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Ceria-modification of H-mordenites The deactivation of external acid sites in the isopropylation of biphenyl and the isomerization of 4,4′-diisopropylbiphenyl

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Abstract

Ceria-modification is an effective method for the deactivation of external acid sites of H-mordenite (HM). The selectivity for 4,4′-diisopropylbiphenyl (4,4′-DIPB) in the isopropylation of BP over dealuminated HM such as HM(128) decreased with raising reaction temperatures or with decreasing propylene pressures. The decrease of the selectivity during the isopropylation is due to the isomerization of 4,4′-DIPB. Ceria-modification of HM(128) was highly effective for the prevention of the isomerization. The selectivity for 4,4′-DIPB was also improved in the case of HM with low SiO_2/Al_2O_3 ratio such as HM(10). The enhancement of the selectivities of 4,4′-DIPB by ceria-modification is ascribed to the decrease of external acid sites which are active in non-regioselective alkylation and isomerization of products.

Keywords: H-mordenite; External acid site; Ceria-modification; Deactivation; Isomerization; Isopropylation; Biphenyl; 4,4′-diisopropylbiphenyl

1. Introduction

Recently, many researchers have drawn attention to shape-selective catalysis for the alkylation of polynuclear aromatics such as the methylation of naphthalene [1,2] and the isopropylation of biphenyl (BP) and naphthalene [3–16]. We have found that a highly selective synthesis of 4,4′-DIPB can be achieved in the isopropylation of BP over dealuminated HMs [3–9]. Lee and his coworkers have also reported that dealuminated HM with a high SiO_2/Al_2O_3 ratio (∼2600) is very active for the isopropylation of BP, because the dealumination not only reduces the number of acid sites, but also modifies pore distribution, resulting in an increase in mesopore volume [10]. From these results, we proposed that the shape-selectivity in the zeolite catalysis is controlled by the stereochemistry of the transition state composed of substrates and acid sites in sterically restricted environment [3,8–10].

Acid sites of zeolites exist mainly in the pores, whereas some of them are on the external surface. The reactions on external surface are controlled kinetically or thermodynamically to produce non-regioselective mixtures of isomers, and their rates are more rapid than those inside the pores. There have been sev-

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eral reports that the shape-selectivity decreased by the non-regioselective reactions and the isomerization of products at the external acid sites [7–9,15]. The deactivation of external acid sites is considered to be essential for the improvement of the selectivities for shape-selective catalysis [16–19].

In this paper, we describe the suppression of external acid sites of H-mordenites by modification with ceria, and their application in the isopropylation of BP and the isomerization of 4,4′-DIPB.

2. Experimental

2.1. Catalysts

H-mordenite (HM; SiO_2/Al_2O_3=10, 128) was obtained from Tosoh Corporation, Tokyo, Japan, and calcined at 550°C just before use. HMs modified with various amounts of cerium (Ce(*x*)HM(*y*), "*x*" refers to the cerium amount (wt.%) based on HM, and "*y*" expresses SiO_2/Al_2O_3 ratio) were prepared by impregnation from ethanol solution of cerium nitrate, drying at 80°C, and calcination at 550°C for 5 h in an air stream.

2.2. Isopropylation

Isopropylation was carried out in a 100 ml SUS-316 autoclave using propylene as an alkylating reagent. Standard conditions for the isopropylation of BP were: 200 mmol of BP, 1 g of catalyst, 0.8 MPa of propylene pressure, 200–300°C, and 4 h of operating period. The autoclave was purged with nitrogen before heating, and then heated to reaction temperature. Propylene was supplied to the autoclave and kept at constant pressure throughout the reaction. The products were analyzed by gas chromatography (Shimadzu GC-14A with an Ultra-1 capillary column from HP, 30 m×0.2 mm, 170°C), and identified by a Shimadzu GC-MS5000 Gas chromatograph–Mass spectrometer.

The yield of every product was calculated on the basis of BP used for the reaction; i.e. the selectivity for each isomer of isopropylbiphenyls (IPBP) and diisopropylbiphenyls (DIPB) is expressed as a percentage of each IPBP and DIPB isomer among total IPBP and DIPB isomers for the isopropylation of BP:

$$\text{Selectivity for a DIPB (IPBP) isomer (\%)} = \frac{\text{Each DIPB (IPBP) isomer (mol)}}{\text{DIPB (IPBP) isomers (mol)}} \times 100$$

The analysis of products encapsulated in the catalyst used for the reaction was carried out as follows: The catalyst was filtered off, washed well with 200 ml of acetone, and dried at 110°C under an air atmosphere during 12 h. The resulting catalyst was destroyed by aqueous hydrofluoric acid (47%) at room temperature. This solution was neutralized with solid potassium carbonate, and the organic layer was extracted three times with 20 ml of dichloromethane. After removal of the solvent in vacuo, the residue was dissolved in 5 ml of toluene and 10 mg of naphthalene was added as an internal standard. The GC analysis was done similar to the case of bulk products.

2.3. Characterization of H-mordenites

The cracking of 1,3,5-triisopropylbenzene (1,3,5-TIPB) and cumene (IPB) was carried out using a conventional pulse reactor. The isopropylation of 2,6-DIPN was carried out by using a 100 ml autoclave under a constant propylene pressure.

The adsorption of naphthalene (NP) and 2,6-diisopropylnaphthalene (2,6-DIPN) was measured at room temperature using their 4 wt.% solutions in 1,3,5-TIPB. Total amounts of the adsorption were determined after 24 h by gas chromatographic analysis.

