH. The resulting alkaline solution was stirred for ca. 10–15 min and, then 0.416 g (14.8 mmol including the silica from BEA) of fumed silica (Cab-O-Sil M5, Cabot) followed by 11.4 g (1033.5 mmol) of deionized water was added. The mixture was stirred for 30 min. Finally, 0.50 g of calcined BEA was added and the mixture was stirred for 4 h. The resulting gel had the composition SiO₂-0.13R²⁺(OH⁻)₂-0.056NaOH-0.0184Al₂O₃-70H₂O. The crystallization was carried out statically at 175 °C under autogenous pressure for 6 days, and the autoclave was finally quenched with cold water. The product was filtered, washed with distilled water, and dried overnight to give the as-synthesized material. To remove the organic SDA encapsulated inside the pores, the as-synthesized zeolite sample was heated in a muffle furnace under air flow (100 ml/min) stepwise from room temperature to 540 °C over a period of 7 h and, then maintained at this temperature for 4 h. The temperature was then raised to 600 °C over period of 4 h, and maintained at that temperature for another 4 h. The sample was

finally allowed to cool naturally to room temperature.

2.2. Post-synthesis treatment

The calcined sample was refluxed with ammonium nitrate (NH_4NO_3) solution for 12 h under constant stirring. The mass of nitrate used was the same as the zeolite, and the H_2O :zeolite ratio was 50:1 (w/w). The zeolite was then filtered. This process was repeated two more times, then the sample was filtered, washed thoroughly with water and dried overnight at room temperature. Finally, the NH_4 -form of the zeolite was calcined under air flow for 8 h at 550°C to obtain the H-form.

2.3. Catalyst characterization

The as-synthesized and calcined SSZ-31 zeolites were examined by powder X-ray diffraction (XRD-6000, Shimadzu Corporation) with $\text{Cu K}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$) to determine the crystallinity and phase purity. Elemental analyses were performed using inductively coupled plasma atomic emission spectroscopy (ICP-AES; JICP-PS-1000 UV, Leeman Labs Inc.). The surface area and pore volumes of calcined samples were measured on a Belsorp 28SA (Bel Japan, Osaka, Japan), and the acidity of the catalyst was measured by ammonia temperature programmed desorption (TPD) using a BEL TPD-66 (Bel Japan). The catalyst (50 mg) was evacuated at 500°C for 0.5 h, exposed to 2.6 kPa ammonia at 100°C during 10 min for adsorption and, then evacuated at this temperature for a further 30 min. The sample was heated from 100 to 710°C at $10^\circ\text{C}/\text{min}$ under constant helium flow of 50 ml/min with the pressure of 13.2 kPa. Desorbed ammonia and other species were detected by mass spectroscopy.

Adsorption of *o*-xylene was analyzed by gravimetry using a microbalance at 120°C after evacuation of the sample at 500°C . Cracking of 1,3,5-triisopropylbenzene (1,3,5-TIPB) and cumene (IPB) was carried out using a conventional pulse reactor at 450°C under nitrogen flow, and the products were analyzed by an inline Shimadzu GC-4C gas chromatograph. Thermogravimetric analysis of the catalysts used for the isopropylation was carried out using a Shimadzu DTG-50 analyzer at programmed rate of $10^\circ\text{C}/\text{min}$ under air flow.

2.4. Catalysis

2.4.1. Reagents

Biphenyl (BP), 4-isopropylbiphenyl (4-IPBP), 4,4'-diisopropylbiphenyl (4,4'-DIPB), 4-*t*-butylbiphenyl (4-TBP) and 4,4'-di-*t*-butylbiphenyl (4,4'-DTBB) were purchased from Tokyo Kasei Kogyo Co. Ltd. (Tokyo, Japan). Propene, 1-butene, and 2-methylpropene were supplied by Tomoe Shokai Co. Ltd. (Tokyo, Japan). These reagents were used without further purification.

2.4.2. Isopropylation

The reactions were carried out in a batch reactor (100 ml SUS-316) at constant pressure of propene in the temperature range of 225 – 325°C . Propene pressure was varied between runs from 0.1 to 0.8 MPa. The typical procedure was as follows. An autoclave containing 0.5 g of SSZ-31 and 15.4 g (100 mmol) of BP (Tokyo Kasei Kogyo Co. Ltd.) was flushed with nitrogen, then heated to the desired temperature. Propene was then introduced to the desired pressure, and this pressure was maintained throughout the reaction period (4 h). After the reaction, the autoclave was cooled, and the catalyst was filtered and washed with toluene (100 ml). The solution (ca. 1.5 ml) was taken from the total bulk products and diluted with toluene (1.5–6.0 ml). The products obtained after the reaction were identified by gas chromatography–mass spectroscopy (GC–MS; QP5000, Shimadzu Corporation Ltd.), and analyzed by Shimadzu-14A gas chromatograph equipped with an Ultra-1 capillary column (25 m \times 0.3 mm).

The conversion of BP and the yield of each product were calculated on the basis of consumed BP. The selectivities of each DIPB and isopropylbiphenyl (IPBP) isomers are expressed as follows.

Selectivity for DIPB (IPBP) isomers (%)

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

The products encapsulated inside the catalysts were analyzed as follows. After collection of the bulk products (as mentioned earlier), the catalyst was washed with acetone (~ 20 ml), and then dried at 110°C for 12 h. A total of 300 mg of the dried catalyst was dissolved carefully in 3 ml of aqueous hydrofluoric acid

(47%) at room temperature. This solution was basified with solid potassium carbonate, and the organic layer was extracted three times with dichloromethane (20 ml). After removing the solvent in vacuo, the residue was dissolved in toluene (5 ml). GC analysis was performed similarly to that for the bulk products.

The *s*- and *t*-butylations were carried out in a similar manner using 1-butene and 2-methylpropene as alkylating agents, respectively. Products were identified by GC–MS, and analyzed by GC in a similar manner as for the bulk products of the isopropylation.

