Korean J. Chem. Eng., **17**(1), 1-11 (2000)

FEATURED REVIEW

Shape-Selective Alkylation of Biphenyl Catalyzed by H-Mordenites

Yoshihiro Sugi†

Department of Chemistry, Faculty of Engineering, Gifu University, Gifu 501-1193, Japan

Abstract–Liquid phase alkylation of biphenyl was studied over large pore zeolites. Selective formation of the narrowest products, 4,4'-diisopropylbiphenyl (4,4'-DIPB), occurred only over HM among the zeolites with twelve-membered pore openings. These shape-selective catalyses are ascribed to steric restriction of transition state and to entrance of bulky substrates into the pores. The dealumination of HM enhanced catalytic activity and the selectivity of 4,4'-DIPB because of the decrease of coke-deposition, while the activity and the selectivity were low over HM with the low SiO_2/Al_2O_3 ratio. Non-regioselective catalysis occurs on external acid sites because severe coke-deposition deactivates the acid sites inside the pores by blocking pore openings. The selectivity of DIPB isomers was changed with propylene pressure and/or with reaction temperature. 4,4'-DIPB yielded selectively under high propylene pressure (<0.3 MPa) at 250 °C, while the selectivity of 4,4'-DIPB decreased under such low propylene pressure as 0.2 MPa. Selective formation of 4,4'-DIPB was observed at moderate temperature such as 250 °C, whereas the decrease of the selectivity of 4,4'-DIPB occurred at higher temperature as 300 °C. However, 4,4'-DIPB was almost exclusively isomer in the encapsulated DIPB isomers inside the pores under every pressure and temperature. These decreases of the selectivity of 4,4'-DIPB are due to the isomerization of 4,4'-DIPB on the external acid sites. The deactivation of external acid sites of HM was examined to reduce non-regioselective alkylation and isomerization. External acid sites were deactivated by calcination after impregnation of cerium on HM without the decrease in pore radii. Selectivities of 4,4'-DIPB were improved even at high temperatures in the isopropylation of biphenyl because of the suppression of non-regioselective alkylation and isomerization at the external acid sites. The selectivity of 4,4'-diethylbiphenyl (4,4'-DEBP) in the ethylation of biphenyl was much lower than that in the isopropylation. Among the DEBP isomers, 4,4'-DEBP has the highest reactivity for the ethylation to polyethylbiphenyls inside the pores, whereas the isopropylation of 4,4'-DIPB was negligibly low inside the pores. These differences are ascribed to the difference in steric restriction at the transition state composed of substrate, alkylating agent, and acid sites inside the pores.

Key words: Alkylation, Biphenyl, Shape-selectivity, Restricted Transition State Mechanism, H-mordenite, Dealumination, External Acid Sites, Ceria Modification

INTRODUCTION

Acid catalysis plays an important role in modern chemical processes. Liquid acids, such as sulfuric acid, hydrochloric acid, and phosphoric acid, or Lewis acids, such as aluminum halides are potential catalysts for those purposes. However, they are environmentally unfriendly because of difficulties, such as separation of products, regeneration of waste catalysts, etc. On the other hand, solid acid catalysts, such as mixed oxides and zeolites are environmentally friendly materials because of easy separation of products and catalysts and easy regeneration of catalysts. Another important point for environmentally friendly process catalysis is high performance of the catalysts, because complete conversion of substrate to target molecule is an essential condition for saving energy in a chemical process. These catalysts are fit for recently proposed concepts of "green chemical process" [1]. In these aspects, the improvement of catalytic activity, selectivity and catalyst life is the most important target for those catalytic processes.

Shape-selective reactions occur by differentiating reactants, products, and/or reaction intermediates according to their shape and size in sterically restricted environments of the pore structures of microporous crystals [2-4]. If all of the catalytic sites are located inside the pore that is small enough to accommodate both reactants and products, the reactant's fate and the product's formation probability are determined by molecular size and configurations of the pore, as well as by the characteristics of its catalytic center, i.e., only a reactant molecule whose dimension is less than a critical size can enter into the pore and react at the catalytic site. Furthermore, only product molecules that can diffuse out through the pore will appear in the product. Zeolites are the most promising microporous crystals for achieving highly shape-selective catalysis because their pores are uniformly distributed and have dimensions allowing both organic reactants and products to enter, to accommodate, and to leave.

Catalytic alkylation of mononuclear aromatics using zeolites has been the subject of much research [2, 3, 5-8]. It is essential to match the dimensions between reactants, products, and zeolite pores in order to achieve shape-selective catalysis. The pores of ten-membered ring zeolites (e.g., HZSM-5) are especially suitable for shape-selective methylation of mononuclear aromatics, while large-pore zeolites, such as H-mordenite (HM), HY, etc., have pore sizes that are too large to control the selectivity for the reaction [5-7]. On the other hand, HM is useful for catalyzing shape-selective alkylation and other related reac-

†To whom correspondence should be addressed.
E-mail: sugi@apchem.gifu-u.ac.jp

tions of mononuclear aromatics such as ethylbenzene using bulky alkylating agents [8].

Recently, the synthesis of symmetrically substituted dialkylpolynuclear aromatic hydrocarbons, such as 4,4'-diisopropylbiphenyl and 2,6-diisopropylnaphthalene, has received attention from many researchers because they are superior candidates of components for advanced materials [9]. Polynuclear aromatics require larger space for the transition state intermediate composed of reactants and acid sites inside the pores than mononuclear reactants. For these reasons, large-pore zeolites, especially HM, are suitable for the formation of the slimmest products for polynuclear aromatics such as biphenyl [10-30] and naphthalene [31-36], although the selectivity varies with reactants and zeolites. In this paper, we would like to review our recent works on shape-selective alkylation of biphenyl catalyzed by zeolites [10-23].

MECHANISMS OF SHAPE-SELECTIVE CATALYSIS

Three types of shape-selective catalyses were proposed as in Fig. 1. They are classified 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]:

(1) *Reactant selectivity mechanism* occurs when some of the molecules in a reaction mixture can enter the pores and react in catalyst pores. However, molecules, which are too large to diffuse through the pores, cannot react.

(2) *Product selectivity mechanism* occurs when some of products formed in catalyst pore are too bulky to diffuse out, being converted to less bulky molecules (e.g., by equilibration or cracking). Large product molecules, cannot diffuse out, may eventually deactivate catalytic sites by blocking the pores.

(3) *Restricted transition-state selectivity mechanism* occurs when certain reactions are prevented because the corresponding transition state would require more space than available inside the pores. Reactions requiring smaller transition states proceed unhindered to form smaller product molecules.

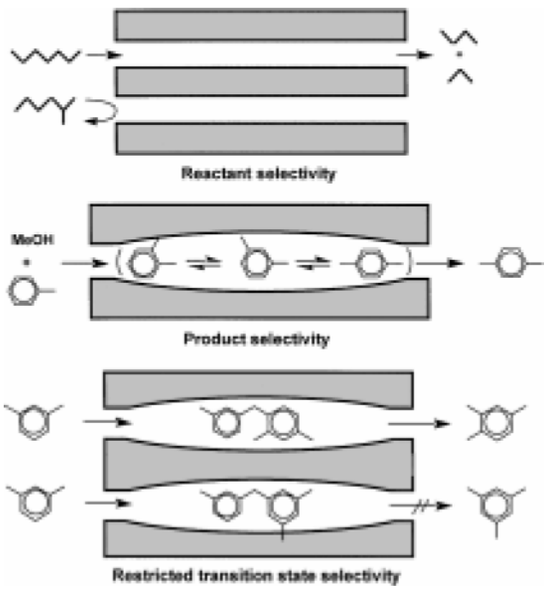

Fig. 1. Mechanisms of shape-selective catalysis.

Although a clear-cut discrimination of *product selectivity* and *restricted transition-state mechanisms* is difficult, a difference between them is considered as follows. In the former mechanism, product composition inside the pores should be close to equilibrium, or at least, the selectivity for 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.

Derouane and Gabelica [37] proposed *molecular traffic control* as another type of shape-selectivity, which could occur in zeolites having more than one type of intersecting pore system. Here, reactant molecules may preferentially enter into the catalyst through one pore system, while the products diffuse out through the other, thereby minimizing counter diffusion, and thus increasing the reaction rate.

Zeolite-catalyzed alkylation of polynuclear aromatics is simultaneously governed by several mechanisms. To achieve highly shape-selective catalysis, it is essential that the pore size precisely corresponds to the molecular dimensions of reactants and products, and to the transition state of the reaction intermediates.

