Lanthanoid Exchanged Mordenites as Catalysts for the Isopropylation of Biphenyl

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Liquid-phase isopropylation of biphenyl (BP) with propene was studied to understand the acidities resulting from lanthanoid exchanged sodium mordenite (Ln,NaMOR; Ln: La, Ce, Pr, Sm, Dy, and Yb). The acidities of La^{3+} exchanged sodium mordenite (La,NaMOR) appeared at around 0.6–0.8 exchange calculated from La/3Al molar ratio. Similar acidities appeared with all Ln,NaMORs. The resultant zeolites have Brønsted acidic sites appearing near unsaturated lanthanoid cations. The isopropylation of BP predominantly afforded 4,4′-diisopropylbiphenyl (4,4′-DIPB) among DIPB isomers over all Ln,NaMORs. These catalyses occur on the acidic sites in the channels. The exchanged catalysts had high selectivities for 4,4′-DIPB even at temperatures as high as 300 °C although the selectivities decreased by the isomerization of 4,4′-DIPB over H-mordenite (HMOR) with similar SiO_2/Al_2O_3 ratio. These results indicate the external acid sites are lowly active for the isopropylation of BP and the isomerization of 4,4′-DIPB. The combustion of coke-deposits on Ln,NaMORs, particularly Ce,NaMOR, used for the isopropylation occurred at lower temperatures than that on HMOR because the lanthanoids dispersed in MOR channels work as an oxidation catalyst.

Lanthanoid exchanges of zeolites are well-known to improve catalytic properties such as activity and life span of zeolite catalysts. Particularly, they are devoted to the improvement of catalysts for cracking heavy hydrocarbons in FCC and reduction of NO_x in flue exhaust.[1–3] Lanthanum exchanged zeolites are also applied to the alkylation of isobutane with alkenes to replace hazardous hydrofluoric acid with environmental benign solid catalysts.[4,5] They enhance thermal and hydrothermal stabilities with acidity different from the conventional protic acidity of H-type zeolite.[6–9] They are also important solid acid catalysts in organic synthesis because the acidities can be designed by cation exchange.[10–15] There have been however no systematic studies on the lanthanoid exchange of zeolites for organic synthesis.

H-Mordenite (HMOR) has been found to be the most potent catalysts for the alkylation of polynuclear aromatics such as biphenyl (BP) and naphthalene (NP).[16–29] The catalysis occurs shape-selectively at acidic sites inside the channels by steric restriction through a restricted transition state mechanism. To clarify how their channels work in the catalysis, we have been much interested in the nature of lanthanoid exchanged sodium mordenite, where new acidities appear by the exchange of sodium mordenite (NaMOR) with lanthanoid cations. We have already published preliminary results in the isopropylation of BP over cerium exchanged mordenites.[15]

In this paper, we describe the acidic properties and the catalysis of lanthanoid exchanged sodium mordenite (Ln,NaMOR; Ln: La, Ce, Pr, Sm, Dy, and Yb) exchanged with La^{3+}, Ce^{3+}, Pr^{3+}, Sm^{3+}, Dy^{3+}, and Yb^{3+} cations in the isopropylation of BP and discuss the mechanism of the catalysis by the MOR channels.

Experimental

Catalyst Preparation. H-Mordenite (HMOR, $SiO_2/Al_2O_3 = 18.7$) was obtained from Tosoh Corporation, Tokyo, Japan. Sodium mordenite (NaMOR) was prepared from HMOR by treatment with aqueous sodium hydroxide solution, thoroughly washed with water, dried at 110 °C, and calcined at 500 °C for 6 h.

Lanthanum exchange of NaMOR was carried out with lanthanum nitrate hexahydrates ($La(NO_3)_3 \cdot 6H_2O$; Nacalai Tesque, Kyoto, Japan) in aqueous solution at 90 °C. The amounts of La were 0.1 to 10 (mmol-La/mmol-Al in NaMOR). The resulting zeolites were dried at 110 °C and calcined at 500 °C. Other lanthanoid exchanged sodium mordenites were also cation-exchanged at the Ln/NaMOR = 5.0 mmol-Ln/mmol-Al in NaMOR similarly to lanthanum cation. All exchanged mordenites were calcined at 500 °C for 6 h just before using.

Lanthanoid to aluminum ratios (Ln/Al) of the zeolite were determined by inductively coupled plasma atomic emission spectroscopy on a JICP-PS-1000 UV spectrometer (Teledyne Leeman Labs Inc., NH, USA). The details of the procedure are as follows: K_2CO_3 powder (100 mg) was taken and mixed with 20 mg of the sample. This mixture was then heated in a platinum crucible using a natural gas–oxygen torch. After the sample melted completely, the entire platinum crucible was placed in 80 mL of water and agitated until the flux was freed from the crucible. The resulting solution with the flux was acidified with ca. 20 mL of ca. 3–4 M HNO_3 with stirring, diluted to 100 mL, and subjected to ICP analysis to quantify sodium, silicon, aluminum, and lanthanoid.

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Table 1. Properties of Ln,NaMORs[a)]

Mordenite	SiO_2/ Al_2O_3	Na/ Al	Ln/ 3Al[b)]	NH_3-TPD peak temperature /°C	Acid amount /mmol g^{-1}
HMOR	18.7	—	—	435	0.512
NaMOR	17.6	1.00	—	—	—
La,NaMOR	17.87	0.34	0.71	396	0.519
Ce,NaMOR	20.25	0.35	0.76	386	0.448
Pr,NaMOR	n.d.[c)]	n.d.	n.d.	403	0.387
Sm,NaMOR	19.32	0.10	0.63	408	0.532
Dy,NaMOR	18.43	0.07	0.89	418	0.595
Yb,NaMOR	18.58	0.03	0.80	406	0.633

a) Ln: La, Ce, Pr, Sm, Dy, and Yb. b) Calculated on the basis of 3Al exchanged to a lanthanoid. c) Not determined.