3. Results and discussion

3.1. Properties of SSZ-31 zeolite

Five SSZ-31 zeolites were synthesized: DG1 ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 136$), DG2 ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 176$), and DG3 ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 251$) by DGC, and HT1 ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 98$) and HT2 ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 235$) by HTS. The X-ray diffraction patterns indicated that all samples were pure and crystalline. Fig. 1 shows typical scanning electron micrographs for SSZ-31 produced by DGC and HTS. The particles were smaller than 1 μm for the DGC samples, and around 5 μm for the HTS samples. No significant differences in surface area and pore volume were observed for any of the SSZ-31 zeolites (350–380 m^2/g and 0.11 ml/g).

Fig. 2 shows the progression of *o*-xylene adsorption on SSZ-31 zeolites (HT2 and DG2) at 120 °C.

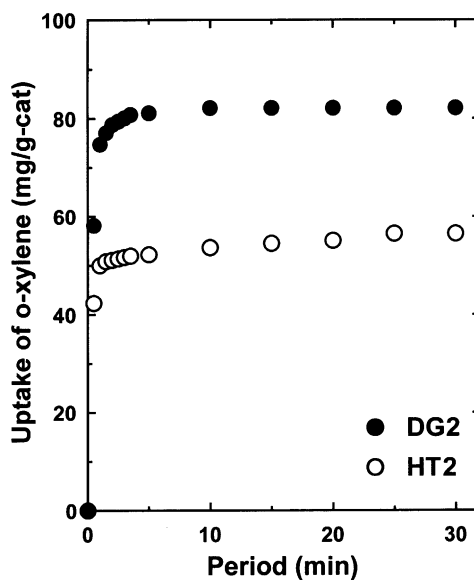


Fig. 2. Adsorption of *o*-xylene over SSZ-31 zeolite.

The adsorption occurs rapidly in all cases, but the rate and amount of *o*-xylene adsorption depend on the synthetic method. The initial rate and total amount of *o*-xylene adsorbed by HT2 were ca. 70% of the values for DG2. Although the two samples have similar surface area, HT2 has larger particles than DG2. The dissimilar rates of *o*-xylene adsorption, therefore, appears to be due to the different diffusion rates corresponding to the different particle sizes, and the lower adsorption by HT2 is due to lower diffusivity to the very deep pores. Furthermore, although HT2 and DG2

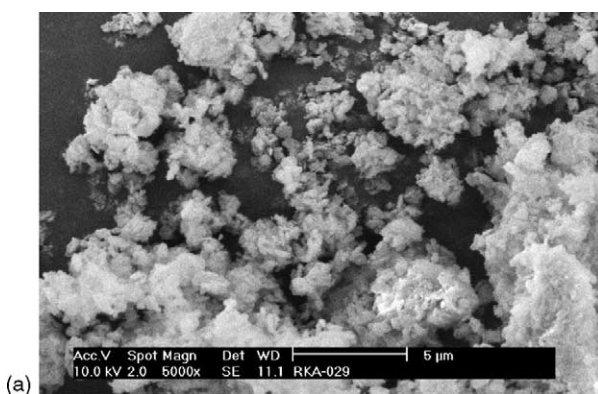


Fig. 1. SEM micrograph of [Al]-SSZ-31 zeolite. (a) DGC (DG2, $\text{SiO}_2/\text{Al}_2\text{O}_3 = 176$); (b) HTS (HT2, $\text{SiO}_2/\text{Al}_2\text{O}_3 = 235$).

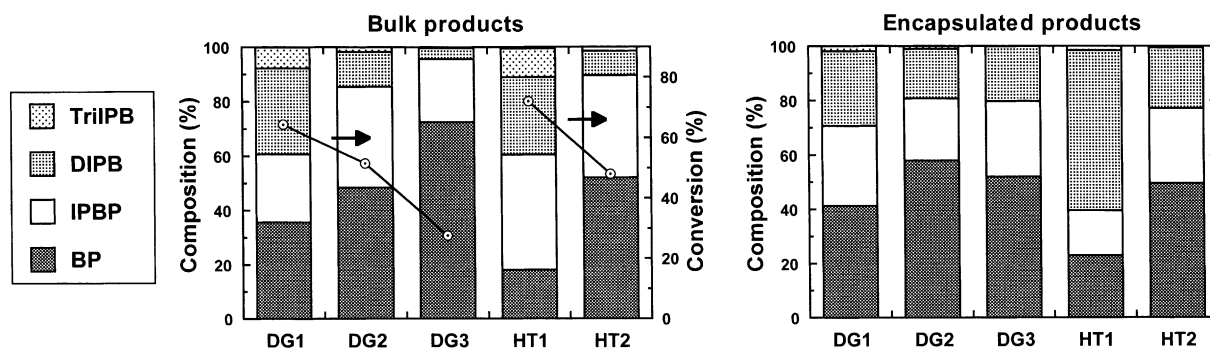


Fig. 3. Effect of SSZ-31 zeolite synthesis method on isopropylation of BP (100 mmol BP, 0.5 g catalyst, 250 °C, 0.8 MPa propene pressure, 4 h).

have similar surface areas and pore volumes according to measurement by N_2 , the adsorptivities for *o*-xylene are quite different. These differences are ascribed to the bulkiness of the adsorbent and the size of particles as mentioned previously.

