THE EFFECT OF PROPYLENE PRESSURE ON SHAPE-SELECTIVE ISOPROPYLATION OF BIPHENYL OVER H-MORDENITE

Y. Sugi, X. Tu[a], T. Matsuzaki, T. Hanaoka, Y. Kubota, J.-H. Kim[b], and M. Matsumoto[a]

National Institute of Materials and Chemical Research, AIST, Tsukuba, Ibaraki 305, Japan
[a]Research and Development Center, Osaka Gas Co., Ltd., Osaka 554, Japan
[b]Department of Materials Science, Tottori University, Tottori 680, Japan

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INTRODUCTION

Catalytic alkylation of aromatics using zeolites has been the subject of much research, because it is essential to match the dimensions between reactants, products, and zeolite pore to achieve highly shape-selective catalysis [1,2]. H-Mordenites have been found as potential catalysts for the shape-selective alkylation of polynuclear aromatics such as biphenyl [3-9], naphthalene [10-14], and terphenyl [15]. We previously described the activity and the selectivity of the slimmest DIPB isomers, 4,4'-DIPB, were enhanced by the dealumination because of reactions inside pores, and discussed the participation of external acid sites for the H-mordenite with the low SiO_2/Al_2O_3 ratio because the pores were choked by coke-deposition [3-7]. However, mechanisms of the catalysis by acid sites and of the steric requirement of substrate and products in mordenite pores have not been fully understood.

In this paper, we describe the effect of propylene pressure on the isopropylation of biphenyl over a highly dealuminated H-mordenite, and discuss the role of acid sites at intracrystalline and external surfaces.

EXPERIMENTAL

Catalysts and reagents. H-Mordenite (HM(220), SiO_2/Al_2O_3 = 220) was obtained from Tosoh Corporation, Tokyo, Japan, and calcined at 500 °C just before use for the reactions. Biphenyl and propylene were purchased from Tokyo Kasei Co. Ltd., Tokyo, Japan, and used without further purifications.

Alkylation. The alkylation was carried out without solvent using a 100 or 200 ml autoclave. Oxygen in the autoclave containing biphenyl and HM(220) was purged out with flashing N_2 before heating. After reaching reaction temperature, propylene was supplied to the autoclave and kept at a constant pressure throughout the reaction. A standard set of the reaction included: 200 mmol of biphenyl, 2 g of HM(220), 0.8 MPa of propylene pressure, and 250 °C of temperature. Propylene pressure was expressed by the difference between before and after the introduction of propylene.

Isomerization of 4,4'-DIPB. The isomerization of 4,4'-DIPB was examined under the condition as follows: 100 mmol of 4,4'-DIPB, 1 g of HM(220), 0-0.8 MPa of propylene pressure, 250 °C of temperature, and 4 h of period.

Product analysis. The products were analyzed with a HP-5890 GC equipped with a 25 ml Ultra-1 capillary column, and identified with a HP-5978 GC-MS. The yield of every product was calculated on the basis of biphenyl used for the reaction, and the selectivities of each IPBP and DIPB isomers are expressed as:

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

RESULTS and DISCUSSION

Effects of propylene pressure on the isopropylation

The isopropylation over HM(220) reached to above 80 % of conversion within 800 min at 250 °C under every propylene pressure among 0.1-0.8 MPa as shown in Fig. 1. No significant effect of propylene pressure was observed in the initial rate of the isopropylation although there were some differences in the late stage. These results showed that primarily principal reaction was the alkylation over HM(220) under every pressure. Figure 2 shows the profile of the formation of isopropylbiphenyl (IPBP), diisopropylbiphenyl (DIPB), and triisopropylbiphenyl (TrIPB) isomers expressed on the basis of the conversion of biphenyl under various propylene pressures. The yield of products under every pressure was on the same plot. These profiles show that the alkylation proceeds by the same reaction paths under every propylene pressure.

Figure 3 shows the effect of pressure on the yield of 4- and 3-IPBP. No significant effects of propylene pressure on the yields were observed. The yield of 4-IPBP reached the maximum at 50-60 % conversion, and decreased as further alkylation proceeded. On the other hand, the yield of 3-IPBP increased monotonously with the conversion of biphenyl. The predominant formation of 4-IPBP in the isopropylation of biphenyl to IPBP isomers occurs through the shape selective catalysis inside the pores at any propylene pressures. The isomerization of IPBP isomers was not observed under these conditions. The difference of the formation of 4- and 3-IPBP isomers can be understood on the difference of their participation to form DIPB isomers. The profiles of 3- and 4-IPBP shows that 4-IPBP is a sole precursor to produce DIPB isomers, and that 3-IPBP does not participate to the formation of 3,4'-DIPB, at least, except the late stage of the reaction. Highly selective formation of 4,4'-DIPB is also ascribed to the shape selective catalysis inside H-mordenite pores. The higher selectivity of 4,4'-DIPB compared to that of 4-IPBP shows that the isopropyl group of 4-IPBP gives more severe restriction than the hydrogen group of biphenyl at the transition states between propylene, biphenyl, and acid sites in the pores.