The heat of adsorption for ammonia was measured by a Tokyo Sinku Riko HAC-450G calorimeter at 200°C. All samples were evacuated at elevated temperatures (450°C) for 5 h before calorimetric experiments. The amounts of adsorbed ammonia were calculated on the basis of the weight of HM(128). XRD patterns were recorded by a Shimadzu XRD-6000 Spectrometer.

3. Results and discussion

3.1. Characterization of ceria-modified H-mordenite

Acid catalyzed reactions, such as a cracking and an alkylation of bulky molecules, the diameter of which is larger than the entrance of the pore of HM,

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

Catalyst	Conversion (%)	
	1,3,5-TIPB	IPB
HM(128)	60.9	98.5
Ce(30)HM(128)	3.9	65.6

[a] Reaction conditions: catalyst, 10 mg (as HM); temperature, 300°C; carrier gas flow rate, 50 ml min^{-1} (N_2); injection amount, 0.02 μl.

give useful information to evaluate the reactivity of acid sites at external surface [20]. We examined the cracking of 1,3,5-TIPB and the isopropylation of 2,6-DIPN to evaluate the change of surface activity by ceria-modification of HM(128). Typical results of the cracking of 1,3,5-TIPB and IPB over HM(128) and Ce(30)HM catalysts are summarized in Table 1. HM(128) itself exhibited high activity for the cracking in spite of its high dealumination. This means that only a small amount of acid sites on external surface of HM(128) is enough to show high activity in the cracking of 1,3,5-TIPB. However, the cracking of 1,3,5-TIPB over Ce(30)HM(128) was suppressed much under the same condition with HM(128). Both of HM(128) and Ce(30)HM(128) have high activity for the cracking of IPB. The different behavior of HM(128) and Ce(30)HM(128) against the cracking of 1,3,5-TIPB and IPB showed that bulky 1,3,5-TIPB cannot enter into the pore of HM, whereas IPB can enter the pore. These results show that HM(128) was modified with ceria with minimum blockage of the pore.

Table 2 summarizes the isopropylation of 2,6-DIPN over HM(128) and Ce(30)HM(128) catalysts at 300°C under 0.8 MPa of propylene pressure. HM(128) exhibited high catalytic activity and high selectivity for 2,6-DIPN [13], and the enhancement of the selectivity for 2,6-DIPN was observed by the modification with ceria [14,15]. In the case of the isopropylation of 2,6-DIPN, HM(128) gave high activity for further alkylation to polyisopropylnaphthalenes (PIPN) and for the isomerization to other DIPN isomers, whereas these reactions were suppressed over Ce(30)HM(128). These results show that the reactions of bulky molecules such as the isopropylation and the isomerization of 2,6-DIPN occur on external acid sites of HM(128), and that cerium modification of HM(128) effectively deactivated external acid sites to reduce the isopropylation and isomerization of 2,6-DIPN on them.

Table 2
The isopropylation of 2,6-DIPN over Ce(30)HM(128)[a]

Catalyst	Conversion (%)	Yield (%)			
		NP	IPN[b]	DIPN[c]	PIPN[d]
HM(128)	32.4	0.2	2.1	15	15.6
Ce(30)HM(128)	8.3	0	1.1	5.8	1.4

[a] Reaction conditions: catalyst, 1 g; 2,6-DIPN, 200 mmol; propylene pressure, 0.8 MPa; temperature, 250°C; period 20 h.
[b] Isopropylnaphthalenes.
[c] Amount of DIPN isomers except 2,6-DIPN.
[d] Polyisopropylnaphthalenes.

Adsorption of NP and 2,6-DIPN gives us information on effective pore diameter of microporous materials. The amounts of NP and 2,6-DIPN adsorbed in HM(128) and Ce(30)HM(128) are summarized in Table 3. The amount of NP adsorbed on HM(128) and Ce(30)HM(128) was the same (50 mg g^{-1}). 2,6-DIPN was also adsorbed in both catalysts although there were differences in adsorbed amount. The decrease of the amount of 2,6-DIPN adsorbed on Ce(30)HM(128) shows that ceria on Ce(30)HM(128) has some pores which discriminate diameters of NP and 2,6-DIPN. These results indicate that effective pore diameter of HM is not reduced significantly by the modification.

Calorimetric measurement of the adsorption of small basic molecules such as ammonia has been used as the method to determine the amount and the strength of acid site in zeolites [21,22]. Fig. 1 shows the heat of adsorption of ammonia on Ce(30)HM(128). The highest heat of adsorption was about 120 kJ mol^{-1} for every sample. The slope of curves changed significantly at the level of ca. 100 kJ mol^{-1}. Heat of adsorption higher than 100 kJ mol^{-1} is assigned to

Table 3
Adsorption of NP and 2,6-DIPN on Ce(30)HM(128)[a]

Catalyst	NP (mg g^{-1})	2,6-DIPN (mg g^{-1})
HM(128)	49.8	24.7
Ce(30)HM(128)	50.1	18.9

[a] Conditions: 1,3,5-TIPB solution of NP (4 wt.%) and 2,6-DIPN (4 wt.%) was treated in the presence of the catalyst during 24 h at room temperature.