ALKYLATION OF BIPHENYL[*1]

1. Catalysis over Typical Zeolites

Table 1 summarizes results of the catalysis with typical zeolites in liquid phase isopropylation of biphenyl [10,11]. The isopropylation over HY(5.8)[*2] and HL(6.1) zeolites as well as amorphous silica-alumina (SA (4.3)) was non-regioselective in the formation of three isopropylbiphenyl (IPBP) isomers. The selectivity for 4-IPBP among IPBP isomers over HY at 200 °C was as low as 41%, whereas selectivities for 2- and 3-IPBP were as high as 36% and 23%, respectively. The formation of diisopropylbiphenyl (DIPB) isomers were also non-regioselective: the selectivity for 4,4'-DIPB was less than 11%. However, the selectivity of thermodynamically more stable isomers, 3-IPBP among IPBP isomers, and 3,4'- and 3,3'-DIPB among DIPB isomers increased at 250 °C. Catalytic features of HL and SA also resembled that of HY. The selectivity for 4-IPBP over HM(23) at 250 °C was more than 70%, whereas it was less than 5% for 2-IPBP. For DIPB isomers, the slimmest isomer, 4,4'-DIPB was also formed in high selectivity (*ca.* 80%). HZSM-5(50) showed low activity even at 300 °C.

2. Isopropylation over H-Mordenite

Fig. 2 shows the changes in the selectivity for IPBP and DIPB isomers over HM(220) at 250 °C under propylene pressure of 0.8 MPa [12,15]. Shape-selective isopropylation occurred to yield predominantly the least bulky 4-IPBP among IPBP isomers, and 4,4'-DIPB among DIPB isomers. 4,4'-DIPB was

*1 The selectivity of the isomer is shown by the percentage in all isomers for each alkylates.

*2 The value in parenthesis expresses the SiO_2/Al_2O_3 ratio of zeolites.

Table 1. Isopropylation of biphenyl catalyzed by typical zeolites[a]

Catalyst (SiO_2/Al_2O_3)	Reaction temperature (°C)	Conversion (%)	Product composiiton (%)		Selectivity for IPBP (%)			Selectivity for DIPB (%)		
			IPBP	DIPB	2-	3-	4-	4,4'-	3,4'-	3,3'-
HM(23)	180	16	89	11	7	20	74	75	16	2
	250	48	73	27	5	24	71	78	14	2
HY(5.8)	200	76	60	40	36	23	41	5	8	7
	250	83	61	33	7	48	45	11	22	13
HL(6.1)	200	82	54	36	39	18	43	10	8	6
	250	84	53	47	29	25	46	10	13	6
SA(4.3)	180	67	62	38	36	15	49	16	9	5
	250	84	48	39	18	32	50	25	26	8
HZSM-5	300	6	100	0	16	30	54	-	-	-

[a]Reaction conditions: catalyst, 1 g; biphenyl, 50 mmol; propylene, 100 mmol; solvent, trans-decalin, 20 ml; Period: 4 h.

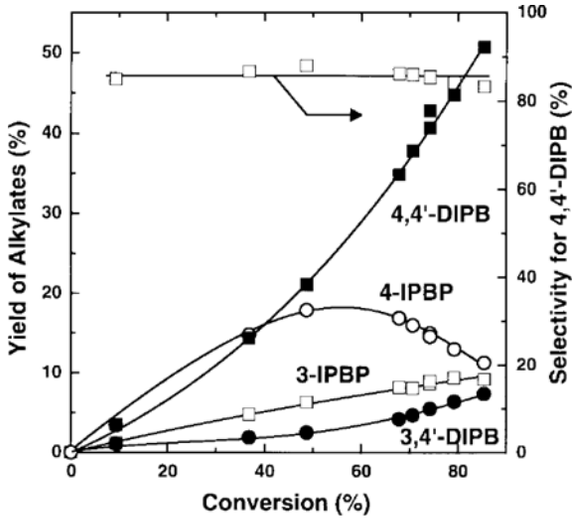

Fig. 2. The isopropylation of biphenyl over HM(220). Reaction conditions: biphenyl, 400 mmol; HM(220), 2 g; propylene pressure, 0.8 MPa; temperature, 250 °C.

yielded with the consumption of 4-IPBP with an accumulation of 2- and 3-IPBP, 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: biphenyl is isopropylated to IPBP isomers with predominant formation of 4-IPBP, and the isopropylation of 4-IPBP yields 4,4'-DIPB regioselectively in the second stage.

H-Mordenite has two types of pores, which are perpendicular to each other: twelve-membered ring elliptical pores (0.67×0.71 nm) and eight-membered ring pores (0.29×0.57 nm) [38]. Active centers in the catalysis should be inside elliptical pores because biphenyl cannot enter into the latter pores; thus these pores restrict the transition state of the isopropylation of biphenyl to form the least bulky products, 4-IPBP among IPBP isomers, and 4,4'-DIPB among DIPB isomers. The formation of IPBP and DIPB isomers with 2- and 3-isopropyl groups was prevented inside pores because corresponding transition states have bulky conformation, which requires larger space than is available at the acid sites.

3. Isopropylation over Dealuminated H-Mordenite

Acid catalysis is usually dependent on the amounts of acid sites on catalysts. However, catalytic activities are not always proportional to acid density of zeolites. In large-pore zeolites, such as HM and HY, the coke deposited inside pores is usually aromatic hydrocarbons having several nuclei. These deposits prevent acid catalysis because they choke catalytic active sites inside pores [39-41]. The major part of dense acid sites does not contribute to acid catalysis, but promotes the coke-deposition on them. For these reasons, the dealumination of zeolites is one of effective method for reduction of coke-deposition and for enhancement of catalyst performance in spite of the decrease of

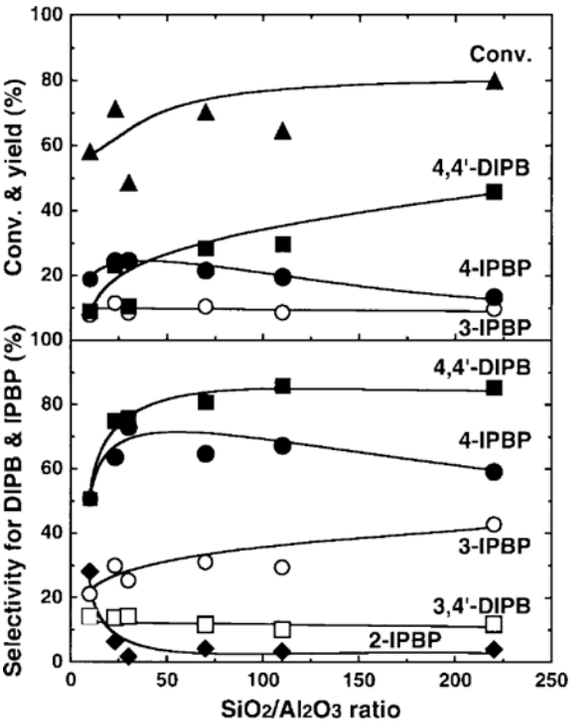

Fig. 3. Effect of the dealumination of HM on the isopropylation of biphenyl. Reaction conditions: biphenyl, 200 mmol; HM, 2 g; propylene pressure, 0.8 MPa; temperature, 250 °C; period, 4 h.

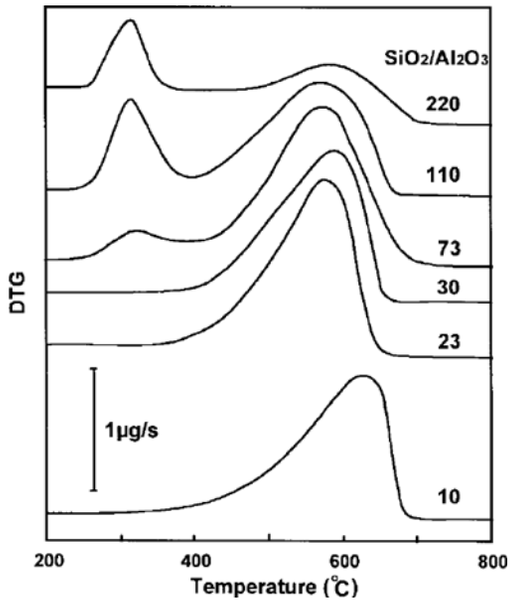

Fig. 4. Effect of the dealumination of HM on coke deposition in the isopropylation of biphenyl. Reaction conditions were as the same as in Fig. 3.

