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The effect of propylene pressure on shape-selective isopropylation of biphenyl over H-mordenite

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Abstract

The effect of propylene pressure on the isopropylation of biphenyl was investigated over highly dealuminated H-mordenite. The selectivity of 4,4′-diisopropylbiphenyl (4,4′-DIPB) in liquid phase products was achieved up to 90% under a high propylene pressure of 0.8 MPa, whereas the decrease of the selectivity of 4,4′-DIPB by the isomerization to 3,4′-DIPB was observed under low pressure of 0.1 MPa. However, the formation of IPBP isomers was not influenced by the pressure. The yield of 4-isopropylbiphenyl (4-IPBP) reached a maximum at 50–60% conversion of biphenyl, whereas that of 3-IPBP increased monotonously. The isomerization of 4,4′-DIPB occurred extensively under low propylene pressure, but decreased with the increase of the pressure. No significant isopropylation of 4,4′-DIPB was observed even under high pressure. The selectivities of 4,4′-DIPB encapsulated in the catalysts were more than 90% in both cases for the isopropylation of biphenyl and for the isomerization of 4,4′-DIPB under every pressure.

These results of the isopropylation and the isomerization suggest that selective formation of 4,4′-DIPB occurred in the pores, and that high selectivity under high pressures is due to the prevention of the adsorption of 4,4′-DIPB at external acid sites because of preferential adsorption of propylene. The isomerization of 4,4′-DIPB under low pressures occurred on external acid sites where no propylene was adsorbed.

Keywords: Effect of propylene pressure; Propylene; Shape-selective isopropylation; Biphenyl; H-mordenite

1. Introduction

Catalytic alkylation of aromatics using zeolites has been the subject of much research from basic and practical points of view since it is essential to match the dimensions between reactants, products and zeolite pores to achieve shape-selective catalysis [1–3]. H-mordenite (HM) has been found as a potential catalyst for the shape-selective alkylation of polynuclear aromatics such as biphenyl [4–13], naphthalene [14–18] and *p*-terphenyl [19]. We previously described that catalytic activity and the selectivity for the slimmest diisopropylbiphenyl (DIPB) isomers, 4,4′-DIPB, were increased by the dealumination of HM in the isopropylation of

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biphenyl. We discussed that high selectivity of 4,4′-DIPB was due to shape-selective reaction in the HM pores, and that the decrease of the selectivity for HM with the low SiO_2/Al_2O_3 ratio was ascribed to the participation of external acid sites because the pores were choked by coke-deposition [6,7]. However, the mechanisms such as the difference of the catalysis on intracrystalline and external acid sites, and the steric requirement of substrates and products in pores are not fully understood.

In this paper, we describe the effect of propylene pressure on the isopropylation of biphenyl over H-mordenite, and on the distribution of encapsulated products in the catalyst used for the reaction. The role of acid sites on intracrystalline and external surfaces is also discussed.

2. Experimental

2.1. Catalysts and reagents

Highly dealuminated H-mordenites (SiO_2/Al_2O_3 = 206 (HM(206)), 220 (HM(220)) were kindly supplied by Tosoh Corporation, Tokyo, Japan, and calcined in an air stream at 500°C before use for the reaction. Biphenyl and propylene were purchased commercially, and used without further purification.

2.2. Isopropylation of biphenyl

The isopropylation was carried out without solvent using a stainless steel 100- or 200-ml autoclave. Biphenyl and the catalyst was placed in the autoclave, and oxygen in the autoclave was purged out with flushing nitrogen before heating. After reaching reaction temperature, propylene was supplied, and the autoclave was kept, with stirring, at a constant pressure throughout the reaction. A standard reaction included: 400 mmol of biphenyl, 2 g of HM, 0.8 MPa of propylene pressure, 250°C of temperature, and a reaction period of 4 h. Propylene pressure was expressed by the difference between before and after the introduction of propylene.

2.3. Isomerization of 4,4′-DIPB

The isomerization of 4,4′-DIPB was examined under following conditions: 100 mmol of 4,4′-DIPB, 1 g of the catalyst, 0–0.8 MPa of propylene pressure, 250°C temperature, and a reaction period of 4 h.