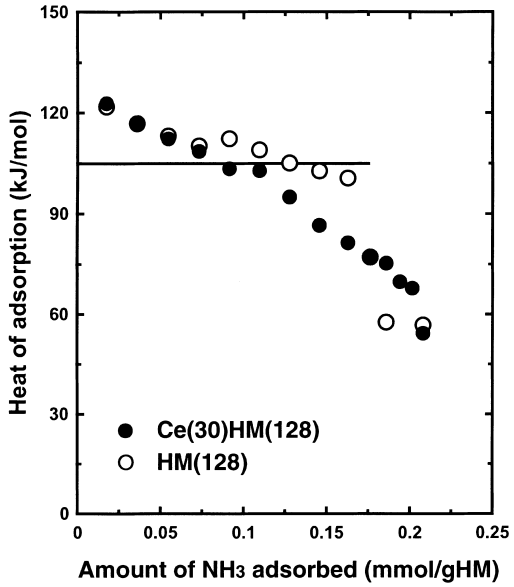

Fig. 1. Heat of adsorption for ammonia on Ce(30)HM(128).

interaction with the structural acidic hydroxyl group at aluminum [22]. In the case of HM(128), strong acid sites were decreased by ceria-modification although total amount of acid site higher than 100 kJ mol^{-1} was not changed significantly. The interaction of two types of oxide such as silica and ceria was reported to form acid sites [23]. However, the results discussed above suggest that there are no acid sites formed newly by ceria-modification of HM(128), and that ceria exists only on external surface of HM(128) with no interaction with acid sites in the pores.

XRD investigations showed that all HMs were of good crystallinity. The peaks of ceria were observed for HM(128) loaded such large amounts as 30–50 wt.% of cerium.

3.2. Effects of reaction temperature on the isopropylation of biphenyl

Fig. 2a shows the effects of reaction temperature on the selectivity for DIPB and IPBP isomers in the isopropylation of BP over unmodified HM(128). The selectivity for these DIPB isomers in bulk products varied with reaction temperature. The isopropylation produced 4,4′-DIPB shape-selectively at moderate temperature up to 250°C. However, it decreased with the increase of the selectivity for 3,4′-DIPB at temperatures higher than 275°C. Moreover, the formation of 3,3′-DIPB was observed above 300°C. The features of encapsulated products[1] are quite different from those of bulk products in the isopropylation of BP. The selectivity for 4,4′-DIPB was higher than 80% at all temperatures, even at 300°C. These results show that shape-selective formation of 4,4′-DIPB in the isopropylation of BP occurs inside the pores of HM(128) even at such a high temperature as 300°C, and that the isomerization of 4,4′-DIPB in the bulk products at high temperatures occurs on external acid sites.

The deactivation of external acid sites is expected to prevent the isomerization of 4,4′-DIPB. We examined the modification of HM with ceria. Ceria-modification effectively deactivated the external acid sites as shown in the cracking of 1,3,5-TIPB and the isopropylation of 2,6-DIPN (see Section 3.1). Fig. 2b shows the effect of reaction temperatures on the isopropylation of BP over Ce(30)HM(128). The selectivity for 4,4′-DIPB was high even at a high temperature such as 300°C. However, the selectivity for 4,4′-DIPB was almost constant over Ce(30)HM(128) during the isopropylation of BP, although catalytic activity was decreased. These results show that ceria-modification is an effective way to maintain high selectivity for 4,4′-DIPB at high temperatures in the isopropylation of BP.

The selectivity for 3-IPBP also increased with the decrease of that of 4-IPBP at higher temperatures in the isopropylation of BP over HM(128) as in Fig. 2. These results suggest that the formation of IPBP isomers is also thermodynamically controlled under high temperatures. However, the ceria-modification prevents the isomerization of 4-IPBP to 3-IPBP.

In order to know the detailed features of the reactions on the external acid sites, we examined the isomerization of 4,4′-DIPB under propylene pressure. Fig. 3 summarized the change of the composition of bulk products in the isomerization of 4,4′-DIPB over HM(128) and Ce(30)HM(128) under propylene pressure. Over HM(128), the isomerization occurred significantly at high temperatures such as 300°C, but

[1] Encapsulated products are defined as the products contained in the catalyst used for the reaction. We considered that most of them are contained inside pores because surface area of zeolite is principally intracrystalline. For these reasons, encapsulated products are a good example of fingerprints of the catalysis.

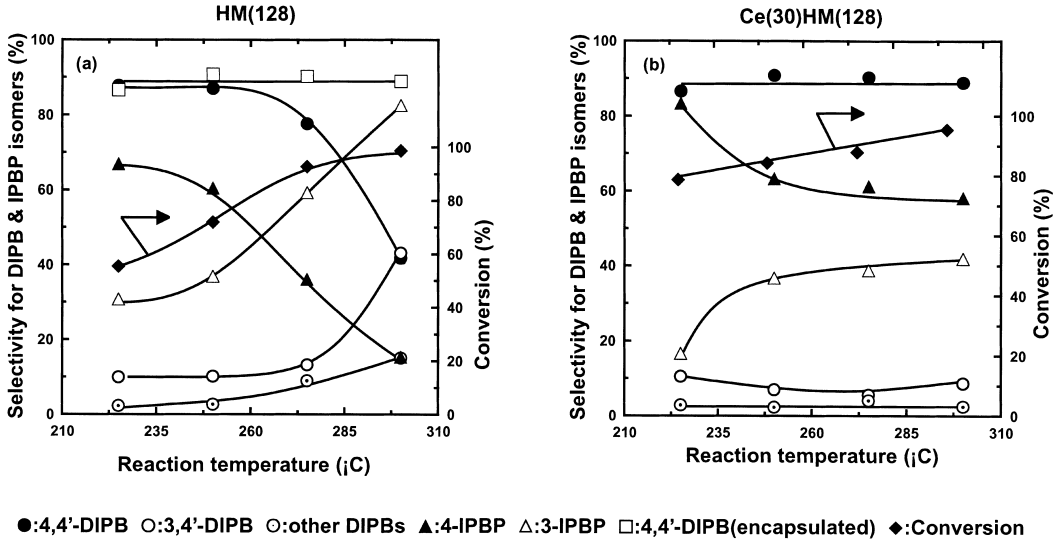

Fig. 2. Effects of reaction temperature on the isopropylation of BP over HM(128) and Ce(30)HM(128). (a) HM(128); (b) Ce(30)HM(128). Reaction conditions: BP, 200 mmol; catalyst, 1 g (as HM(128)); propylene pressure, 0.8 MPa; period, 4 h.