The formation of 4,4'-DIPB over HM(220) was much influenced by propylene pressure as shown in Fig. 4. The selectivities were as high as 80 % under all pressure conditions at early stages, and kept almost constant during the reaction under higher pressures than 0.3 MPa. However, the decrease of the selectivity was observed under lower pressures than 0.2 MPa, although no significant effects of pressure on the selectivities were observed in the formation of IPBP isomers. The decrease of the selectivity of 4,4'-DIPB corresponded to the increase of that of 3,4'-DIPB. The yields of 4,4'- and 3,4'-DIPB were in linear relations to the yield of combined DIPB isomers under higher pressure than 0.3 MPa. These results show that the alkylation occurs in steady state under high propylene pressures. The yield of 4,4'-DIPB under such a low pressure as 0.1 MPa was deviated downwards from the linear plot under higher pressures, and the upward deviation occurred for the yield of 3,4'-DIPB. The amount of 4,4'-DIPB decreased after reaching the maximum at higher conversion. The increase of the yield of 3,4'-DIPB corresponded to the decrease of the case of 4,4'-DIPB. These results show that the decrease of the selectivity of 4,4'-DIPB is not due to the change of shape-selectivity of the pore, but to its isomerization to 3,4'-DIPB because 3,4'-DIPB is more thermodynamically stable isomer than 4,4'-DIPB. The analysis of the products encapsulated inside the pores after the reaction showed that the distribution of 4,4'-DIPB was as high as 90 % under every propylene pressure [16].

Further isopropylation of 4,4'-DIPB occurred only in a small amount even under high propylene pressure. This means that alkylation of 4,4'-DIPB is prevented in the pore. H-mordenite pore allows the formation of 4- and 3-IPBP, and 4,4'- and 3,4'-DIPB, while the formation of TrIPB is forbidden in the pore.

Takahata and his co-workers found also the increase of the selectivity of 4,4'-DIPB with raising propylene pressure over H-mordenite with the low SiO_2/Al_2O_3 ratio [17]. Fellmann proposed that the increase of the selectivity was ascribed to the steric crowding with accumulation of propylene at the active sites [18]. However, our results show that the change of the selectivity of 4,4'-DIPB with propylene pressure is due to the isomerization of 4,4'-DIPB by preferential adsorption of propylene at the external surface as discussed above.

The behavior of 4,4'-DIPB under propylene pressure

The behavior of 4,4'-DIPB during the reaction is one of the essential factors for product distributions. Figure 5 shows the stability of 4,4'-DIPB in the presence of propylene pressure over HM(220). Without propylene or under low propylene pressure, 4,4'-DIPB was isomerized significantly to 3,4'-DIPB accompanying IPBP isomers formed by the dealkylation. However, the formation of 3,4'-DIPB decreased with the increase of propylene pressure. These tendencies correspond well with the influences of propylene pressure in the alkylation. 4,4'-DIPB was found as exclusive isomer encapsulated in H-mordenites under these conditions (16). These results lead us to conclude that active sites for the isomerization of 4,4'-DIPB are not inside the pores, but at external surface. The inhibition of the isomerization under high propylene pressure show that propylene adsorbs more preferentially than 4,4'-DIPB does. Adsorbed propylene prevents the adsorption of 4,4'-DIPB, and retards its isomerization. However, the adsorption of 4,4'-DIPB predominates over that of propylene under low propylene pressure to result in the enhancement of its isomerization.

Further isopropylation of 4,4'-DIPB under the conditions was observed only in small amounts even under high propylene pressure; *i.e.,* the alkylation of 4,4'-DIPB is prevented inside the pores. This is one of the reasons why shape-selective isopropylation occurs in the catalysis of H-mordenite. H-mordenite pore allows the formation of 3- and 4-IPBP, and 4,4'- and 3,4'-DIPB, while the formation of TrIPB is forbidden in the pores. The higher steric restriction of 3,4'-DIPB compared with that of 4,4'-DIPB results in the lowly formation of 3,4'-DIPB because molecular diameter of the former isomer is bigger than that of the latter. The relatively high amount of TrIPB was observed in the isomerization of 4,4'-DIPB under 0.1 MPa. TrIPB is formed by the alkylation of DIPB isomers at the external surface because of low propylene pressure.

Mechanistic aspects on the catalysis

The isopropylation of biphenyl over H-mordenite occurred inside the pores by successive addition of propylene to biphenyl. Principal factor controlling the catalysis is ascribed to steric restriction at the transition state composing biphenyl, propylene, and acid sites. Predominant formation of 4-IPBP in the isopropylation of biphenyl to IPBP isomers proceeds through the shape selective catalysis inside the pores. The difference of 4- and 3-IPBP isomers for their formation and for their alkylation to DIPB isomers is ascribed to the difference of their accommodations inside the pores. 4-IPBP is a sole precursor to form DIPB isomers, and that 3-IPBP does not participate in the formation of 3,4-DIPB. Higher selectivity of 4,4'-DIPB compared with that of 4-IPBP is due to the bulkiness of 4'-isopropyl group in 4-IPBP.