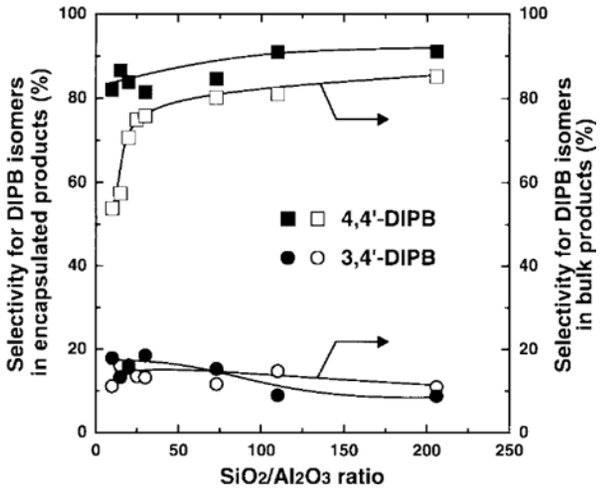

Fig. 5. Effect of the dealumination on the product distribution of encapsulated DIPB isomers inside pores and of bulk products in the isopropylation of biphenyl. Reaction conditions are the same as in Fig. 3.

acid density [42-44].

Fig. 3 shows the effect of the dealumination of HM in the isopropylation of biphenyl under propylene pressure of 0.8 MPa [12,13]. The change of the activity depending on SiO_2/Al_2O_3 ratio corresponds well to the change of the selectivity for products. The activity and the selectivity for 4,4'-DIPB was low over HM with low SiO_2/Al_2O_3 ratio although they have dense acid sites. However, catalyst performance to yield 4,4'-DIPB was enhanced by the dealumination, and thus HM(220) exhibited the highest value in spite of decreasing the number of acid sites.

Fig. 4 shows TG profiles of catalysts used in the isopropylation [12,13]. The amounts of cokes observed at around 600 °C decreased with the dealumination. Volatile organic compounds, which are ascribed to isopropylated biphenyls encapsulated inside pores, were also found at 300-350 °C for dealuminated HM with the SiO_2/Al_2O_3 ratio higher than 70 (*see below*). These results suggest that most of the volatile compounds were converted to coke-deposits inside pores for HM with low SiO_2/Al_2O_3 ratio, and that the major part of the acid sites inside pores cannot work as catalytic active sites. A high silica HM such as HM(220) effectively catalyzes shape-selective alkylation with the minimum coke deposition.

The coke-deposits were formed from biphenyl over dealuminated HM only in the presence of propylene, although the amounts were not so much [15]. Coke-deposition occurred in a short period after starting the reaction, and by the contact of 4,4'-DIPB with HM even in the absence of propylene pressure: coke-deposits are yielded from isopropylated biphenyls by de-hydrogenative alkylation at isopropyl groups and condensation to form polynuclear aromatics on acid sites. Propylene oligomers were formed during the reaction [18]. They are alternative precursors of deposited coke.

The effect of the dealumination on encapsulated products inside catalysts used for the reaction is shown in Fig. 5 [13,17]. The selectivity for 4,4'-DIPB inside pores was almost constant over all HM zeolites although the selectivity for 4,4'-DIPB in bulk products varied with SiO_2/Al_2O_3 ratio. These results suggest that shape-selective isopropylation occurs inside pores even over HM with the low ratio. Low catalytic activity and selectivity for 4,4'-DIPB in bulk products over HM with low SiO_2/Al_2O_3 ratios were due to non-regioselective catalysis at external acid sites which were still alive after choking the pores. High selectivity for 4,4'-DIPB in encapsulated DIPB isomers indicates that a *restricted transition-state mechanism* is operated in the catalysis over HM, and a *product selectivity mechanism* is not.

Lee and his co-workers [24] reported that highly dealuminated mordenites were exceptionally highly active for the isopropylation of biphenyl at 250 °C, and the yield of 4,4'-DIPB increased with increasing the SiO_2/Al_2O_3 ratio as shown in Table 2. After 20 h, DHM-2X with SiO_2/Al_2O_3 ratio of 2600 prepared from zeolon 100 gave an extremely high conversion of biphenyl (98 %) and a high yield of 4,4'-DIPB (72%). These phenomena occur because the dealumination not only reduces the number of acid sites, but also modifies pore distribution resulting in an increase in the volume of mesopore with radii of 2-200 nm. If the alkylation is diffusion limited, then high yield by DHM-2X may be due to improved diffusion caused *via* the creation of mesopores. High

Table 2. Isopropylation of biphenyl over dealuminated HM[a]

Catalyst	SiO_2/Al_2O_3 ratio	Yield of 4,4'-DIPB (%)		Surface area (m^2/g)	Pore volume (cm^3/g)	
		1 h	20 h		mico	macro[b]
Zeolon 100	10	0	0.8	319	0.133	0.061
Zeolon 1X	144	3	28.6	465	0.184	0.087
Zeolon 2X	213	15	41.4	496	0.17	0.123
DHM-1X	256	35	56.2	428	0.208	0.2
DHM-2X	2600	56	72	382	0.149	0.227

[a] Reaction conditions: biphenyl, 500 g; propylene, 0.7 Mpa; temperature, 250 °C; stirring rate, 2,000 rpm. [b] pore radius, 2-200 nm.

yield of 4,4'-DIPB could also be related to lower deactivation rate in the DHM. From XRD and adsorption data, they proposed a biphenyl packing mechanism involving a partial overlap of aromatic rings, being similar to two layer packing of benzene in twelve-membered ring pores of mordenite as originally described by Itabashi and his co-workers [45]. Since the shape-selectivity appears to be related to both the packing of the reactants and the geometry of the mordenite pore, this phenomenon is termed as *reactant assisted shape-selectivity* [24]. The occupation of 12-membered ring pores in mordenite by polynuclear aromatics suggests that propylene may diffuse into zeolite pores, at least partially, *via* eight-membered ring pores. The high yield of 4,4'-DIPB is considered to be a good example of *molecular traffic control* [24, 25].

4. Influences of Propylene Pressure on the Isopropylation

Pressure of propylene is one of key factors for selective formation of 4,4'-DIPB. High pressure of propylene effectively enhanced the isopropylation, but a decrease of the selectivity for 4,4'-DIPB was observed during the reaction under the low pressures over HM(220) as shown in Fig. 6 [14,15,17]. Because 3,4'-DIPB is thermodynamically more stable isomer than 4,4'-DIPB [19], the decrease of the selectivity was ascribed to the isomerization of 4,4'-DIPB to 3,4'-DIPB, but not to the decrease of the selectivity to form 4,4'-DIPB. Fig. 7 shows the effect of propylene pressure on the selectivities for 4,4'-DIPB in bulk and encapsulated products [15,17]. The selectivity for 4,4'-DIPB inside pores was almost constant under all pressures. These results indicate that the isomerization does not occur inside pores, but at external acid sites.

The isomerization of 4,4'-DIPB under high pressures is considered to be retarded by preferential adsorption of propylene on acid sites [15,17]. However, the adsorption of 4,4'-DIPB should predominate over that of propylene under low pressure, and thus, the isomerization of 4,4'-DIPB occurs at external acid sites. Another interesting feature is that no further isopropylation of 4,4'-DIPB to polyisopropylbiphenyls (PIPB) was observed even under high pressure of propylene [15,17]. These results are explained by no

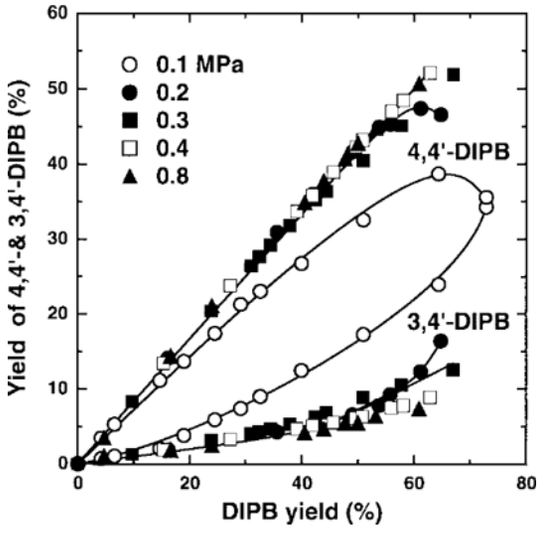

Fig. 6. Effect of propylene pressure on the yield of 4,4'- and 3,4'-DIPB in the isopropylation of biphenyl. Reaction conditions biphenyl, 400 mmol; HM(220), 2 g; propylene pressure, 0.1-0.8 MPa; temperature, 250 °C.