3.2. Influence of SSZ-31 zeolite synthetic method on isopropylation of biphenyl

Fig. 3 shows typical results for the isopropylation of BP over SSZ-31 synthesized by DGC and HTS at 250 °C under 0.8 MPa propene pressure. The conversion of BP decreased with increasing SiO_2/Al_2O_3 ratio of SSZ-31 synthesized by both methods. The yield of isopropylbiphenyl (IPBP) isomers increased with the ratio, whereas the yield of diisopropylbiphenyl (DIPB) isomers decreased. The isopropylation of IPBP to DIPB may be retarded due to the decrease of acid sites. Triisopropylbiphenyls (TriIPBs) were observed only in small amounts. The encapsulated products exhibited an increase in BP and decreases in IPBP and DIPB with increasing ratio of SiO_2/Al_2O_3 , attributed to the decrease in catalytically active acid sites at high ratios. These results are different from the case for HM, for which the DIPB isomer content was high in encapsulated products [3–5,7]. Some TriIPBs were observed for DG1 and HT1, due to the relatively high amounts of acidic sites in these zeolites.

There is a relatively large difference between the catalytic performance of SSZ-31 zeolites synthesized by the DGC and HTS methods, although HT1 and HT2

are sufficiently fine particles for catalytic purposes. Further studies on these characteristics are currently in progress.

As shown in Fig. 4, the isopropylation of BP gave predominantly 4,4'-DIPB over SSZ-31 zeolites. The selectivity for 4,4'-DIPB over SSZ-31 remained almost constant during the reaction under moderate conditions. The selective formation of 4,4'-DIPB was observed for all SSZ-31 zeolites, although the catalytic performance and the selectivity varied according to the synthetic method. These results show that the selective formation of 4,4'-DIPB is probably due to the characteristics of the SSZ-31 pores. The synthetic method is, therefore, not the principal factor governing the shape-selective nature of SSZ-31.

The selectivity for 4,4'-DIPB was similar in the bulk and encapsulated products over SSZ-31 synthesized by DGC, although the catalytic activity decreased with increasing SiO_2/Al_2O_3 ratio. However, the selectivity for 4,4'-DIPB was influenced by the SiO_2/Al_2O_3 ratio of SSZ-31 synthesized by HTS. The selectivity of HT1 for 4,4'-DIPB was lower than that of HT2 in the bulk products, but the selectivities were similar in the encapsulated products. This difference is ascribed to the isomerization of 4,4'-DIPB to a thermodynamically more stable isomer, 3,4'-DIPB, at external acid sites similarly to the isopropylation of BP over HM [7].

The selective formation of 4,4'-DIPB is due to the shape-selective catalysis within the pores of SSZ-31. The shape-selective nature originates from the pore structure, and does not depend on the size of

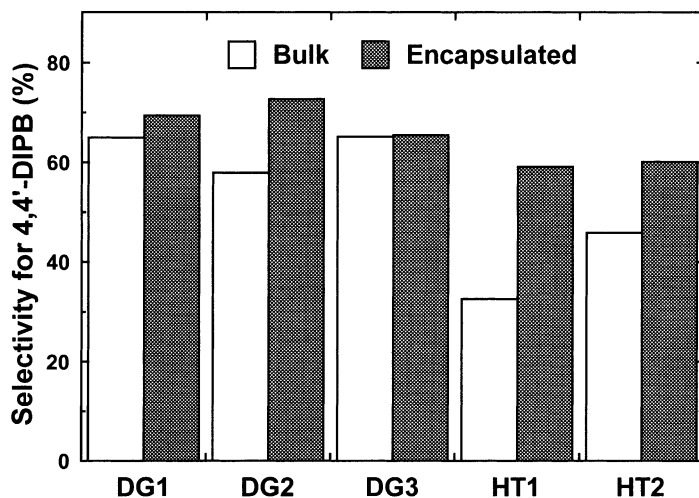


Fig. 4. Effect of synthesis method on selectivity for 4,4'-DIPB. Reaction conditions are the same as shown in Fig. 3.

crystals, which is affected by the synthetic method. The restricted transition state mechanism operates principally to form predominantly 4,4'-DIPB, as is the case for H-mordenite (HM) [1,3–5,7]. A less steric restriction by the pores of SSZ-31 should enhance the formation of 3,4'-DIPB.

The SSZ-31 zeolites synthesized by DGC and HTS had essentially identical shape-selective character judging from the selectivity of the encapsulated products for 4,4'-DIPB. The observed differences are, therefore, attributed to the acidic character of the external surface. This may be due to differences in acid distribution in particles according to the synthetic method of synthesis. Such surface enrichment has been seen for aluminum in the hydrothermal synthesis of zeolite [27]. Further studies on this topic will, therefore, be necessary for a detailed discussion.

Fig. 5 shows TG profiles of SSZ-31 zeolite used in the isopropylation of BP. Peaks due to coke formed during the reaction were observed at around 600 °C. The amount of coke deposits was estimated to be around 7% for HT1 and 4% for HT2, whereas coke formation was negligibly low for DG1, DG2, and DG3. These large amounts of coke are due to the higher acid amounts on the external surface of SSZ-31 produced by HTS. The differences in coke production between HT2 and DG2 were also ascribed to differences

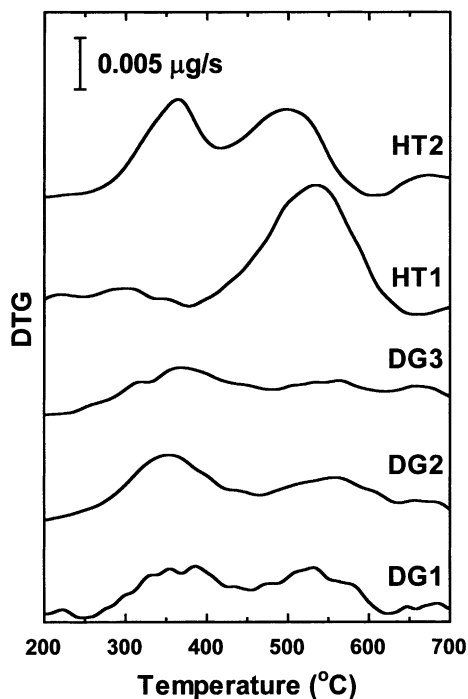


Fig. 5. TG profiles for SSZ-31 zeolite used in the isopropylation of BP. Reaction conditions are the same as shown in Fig. 3.

in particle sizes: coke deposits are easily formed on larger crystals with a large amount of acid. Volatile organic compounds from encapsulated products were also found at around 300–400 °C in addition to coke deposits, as shown in Fig. 6. The analysis of these compounds is useful for discussing the processes within pores.