the isopropylation of 4,4′-DIPB to polyisopropylbiphenyls (PIPB) did not occur significantly at 300°C. The isomerization of 4,4′-DIPB is controlled thermodynamically to yield stable isomers, 3,3′- and 3,4′-DIPB [11,24]. However, 4,4′-DIPB was exclusive in encapsulated products in the isomerization even at high temperatures such as 300°C. These results show that the isomerization occurs not inside pores, but at the external surface.

No significant isomerization of 4,4′-DIPB was observed over Ce(30)HM(128) even at high temperatures. These results show that ceria on HM(128)

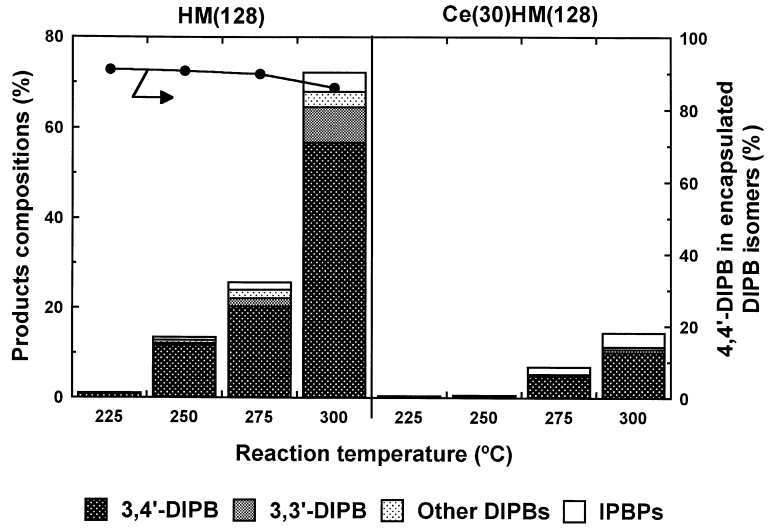

Fig. 3. Effects of reaction temperature on the isomerization of 4,4′-DIPB over HM(128) and Ce(30)HM(128): (a) HM(128); (b) Ce(30)HM(128). Reaction conditions: 4,4′-DIPB, 100 mmol; catalyst, 1 g (as HM(128)); propylene pressure, 0.8 MPa; period, 4 h.

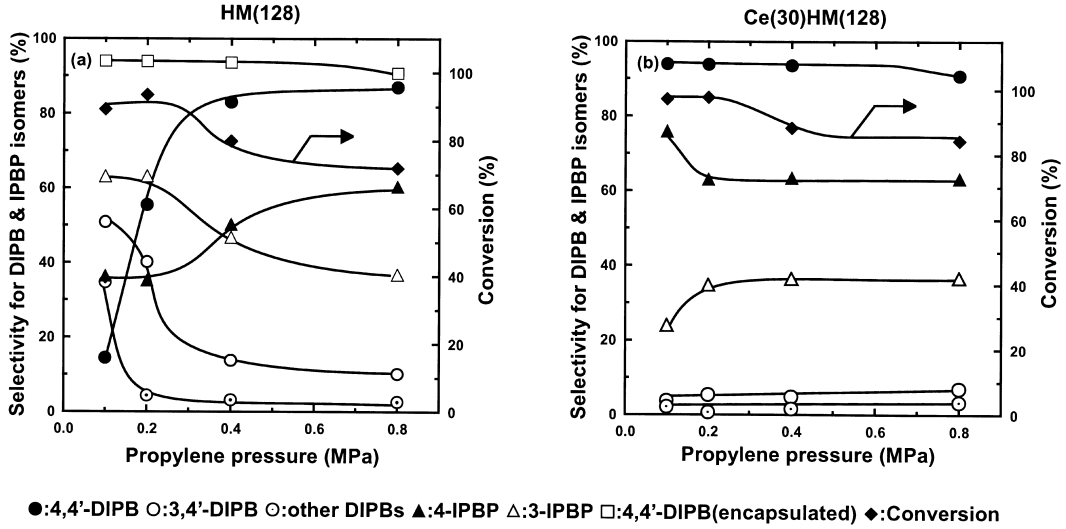

Fig. 4. Effects of propylene pressure on the isopropylation of BP over HM(128) and Ce(30)HM(128). Reaction conditions: BP, 200 mmol; catalyst, 1 g (as HM(128)); temperature, 250°C; period, 4 h.

deactivates the external acid sites, and that the isomerization of 4,4′-DIPB was prevented effectively by the ceria-modification. For these reasons, shape-selective isopropylation of BP over ceria-modified HM(128) proceeded inside the pores to yield selectively 4,4′-DIPB at high temperatures such as 300°C although there was not any information on encapsulated products. [2]

The selectivity for IPBP isomers increased with the reaction temperature in the isomerization of 4,4′-DIPB over HM(128) as shown in Fig. 3. These are due to the dealkylation at the external acid sites. In fact, no significant isomerization was observed over Ce(30)HM(128).