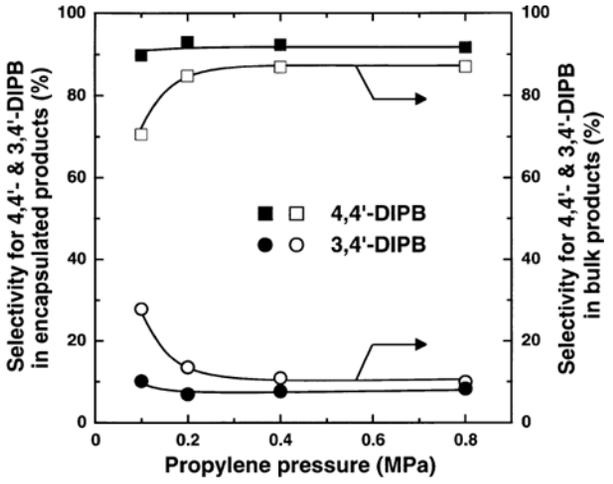

Fig. 7. Effect of propylene pressure on the product distribution of encapsulated 4,4'- and 3,4'-DIPB inside the pores and of the bulk products in the isopropylation of biphenyl. Reaction conditions: biphenyl, 200 mmol; HM(206), 1 g; propylene pressure, 0.1-0.8 MPa; temperature, 250 °C; period, 4 h.

enough space inside pores for the transition state of further isopropylation of 4,4'-DIPB. This should be one of the reasons for highly regioselective formation of 4,4'-DIPB.

Takahata and his co-workers found the increase of the selectivity for 4,4'-DIPB with raising propylene pressure over HM with the low SiO_2/Al_2O_3 ratio [25, 26]. Fellman proposed that the increase of the selectivity was ascribed to crowding with the accumulation of propylene at active sites [27]. However, it is obvious from above discussion that the change of the selectivity for 4,4'-DIPB with propylene pressure is due to the decrease of the isomerization of 4,4'-DIPB.

Matsuda and his co-workers also noted that extensive isomerization of 4,4'-DIPB for HM(20) catalyst was observed at high conversion of biphenyl in the presence of limited amounts of propylene (initial propylene/biphenyl=1.0) [28]. However, the selectivity was almost constant during the reaction although the selectivity for 4,4'-DIPB was less selective than that of HM(10) catalyst. They considered that low isomerization activity of HM (10) is related to its weak acid strength.

5. Influences of Reaction Temperature on the Isopropylation

Reaction temperature is also a key factor for the selective formation of 4,4'-DIPB because reactions at high temperature enhanced many side-reactions such as further alkylation, isomerization, de-alkylation, *etc*. Fig. 8 shows the effects of reaction temperature on the yield of DIPB and IPBP isomers in the isopropylation of biphenyl [16,17]. The yield of 4,4'-DIPB increased with the temperature, and reached the maximum at 250 °C. However, it decreased with the increase of the yield of 3,4'-DIPB at temperatures high than 275 °C. Moreover, further isomerization of 3,4'-DIPB to 3,3'-DIPB occurred above 300 °C. These changes are due to the isomerization of 4,4'-DIPB to thermodynamically stable isomers, 3,3'- and 3,4'-DIPB [19]. Fig. 9 shows the effects of reaction temperature on the selectivity for 3,3'-, 3,4'- and 4,4'-DIPB in the isopropylation of biphenyl [16, 17]. Product distribution of encapsulated products is quite different from

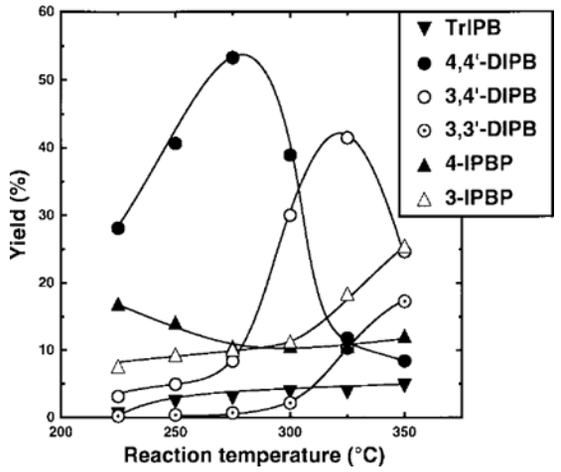

Fig. 8. Effect of reaction temperature on the yield of IPBP and DIPB isomers in bulk products. Reaction conditions: biphenyl, 200 mmol; HM, 1 g; propylene, 0.8 MPa; period, 4 h.

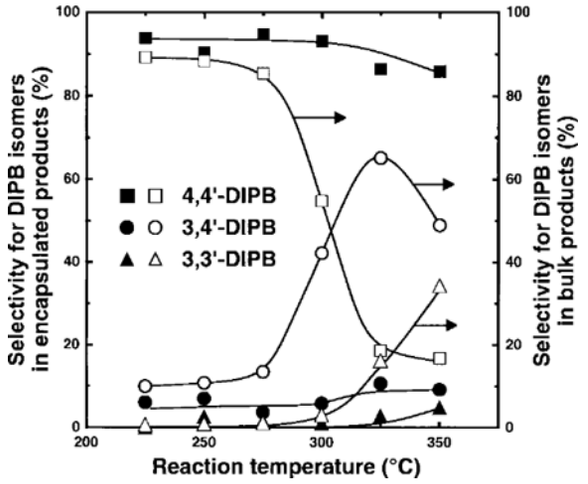

Fig. 9. Effect of reaction temperature on the selectivity for DIPB isomers in bulk and encapsulated products. The reaction conditions are the same as Fig. 8.

that of bulk products. The selectivity for 4,4'-DIPB in encapsulated products was higher than 80% at all temperatures, even at 350 °C. However, the selectivity for 4,4'-DIPB in bulk products varied with reaction temperature, and the changes of the selectivities corresponded well to the yield of DIPB isomers. Selective formation of 4,4'-DIPB was observed at temperatures below 275 °C, whereas the decrease of the selectivity for 4,4'-DIPB in DIPB isomers was compensated with the increase in that for 3,3'- and 3,4'-DIPB. The results indicate that shape-selective isopropylation occurs inside HM pores even at such high temperatures as 350 °C, and that low selectivities for 4,4'-DIPB in the bulk products at high temperatures are due to the isomerization on external acid sites and not to the lack of shape-selectivity inside the pores.

The discrepancies of bulk and encapsulated products on reaction temperature are also explained by preferential adsorption of propylene [16,17]. At such a moderate temperatures as 250 °C, the high selectivity for 4,4'-DIPB shows that the isomerization was effectively prevented by preferential adsorption of propylene

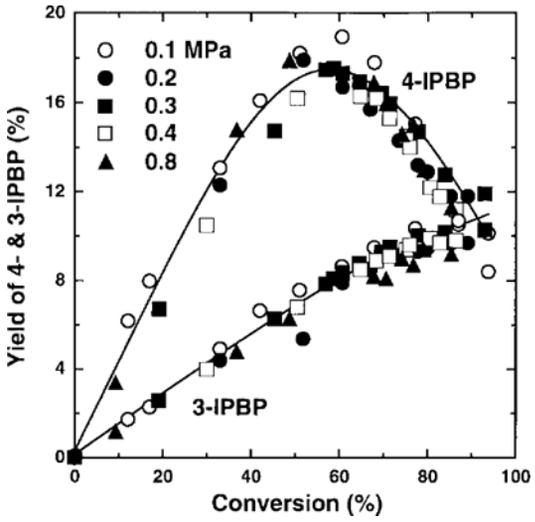

Fig. 10. Effect of propylene pressure on the yield of 4- and 3-IPBP in the isopropylation of biphenyl. Reaction conditions are the same as Fig. 6.

at external acid sites. However, at high temperatures, the adsorption of propylene could not play a primary role in controlling the isomerization of 4,4'-DIPB at external acid sites.