Propylene pressure changed significantly the selectivity of DIPB isomers in the isopropylation of biphenyl over H-mordenite. The isomerization of 4,4'-DIPB occurred under low pressure of propylene. However, total formations of IPBP and DIPB isomers were on the same profiles under any propylene pressure. This means that the isomerization occurs after the formation of 4,4'-DIPB. The distribution of 4,4'-DIPB encapsulated in the pores was highly selective under any pressures [16]. These results support that the isomerization of 4,4'-DIPB occurs at the external acid sites. The isomerization under high propylene pressures is prevented by the preferential adsorption of propylene on the acid sites, whereas under low propylene pressure, the adsorption of 4,4'-DIPB predominates over that of propylene, and thus, the isomerization of 4,4'-DIPB occurs at external acid sites.

The high selectivity of 4,4'-DIPB during the isopropylation suggests that the difference of the rate among acid sites at intracrysatlline and external surface is not so significant. It also reflects the amount of acid sites at the surfaces.

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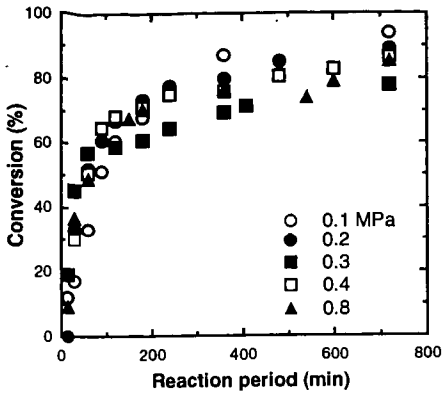

Fig. 1 Effect of propylene pressure on catalytic activity of HM(220) in the isopropylation of biphenyl. Reaction conditions: biphenyl 400 mmol, HM(220) 2 g, propylene pressure 0.1-0.8 MPa, temperature 250 °C.

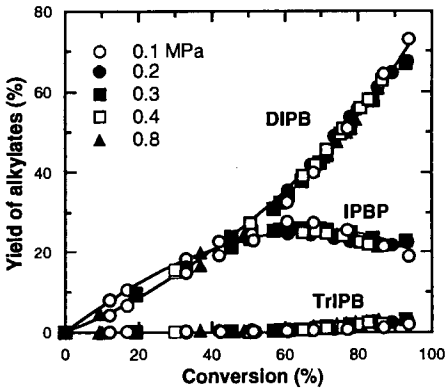

Fig. 2 Product Profile of the isopropylation of biphenyl. Reaction conditions were the same as Fig. 1.

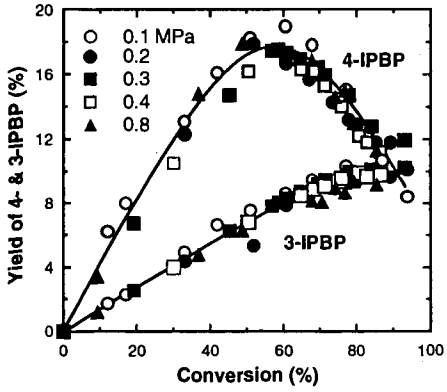

Fig. 3 Effect of propylene pressure on the yield of 4- and 3-IPBP over HM(220). Reaction conditions were the same as Fig. 1.

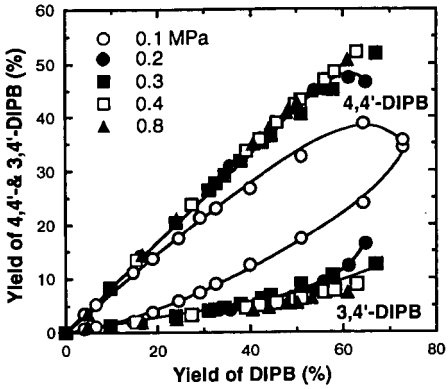

Fig. 4 Effect of propylene pressure on the yield of 4,4'- and 3,4'-DIPB over HM(220). Reaction conditions were the same as Fig. 1.

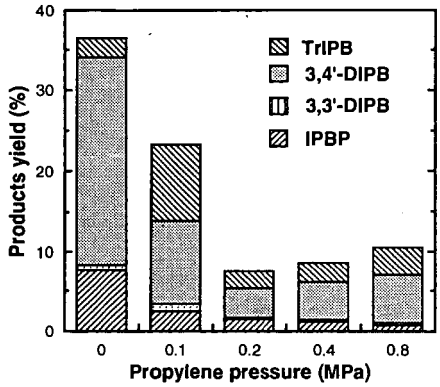

Fig. 5 Effect of propylene pressure on the isomerization of 4,4'-DIPB over HM(220). Reaction conditions: 4,4'-DIPB 100 mmol, HM(220) 1 g, temperature 250 °C, period 4 h.