3.3. Effects of propylene pressure on the isopropylation

Fig. 4a shows effects of propylene pressure on the selectivity for DIPB and IPBP isomers in the isopropylation of BP over HM(128). The selectivity for 4,4′-DIPB varied with propylene pressure. Under high pressures, such as 0.8 MPa, the selectivity for 4,4′-DIPB was as high as 90%, while the selectivity decreased with the increase of 3,4′-DIPB under the propylene pressure less than 0.2 MPa. However, 4,4′-DIPB was exclusive in encapsulated products in the isopropylation of BP. These results show that the decrease of propylene pressure enhanced the isomerization of 4,4′-DIPB at external acid site [7]. The isomerization was prevented effectively under high pressure by preferential adsorption of propylene on acid sites. However, the adsorption of 4,4′-DIPB should predominate over that of propylene under the low pressure, and thus, the isomerization of 4,4′-DIPB occurs at external acid sites.

Fig. 4b shows the effect of propylene pressure on the isopropylation of BP over Ce(30)HM(128). The selectivity for 4,4′-DIPB was almost constant under every propylene pressure, although catalytic activity was decreased. The ceria-modification effectively prevented the isomerization at the external acid sites under low propylene pressure.

Fig. 5 summarizes the effect of propylene pressure on the isomerization of 4,4′-DIPB over HM(128) and Ce(30)HM(128). The isomerization of 4,4′-DIPB to 3,4′- and 3,3′-DIPB was enhanced over HM(128) with the decrease of propylene pressure, although 4,4′-DIPB was almost exclusively an encapsulated product. These results mean the isomerization

[2] Unfortunately, we could not find any definite information on encapsulated products because ceria was difficult to dissolve and remove from organic products.

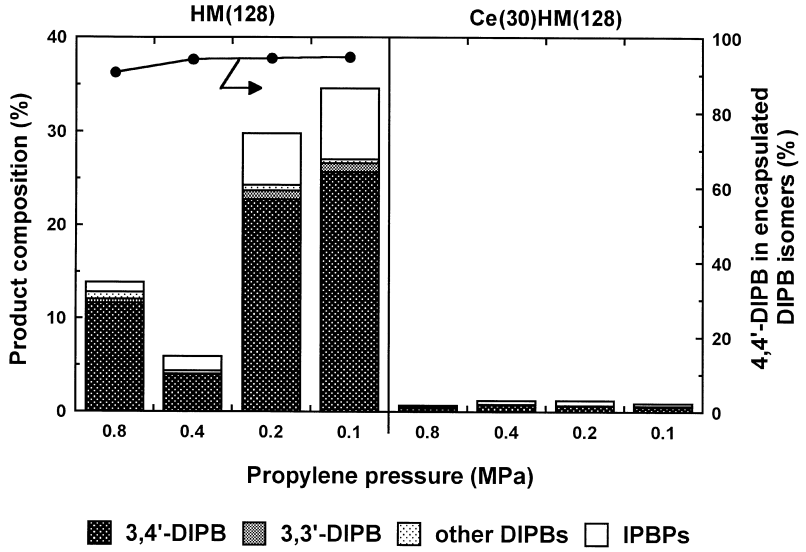

Fig. 5. Effects of propylene pressure on the isomerization of 4,4′-DIPB over HM(128) and Ce(30)HM(128): (a) HM(128); (b) Ce(30)HM(128). Reaction conditions: 4,4′-DIPB, 100 mmol; catalyst, 1 g (as HM(128)); temperature, 250°C; period, 4 h.

occurs on the external acid sites [8,11]. However, the isomerization was suppressed by ceria-modification even under low propylene pressures. These results show that ceria on HM(128) deactivates external acid sites and prevents effectively the isomerization of 4,4′-DIPB, even under 0.2 MPa of propylene.

The dealkylation of 4,4′-DIPB was observed over HM(128) under low propylene pressure as shown in Fig. 5. However, ceria-modification suppresses effectively the dealkylation in the isomerization of 4,4′-DIPB even under low propylene pressure. This is due to the removal of acid sites by ceria-modification.

The formation of IPBP isomers was enhanced with the decrease of propylene pressure in the isomerization of 4,4′-DIPB over HM(128) as shown in Fig. 5. These are due to the dealkylation at the external acid sites because of decreasing the amount of propylene adsorbed on the acid sites. However, no significant isomerization was observed over Ce(30)HM(128).

3.4. Effects of cerium amount on the isopropylation

Fig. 6 summarizes the effects of ceria amount on the selectivity for 4,4′-DIPB at 300°C over Ce(30)HM(128). The selectivity was only 50% for unmodified HM(128) whereas it was increased to 80% by the modification with 10 wt.% cerium against HM(128) although it was accompanied by a small decrease of catalytic activity. Fig. 7 shows the effects of ceria-modification of HM(128) on the isomerization

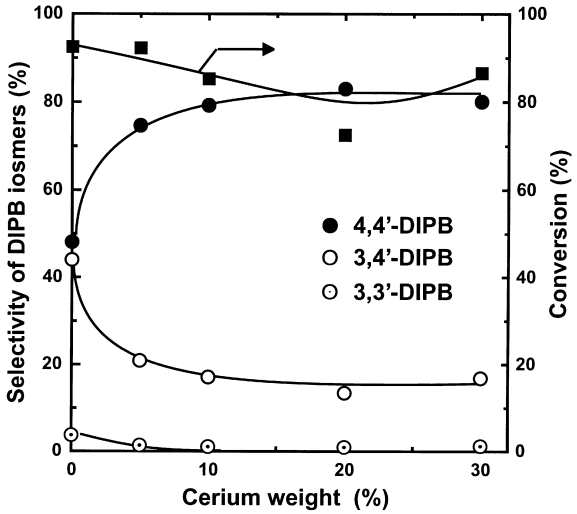

Fig. 6. Effect of cerium amount over HM(128) on the isopropylation of BP. Reaction conditions: BP, 200 mmol; catalyst, 1 g (as HM(128)); temperature, 250°C; propylene pressure, 0.8 MPa; period, 4 h.