6. Role of 3- and 4-IPBP in the Isopropylation of Biphenyl

Fig. 10 shows the yield of 3- and 4-IPBP against the conversion in the isopropylation of biphenyl under various pressures of propylene [15]. The yields of 3- and 4-IPBP are plotted on the line. The yield of 4-IPBP had maximum selectivities at the conversion of 40-60%, and then decreased with the conversion, whereas the yield of 3-IPBP increased steadily with the conversion except the late stage of the reaction. These results show that 4-IPBP is the principal precursor in second stage isopropylation to yield DIPB isomers, and that 3-IPBP may not participate to the formation of 3,4'- and 3,3'-DIPB.

The isopropylation of mixtures of 3- and 4-IPBP was examined to clarify further roles of 3- and 4-IPBP. Fig. 11 summarizes influences of ratio of 3- and 4-IPBP in their isopropylation over HM(128) at 250 °C under 0.8 MPa of propylene [20]. 4-IPBP was consumed more rapidly than 3-IPBP: apparent conversions of 4-IPBP were 78.4%, 85.0%, and 97.8% for 1:4, 1:1, and 4:1 of ratios of mixtures, 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 was isopropylated selectively to 4,4'-DIPB if it is present in large amounts, and that 3-IPBP was isopropylated after disappearance of 4-IPBP to products which are principally composed of 3,3'- and 3,4'-DIPB.

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 [20]. 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 at relatively high amounts inside the pores. These results mean that 4-IPBP is highly reactive and selective to the formation of 4,4'-DIPB.

The isopropylation of mixtures of 3- and 4-IPBP showed that the isopropylation of 4-IPBP was almost the only precursor of

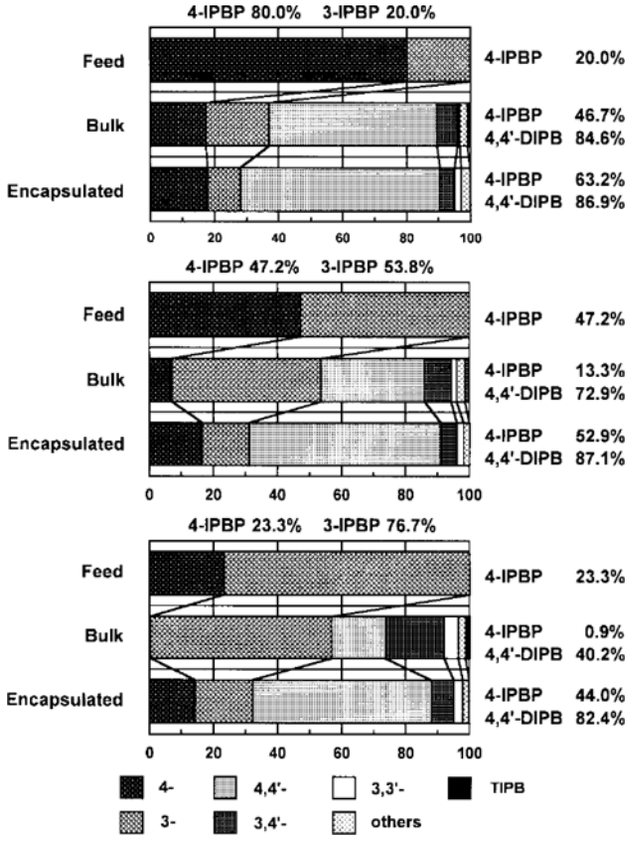

Fig. 11. Influences of 3- and 4-IPBP on their isopropylation. Reaction conditions: 3-/4-IPBP, 200 mmol (total); HM(128), 1 g; propylene, 0.8 MPa; period, 4 h.

the isopropylation. 4-IPBP can allow establishment of active complex with propylene and acid site in HM pores, whereas 3-IPBP cannot. These shape-selective catalyses occurred through a *restricted transition state mechanism*, and a *reactant selectivity mechanism* was not operated in the isopropylation of biphenyl over HM.

7. Effects of the Modification of H-Mordenite

As discussed above, the prevention of the isomerization of 4,4'-DIPB at external acid sites is the important factor for selective synthesis of 4,4'-DIPB. For this purpose, we attempted the deactivation of external acid sites by ceria modification [21]. Dealuminated HM has acid sites active for the cracking of 1,3,5-triisopropylbenezene (1,3,5-TIPB) as shown in Table 3. The cracking of 1,3,5-TIPB occurs only on external acid sites because it is too bulky to enter HM pores. Ceria-modification effectively deactivated the cracking. The pores are open for the adsorption of naphthalene and 2,6-diisopropylnaphthalene as shown in Table 4. These results show that ceria modification effectively deacti-

Table 3. Cracking of 1,3,5-TIPB over Ce(30)HM(128)[a]

Catalyst	Conversion of 1,3,5-TIPB (%)
HM(128)	35.9
Ce(30)HM(128)	0.6

[a]Reaction conditions: temperature, 350 °C; flow rate: W/F, 3.5 g·h/mol.

Table 4. Adsorption of NP and 2,6-DIPN on Ce(30)HM(128)[a]

Catalyst	Naphthalene (mg/g)	2,6-DIPN[b] (mg/g)
HM(128)	49.8	24.7
Ce(30)HM(128)	50.1	18.9

[a]Conditions: 1,3,5-TIPB solution of naphthalene (4 wt%) and 2,6-DIPN (4 wt%) was contacted with the catalyst during 24 h at room temperature. [b]2,6-diisopropylnaphthalene.

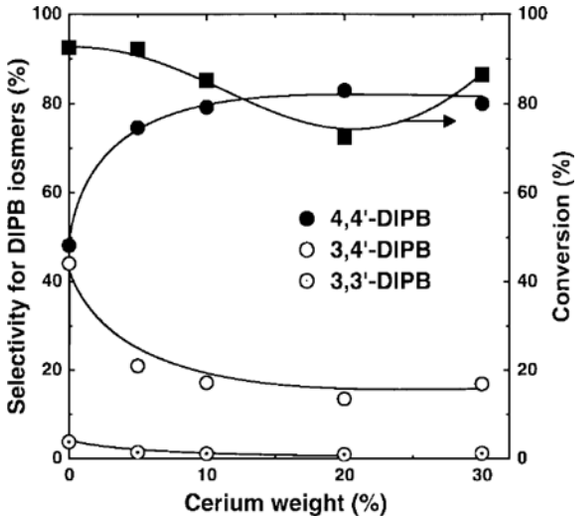

Fig. 12. Effects of cerium amounts on the selectivity of 4,4'-DIPB in the isopropylation of biphenyl. Reaction conditions: biphenyl, 200 mmol; catalyst 1 g (as unmodified HM(128)); propylene pressure, 0.8 MPa, temperature, 300 °C; period, 4 h.

vated external acid sites with a minimum choking of the pores.

Fig. 12 summarizes the effects of ceria amount on the selectivity for 4,4'-DIPB at 300 °C [21]. The selectivity was only 50% for HM. However, it was enhanced by ceria-modification, and reached to 80% by the modification with 10 wt% cerium against HM although a slight decrease of catalytic activity was accompanied.

The effects of reaction temperature on the selectivity for 4,4'-DIPB in the isopropylation of biphenyl under 0.8 MPa of propylene over Ce(30)HM(128)[*3] are shown in Fig. 13 [21]. The selectivity for 4,4'-DIPB over Ce(30)HM(128) was high even at such a high temperature as 300 °C: the isomerization of 4,4'-DIPB was effectively prevented although catalytic activity was decreased. Neither significant formation of 3,4'-DIPB was found in the isomerization of 4,4'-DIPB at 300 °C under propylene pressure of 0.8 MPa (*see previous sections*). These results show that the formation of 4,4'-DIPB occurs inside HM pores, and that the isomerization of 4,4'-DIPB at the external acid sites is prevented by ceria-modification. Similar improvement of 2,6-diisopropylnaphthalene was found by ceria-modification of HM [32, 33].

Matsuda and his co-workers [28, 29] showed that the modifi-

[*3] Values in parenthesis after Ce expresses the amount in weight percentage of Cerium on HM.