3.3. Influence of reaction temperature on the isopropylation of biphenyl

Fig. 6 shows the influence of reaction temperature on the isopropylation of BP over SSZ-31 zeolite (DG2) for both bulk and encapsulated products under propene pressure of 0.8 MPa. The conversion increased with temperature, and the yield of DIPB isomers increased while that of IPBP isomers decreased for both the bulk products. However, the influence of reaction temperature was smaller for the encapsulated products. These observations for SSZ-31 differ from those for HM, for which the IPBP yield increased and the DIPB yield decreased at high temperatures (>300 °C) due to the dealkylation of DIPB isomers. Selectivity for TriIPB increased with temperature, which may be attributed to non-selective reactions taking place on the external acid surface of the catalyst, or to the weaker steric hindrance in pores of SSZ-31 zeolite [2–5].

As evident in Fig. 6, the selectivity for 4,4'-DIPB was about 60% at moderate temperatures below 275 °C. Each amount of DIPB isomers other than 3,3', 3,4'- and 4,4'-DIPB accounted for <10%. However, the higher selectivity for 4,4'-DIPB was observed in the encapsulated products. These results show that the formation of DIPB occurs by shape-selective catalysis inside the pores of SSZ-31, as is the case for HM [7]. The selectivity for 4,4'-DIPB in the bulk products decreased, with a complementary increase in 3,4'-DIPB, above 275 °C, although the amount of 3,3'-DIPB produced remained almost constant. This decrease in selectivity for 4,4'-DIPB was not observed in the encapsulated products, and is considered in the bulk products to be due to the isomerization of 4,4'-DIPB to 3,4'-DIPB at external acid sites, as discussed for HM [7]. The selectivity of IPBP isomers also changed with temperature. The selectivities for 4-, 3- and 2-IPBP were ca. 50, 25, and 25%, and that for 3-IPBP increased with temperature with a

corresponding decrease in the selectivity for 2- and 4-IPBP. These changes are also considered to be due to the isomerization of 4- and 2-IPBP to 3-IPBP. As 2-IPBP was found only in small amounts in encapsulated products, it is considered to be formed at external acid sites. These results indicate that some of the IPBP isomers are formed at external acid sites.

The situation for 4-IPBP and 4,4'-DIPB in the encapsulated products was somewhat different from that in the bulk products. The IPBP and DIPB isomers content in the encapsulated products inside the pores was lower than in the bulk products at high temperatures (>300 °C), and the selectivities for 4-IPBP and 4,4'-DIPB were higher at all temperatures. As shown in Fig. 6, the selectivity for 4,4'-DIPB in encapsulated products increased with temperature, and the selectivities for 3,4'-DIPB and 3,3'-DIPB were correspondingly reduced. This variation differs from that of HM, where the selectivity for 4,4'-DIPB remained constant even at high temperature. Although these results do not lead to definitive mechanism, most of the reaction is considered to take place inside the pores of SSZ-31 zeolite, in particular near the pore mouth. The participation of deep acid sites away from the pore mouth in the catalysis of SSZ-31 will increase with reaction temperature due to higher diffusion of BP and propene, enhancing the generation of 4,4'-DIPB, and eventually resulting in an increase in selectivity for 4,4'-DIPB in the encapsulated products. However, it is difficult to determine exactly how much of a role such deep acids sites play in the formation of bulk products. Similar increases in selectivity were observed for 4-IPBP. Details of the mechanism and comparisons with other large-pore zeolites are currently under investigation.

Fig. 7 summarizes the effect of reaction temperature on the product distribution and selectivity for 4,4'-DIPB in bulk and encapsulated products for the isomerization of 4,4'-DIPB over SSZ-31 zeolite (DG2) at propene pressure of 0.8 MPa. Although the isomerization of 4,4'-DIPB to 3,4'-DIPB was not extensive at moderate temperatures (below 275 °C), it increased considerably at higher temperatures. 3,4'-DIPB was also found in the encapsulated products even at lower temperatures. From these results, the isomerization of 4,4'-DIPB appears to occur to a certain extent in