2.4. Product analysis

Products of the isopropylation and the isomerization were analyzed with a Hewlett-Packard model 5890 series II gas chromatograph using an Ultra-1 capillary column (30 m × 0.3 mm), and identified with a Hewlett-Packard model 5890 series II equipped with a 5971A mass selective detector system using the same column. The yield of every product was calculated on the basis of biphenyl consumed for the reaction, and the selectivities of each isopropylbiphenyl (IPBP) and DIPB isomers are expressed as:

$$\text{Selectivity of DIPB (IPBP) isomers} = \frac{\text{Each DIPB (IPBP) isomer (mmol)}}{\text{Total DIPB (IPBP) isomers (mmol)}}$$

2.5. Analysis of encapsulated products in the catalysts used for the reaction

The catalyst used for the reaction was washed well with acetone, and dried at 110°C in an air atmosphere. The catalyst (0.5 g) was placed in 3 ml of aqueous hydrofluoric acid solution (47%). The resulting suspension was kept overnight with stirring, and neutralized with potassium carbonate. Organic products were extracted three times with 20 ml of dichrolomethane, and the organic layer was dried over anhydrous sodium sulfate. After filtration of sodium sulfate and removal of solvent in vacuo, the residue was dissolved in 5 ml of toluene, and 10 mg of naphthalene was added as an internal standard. The analysis and the identification was done by the method described above. The selectivities of DIPB isomers encapsulated products were also calculated based on the percentage of the peak area of each DIPB isomer against the total area of all isomers.

2.6. *Thermogravimetric analysis of the catalyst used for the reaction*

Thermogravimetric (TG) analysis of HM used for reaction was carried out using 10 mg of a sample in an air stream at a rate of 10°C/min up to 800°C with a MAC Science TG-DTA 2000 apparatus.

3. Results

3.1. *Isopropylaiton of biphenyl under high propylene pressure*

Fig. 1 shows a typical profile of the isopropylation of biphenyl over HM(220) under high propylene pressure. At an early stage of the reaction, biphenyl converted to isopropylbiphenyl (IPBP) isomers, especially to 4-IPBP. The yield of 4-IPBP reached a maximum at 50–60% of the conversion, and then, decreased with further reaction. However, the yield of 3-IPBP increased monotonously with the conversion. This shows that 4-IPBP was much reactive than 3-IPBP for the formation of DIPB isomers. The yield of DIPB isomers, especially, 3,4′- and 4,4′-DIPB increased with the consumption of 4-IPBP. The formation of 4,4′-DIPB was highly selective and the selectivity was almost constant throughout the reaction. These results indicate that the isopropylation of biphenyl to 4,4′-DIPB proceeded by a consecutive reaction mechanism via 4-IPBP. Biphenyl converts predominantly to 4-IPBP. 4-IPBP is a precursor to produce 4,4′-DIPB, but 3-IPBP does not participate significantly in the formation 3,4′-DIPB except at a late stage.

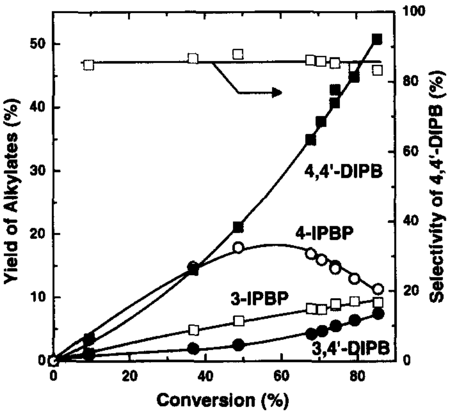

Fig. 1. The isopropylation of biphenyl over HM(220). Reaction conditions: biphenyl 400 mmol, HM(220) 2 g, propylene pressure MPa, temperature 250°C.

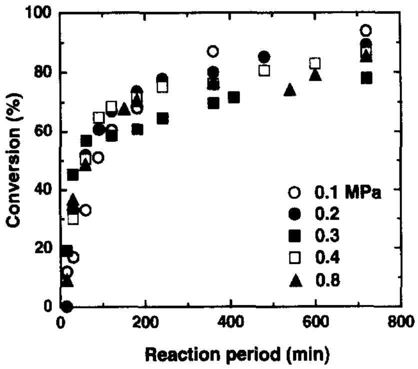

Fig. 2. Effect of propylene pressure on catalytic activity in the isopropylation of biphenyl. Reaction conditions: biphenyl 400 mmol, HM(220) 2 g, propylene pressure 0.1–0.8 MPa, temperature 250°C.

