Shape-Selective Catalysis over Zeolite. An Attempt in the Alkylation of Biphenyl

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Liquid phase alkylation of biphenyl (BP) was studied over large pore zeolites. Selective formation of the least bulky products, 4,4'-disopropylbiphenyl (4,4'-DIPB) occurred only in the isopropylation of BP over some large pore molecular sieves. H-mordenites (MOR) gave the highest selectivity among them. The dealumination of MOR enhanced catalytic activity and the selectivity of 4,4'-DIPB because of the decrease of coke-deposition. Non-selective catalysis occurs on external acid sites over MOR with the low SiO2/Al2O3 ratio because severe coke-deposition deactivates the acid sites inside the pores by blocking pore openings. The selectivity of DIPB isomers was changed with reaction temperature. Selective formation of 4,4'-DIPB was observed at moderate temperatures such as 250 °C, whereas the decrease of the selectivity of 4,4'-DIPB occurred at higher temperatures as 300 °C. However, 4,4'-DIPB was almost exclusive isomer in the encapsulated DIPB isomers inside the pores even at high temperatures. These decreases of the selectivity of 4,4'-DIPB are due to the isomerization of 4,4'-DIPB on the external acid sites. Some 12-membered molecular sieves, such as SSZ-24, MAPO-5 (M: Mg, Zn, Si), SSZ-31, and ZSM-12, which have straight channels, gave 4,4'-DIPB with moderate to high selectivity; however, SSZ-55, SSZ-42, and MAPO-36 (M: Mg, Zn) gave lower selectivity because of cages in 12-membered one dimensional channels. Three dimensional H-Y and Beta zeolites also yield 4,4'-DIPB in low yield because of their wide circumstances for the isopropylation of BP. The increasing the size of alkylation agent enhanced the shape-selective alkylation even for the zeolites, such as UTD-1. The ethylation of BP to ethylbiphenyls (EBPs) and diethylbiphenyls (DEBPs) over MOR was non-selective. The ethylation of BP to EBPs was controlled kinetically. However, there was difference in reactivity of EBPs and DEBPs for their further ethylation. 4-EBP was ethylated preferentially among the isomers, although the formation of 4,4'-DEBP was less selective. The least bulky 4-EBP and 4,4'-DEBP have the highest reactivity among EBPs and DEBPs for the ethylation to polyethylbiphenyls (PEBPs). These results show that the environments of MOR pores are too loose for shape selective formation of the least bulky isomers, 4-EBP and 4,4'-DEBP in the ethylation of BP, and that MOR pores have enough space for the further ethylation of 4,4'-DEBP.

Keywords: alkylation, biphenyl, shape-selectivity, large pore molecular sieves, H-mordenite, dealumination, external acid sites

1. Introduction

The synthetic processes of fine organic chemicals using solid catalysts are urgent issues for the reduction of environmental burden for manufacturing advanced materials[1]. Shape-selective catalyses using microporous crystals are promising ways for the slimmest symmetrical chemical targets for the advanced materials. Molecular sieves, such as zeolites are the most probable candidate for the purposes because their pores are uniformly distributed and have dimensions allowing both reactants and products to enter, to reside, and to leave in the catalysis[2,3]. Among them, large-pore molecular sieves, particularly H-mordenite (MOR), are suitable for the formation of the least bulky products from polynuclear aromatics such as biphenyl (BP) and naphthalene (NP), although the selectivity changes with types of reactants and zeolites[3-18].

The most important keys for the catalyst design are how to find the molecular sieves to exclude the formation of bulky molecules by the steric circumstance of their pores. Usually, organic molecules are attacked at many positions to give mixtures of many products by use of non-sterically controlled catalysts because the catalysis proceeds by kinetic control or by thermodynamical control. However, the selective synthesis of the slimmest isomers can be achieved if the micropores of molecular sieves exclude the formation of bulky isomers.

Authors have been studied the shape-selective catalysis of polynuclear aromatics, such as biphenyl (BP) and naphthalene (NP) during the decades how and where shape-selective catalysis occurs[4-14]. In this paper, we would like to review our recent works on shape-selective alkylation of BP catalyzed by large pore molecular sieves.

2. Mechanisms of Shape-Selective Catalysis

Shape-selective catalysis occurs by differentiating reactants, products, and/or reaction intermediates according to their shape and size[2,3], with sterically restricted environments being essential in this process. If all of the catalytic sites are located in the pore structure of a molecular sieves that is small enough to accommodate both the
reactants and products, the reactant’s fate and the product’s formation probability are determined by the molecular size and configurations, as well as by the characteristics of its catalytic centers, i.e., only molecules whose dimensions are less than a critical size can enter the pore and react at the internal catalytic sites. Furthermore, only molecules which can diffuse through the pores will appear in the products.