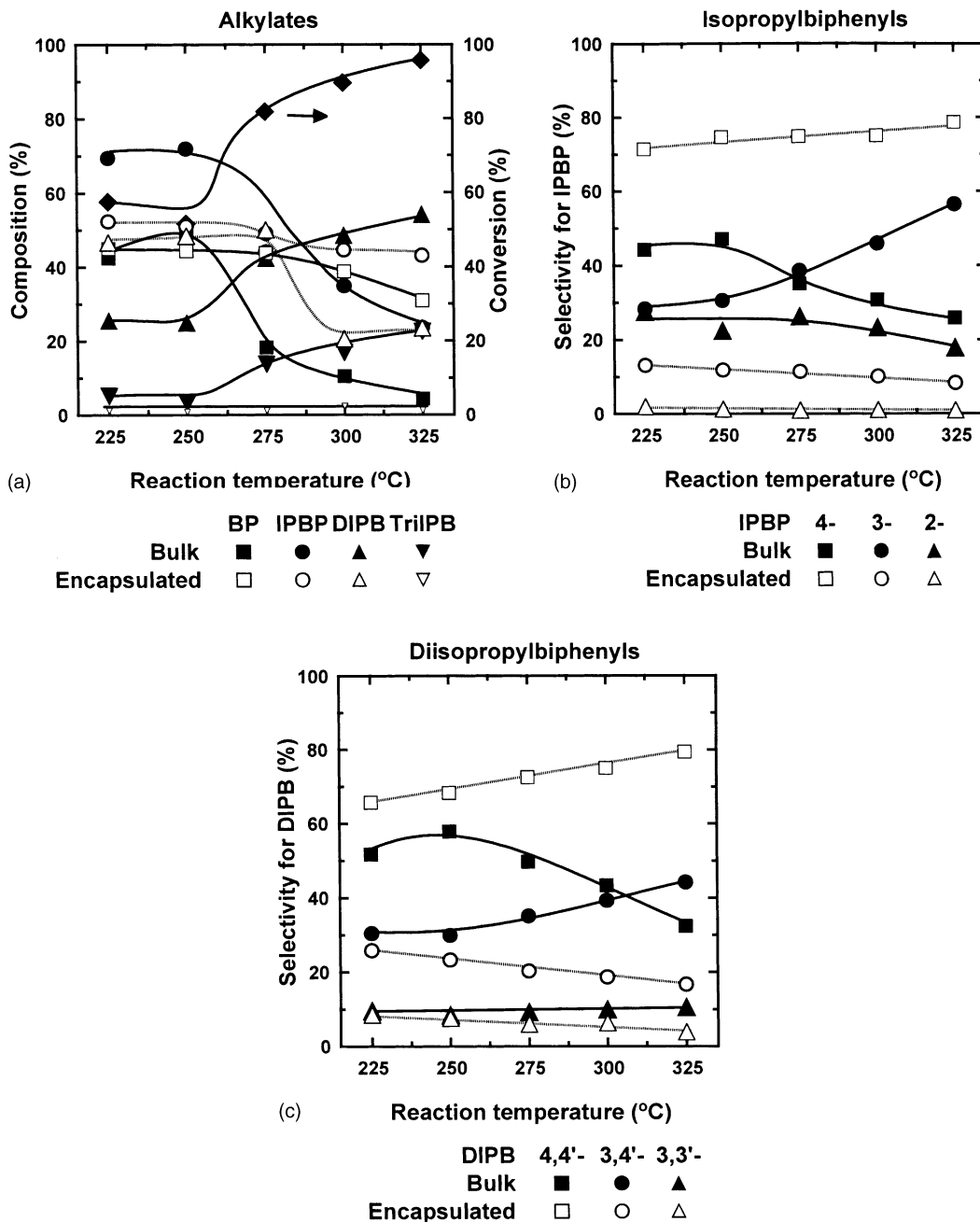


Fig. 6. Effect of reaction temperature on isopropylation of BP (100 mmol BP, 0.5 g DG2 catalyst, 0.8 MPa propene pressure, 4 h).

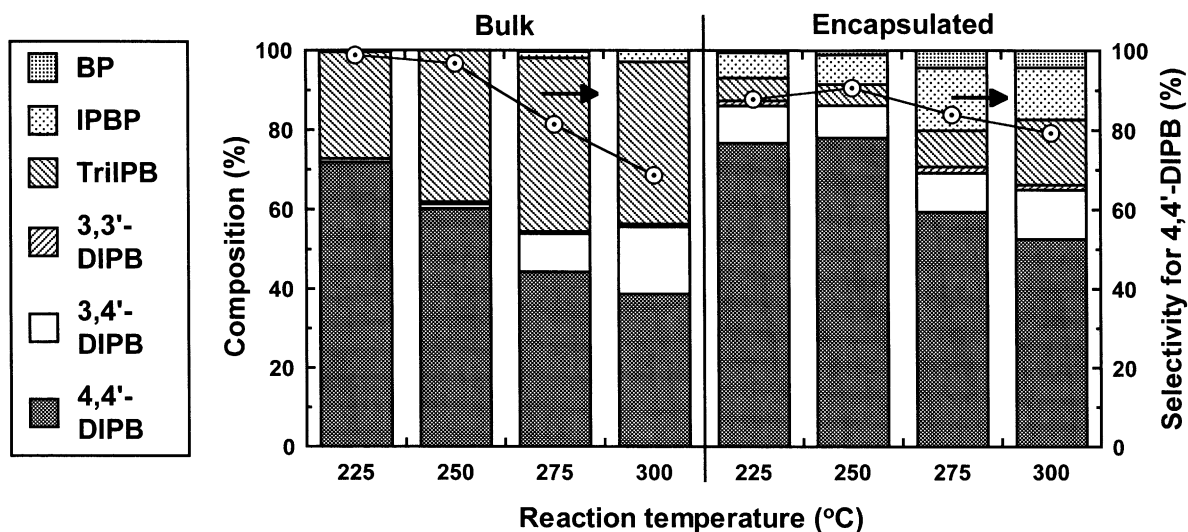


Fig. 7. Effect of reaction temperature on isomerization of 4,4'-DIPB (50 mmol 4,4'-DIPB, 0.5 g DG2 catalyst, 0.8 MPa propene pressure, 4 h).

the pores of SSZ-31 during the isopropylation of BP. Extensive formation of TriIPBs was also observed in bulk products, and in encapsulated products most noticeably at higher temperatures. The formation of TriIPBs is thought to occur principally at external acids sites, and to a lesser extent inside pores. BP and IPBP isomers were found in the encapsulated products, presumably formed by the dealkylation of 4,4'-DIPB and TriIPBs inside pores.

3.4. *s*-Butylation of biphenyl with 1-butene over SSZ-31 zeolite

As shown in Fig. 8, the conversion increased with temperature in the *s*-butylation of BP with 1-butene over SSZ-31 zeolite (DG2). The yield for *s*-butylbiphenyl (SBBP) decreased while that for di-*s*-butylbiphenyl (DSBB) increased with temperature. The selectivity for the least bulky 4,4'-di-*s*-butylbiphenyl (4,4'-DSSB) of the di-*s*-butylbiphenyl (DSBB) was highest, remaining constant at 70% over the entire temperature range (225–300 °C). Furthermore, the selectivity for 3,4'-DSSB also remained constant in the bulk products, with little isomerization of 4,4'-DSSB to 3,4'-DSSB. Encapsulated products exhibited a higher selectivity for

4,4'-DSSB, however, the difference between the selectivities for bulk and encapsulated products was not very significant. The selectivity for SBBP changed only slightly with temperature. The selectivities for 4-, 3- and 2-SBBP were ca. 65–60%, 20–35%, and 5–10%, and the selectivity for 4-SBBP was higher in the encapsulated products than in the bulk products, demonstrating the shape-selective nature of catalysis. 2-SBBP, in this case, was formed on the external surface.