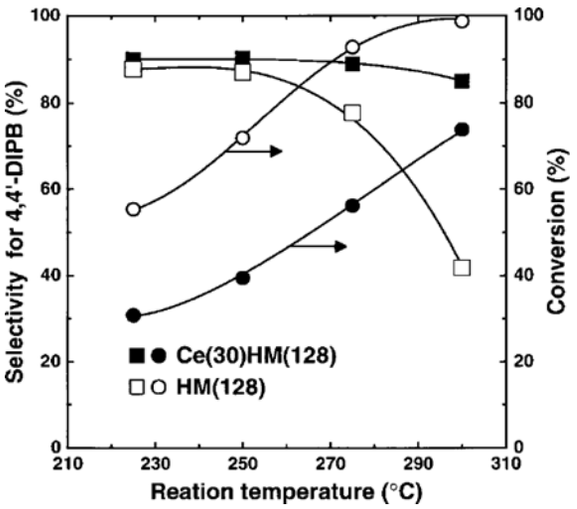

Fig. 13. Effects of reaction temperature on the isopropylation of biphenyl over unmodified and ceria modified HM. Reaction conditions: biphenyl, 200 mmole; catalyst 1 g (as unmodified HM(206)); propylene pressure, 0.8 MPa; period, 4 h. Solid marks: Ce(30)HM(128). Open mark: HM(128).

cation of the external surface of HM with tributyl phosphonate (TBP) reduces the decrease in 4,4'-DIPB yield during the reaction. The selectivity for 4,4'-DIPB was enhanced by the modification, and modified HM(10) catalyst showed the highest selectivity. Because TBP cannot enter into the pores, the modification deactivates acid sites only at external surfaces without changing the properties of acid sites inside the pores. Actually, the cracking activity of 1,3,5-TIPB was extensively reduced by the modification although that of cumene was unchanged. These results indicate that the modification with TBP prevents the isomerization of 4,4'-DIPB.

8. Isopropylation over HY, HL, and Other Zeolites

The catalysis over HY and HL zeolites is quite different from that over HM. The product distribution over these zeolites resembled the case of SA: the formation of 4,4'-DIPB was nonregioselective (Table 1) [11]. These catalyses are not controlled by the environments of the pores because both zeolites have enough space of pores for the transition states which allow the formation of all the IPBP and DIPB isomers. Instead, the product distribution markedly changes by the reaction temperature [19]. At low temperatures, the catalyses are controlled by higher reactivity at 2- and 4-positions for alkylation than case of 3-position. However, amounts of 3- and 4-IPBP, and 3,4'- and 3,3'-DIPB increased with increasing temperature. These isomers may be formed by the isomerization of IPBP and DIPB isomers with 2-isopropyl groups because the former isomers are thermodynamically more stable isomers than the latter. These results show that the isopropylation of biphenyl over HY, HL, and SA is controlled by the reactivity of the reactant molecules at low temperatures, and by the thermodynamic stability of the product molecules at higher temperatures.

Matsuda and his co-workers examined the isopropylation of biphenyl over H-offretite and SAPO-11 [30]. H-Offretite has pore size of 0.67×0.68 nm, but its pore has cages in channels [38]. SAPO-11 has pores of 0.63×0.39 nm [38]. H-Offretite was less selective for the formation of 4,4'-DIPB than HM although their catalytic activities were comparable. SAPO-11 exhibited a comparable selectivity for 4,4'-DIPB to HM although catalytic activity was low. The formation of 4,4'-DIPB over these two zeolites was shape-selective in comparison with the thermodynamically attainable level.

9. Alkylation with Other Alkenes over H-Mordenite

As discussed above, the steric requirement at the transition state is essential for high selectivity in the isopropylation of biphenyl. The selectivity should be highly dependent on the bulkiness of alkene. We investigated the nature of catalysis against the bulkiness of alkene.

The ethylation of biphenyl gave quite different feature from the isopropylation [36-40]. Selectivities for ethylbiphenyl (EBP) isomers were nearly in the ratio 4-EBP:3-EBP:2-EBP=1:2:2 at an early stage [22, 23]. This means that the ethylation of biphenyl to EBP isomers is controlled kinetically. However, these three isomers act differently at higher conversion. 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 increased at early and middle stages, and was saturated at the late stage. However, the formation of 2-EBP increased steadily during the reaction. These results suggest that these three isomers have different reactivities for further ethylation to give diethylbiphenyl (DEBP) isomers. Especially, the slimmest isomer, 4-EBP, was consumed at the highest rates to yield predominantly DEBP isomers having 4-ethyl group, 2,4-, 3,4-, 3,4'-, 2,4'-, and 4,4'-DEBP. The formation of 3,3'-DEBP suggests the participation of 3-IPBP. The yield of 2,4-, 3,4-, 3,4'-, and 2,4'-DEBP increased with the conversion, while the yield of 4,4'-DEBP kept constant during the re-

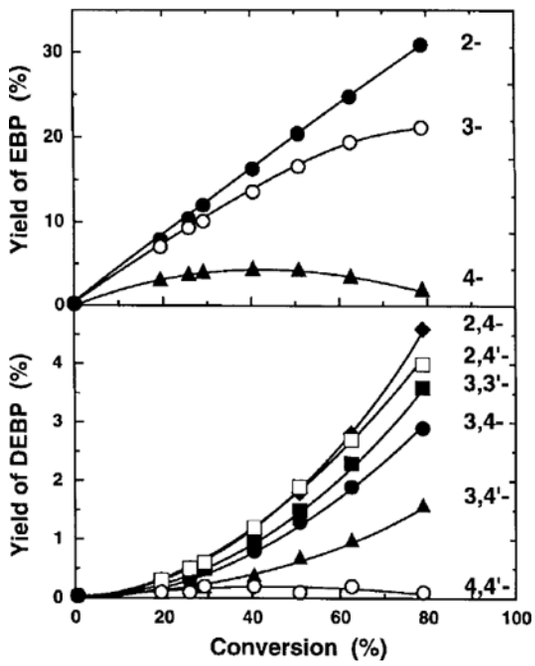

Fig. 14. Profile of formation of EBP and DEBP isomers in the ethylation of biphenyl. Reaction conditions: biphenyl, 200 mmol; HM(206), 1 g; ethylene, 0.8 MPa; temperature, 220 °C.

Table 5. Effect of alkene on isopropylation of biphenyl over HM[a]

Alkene	Reaction temperature (°C)	Conversion (%)	Product composition (%)		Selectivity for MABP (%)			Selectivity for DABP (%)		
			MABP[b]	DABP[c]	2-	3-	4-	4,4'-	3,4'-	3,3'-
Ethylene	250	20	86	14	36	45	19	7	n.d.[d]	n.d.
Propylene	250	48	73	27	5	24	71	78	14	2
Butene-1	220	35	82	17	3	13	82(2[e])	82	7	6
2-Methylpropene	220	41	67	33	-	4	94(2[f])	100	-	-
Hexene-1	220	39	91[i]	9	2[g] 12[h]	8[g] 14[h]	90[g] 75[h]	n.d. n.d.	n.d. n.d.	n.d. n.d.

[a] Reaction conditions: biphenyl, 50 mmol; alkene, 100 ml; solvent, *trans*-decalin, 20 ml; HM, 1 g period, 4 h. [b] Alkylbiphenyl. [c] dialkylbiphenyl. [d] not determined. [e] 2-t-butylbiphenyl. [f] 4-isobutylbiphenyl. [g] 2-hexylbiphenyl (2-HBP). [h] 3-hexylbiphenyl. [i] 2-HBP:3-HBP=77:23.

action. This means that 4,4'-DEBP is the most reactive isomer for further ethylation to polyethylbiphenyls. These results show that the steric restriction at the transition state composed of biphenyl, ethylene, and acid sites is too loose for the shape-selective formation of the slimmest isomer, 4,4'-DEBP.

The alkenes higher than butenes gave similar product patterns for alkylbiphenyls (4-ABP) and 4,4'-dialkylbiphenyls (4,4'-DABP) in the alkylation of biphenyl [11]. Especially, 2-methylpropene, which gives the most bulky carbonium ions, yielded selectively 4-*t*-butylbiphenyl and 4,4'-di-*t*-butylbiphenyl. With hexene-1, a mixture of biphenyls with 2- and 3-hexyl groups (2- and 3-HBP) was produced in an approximate ratio of 3:1. 3-HBP was formed by the alkylation after the isomerization of hexene-1 to hexene-2, and had a higher *para*-selectivity than 2-HBP.