Figure 1 shows three types of mechanism of zeolite catalyzed isopropylation of BP originally proposed by Csiscery[2]. Shape-selective catalysis is due to the steric control of the catalysis by the nano-sized circumstances of zeolites, and not due to kinetic and thermodynamic controls. Three types of catalysis are proposed as Reactant selectivity mechanism, Product selectivity mechanism, and Restricted transition-state selectivity mechanism. They are distinguished depending on whether the pore size limits the entrance of reactant molecules, the departure of product molecules, or the formation of certain transition states[2,4,5].

(1) “Reactant selectivity mechanism” operates when some of the molecules in a reaction mixture can enter and react in catalyst pores. However, molecules, which are too large to diffuse through, cannot react. Only 4-IPBP among IPBP isomers will enter into pores and yield 4,4'-DIPB if this mechanism operates in the isopropylation of BP.

(2) “Product selectivity mechanism” operates when some of products formed in catalyst pore are too bulky to diffuse out. Large product molecules will convert to less bulky molecules (e.g., by equilibration or cracking), and some of them, which cannot diffuse out, may eventually deactivate catalytic sites by blocking pores. The least bulky 4,4'-DIPB will diffuse out preferentially from DIPB mixture inside pores if this mechanism operates in the isopropylation of BP. Composition of DIPB isomers inside pores pore will be in or near equilibrium inside pores.

(3) “Restricted transition-state selectivity mechanism” operates when certain reactions are prevented because corresponding transition state would require more space than available inside pores. Reactions requiring smaller transition states proceed unhindered to form smaller product molecules. 4,4'-DIPB will be obtained preferentially because transition state will be restricted the least among its isomers inside pores if this mechanism operates in the isopropylation of BP. 4,4'-DIPB will be contained predominantly in encapsulated products as well as in bulk products.

Although it is difficult to distinguish clearly “product selectivity mechanism” and “restricted transition-state selectivity mechanism”, a difference between them is considered as follows. In the former mechanism, product composition inside pores should be close to equilibrium, or at least, the selectivity for preferred products inside pores should be lower than that for bulk products. However, the selectivity for the slimmest isomer of encapsulated products should be as high as that of bulk products in the latter mechanism.

3. The Isopropylation of Biphenyl

3.1. The Catalysis over Conventional Zeolites

In the early stages of our research, we tried liquid phase isopropylation of BP over some conventional large pore zeolites[8-10]. Figure 2 shows the catalytic activity and the selectivity of diisopropylbiphenyl (DIPB) in the isopropylation of BP over the conventional 12-membered zeolites, MOR, FAU, LTL, and amorphous silica-alumina (SA) only shape-selective formation of the least bulky 4,4'-disopropylbiphenyl (4,4'-DIPB) were observed over MOR as shown in Figure 2. However, FAU and LTL, and amorphous silica-alumina gave 4,4'-DIPB only in low selectivity. On the other hand, MFI, which has 10-membered ring pore system, had very low catalytic activity with low

1) Value in parenthesis is SiO2/Al2O3 ratio of zeolites.
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selectivity for 4,4'-DIPB. The results suggested that the type of zeolites are important keys for the highly selective formation of 4,4'-DIPB. From these results, we focused on MOR for the elucidation of shape-selective catalysis.

3.2. The Isopropylation of BP over H-mordenite

Figure 3 shows reaction profiles of the isopropylation of BP over MOR (220) at 250 °C under propylene pressure of 0.8 MPa[10]. The least bulky isomers, 4,4'-DIPB among DIPB isomers, were observed predominantly throughout the reaction. The formation of 4,4'-DIPB occurred with a consumption of 4-IPBP and corresponding accumulation of 2- and 3-IPBP isomers, and the selectivity for 4,4'-DIPB was almost constant during the reaction. Highly selective formation of 4,4'-DIPB shows that the isopropylation proceeds by a consecutive mechanism: BP is isopropylated with predominant formation of 4-IPBP in the first stage, and the isopropylation of 4-IPBP yields selectively 4,4'-DIPB in the second stage.