3.2. *The effects of propylene pressure on the isopropylation of biphenyl*

The conversion of biphenyl in the isopropylation reached more than 80% within 800 min at 250°C under a propylene pressure of 0.1–0.8 MPa as shown in Fig. 2. No significant influence of propylene pressure on the initial rate was observed in the isopropylation although some differences were found at a later stage. Fig. 3 shows the profile of the formation of IPBP, DIPB, and triisopropylbiphenyl (TIPB)

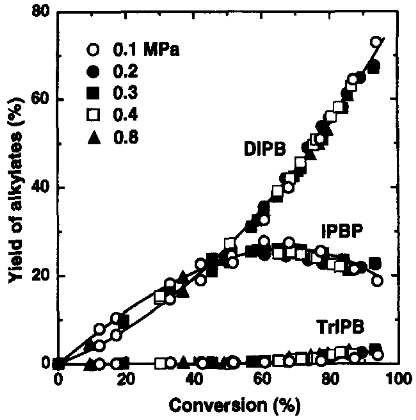

Fig. 3. Product profile of the isopropylation of biphenyl. Reaction conditions were the same as Fig. 2.

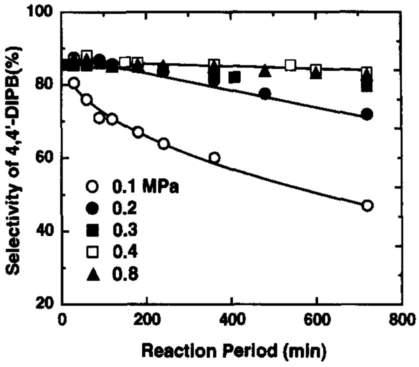

Fig. 5. Effect of propylene pressure on the selectivity of 4,4′-DIPB. Reaction conditions were the same as Fig. 2.

isomers expressed on the basis of conversion under various propylene pressures. The yields of the products are on the same plot under all pressures. Isopropylation proceeded by successive addition of propylene under every pressure. These results show that the change of product distribution shown below occurs after the formation of IPBP and DIPB isomers.

Fig. 4 shows the effect of the conversion of biphenyl on the yield of 4- and 3-IPBP under various propylene pressures. 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, but decreased with further reaction. No significant influence of propylene pressure on the yields of IPBP isomers was observed. However, the selectivity of 4,4′-DIPB was much influenced by propylene pressure as shown in Fig. 5. Under pressures higher than 0.3 MPa, the selectivity was as high as 80% in the early stages, and remained almost constant during the reaction. However, the selectivity decreased gradually under pressures less than 0.2 MPa. Fig. 6 shows the effect of propylene pressure on the formation of 4,4′- and 3,4′-DIPB. The yields of 4,4′- and 3,4′-DIPB were in a linear relationship to the yield of all DIPB isomers under pressures

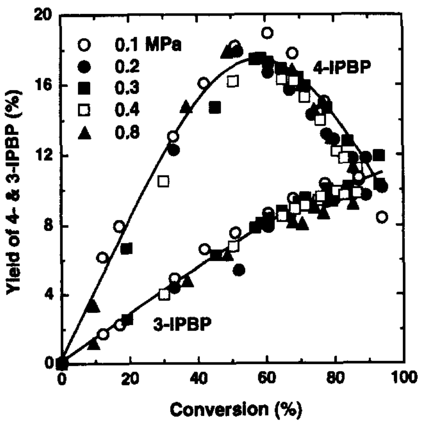

Fig. 4. Effect of propylene pressure on the yield of 4- and 3-IPBP. Reaction conditions were the same as Fig. 2.

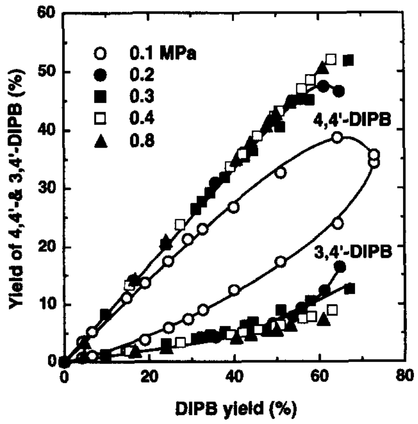

Fig. 6. Effect of propylene pressure on the yield of 4,4′- and 3,4′-DIPB. Reaction conditions were the same as Fig. 2.