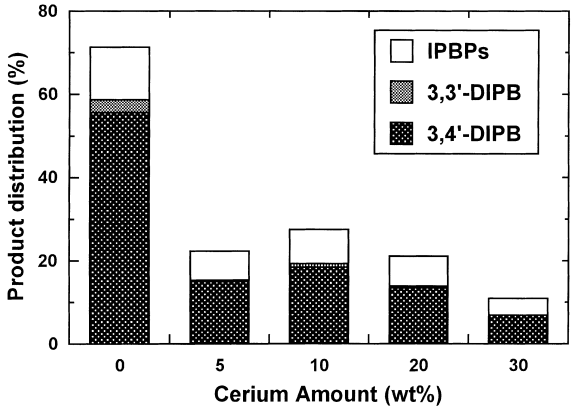

Fig. 7. Effect of cerium amount over HM(128) on the isomerization of 4,4′-DIPB. Reaction conditions: 4,4′-DIPB, 100 mmol; catalyst, 1 g (as HM(128)); temperature, 250°C; period, 4 h.

of 4,4′-DIPB in the absence of propylene pressure. The isomerization of 4,4′-DIPB was significant over unmodified HM(128), whereas it was decreased with increase of ceria amount. The deactivation of acid sites for the isopropylation of BP was enough by the ceria-modification with 10 wt.% of cerium. These results lead to the conclusion that the enhancement of the selectivity for 4,4′-DIPB in the isopropylation of BP is apparently due to the decrease of the isomerization of 4,4′-DIPB by the deactivation of external acid sites. Similar deactivation of the external acid sites was observed in the isopropylation of NP [14,15]. However, the deactivation in the isopropylation of BP was highly effective compared to the case of NP. These differences are due to the easy isomerization of products.

3.5. The isopropylation of BP over CeHM(10)

Fig. 8 shows the effect of cerium amounts over HM(10) on the isopropylation of BP over HM(10) at 250°C under 0.8 MPa of propylene. As previously described, the selectivity for 4,4′-DIPB and 4-IPBP was low over unmodified HM(10) [3,5,6]. Non-regioselective alkylation at external acid sites occurred after blockage of the pores by coke-deposition at acid sites inside the pores. Although the catalytic activity decreased significantly, the selectivity for 4,4′-DIPB was improved and that for 3,4′-DIPB was kept constant by the modification of HM(10).

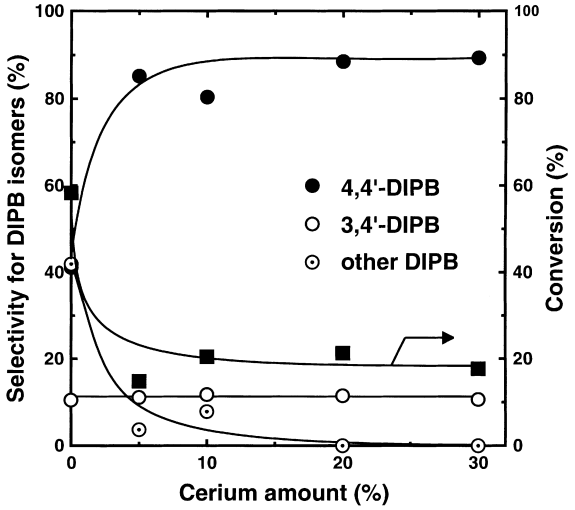

Fig. 8. Effect of cerium amount over HM(10) on the isopropylation of BP. Reaction conditions: BP 200 mmol; catalyst, 1 g (as HM(10)); temperature, 250°C; propylene pressure, 0.8 MPa; period, 4 h.

Significant isomerization of 4,4′-DIPB was not observed over ceria-modified HM(10) in the absence of propylene pressure, as shown in Fig. 9. The low activity for the isomerization is due to the coke-deposition on external acid sites. Further, ceria-modification of HM(10) reduced isomerization to 3,4′-DIPB, dealkylation to IPBP, and alkylation to PIPB.

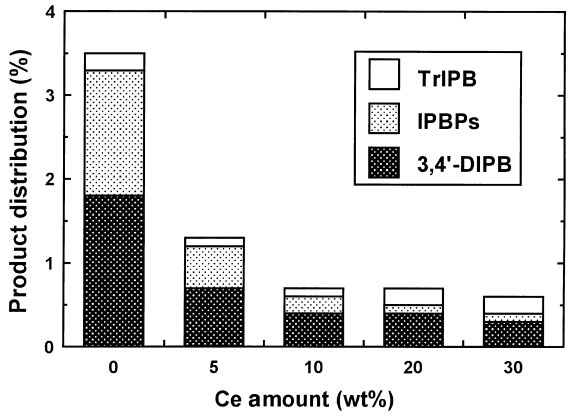

Fig. 9. Effect of cerium amount over HM(10) in the isomerization of 4,4′-DIPB. Reaction conditions: 4,4′-DIPB, 100 mmol; catalyst, 1 g (as HM(10)); temperature, 250°C; period, 4 h.