10. Isopropylation and Ethylation of 4-Alkylbiphenyls over H-Mordenite

The isopropylation and the ethylation of 4-alkylbiphenyls (4-ABP) (alkyl=methyl, ethyl, isopropyl) were examined to elucidate the interaction at the transition state in the pores [22, 23]. 4-Methyl-4'-isopropylbiphenyl (4,4'-MIPB), 4-ethyl-4'-isopropylbiphenyl (4,4'-EIPB), and 4,4'-DIPB, were obtained selectively from corresponding 4-ABP in the isopropylation. The selectivity for 4,4'-DABP increased in the order: 4,4'-MIPB<4,4'-EIPB <4,4'-DIPB. The selectivity for 4-IPBP was *ca.* 70% at the early stage of the isopropylation of biphenyl. Moreover, in the isopropylation of *p*-terphenyl, the selectivity for 4-isopropyl-*p*-terphenyl was higher than 90% at the early stage of the reaction. These results show that the 4-substituted group enhanced shape-selective catalysis inside the pores in the order: none<methyl< ethyl<isopropyl≤phenyl. This is the order of bulkiness of substrate. On the other hand, the selectivity for 4,4'-DABP in the ethylation was much lower than that in the isopropylation although bulkiness of the 4-substituted group reflected on the selectivity for the former reaction. The selectivity for 4,4'-EIPB in the isopropylation of 4-EBP was much lower than that in the ethylation of 4-IPBP. These results show that the influence of bulkiness of alkene on the selectivity is much higher than that of 4-substituted group.

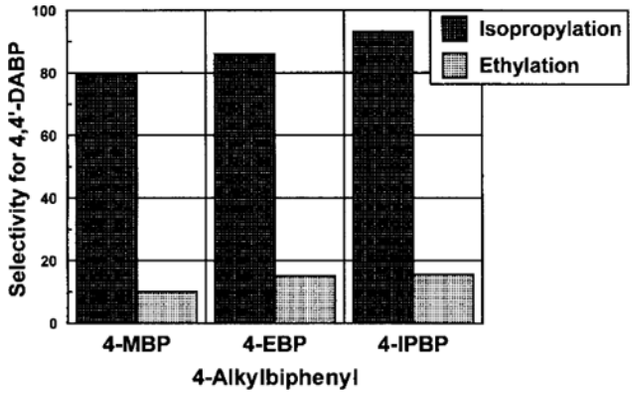

Fig. 15. The isopropylation and the ethylation of 4-alkylbiphenyl. Reaction conditions. Isopropylation: substrate, 100 mmol. HM(206), 1 g. temperature, 250 °C, propylene, 0.8 MPa, period, 4 h. Ethylation: substrate, 100 mmol; HM (206), 1 g; temperature, 220 °C; ethylene, 0.8 MPa; period, 0.5 h.

CONCLUSION

Product distribution in zeolite-catalyzed alkylation of biphenyl depends on the structure of zeolite pores. High regioselectivities were observed in the HM catalyzed isopropylation of biphenyl to yield predominantly the least bulky products 4,4'-DIPB among DIPB isomers. 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. On the other hand, the catalyses with large pore HY and HL zeolite are controlled at low temperature by the electron density of the reactant molecule and at higher temperature by the stability of the products molecules because their pores have enough space for a transition state, which allows the formation of all corresponding isomers.

The dealumination of HM decreases the choke of the pores by the coke deposition because of the decrease of acid sites at intracrystalline and external surfaces. It also reduced the non-regioselective isopropylation at external acid sites, and enhanced the reaction to yield the least bulky product molecules. The pressure of propylene is also an important key factor for high yield of 4,4'-DIPB in the isopropylation of biphenyl, because the isomerization of 4,4'-DIPB occurred significantly under low pressure of propylene at external acid sites.

H-Mordenite has active external acid sites for acid catalysis

even after the deep dealumination. It is important to deactivate the external acid sites, because the reaction on them is more rapid and less regioselective than that inside the pores. The modification with ceria and phosphorus oxide could selectively deactivate the external acid sites in the isopropylation of biphenyl. Especially, the modifications with ceria prevent the isomerization of 4,4'-DIPB in the isopropylation of biphenyl.

Shape-selective catalysis is the most promising way for an environmentally friendly process. It is important to develop high performance catalysts to attain the purpose. To achieve high selectivity and catalytic activity for the synthesis of symmetrically dialkylated polynuclear aromatics, it is essential to design the zeolite pores and the stereochemistry of the transition state composed of reactant aromatic compounds, alkylating agents, 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 in the zeolite pore, 2) the prevention of reactions at the external surface, 3) the control of number of acid sites inside the pores, and 4) the control of acid strength.

ACKNOWLEDGEMENTS

The authors thank Professor C. Song of Pennsylvania State University, and Professor S. Namba of Teikyo University of Science & Technology for their valuable discussions, and Drs. T. Matsuzaki and T. Hanaoka of National Institute of Materials and Chemical Research, Professor K. Kunimori of University of Tsukuba, Professor J.-H. Kim and Professor G. Seo of Chonnam National University, and Professor Y. Kubota of Gifu University for their continuing cooperation.

REFERENCES

1. Anastas, P. T. and Williamson, T. C. (eds.), in "Green Chemistry. Frontiers in Benign Chemical Synthesis and Processes," Oxford University Press, Oxford (1998).
2. Csicsery, S. M., "Shape-selective Catalysis in Zeolites," *Zeolite*, **4**, 202 (1984).
3. Venuto, P. B., "Organic Catalysis over Zeolites: A Perspective on Reaction Paths with Micropores," *Micropor. Mater.*, **2**, 297 (1994).
4. Sugi, Y. and Kubota, Y., "Shape-selective Catalysis of Zeolite in the Alkylation of Aromatics," in Catalysis, Spivey, J. J. (ed.), Specialist Periodical Report, Royal Soc. Chem., London, Chapter 3, **13**, 55 (1997).
5. Kaeding, W. W., Chu, C., Young, L. B., Weinstein, B. and Butter, J., "Selective Alkylation of Toluene with Methanol to Produce para-Xylene," *J. Catal.*, **67**, 159 (1981).
6. Namba, S., Kim, J.-H. and Yashima, T., "Para-selectivity of Zeolites and Metalosilicates with MFI Structure," *Stud. Surf. Sci. Catal.*, **83**, 279 (1994) and their earlier papers cited in.
7. Young, L. B., Butter, S. A. and Kaeding, W. W., "Shape Selective Reaction with Zeolite Catalysis. III. Selectivity in Xylene Isomerization, Toluene-Methanol Alkylation, and Toluene Disproportionation over ZSM-5 Catalysts," *J. Catal.*, **76**, 418 (1982).
8. Karge, H. G., Laderbeck, J., Sarbak, Z. and Hatada, K., "Conversion of Alkylbenzenes over Zeolite Catalysts. I. Dealkylation and Disproportionation of Ethylbenzenes over Mordenites," *Zeolites*, **2**, 94 (1982).
9. Polym. Soc. Japan (ed.), in "High Performance Polynuclear Aromatics Materials," Maruzen, Tokyo (1990).
10. Matsuzaki, T., Sugi, Y., Hanaoka, T., Takeuchi, K., Arakawa, H., Tokoro, T. and Takeuchi, G., "Shape-selectivity of Zeolite Catalysts in the Alkylation of Biphenyl," *Chem. Express*, **4**, 413 (1989).
11. Sugi, Y., Matsuzaki, T., Hanaoka, T., Takeuchi, K., Tokoro, T. and Takeuchi, G., "Alkylation of Biphenyl Catalyzed by Zeolites," *Stud. Surf. Sci. Catal.*, **60**, 303 (1991).
12. Sugi, Y., Matsuzaki, T., Hanaoka, T., Kubota, Y., Kim, J.-H., Tu, X. and Matsumoto, M., "Shape-selective Isopropylation of Naphthalene and Biphenyl over Dealuminated H-Mordenites," *Stud. Surf. Sci. Catal.*, **90**, 397 (1994).
13. Hanaoka, T., Nakajima, K., Sugi, Y., Matsuzaki, T., Kubota, Y., Tawada, S., Kunimori, K. and Igarashi, A., "Effects of SiO_2/Al_2O_3 Ratio of H-Mordenite on Encapsulated Products inside the Pores in Shape-selective Isopropylation of Biphenyl," *Catal. Lett.*, **50**, 149 (1998).
14. Tu, X., Matsumoto, M., Matsuzaki, T., Hanaoka, T., Kubota, Y. and Sugi, Y., "Shape-selective Isopropylation of Biphenyl over a Highly Dealuminated Mordenite: Effect of Propylene Pressure," *Catal. Lett.*, **21**, 71 (1993).
15. Sugi, Y., Tu, X., Matsuzaki, T., Hanaoka, T., Kubota, Y., Kim, J.-H., Matsumoto, M., Nakajima, K. and Igarashi, A., "The Effect of Propylene Pressure on Shape-selective Isopropylation of Biphenyl over H-Mordenite," *Catal. Today*, **31**, 3 (1996).
16. Tawada, S., Kubota, Y., Sugi, Y., Hanaoka, T. and Matsuzaki, T., "Effects of Reaction Temperature on the Isopropylation of Biphenyl over H-Mordenite," *Catal. Lett.*, **57**, 217 (1999).
17. Sugi, Y., Tawada, S., Sugimura, T., Kubota, Y., Hanaoka, T., Matsuzaki, T., Nakajima, K. and Kunimori, K., "Shape-selective Isopropylation of Biphenyl over H-Mordenites. Relationships of Bulk Products and Encapsulated Products," *Appl. Catal. A: General*, **189**, 251 (1999).
18. Sugi, Y., Matsuzaki, T., Hanaoka, T., Kubota, Y., Kim, J.-H., Tu, X. and Matsumoto, M., "Coke-Deposition, Product Encapsulation, and Propylene Oligomerization during the Isopropylation of Biphenyl over a Highly Dealuminated H-Mordenite," *Sekiyu Gakkaishi*, **37**, 557 (1994).
19. Takeuchi, G., Okazaki, H., Kito, T., Sugi, Y. and Matsuzaki, T., "Isomer Selectivity in Isopropylation of Biphenyl over Solid Acid Catalysts," *Sekiyu Gakkaishi*, **34**, 242 (1991).
20. Sugi, Y., Tawada, S., Sugimura, T. and Kubota, Y., manuscript in preparation
21. Nakajima, K., Tawada, S., Sugi, Y., Kubota, Y., Hanaoka, T., Matsuzaki, T. and Kunimori, K., "Deactivation of External Acid Sites of H-Mordenite with Ceria Modification in the Isopropylation of Biphenyl," *Chem. Lett.*, 215 (1999).
22. Matsumoto, M., Tu, X., Sugi, Y., Matsuzaki, T., Hanaoka, T., Kubota, Y., Kim, J.-H., Nakajima, K., Igarashi, A. and Kunimori, K., "The Influences of Reagents on Shape-selective Alkylation of Biphenyls over H-Mordenite," *Stud. Surf. Sci. Catal.*, **105**, 1317 (1997).
23. Nakajima, K., Hanaoka, T., Sugi, Y., Matsuzaki, T., Kubota, Y.,