Before starting our research, it has been known that the deactivation of MOR occurs during the catalysis because its one-dimensional channels are easy to be blocked by coke-deposition[19-21]. However, the dealumination is the key technology to enhance catalytic performances of MOR[22-24]. The dealumination of MOR was enhanced catalyst performances in the isopropylation of BP, and the selectivity for 4,4'-DIPB was highly improved in spite of decreasing the number of acid sites: MOR (220) has the highest catalytic performance in all H-mordenites examined. The peaks due to coke-deposition were observed at ca. 600 °C; however, decreased significantly by the dealumination. The peaks due to volatile organic compounds due to encapsulated product inside the channels, were also found at 300 ~ 350 °C for the dealuminated MOR. These encapsulated products were considered finger prints to elucidate the features of the catalysis in zeolite pores. The selectivities for 4,4'- and 3,4'-DIPB in encapsulated products were also shown in Figure 5. The selectivity for 4,4'-DIPB in encapsulated products was almost constant over all MOR catalysts although the MOR with low SiO2/Al2O3 ratio have the low selectivity for 4,4'-DIPB in bulk products: these low selectivities were due to the non-selective catalysis at the external surface because of choking of pores by coke-deposition.

Reaction temperature is also a key factor for shape-selective catalysis because many side reactions such as further alkylation, isomerization, de-alkylation, etc., were enhanced at high temperatures[10]. Figure 5 shows the influences of reaction temperature on the isopropylation of BP over MOR (128). 4,4'-DIPB was principal products in low and moderate temperatures, and the yield was reached maximum at 275 °C, and the increase in temperature decreased the yield of 4,4'-DIPB with accompanying the yield of 3,4'-DIPB. Further increase in temperature resulted the increase in the formation of 3,3'-DIPB with decrease in 3,4'-DIPB (Figure 5a). The decrease in the selectivity of 4,4'-DIPB at higher temperatures is due to the isomerization of 4,4'-DIPB to thermodynamically stable 3,4'-DIPB to 3,4'- and 3,3'-DIPB. Similar changes were observed in the selectivity for DIPB isomers in bulk products; however, the selectivity for 4,4'-DIPB was kept constant even at higher temperatures as 350 °C (Figure 5b). These results mean that the isomerization of 4,4'-DIPB occurs at the external acid sites because These discrepancies of bulk and encapsulated products on reaction temperature are explained by preferential adsorption of propylene. At such a moderate temperature as 250 °C, high selectivity for 4,4'-DIPB shows that the isomerization was effectively prevented by preferential adsorption of propylene. At such a moderate temperature as 250 °C, high selectivity for 4,4'-DIPB shows that the isomerization was effectively prevented by preferential adsorption of propylene. At such a moderate temperature as 250 °C, high selectivity for 4,4'-DIPB shows that the isomerization was effectively prevented by preferential adsorption of propylene. 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precursor because it is reactive compared with 2- and 3-IPBP over MOR. However, the behavior of 3-IPBP is still unclear because the amounts of 3-IPBP is low in the isopropylation. The isopropylation of 3- and 4-IPBP mixtures was examined in order to understand the role of these isomers[11]. Figure 6 summarizes influences of initial 3/4-IPBP ratio in their isopropylation over MOR (128) at 250 °C under 0.8 MPa of propylene. 4-IPBP was consumed more rapidly than 3-IPBP: apparent conversions of 4-IPBP were 78.4%, 85.0%, and 97.8% for mixture of 3- and 4-IPBP in the ratios of 1:4, 1:1, and 4:1, and 3-IPBP was consumed only 1.5%, 12.1%, and 26.5%, respectively. The selectivity for 4,4'-DIPB was decreased with the increase of 3-IPBP: 40% in the excess of 3-IPBP. These results show that 4-IPBP gave selectively to 4,4'-DIPB and that 3-IPBP yielded very slowly to products probably after disappearance of 4-IPBP. The distribution of encapsulated products was quite different from that of bulk products. 4,4'-DIPB was highly selective for all different mixtures of 3- and 4-IPBP. Even for a 4:1 mixture of 3- and 4-IPBP, the selectivity for 4,4'-DIPB was over 80% although 3-IPBP was found in a relatively high amount in encapsulated products. These results mean that 4-IPBP is highly reactive and exclusive precursor of the isopropylation of BP. Only 4-IPBP can establish transition states with propylene and acid sites in MOR pores, and 3-IPBP cannot be isopropylated although it can enter into pores. These results show that the second stage isopropylation of DIPB isomers occurs through 4-IPBP by “reaction selectivity mechanism” due to the difference of the reactivity in 3- and 4-IPBP.