Table 4
The isopropylation of BP over Ce(30)HM(10)[a]

	Reaction period (h)	Conversion (%)	Selectivity for IPBP (%)			Selectivity for DIPB (%)			
			4-IPBP	3-IPBP	2-IPBP	4,4′-DIPB	3,4′-DIPB	3,3′-DIPB	Others
HM(10)	2	34	57	20	24	55	12	5	28
Ce(30)HM(10)	18	35	75	22	3	85	11	2	2

[a] Reaction conditions: BP, 200 mmol; catalyst, 1 g (as HM); temperature, 250°C; propylene pressure, 0.8 MPa.

Table 4 shows the isopropylation of BP over HM(10) and Ce(30)HM(10) catalysts at 250°C under 0.8 MPa of propylene at the same conversion level. Over HM(10), the selectivity for 2-IPBP was as high as 24%, and that for DIPB isomers other than 4,4′- and 3,4′-DIPB, which are mainly DIPB with 2-isopropyl groups were as high as 28%. On the other hand, 2-IPBP and DIPB isomers other than 4,4′- and 3,4′-DIPB was suppressed in the isopropylation of BP over Ce(30)HM(10). These results show that DIPB isomers other than 4,4′- and 3,4′-DIPB formed by non-regioselective alkylation, and that the shape-selective alkylation inside pores enhanced by deactivation of external acid sites through ceria-modification. The change of the selectivity against the amounts of ceria was not observed in the isopropylation of BP at 250°C over Ce(30)HM(128) because the isopropylation was shape-selective over HM(128).

3.6. TG analysis of the catalysts used for the isopropylation

Fig. 10 shows TG profiles of ceria-modified HM(128) used for the isopropylation of BP. The peak due to the combustion of coke inside the pores was observed around 550°C, and it is shifted by the ceria-modification. The amount of coke was decreased by the ceria-modification as shown in Table 5. The peaks due to organic compounds encapsulated inside pores were observed around 350°C for ceria-modified HM(128). The shift should be due to enhancement of combustion of coke by ceria [14]. Fig. 11 also shows TG profiles of ceria-modified HM(10) for the isopropylation of BP. No significant shift of combustion and deposited coke occurred by ceria-modification of HM(10). These results show that coke-formation

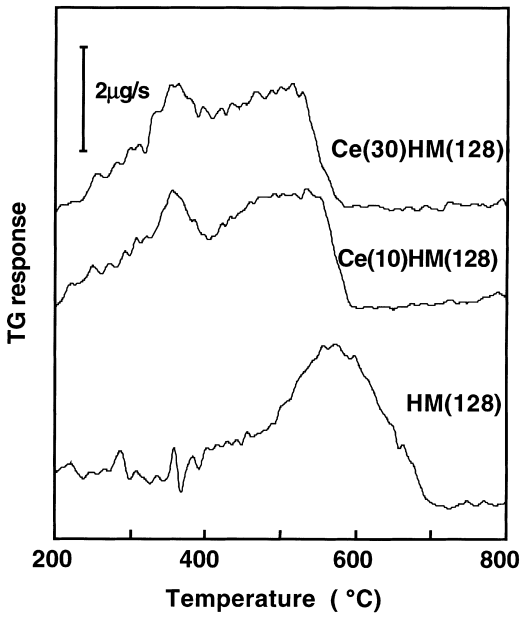

Fig. 10. TG profiles of ceria-modified HM(128) used for the isopropylation of BP. Reaction conditions: BP, 200 mmol; catalyst, 1 g (as HM(128)); temperature, 250°C; propylene pressure, 0.8 MPa; period, 4 h. TG conditions: sample, 10 mg; programmed rate, 10°C min^{-1}; in an air stream.

Table 5
Amounts of coke-deposit on ceria-modified HM(128)[a]

Catalyst	Coke-deposit (wt.%)[b]
HM(128)	11.0
Ce(10)HM(128)	8.0
Ce(30)HM(128)	6.2

[a] Reaction conditions: BP, 200 mmol; catalyst, 1 g (as HM); temperature, 250°C; propylene pressure, 0.8 MPa; period, 4 h.
[b] Coke-deposit was calculated on the basis of HM(128).

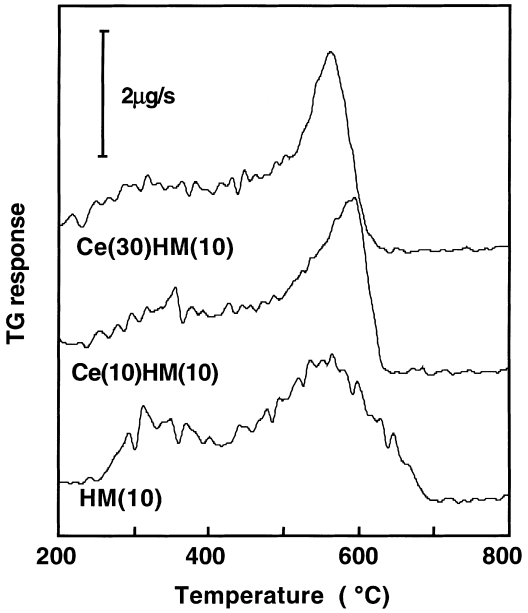

Fig. 11. TG profiles of ceria-modified HM(10) used for the isopropylation of BP. Reaction conditions: BP, 200 mmol; catalyst, 1 g (as HM(10)); temperature, 250°C; propylene pressure, 0.8 MPa; period, 4 h. TG conditions: sample, 10 mg; programmed rate, 10°C min^{-1}; in an air stream.

was severe even over HM(10), and that principal active sites were on external surface. Ceria on HM(10) deactivates external acid sites. The isopropylation over ceria-modified HM(10) occurs at acid sites inside pores, which are not choked by coke-deposition. This is one of principal reasons why the catalytic activity decreases by ceria-modification of HM(10).