3.5. *t*-Butylation of biphenyl with 2-methylpropene over SSZ-31 zeolite

Fig. 9 shows influences of temperature on bulk and encapsulated products in the *t*-butylation of BP with 2-methylpropene over SSZ-31 zeolite (DG2). The conversion increased with temperature in the *t*-butylation of BP. The yield of *t*-butylbiphenyl (TBBP) was higher than that of di-*t*-butylbiphenyl (DTBB) in the temperature range from 225 to 300 °C. Dialkylation is less favored in this case because of the severe restriction of the bulky substrate and products inside the pores of SSZ-31 zeolite. This behavior is analogous to that observed for the zeolites HY and H β by Moreau and co-workers [13], who reported the appreciable

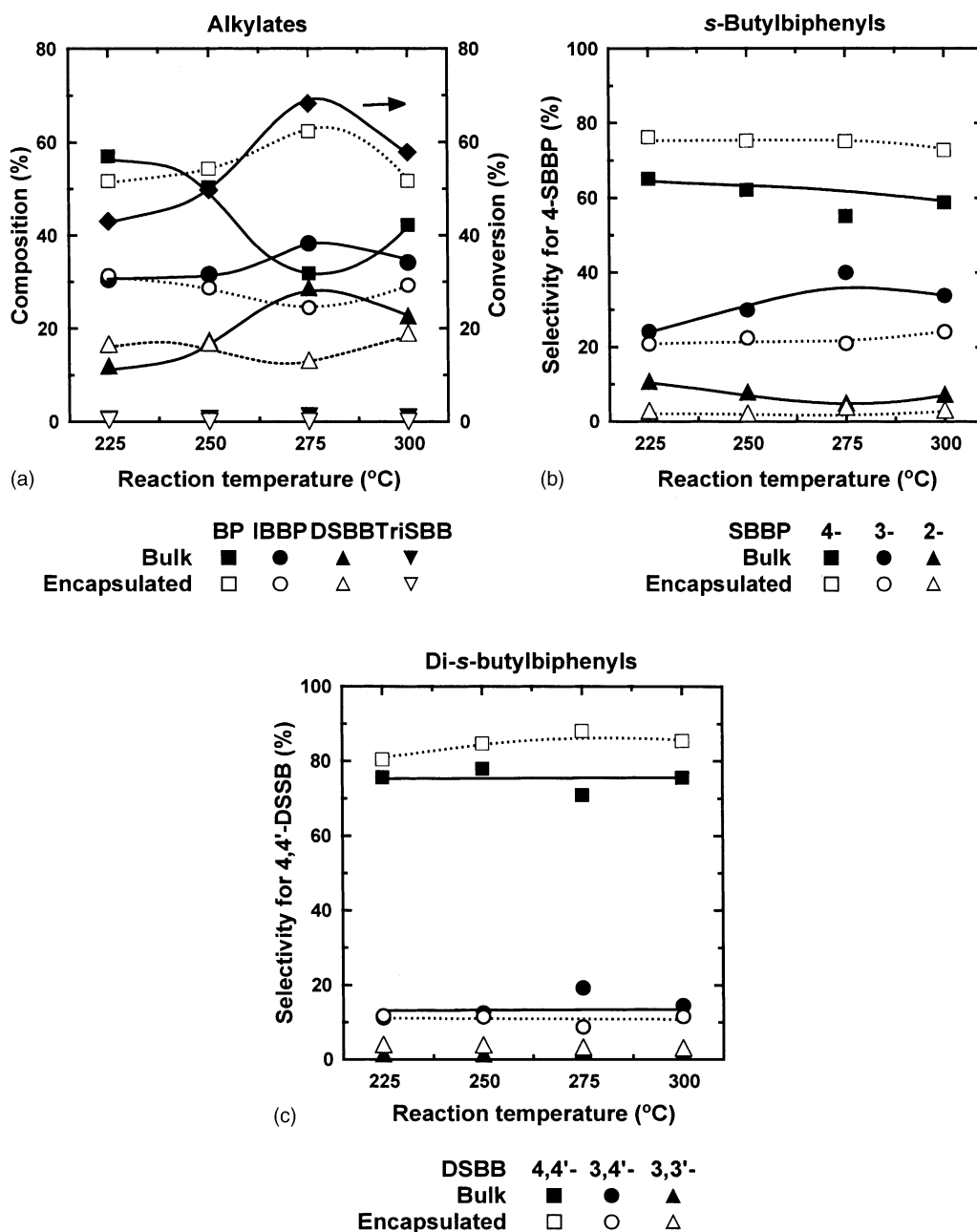


Fig. 8. Effect of reaction temperature on *s*-butylation of BP (100 mmol BP, 0.5 g DG2 catalyst, 0.5 MPa 1-butene pressure, 4 h).

generation of mono-alkylated products. However, the selectivity for 4,4'-di-*t*-butylbiphenyl (4,4'-DTBB) over SSZ-31 was higher than for 4-*t*-butylbiphenyl (4-TBBP) in contrast to HY and H β zeolites. These

differences are attributed to the structural differences between HY, H β and SSZ-31. The selectivity of 4-TBBP and 4,4'-DTBB over SSZ-31 zeolite was lower in the bulk products at high temperatures (ca.