Igarashi, A. and Kunimori, K., "Influences of Bulkiness of Reagents in the Alkylation of Biphenyl over H-Mordenite," in "Shape Selective Catalysis-Chemicals Synthesis and Hydrocarbon Processing," ACS Symposium Series 738, Song, C., Garces, J. M. and Sugi, Y. (eds), Am. Chem. Soc., Chapter 19, 260 (1999).
24. Lee, G. S., Maj, J. J., Rocke, S. C. and Garces, J. M., "Shape-selective Alkylation of Polynuclear Aromatics with Mordenite-type Catalysts. A High Yield Synthesis of 4,4'-Diisopropylbiphenyl," *Catal. Lett.*, **2**, 243 (1989).
25. Taniguchi, T., Tanaka, M., Takahata, K., Sakamoto, N., Takai, T., Kurano, Y. and Ishibushi, M., "Process for Producing Alkyl-group-substituted Aromatic Hydrocarbons," PCT Int., Appl., WO 88 03523 (assigned to Mitsui Petrochem. Ind. Ltd.).
26. Sakamoto, N., Takai, T., Taniguchi, K. and Takahata, K., "Process for the Catalytic Preparation of *p,p'*-Dialkylbiphenyls," Jpn. Tokkyo Kokai Koho, 88-122635 (assigned to Mitsui Petrochem. Ind. Ltd).
27. Fellmann, J., in Catalytica Highlights, **17**(#1), 1 (1991).
28. Matsuda, T. and Kikuchi, E., "Selective Synthesis of 4,4'-Diisopropylbiphenyl using Mordenite Catalysts," *Stud. Surf. Sci. Catal.*, **83**, 295 (1994).
29. Matsuda, T., Urata, T., Saito, U. and Kikuchi, E., "Effect of SiO_2/Al_2O_3 Ratio on the Catalytic Properties of Mordenite for Alkylation of Biphenyl with Propene," *Appl. Catal. A: General*, **131**, 215 (1995).
30. Matsuda, T., Kimura, T., Herawati, E., Kobayashi, C. and Kikuchi, E., "Shape Selective Alkylation of Biphenyl with Propene on SAPO-11 Catalysts," *Appl. Catal., A: General*, **136**, 19 (1996).
31. Kim, J.-H., Matsuzaki, T., Hanaoka, T., Kubota, Y., Sugi, Y., Matsumoto, M. and Tu, X., "Effect of SiO_2/Al_2O_3 Ratio of H-Mordenite on the Isopropylation of Naphthalene," *Micropor. Mater.*, **5**, 113 (1995).
32. Sugi, Y., Kim, J.-H., Matsuzaki, T., Hanaoka, T., Kubota, Y., Tu, X. and Matsumoto, M., "The Isopropylation of Naphthalene over Cerium-Modified H-Mordenite," *Stud. Surf. Sci. Catal.*, **84**, 1837 (1994).
33. Kim, J.-H. Sugi, Y., Matsuzaki, T., Hanaoka, T., Kubota, Y., Tu, X., Matsumoto, M., Kato, A., Seo, G. and Pak, C., "Cerium Impregnated H-Mordenite as a Catalyst for Shape-selective Alkylation of Naphthalene," *Appl. Catal., A: General*, **131**, 15 (1995).
34. Katayama, A., Toba, M., Takeuchi, G., Mizukami, F., Niwa, S. and Mitamura, S., "Shape-selective Synthesis of 2,6-Diisopropylnaphthalene over H-Mordenite Catalyst," *J. Chem. Soc., Chem. Commun.*, 39 (1991).
35. Song, C. and Schmitz, A. D., "Shape-selective Isopropylation of Naphthalene over Hydrogen-Mordenite Catalysts. -Effect of Mordenite Dealumination," *Sekiyu Gakkaishi*, **42**, 275 (1999), and their previous papers cited in.
36. Chu, S.-J. and Chen, Y.-W., "Shape-selective Alkylation of Naphthalene with Isopropanol with Large Pore Zeolites," *Appl. Catal. A: General*, **123**, 51 (1995).
37. Derouane, E. G. and Gabelica, Z., "A Novel Effect of Shape Selectivity Molecular Traffic Control in Zeolite ZSM-5," *J. Catal.*, **65**, 486 (1980).
38. Meier, W. M., Olson, D. H. and Baerlocher, Ch., in "Atlas of Zeolite Structure Types," 4th revised edition, Elsevier, Amsterdam (1996).
39. Dejaifve, P., Auroux, A., Gravelle, P. C., Vedrine, J. C., Gabelica, Z. and Derouane, E. G., "Methanol Conversion on Acidic ZSM-5, Offretite, and Mordenite Zeolites: A Comparative Study of the Formation and Stability of Coke Deposits," *J. Catal.*, **70**, 123 (1981).
40. Guisnet, M. and Magnoux, P., "Coking and Deactivation of Zeolites. Influences of Pore Structure," *Appl. Catal.*, **54**, 1 (1989).
41. Bhatia, S., Beltramini, J. and Do, D. D., "Deactivation of Zeolite Catalysts," *Catal. Rev. Sci,. Eng.*, **31**, 431 (1989-90).
42. Karge, H. G. and Weitkamp, J., "Untersuchungen an Dealuminierten Mordenit-Katalysatoren," *Chem. Ind. Tech.*, **58**, 946 (1986).
43. Meyers, L., Fleisch, T. H., Ray, G. J., Miller, J. T. and Hall, J. B., "A Multitechnique Characterization of Dealuminated Mordenites," *J. Catal.*, **110**, 82 (1988).
44. Sawa, M., Niwa, M. and Murakami, Y., "Acid-Leached Dealuminated Mordenite: Effect of Conversion. Acid Concentration on Catalyst Life in Methanol Conversion," *Appl. Catal.*, **53**, 169 (1989), and their earlier papers cited in.
45. Itabashi, K., Fukushima, T. and Igawa, K., "Synthesis and Characteristic Properties of Siliceous Mordenite," *Zeolites*, **6**, 30 (1986).