4. Conclusion

The shape-selective catalysis over zeolites occurs inside pores. However, the non-regioselective reactions on the external acid sites are one of the lowering factors for shape-selectivity in the reactions inside the zeolite pores. The isomerization of 4,4′-DIPB at external acid sites is the reason for the decrease of the selectivity for 4,4′-DIPB formed inside the pores in the isopropylation of BP. The isomerization of 4,4′-DIPB was suppressed effectively by ceria-modification, and the selective formation of 4,4′-DIPB occurred even at high reaction temperatures over ceria-modified HMs.

Ceria-modification of HM is an effective method for the suppression of surface reaction on external acid sites. The enhancement of the selectivity is ascribed to the deactivation of external acid sites judging from the activity of the cracking reaction of 1,3,5-TIPB and the isopropylation of 2,6-DIPN. It is concluded that ceria deactivates effectively external acid sites without choking the pores of HMs judging from the adsorption of NP and 2,6-DIPN.

References

[1] D. Fraenkel, M. Cherniavsky, B. Ittah, M. Levy, J. Catal. 101 (1986) 273.
[2] T. Komatsu, Y. Araki, S. Namba, T. Yashima, Stud. Surf. Sci. Catal. 84 (1994) 1821.
[3] Y. Sugi, Y. Kubota, in: R.J. Spivey (Ed.), Catalysis, Vol. 13, A Specialist Periodical Report, Royal Society of Chemistry, 1997, p. 55.
[4] T. Matsuzaki, Y. Sugi, T. Hanaoka, K. Takeuchi, T. Tokoro, G. Takeuchi, Chem. Express 4 (1989) 413.
[5] Y. Sugi, T. Matsuzaki, T. Hanaoka, K. Takeuchi, T. Tokoro, G. Takeuchi, Stud. Surf. Sci. Catal. 60 (1991) 303.
[6] X. Tu, M. Matsumoto, T. Matsuzaki, T. Hanaoka, Y. Kubota, J.-H. Kim, Y. Sugi, Catal. Lett. 21 (1993) 71.
[7] Y. Sugi, T. Matsuzaki, T. Hanaoka, Y. Kubota, J.-H. Kim, X. Tu, M. Matsumoto, Catal. Lett. 27 (1994) 315.
[8] Y. Sugi, X. Tu, T. Matsuzaki, T. Hanaoka, Y. Kubota, J.-H. Kim, M. Matsumoto, K. Nakajima, A. Igarashi, Catal. Today 31 (1996) 3.
[9] T. Hanaoka, K. Nakajima, Y. Sugi, T. Matsuzaki, Y. Kubota, A. Igarashi, K. Kunimori, Catal. Lett. 50 (1998) 149.
[10] S. Tawada, Y. Kubota, Y. Sugi, T. Hanaoka, T. Matsuzaki, Catal. Lett. 57 (1999) 217.
[11] Y. Sugi, S. Tawada, T. Sugimura, Y. Kubota, T. Hanaoka, T. Matsuzaki, K. Nakajima, K. Kunimori, Appl. Catal. 189 (1999) 251.
[12] G.S. Lee, J.J. Maj, S.C. Rocke, J.M. Garces, Catal. Lett. 2 (1989) 243.
[13] A. Katayama, M. Toba, G. Takeuchi, F. Mizukami, S. Niwa, S. Mitamura, J. Chem. Soc., Chem. Commun. (1991) 39.
[14] C. Song, S. Kirby, Micropor. Mater. 2 (1994) 467.
[15] J.-H. Kim, T. Matsuzaki, T. Hanaoka, Y. Kubota, Y. Sugi, M. Matsumoto, X. Tu, Micropor. Mater. 5 (1995) 113.
[16] Y. Sugi, J.-H. Kim, T. Matsuzaki, T. Hanaoka, Y. Kubota, X. Tu, M. Matsumoto, Stud. Surf. Sci. Catal. 84 (1994) 1837.
[17] J.-H. Kim, Y. Sugi, T. Matsuzaki, T. Hanaoka, Y. Kubota, X. Tu, M. Matsumoto, A. Kato, G. Seo, C. Pak, Appl. Catal. A 131 (1995) 15.
[18] E. Kikuchi, K. Sawada, M. Maeda, T. Matsuda, Stud. Surf. Sci. Catal. 90 (1994) 391.

[19] P. Moreau, A. Finiels, P. Geneste, F. Moreau, J. Solofo, J. Catal. 136 (1992) 487.
[20] S. Namba, J.-H. Kim, T. Yashima, Stud. Surf. Sci. Catal. 90 (1994) 279.
[21] A.L. Klyacho, G.I. Kapustin, T.R. Brueva, A.M. Rubinstein, Zeolites 7 (1987) 119.
[22] M. Niwa, K. Kato, T. Hattori, Y. Murakami, J. Phys. Chem. 90 (1986) 6233.
[23] K. Tanabe, M. Misono, Y. Ono, H. Hattori, Stud. Surf. Sci. Catal. 51 (1989) 108–128.
[24] G. Takeuchi, H. Okazaki, T. Kito, Y. Sugi, T. Matsuzaki, Sekiyu Gakkaishi 34 (1991) 242.