From these results, we recognized that 4-IPBP is highly reactive and exclusive precursor of the isopropylation of BP over MOR, but not through “product selectivity mechanism”.

Figure 5. The influences of reaction temperature on the isopropylation of BP. (a) Yield of isopropylates, (b) Selectivity for DIPB isomers. Reaction conditions: BP, 200 mmol; MOR, 1 g; propylene, 0.8 MPa; period, 4 h.

Figure 6. The isopropylation of 3- and 4-IPBP isomers. Reaction conditions: 3- and 4-IPBP 100 mmol (total); MOR (128), 1 g; propylene, 0.8 MPa; temperature 250 °C.

3.3. The Isopropylation of BP over Some Large-pore Zeolites

As previously discussed, H-MOR pores fit the transition state to lead 4,4'-DIPB, and exclude the other transition states to bulkier isomers. From these results, we have been interested how types of zeolites influence the shape-selective character. We have examined the synthesis of some recently found molecular sieves, aluminosilicates and metaloaluminophosphates, and applied for the alkylation of BP[25-35]. The selectivities for 4,4'-DIPB over large-pore molecular sieves are summarized in Figure 7. The data were taken under our typical conditions, i.e. reaction temperature: 250 °C and propylene pressure: 0.8 MPa.

We first tried molecular sieves with AFI topology, which have 12-membered straight channels of 0.72×0.72 nm symmetrical pore entrance[25-32]. These AFI molecular sieves involve SSZ-24 as aluminosilicate and MAPO-5 (M: Mg, Zn, Si) as metaloaluminophosphate, in which the acidity appears due to imbalance of metal substitution. The shape-selective natures appeared for the isopropylation of BP: the selectivity for 4,4'-DIPB at moderate temperatures were in the level of...
higher temperature because spaces in the channels are larger compared to those of MOR. We can realize that shape-selective catalysis occurs only over one-dimensional 12- or 14-membered straight channels. MOR has the shape-selective characters to allow predominantly the transition states to bulky DIPB isomers because of loose steric restriction by their pores. Among them, MCM-68 yielded 4,4'-DIPB in the level of 60 ~70% of the selectivity for 4,4'-DIPB is due to the difference in spatial constraints for the catalysis inside the zeolites. Conventional H-Y zeolite with FAU topology had not the shape-selective character in the isopropylation of BP because their pores are too loose to exclude the formation of bulky isomers[36]. The catalysis over H-Y zeolites is controlled kinetically at lower temperatures to yield predominantly the bulky 2,x'-DIPB (x: 2,3,4); however, thermodynamically at higher temperatures to yield predominantly a mixture of 3,4'- and 3,3'-DIPB. The 3-dimensional zeolites, Beta with BEA topology, CIT-1 with CON topology, MCM-22 with MWW topology, also gave low selectivities for 4,4'-DIPB: they can allow the formation of bulky isomers because of loose steric restriction by their pores. Among them, MCM-68 yielded 4,4'-DIPB in the level of 60 ~70% of the selectivity [34]. This shape-selective catalysis is due to the structure of MCM-68. MCM-68 has 12-10-10 three dimensional structures with large cavity [37]; however the access to cavity is possible only via 10-membered pores. This structure means that 12-membered ring channels work as straight channels with 0.87×0.64 nm. This is reason why shape-selective character appeared in the isopropylation of BP. We can realize that shape-selective catalysis occurs only over one-dimensional 12- or 14-membered straight channels. MOR has the highest selectivity for 4,4'-DIPB than other four 12-membered zeolites, and CIT-5 with 14-membered ring. Their pore-structures fit to restrict effectively to exclude the transition state to bulky DIPB isomers.

3.4. The Alkylation of BP over Some Large-pore Zeolites

We found the difference in the selectivity for 4,4'-DIPB by the type of zeolites in the isopropylation of BP. We consider that these differences of the selectivity are due to the difference of steric restriction of the transition states to yield DIPB isomers. To elucidate our hypotheses, we investigated the influences of alkylation agents for the selectivity of the least bulky isomer, 4,4'-dialkylbiphenyl in the sec- and tert-alkylations, and ethylation of BP. Figure 8 shows the influences of the selectivity for 4,4'-dialkylbiphenyl in the alkylation of BP. As discussed previously, MOR gave the best selectivity for 4,4'-DIPB. SSZ-24 and CIT-5 gave the moderately high level of 10 ~15% even at moderate temperatures. The difference of the selectivity for 4,4'-DIPB is due to the difference in spatial constraints for the catalysis inside the zeolites.