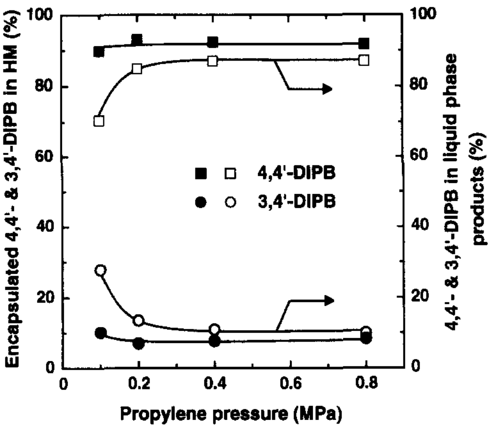

Fig. 7. The selectivity of 4,4′- and 3,4′-DIPB in encapsulated and liquid phase products in the isopropylation of biphenyl. Reaction conditions: biphenyl 200 mmol, HM(206) 1 g, propylene pressure 0.1–0.8 MPa, temperature 250°C. reaction period 4 h.

greater than 0.3 MPa. On the other hand, under a low pressure of 0.1 MPa, the yield of 4,4′-DIPB deviated downwards from the linear plot at higher pressures, and an upward deviation occurred for the yield of 3,4′-DIPB. The yield of 4,4′-DIPB decreased after reaching a maximum at 60% of DIPB isomers (at 85% conversion). The increase of the yield of 3,4′-DIPB corresponded closely to the decrease of that of 4,4′-DIPB. These results show that the decrease of the selectivity of 4,4′-DIPB under low pressure is due to the isomerization of 4,4′-DIPB to 3,4′-DIPB, because 3,4′-DIPB is thermodynamically more stable than 4,4′-DIPB [8], and that no extensive isomerization occurs under high propylene pressures.

Fig. 7 shows the comparison of the selectivity of 4,4′- and 3,4′-DIPB in encapsulated and liquid phase products of the isopropylation of biphenyl. The selectivity of 4,4′-DIPB in the liquid phase products for 0.1 MPa of propylene was lower than that for higher pressures. This coincides well with the results as described above. However, the selectivity of 4,4′-DIPB in encapsulated products was as high as 90% under all propylene pressures. These results also suggest that the decrease of the selectivity was not due to the reaction in pores but the isomerization of 4,4′-DIPB at external acid sites as discussed above.

3.3. Isomerization of 4,4′-DIPB under propylene pressure

The behavior of 4,4′-DIPB during the reaction under propylene pressure is one of important factors controlling the product distribution. Fig. 8 shows the isomerization of 4,4′-DIPB over HM(220) under propylene pressure. 4,4′-DIPB was isomerized extensively to 3,4′-DIPB without propylene or under low pressure pressures. This was accompanied by the formation of IPBP isomers via dealkylation. However, the formation of 3,4′-DIPB decreased with increasing pressure. These results correspond closely with the formation of 3,4′-DIPB in the isopropylation of biphenyl, and thus show that no extensive isomerization of 4,4′-DIPB occurred under high pressure conditions. No extensive isopropylation of 4,4′-DIPB was observed under high pressure, but a small amount of TIPB was found under a low pressure of 0.1 MPa. These results suggest that the isopropylation of 4,4′-DIPB is prevented in the pores under high pressure, and that TIPB likely formed from 3,4′-DIPB formed by the isomerization of 4,4′-DIPB.

The effect of propylene pressure on the dis-

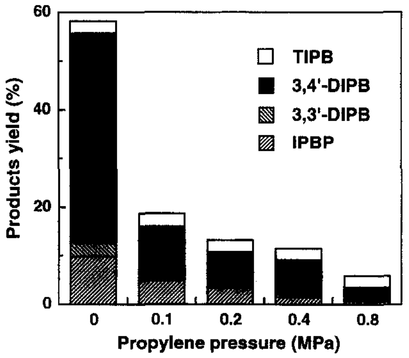

Fig. 8. The isomerization of 4,4′-DIPB under propylene pressure. Reaction conditions: 4,4′- DIPB 100 mmol, HM(220) 1 g, propylene pressure 0–0.8 MPa, temperature 250°C, reaction period 4 h.