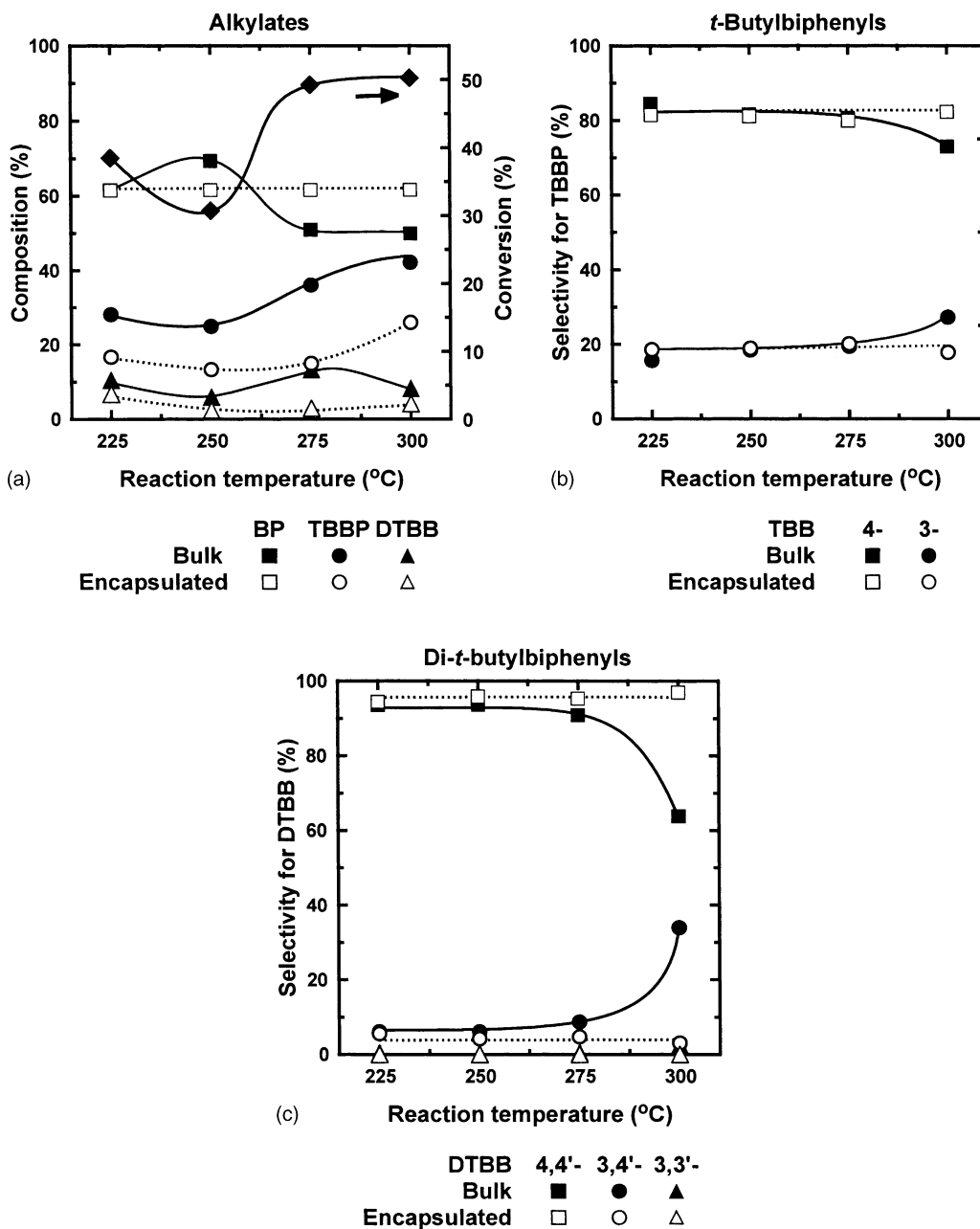


Fig. 9. Effect of reaction temperature on *t*-butylation of BP (100 mmol BP, 0.5 g DG2 catalyst, 0.5 MPa 2-methylpropene pressure, 4 h).

300 °C), but remained high for the encapsulated products at all the temperatures examined. These results indicate that 4-TBBP and 4,4'-DTBB are formed inside the pores, and that a decrease in selectivity occurs

due to the isomerization of 4-TBBP and 4,4'-DTBB at external acid sites. Other secondary reactions such as dealkylation and oligomerization also take place at high temperatures.

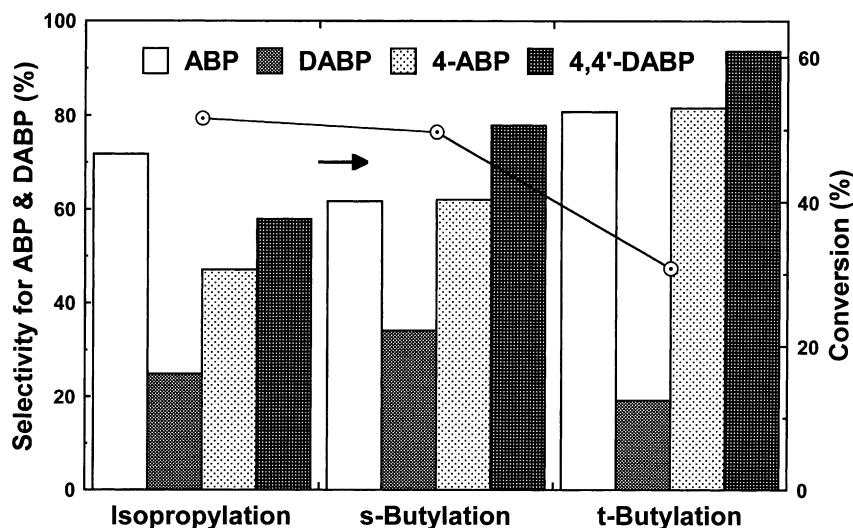


Fig. 10. Comparison of catalytic activity and selectivity for 4,4'-DABP in isopropylation, *s*- and *t*-butylation of BP (100 mmol BP, 0.5 g DG2 catalyst, 250 °C, 4 h. Isopropylation, 0.8 MPa propene; *s*-butylation, 0.5 MPa 1-butene; *t*-butylation, 0.5 MPa 2-methylpropene).