Figure 7. The selectivity for 4,4'-DIPB over large pore molecular sieves in the isopropylation of BP, and their properties. Reaction conditions: temperature, 250 ℃; propylene pressure, 0.8 MPa.

Figure 8. The selectivity for 4,4'-dialkylbiphenyl over large pore zeolites in the alkylation. Reaction conditions: temperature, 250 ℃; pressure: propylene, 0.8 MPa; butene-1 and isobutene, 0.5 MPa.
selectivity for 4,4'-DIPB, however, the selectivities of UTD-1 and Beta were less than 15%. On the other hand, the selectivity for 4,4'-di-sec-butylbiphenyl (4,4'-DSBB) were improved for all zeolites in the sec-butylation of BP: SSZ-24 and CFI-5 gave the selectivity higher than 80 ~ 85%, and the selectivities of UTD-1 and Beta were enhanced to 45 ~ 55%. The similar improvements of the selectivity for 4,4'-tert-butylbiphenyl (4,4'-DTBB) were also observed in the tert-butylation of BP over the zeolites. Particularly, UTD-1 gave 4,4'-DTBB in high selectivity. Similar observation of high selective formation of 4,4'-DTBB was also reported over H-Y and BEA catalysts[38,39]. These differences of the selectivities for the least bulky 4,4'-dialkylbiphenyls show the keys for the shape-selective catalysis is the steric interaction of the transition states with pore environments of zeolites.

It is interesting target to synthesize 4,4'-diethylbiphenyl (4,4'-DEBP) in the ethylation of BP over zeolites. As shown above, the shape-selective ethylation of BP to yield 4,4'-DEBP should be important to use zeolites with small pores. First we examined the ethylation of BP over MOR (128). The ethylation of BP over MOR (128) showed quite different feature from the isopropylation as in Figure 9[40,41]. Selectivities for ethylbiphenyl (EBP) isomers were nearly in the ratio 4-EBP:2-EBP:3-EBP=1:2:2 at an early stage. This means that shape-selective catalysis did not occur in the ethylation of BP to EBP isomers: the formation of EBP isomers was kinetically controlled. However, these three EBP isomers acted differently in further reactions. The yield of 4-EBP had a maximum at 40 ~ 50% of the conversion, and decreased with the further reaction. The yield of 3-EBP was increased at early and middle stages; however, saturated at the late stages. However, the formation of 2-EBP increased steadily during the reaction. These results mean that three EBP isomers have different reactivities for further ethylation to diethylbiphenyl (DEBP) isomers, and that “reactant selectivity” mechanism operates in the step. Particularly, the least bulky isomer, 4EBP, was consumed at the highest rates to yield predominantly DEBPs having 4-ethyl group, 2,4-, 3,4-, 3,4', 2,4', and 4,4'-DEBPs; combined selectivity for these isomers were higher than 70% even at the late stage of the reaction. The formation of 3,3'-DEBP suggests the participation of 3-EBP. The yields of 4,4'-DEBP was less than 1.0% during the reaction: it increased at early stage of the reaction to reach the maximum at 40 ~ 60% of the conversion, and then decreased. This means that 4,4'-DEBP is the most reactive isomer for further ethylation to polyethylbiphenyls (PEBPs) as is the case of 4-EBP, and that reactant selectivity mechanism also operates in the step. The results show that the particular EBP and DEBP isomers are selected as reactant for further ethylation by “reactant selectivity” mechanism, and that the steric restriction at the transition state composed of BP, ethylene, and acid sites is loose for the shape-selective formation of the least bulky isomers, 4-EBP and 4,4'-DEBP by “restricted transition state selectivity” mechanism.

Currently, we study the vapor phase ethylation of BP over ZSM-12, which has the smaller pores compared to MOR; We observed the selectivity for 4,4'-DEBP in the level of 30 ~ 40%. We have not succeeded in the selective synthesis of 4,4'-DEBP by zeolites[42].