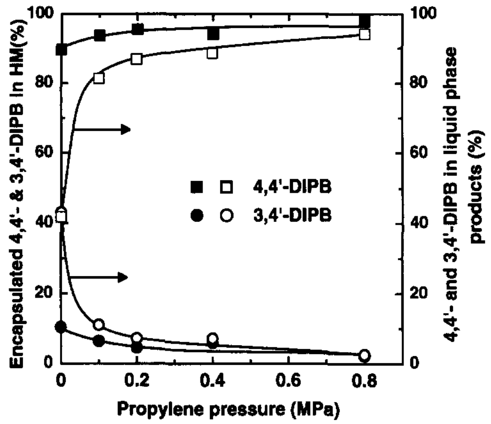

Fig. 9. The distribution of 4,4'- and 3,4'-DIPB in encapsulated and liquid phase products in the isomerization of 4,4'-DIPB. Reaction conditions were the same as Fig. 8.

tribution of 4,4'- and 3,4'-DIPB in encapsulated and liquid phase products of the isomerization of 4,4'-DIPB is summarized in Fig. 9. The percentage of 4,4'-DIPB in DIPB isomers was as high as 90% in encapsulated products under all pressure conditions. However, extensive isomerization was observed in liquid phase products without propylene or under low pressures. These results also show that the isomerization of 4,4'-DIPB did not occur in the pores under any pressures, and that 3,4'-DIPB in the liquid phase without propylene or under low pressure was formed by the isomerization of 4,4'-DIPB at the external surfaces.

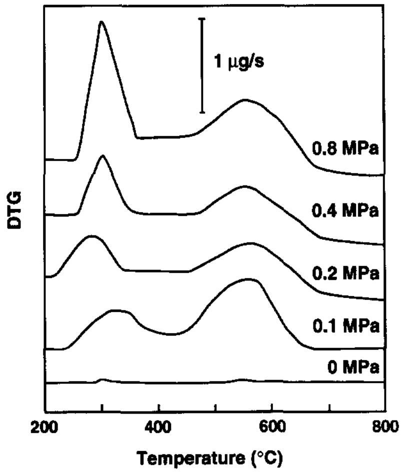

Fig. 10. TG profiles of the catalyst used for the isopropylation of biphenyl. Conditions for TG measurements: catalyst 10 mg, temperature programmed rate 10°C/min in an air stream. Reaction conditions were the same as Fig. 7.

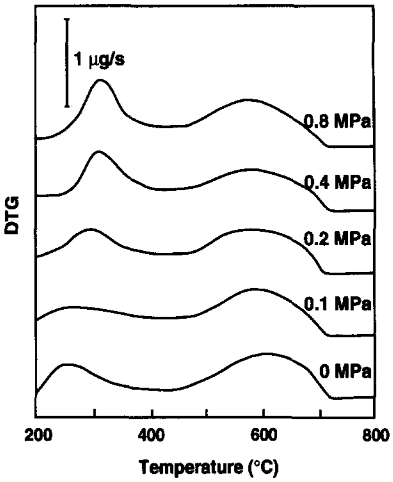

Fig. 11. TG profiles of the catalyst used for the isomerization of 4,4'-DIPB. Conditions for TG measurements were the same as Fig. 10, and reaction conditions were the same as Fig. 9.

3.4. Coke deposition in the catalysts

Figs. 10 and 11 show TG profiles of the catalysts used for the isopropylation of biphenyl and for the isomerization of 4,4'-DIPB in an air stream, respectively. The peaks at lower temperatures of around 250–350°C were ascribed to encapsulated organic products in the catalysts. The peaks at higher temperatures of 500–650°C due to combustion of deposited coke were observed both in the isopropylation of biphenyl and in the isomerization of 4,4'-DIPB under propylene pressure. No significant coke-deposition occurred by contact of biphenyl with HM in the absence of propylene. However, a peak appeared in the isomerization of 4,4'-DIPB even in the absence of propylene. These results show the principal precursor of deposited coke is isopropylated biphenyls.