3.6. Comparison of bulkiness of alkylating agents in the alkylation of biphenyl

Fig. 10 compares the catalytic behavior of isopropylation, *s*-butylation and *t*-butylation of BP over SSZ-31 zeolite (DG2). The conversion is highest for propene, followed by 1-butene and then 2-methylpropene, considered to be due to the decrease in diffusion through pores with increasing size of the alkylating agent and products. The yield for alkybiphenyl (ABP) was consistently higher than that for dialkybiphenyl (DABP), which is attributed to diffusion constraints through 1D channels of SSZ-31 zeolite. The yield of ABP was the highest, and the yield of DABP was the lowest in the *t*-butylation of BP over SSZ-31 zeolite.

The least bulky products, 4-ABP and 4,4'-DABP, were the predominant isomers for all alkylating agents, although the selectivities for these isomers varied according to bulkiness. These alkylations, therefore, proceed via a sequential reaction mechanism: in the first step, the least bulky 4-ABP forms preferentially and, in the second step, further alkylation of 4-ABP yields the least selective bulky 4,4'-DABP. These alkylations occur principally inside pores through shape-selective catalysis by a restricted transition mechanism [4,5,7].

The selectivity for 4,4'-DABP was highest in *t*-butylation, followed by *s*-butylation and then isopropyla-

tion with the lowest selectivity. This variation is ascribed to steric interaction during the formation and diffusion of products because of the bulkiness of the alkylating agent and products. 4,4'-DABP is the least bulky of the DABP isomers, and diffuses relatively easily. Such preferential diffusion of 4,4'-DABP has also been observed for H β zeolite in the *t*-butylation of BP [14] and for HM in the isopropylation of NP [28].

3.7. Comparison of shape-selective isopropylation over SSZ-31 and other zeolites

As discussed in the previous paper, among the conventional 12-membered zeolites, HM, HY, HL, and H β , the shape-selective isopropylation of BP was observed only over HM [3,4]. The shape-selective catalysis appears to occur inside pores by a restricted transition state mechanism.

The isopropylation of BP yielded 4,4'-DIPB shape-selectively over SSZ-31 at lower selectivity than over HM. Although larger than for HM, the pores of SSZ-31 selectively permit the transition state that forms 4,4'-DIPB. The difference is thought to originate in the pore structure. Both the zeolites have 1D pores, with similar elliptical channels. The pores of SSZ-31 are larger than those of HM: 0.78 nm \times 0.65 nm for SSZ-31 and 0.70 nm \times 0.65 nm for HM. This will

be reflected in the space available for catalysis. The steric restriction for SSZ-31, particularly for the transition state, is looser than that for HM, resulting in the increased formation of 3,4'-DIPB in comparison to HM. Further isopropylation of 4,4'-DIPB occurs in small amount over SSZ-31, whereas such further reaction does not occur over HM, suggesting that the pore-wise steric restriction of SSZ-31 is looser than in HM.

The shape-selective formation of 4,4'-DIPB was not observed in the isopropylation of BP over UTD-1 with 14-membered pores of dimensions 0.75 nm × 1.00 nm [29], whereas CIT-5 with 14-membered pores of dimensions 0.72 nm × 0.75 nm [30] gave 4,4'-DIPB as the predominant product [12,31]. It is clear that shape-selective catalysis occurs inside the pores of 1D zeolite, and that the thresholds for shape-selective catalysis in the isopropylation of BP depend on the space associated with reaction sites in these zeolites.

4. Conclusion

H-[Al]-SSZ-31 (SSZ-31) zeolite was found to be active in the alkylation of BP by propene, 1-butene, and 2-methylpropene. Analogous to HM, among all the IPBP and DIPB isomers, SSZ-31 zeolite selectively formed 4-IPBP and 4,4'-DIPB in the isopropylation of BP. However, the selectivities for these isomers were relatively low compared to HM. The selective formation of 4,4'-DIPB was concluded to occur via a restricted-transition state mechanism, and the relatively low selectivity may be, therefore, due to the larger pores of SSZ-31, which provide a looser steric restriction at the transition state. The selectivity of SSZ-31 for 4,4'-DIPB was higher than that of HM, attributed mainly to the differences in pore size and the correspondingly difference in steric restriction at the transition state.

The selective formation of 4,4'-DIPB is probably due to the particular character of pores in SSZ-31 zeolite. The synthetic method is, therefore, not a principal factor in determining the shape-selective nature of SSZ-31, although the catalytic performance was found to vary according to the synthetic method employed. Encapsulated products exhibited higher selectivity for 4,4'-DIPB than the bulk products, particularly SSZ-31 synthesized by HTS. Isomerization of 4,4'-DIPB also

occurred at external acid sites due to the isomerization of 4,4'-DIPB to 3,4'-DIPB.

The selectivity for 4,4'-DIPB decreased with increasing in temperature in the bulk products due to the isomerization of 4,4'-DIPB to thermodynamically stable 3,4'-DIPB. In contrast, the selectivity for 4,4'-DIPB in encapsulated products increased with temperature. Although the reaction primarily takes place inside pores, and in particular near the pore mouth of the catalyst, the participation of deep acid sites away from the pore mouth at higher reaction temperatures enhances the generation of 4,4'-DIPB in the encapsulated products.

The bulkiness of the alkylating agent also influenced the catalysis proceeding inside the pores of SSZ-31 zeolite. The selectivity for 4,4'-dialkylbiphenyl was highest in *t*-butylation, followed by *s*-butylation and isopropylation. This order reflects the steric restriction at the transition state inside the pores.

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