3.5. Deactivation of External Acid Site of H-mordenite

We discussed the shape-selective catalyses in the alkylation of BP over some types of zeolites. However, the decrease in the selectivity for the least bulky isomers by the isomerization and non-selective reaction were observed during the catalysis. It is important to deactivate the external acid sites to attain the high shape-selective catalysis, because the reactions on them are more rapid than that inside pores, and usually lower the selectivity for target molecules. We observed the decrease of the selectivity for 4,4'-DIPB due to the isomerization of 4,4'-DIPB at the external acid sites. The acidity measured by the cracking of 1,3,5-trisopropylbiphenyl (1,3,5-TIPB), which cannot enter the pores of MOR, showed that MOR is active even after the dealumination in spite of the decrease of the number of acid sites on external surface[10]. A small number of acid sites on external surface over highly dealuminated MOR are sufficient for the cracking reaction although these results did not always correspond to catalytic activity of the isopropylation of BP.

Ceria-modification is also an effective method for the deactivation of external acid sites of MOR in the isopropylation of BP and NP [12-14]. Figure 10 summarizes the influences of ceria amount on the selectivity for 4,4'-DIPB at 300 ℃ over Ce (30) MOR (128). The selectivity was only 50% for unmodified MOR (128), whereas it was improved to 80% by the modification with 10 wt% cerium against

2) Value in parenthesis after Ce is amount of cerium on weight basis.

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MOR (128) although small decrease of catalytic activity was accompanied. The deactivation of acid sites for the isopropylation of BP was enough by ceria-modification with 10 wt% of cerium. These results lead to the conclusion that the enhancement of the selectivity for 4,4'-DIPB was apparently due to the decrease of the isomerization of 4,4'-DIPB by the deactivation of external acid sites.

The modification of other rare earth metal oxides was also effective for the deactivation of external acid sites as shown in Figure 11 [33,43]. Optimal loading amounts varied with types of rare earth metal oxide: large amounts of ceria (at least 10 wt% as cerium against MOR (128)) were necessary for effective deactivation. However, the modification with rare earths such as lanthanum, praseodymium, samarium, dysprosium, and ytterbium oxides was effective in a small amount, and catalytic activities were lost by their high loading. Why external acid sites are deactivated by loading with rare earths is now under investigation.

4. Conclusion

The shape-selective alkylation over some types of zeolites is reviewed from our recent research. Product distribution in the alkylation of biphenyl (BP) depends on the structure of zeolite pores. The selective formation of the least bulky 4,4'-disisopropylbiphenyl (4,4'-DIPB) were observed in MOR catalyzed isopropylation of BP. These reactions are controlled by steric restriction at the transition state inside the pores and by the entrance of intermediate products molecules into the pores. Twelve-membered straight zeolites, SSZ-24, MAPO-5 (M: Mg, Zn, and Si), SSZ-31, MCM-68, and ZSM-12 gave moderate to moderate selectivity for 4,4'-DIPB. SSZ-55, SSZ-42, and MAPO-36 (M: Mg, Zn), which have 12-membered one dimensional channels with cages, gave lower selectivity. FAU and Beta zeolites did not give high selectivity for 4,4'-DIPB, either. Among 14-membered zeolites, CIT-5 gave shape-selectivity for the formation of 4,4'-DIPB; however, SSZ-53 and UTD-1 not. These results are due to the difference of the exclusion of the transition state to 4,4'-DIPB by their pores. These features of zeolite catalysis on the alkylation of BP can summarize that the effective steric control of the transition states is the key for the high selectivity for the least bulky dialkylbiphenyl, and the fitting of transition state to the pore is the most important key for the highly shape-selective catalysis.

The dealumination of HM decreases the choke of the pores by the coke-deposition because of the decrease of acid sites at intra-crystalline and external surfaces. It also reduced the non-selective isopropylation at external acid sites, and enhanced the reaction to yield the least bulky product molecules. H-mordenites have active external acid sites for acid catalysis even after deep dealumination. The modification with ceria and other rare earth metal oxides could deactivate selectively the external acid sites in the isopropylation of BP. It is important to adjust the zeolite by the modification, such as the dealumination and the modification with rare earth metal oxides, to improve the shape-selective catalysis.

The shape-selective catalyses in industry use have been widely operated in the wide range of manufacturing chemicals; however, they are limited for the simple mono-nuclear aromatics. We expect that they are one of promising way to manufacturing advanced materials. To achieve high selectivity and activity in the catalysis, it is essential to design the zeolite pores and the stereochemistry of the transition state composed of reactant aromatic compound, alkylating agent, and acid sites inside the pore. The investigation should be focused on the following points: 1) the minimization of steric restriction of transition states composed of polynuclear aromatics, alkylating agent and acids sites inside the pore, 2) the prevention of the reactions at the external surface, 3) the control of number of acid sites inside the pores, and 4) the control of acid strength.

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References

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