4. Discussion

H-mordenite is an excellent catalyst for the shape-selective isopropylation of biphenyl. The principal factor controlling the shape-selective catalysis is fitting of the pore environment for the transition state composed of biphenyl, propylene and an acid site to form the slimmest isomers, 4-IPBP and 4,4′-DIPB [2,4–9]. The isopropylation of biphenyl over HM proceeded by successive addition of propylene. Selective formation of 4-IPBP and 4,4′-DIPB occurred in the HM pores by shape-selective catalysis. 4-IPBP is the principal precursor to form DIPB isomers, and the participation of 3-IPBP for the formation of DIPB isomers is not significant except at a late stage of the reaction. These differences of reactivity between 3- and 4-IPBP can be explained by reactant selectivity due to the difference of their bulkiness [1]. The selectivity of 4,4′-DIPB was higher than that of 4-IPBP throughout the reaction even at the initial stages. The isopropyl group of 4-IPBP may give more severe restriction than the 4-hydrogen atom of biphenyl in the transition state. These mechanisms were supported by high selectivity of 4,4′-DIPB in encapsulated products in the HM pores after the isopropylation.

As shown in Fig. 6, the isomerization of 4,4′-DIPB in the isopropylation of biphenyl occurred under low propylene pressures. However, the total amounts of each of IPBP and DIPB isomers had the same profiles under all pressure conditions as shown in Fig. 3. The selectivity of 4,4′-DIPB encapsulated in the HM pores after the reaction shown in Fig. 7 indicated 4,4′-DIPB was formed selectively in the pores under all pressure conditions. This means that the isomerization occurs after 4,4′-DIPB was formed. As shown in Fig. 8, 4,4′-DIPB itself was not isomerized significantly under high propylene pressures, but extensive formation of 3,4′-DIPB was observed without propylene or under low pressures. However, the percentage of 4,4′-DIPB encapsulated in the pores was as high as 90% in the isomerization of 4,4′-DIPB as shown in Fig. 9: this corresponds closely with the case of isopropylation. These results show that active sites for the isomerization of 4,4′-DIPB are not in the pores, but at the external surfaces. The isomerization of 4,4′-DIPB under high pressures is retarded by the preferential adsorption of propylene on acid sites. However, the adsorption of 4,4′-DIPB predominates over that of propylene under low pressure, and thus, the isomerization of 4,4′-DIPB occurs at the external sites.

Takahata and co-workers found the increase of the selectivity of 4,4′-DIPB with raising propylene pressure over HM with a low SiO_2/Al_2O_3 ratio [13]. Fellmann proposed that the increase of the selectivity was ascribed to crowding with the accumulation of propylene at active sites [20]. However, our results show that the change of the selectivity of 4,4′-DIPB with propylene pressure is due to the decrease of the isomerization of 4,4′-DIPB as discussed above.

Further isopropylation of 4,4′-DIPB occurred only in small amounts under high propylene pressure. However, almost no TIPB isomers were found in encapsulated products in HM pores after the isopropylation of biphenyl and after the isomerization of 4,4′-DIPB. HM pores are considered to allow the formation of 4- and 3-IPBP and 4,4′- and 3,4′-DIPB as discussed above, while the formation of TIPB is forbidden in the pores. Low reactivity of 4,4′-DIPB under high propylene pressure shows that external acid sites do not participate significantly in the further isopropylation of 4,4′-DIPB. The formation of TIPB in the isomerization of 4,4′-DIPB under low propylene pressure likely occurred at acid sites on the external surfaces by the isopropylation of 3,4′-DIPB.

Coke-deposition was observed under our conditions as shown in Figs. 10 and 11. Coke was deposited even under low propylene pressure in the isopropylation of biphenyl. The deposited coke was formed from biphenyl with HM only in the presence of propylene. However, coke-formation occurred by the contact of 4,4′-DIPB even in the absence of propylene pressure. Coke was deposited in a short period after the isopropylation of biphenyl was started [9]. These results suggest that the isopropylated biphenyls gave deposited coke by dehydrogenative condensation of their isopropyl group on acid sites as discussed in a previous paper [6,8,9]. Propylene oligomers were formed during the reaction [9]. They are also candidates for alternative precursors of deposited coke.

5. Conclusion

The effect of propylene pressure on the isopropylation of biphenyl was investigated over a highly dealuminated HM. The selectivity of 4,4′-DIPB was up to 90% under 0.8 MPa of propylene pressure, whereas the selectivity decreased by isomerization to 3,4′-DIPB under 0.1 MPa of the pressure. However, the formation of 3- and 4-IPBP was not influenced by pressure. The yield of 4-IPBP reached a maximum at 50–60% conversion, whereas that of 3-IPBP increased monotonously. These results indicate that the isopropylation of biphenyl proceeds by a consecutive reaction mechanism in the HM pores. In the first step, 4-IPBP was yielded shape-selectively from biphenyl. In the second step, 4-IPBP is the principal substrate to form DIPB isomers, and 3-IPBP does not participate significantly in the formation of DIPB isomers.

The isomerization of 4,4′-DIPB during the isopropylation of biphenyl occurred extensively under low propylene pressures, but decreased with increasing the pressure. However, further isopropylation of 4,4′-DIPB was not observed significantly even under high pressures. Percentages of 4,4′-DIPB in encapsulated products for the isopropylation of biphenyl and for the isomerization of 4,4′-DIPB was more than 90% under all pressures. These results show that the decrease of the selectivity of 4,4′-DIPB during the isopropylation of biphenyl is not ascribed to non-selective reaction in the pores, but to the isomerization at external acid sites.

The isopropylated biphenyls were considered principal precursors of deposited coke which was formed by dehydrogenative condensation at the isopropyl groups on acid sites.

In conclusion, the results in this work showed that selective formation of 4,4′-DIPB occurred in the HM pores under any propylene pressures, that high selectivity under high pressures is due to the prevention of the adsorption of 4,4′-DIPB on acid sites because of preferential adsorption of propylene, and that the isomerization of 4,4′-DIPB under low pressures occurred on external acid sites where no propylene was adsorbed.

References

[1] S. Csicsery, Zeolites, 4 (1984) 203.
[2] Y. Sugi and M. Toba, Catal. Today, 19 (1994) 187.
[3] P. B. Venuto, Microporous Mater. 2 (1994) 297.
[4] T. Matsuzaki, Y. Sugi, T. Hanaoka, K. Takeuchi, T. Tokoro and G. Takeuchi, Chem. Express, 4 (1989) 413.
[5] Y. Sugi, T. Matsuzaki, T. Hanaoka, K. Takeuchi, T. Tokoro and G. Takeuchi, Stud. Surf. Sci. Catal., 60 (1991) 303.
[6] Y. Sugi, T. Matsuzaki, T. Hanaoka, Y. Kubota, J.-H. Kim, X. Tu and M. Matsumoto, Catal. Lett., 27 (1994) 315.
[7] Y. Sugi, X. Tu, T. Matsuzaki, T. Hanaoka, Y. Kubota, J.-K. Kim, M. Matsumoto, T. Nakajima and A. Igarashi, Shokubai, 37 (1995) 152.
[8] G. Takeuchi, H. Okazaki, T. Kito, Y. Sugi and T. Matsuzaki, Sekiyu Gakkaishi, 34 (1991) 242.
[9] Y. Sugi, T. Matsuzaki, T. Hanaoka, Y. Kubota, J.-H. Kim, X. Tu and M. Matsumoto, Sekiyu Gakkaishi, 37 (1994) 557.
[10] G. S. Lee, J.J. Maj, S. C. Rocke and J.M. Garces, Catal. Lett., 2 (1989) 243.
[11] T. Matsuda and E. Kikuchi, Stud. Surf. Sci. Catal., 83 (1994) 295.
[12] T. Matsuda and E. Kikuchi, Appl. Catal. A, 123 (1995) 205.
[13] K. Takahata, M. Yasuda and H. Miki, Jpn. Tokyo Kokai, 88-122635.
[14] A. Katayama, M. Toba, G. Takeuchi, F. Mizukami, S. Niwa and S. Mitamura, J. Chem. Soc., Chem. Commun., (1991) 31.
[15] P. Moreau, A. Finiels, P. Geneste and J. Solofo, J. Catal., 136 (1992) 487.
[16] C. Song and S. Kirby, Microporous Mater., 2 (1994) 467.
[17] J.-H. Kim, Y. Sugi, T. Matsuzaki, T. Hanaoka, Y. Kubota, M. Matsumoto and X. Tu, Microporous Mater., 5 (1995) 31.
[18] J.-H. Kim, Y. Sugi, T. Matsuzaki, T. Hanaoka, Y. Kubota, X. Tu, M. Matsumoto, S. Nakata, A. Kato, G. Seo, and C. Pak, Appl. Catal. A, 131 (1995) 15.
[19] G. Takeuchi, H. Okazaki, M. Yamae and K. Kito, Appl. Catal., 76 (1991) 49.
[20] J. Fellmann, Catal. Highlights, 17 (1991) 1.