Textural and acidic properties of lanthanoid exchanged sodium mordenites (Ln,NaMOR) are summarized in Table 1. The degree of lanthanoid exchange was calculated based on a Ln/3Al ratio (mol/mol), and complete exchange was assumed to be Ln/3Al ratio = 1.

Characterization of Catalysts. XRD was measured using a Shimadzu XRD-6000 apparatus with Cu Kα radiation (λ = 1.5418 Å). NH_3-TPD was measured with a BEL-TPD-66 apparatus (Bell Japan, Osaka, Japan) in a helium stream at 100 °C after evacuation at 500 °C. TG analysis was performed on a Shimadzu DTG-50 analyzer with temperature-programmed rate of 10 °C min^{-1} in an air stream.

Cracking of 1,3,5-Triisopropylbenzene (1,3,5-TIPB) and Cumene (IPB). Cracking of 1,3,5-TIPB and IPB was carried out using a conventional pulse reactor under N_2 flow (catalyst amount: 20 mg; pulse size: 0.02 µL for IPB and 1,3,5-TIPB; temperature: 400 °C; N_2 pressure: 0.2 MPa). The products were analyzed with a Shimadzu GC-4C gas chromatograph directly connected to the reactor: column: 10 wt.% Carbowax 6000 on Celite 545 with 2 m length (GL Science, Tokyo, Japan); temperature: 80 °C.

Isopropylation of BP. The isopropylation of BP was carried out in a 100 mL SUS-316 autoclave using propene as an alkylating reagent. Standard conditions were: 50 mmol (7.7 g) of BP, 250 mg of catalyst, 0.8 MPa of propene pressure, and 4 h time at 200–300 °C. The autoclave was purged with nitrogen before heating, and heated to reaction temperature. Then, propene was supplied to the autoclave, and temperature was maintained under constant propene pressure throughout the reaction. After cooling the autoclave, the products were separated from catalysts by filtration. The solution (ca. 1.5 mL) taken from the combined filtrate and washings was diluted with toluene (1.5–6.0 mL), and an aliquot was subjected to analysis by gas chromatography (Shimadzu GC-14C or GC-18A; FID detector) equipped with an Ultra-1 capillary column (25 m × 0.2 mm; film thickness: 0.25 µm; Agilent Technologies Co., Ltd., MA, USA). The products were also confirmed by using a Shimadzu GC-MS-5000 Gas Chromatograph-Mass Spectrometer using the same type of column.

The yield of every product in the isopropylation of BP 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.

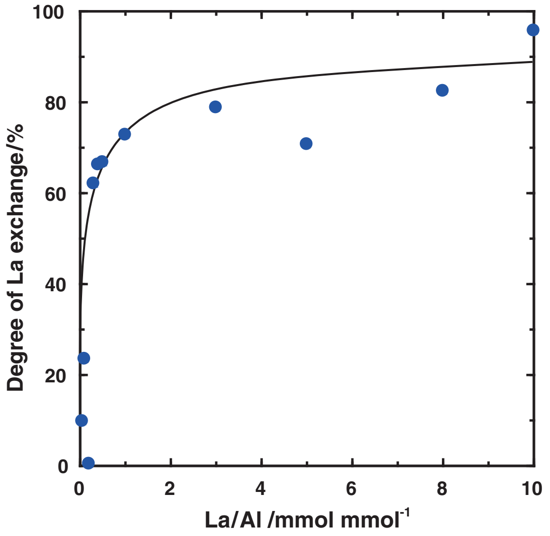


Figure 1. Effects of cation exchange on the lanthanum amounts against Al content of La,NaMOR.

Results and Discussion

Properties of Lanthanoid Exchanged Sodium Mordenites. Figure 1 shows the changes of acidity by lanthanum exchange of sodium mordenite (NaMOR), where the degree of lanthanum exchange was calculated based on a La/3Al ratio (mol/mol). Thus, complete exchange corresponds to La/3Al = 1 because La^{3+} can be exchanged with 3NaOAl moieties. The cation exchange occurred very rapidly up to around 60–70% with an increase in the amount of $La(NO_3)\cdot 6H_2O$ relative to aluminum content of NaMOR, however large lanthanum amounts were necessary for further exchange. No changes of XRD patterns were observed after the exchange. This means there is no significant change of zeolite structure and formation of agglomerates of lanthanoid oxide in the resulting mordenites.

Figure 2 shows the changes of acidity of lanthanum exchanged sodium mordenite (La,NaMOR) with the degree of lanthanum exchange, where the acidities and acid amounts were calculated from peak temperatures and peak area of NH_3-TPD profiles. The acidities appeared at around 60%, and they were enhanced rapidly to around 80% exchange. However, they were saturated by further exchange. The acid strength remained almost constant by the exchange, because the peak temperatures were around 400 °C for all samples. The acidities did not appear at lower exchange because of the formation of saturated triexchanged (La-3Al) species with only low acidity. However, the diexchanged (La-2Al) and/or monoexchanged (La-Al) species appear at higher lanthanum exchange, resulting in the appearance of Brønsted acidity.[1,9]

Table 1 summarizes properties of lanthanoid exchanged sodium mordenites (Ln,NaMOR; Ln: La, Ce, Pr, Sm, Dy, and Yb) with La^{3+}, Ce^{3+}, Pr^{3+}, Sm^{3+}, Dy^{3+}, and Yb^{3+} cations at around 0.7 of Ln/3Al ratio. The cation exchanges were carried out in a similar manner to lanthanum. The XRD patterns show

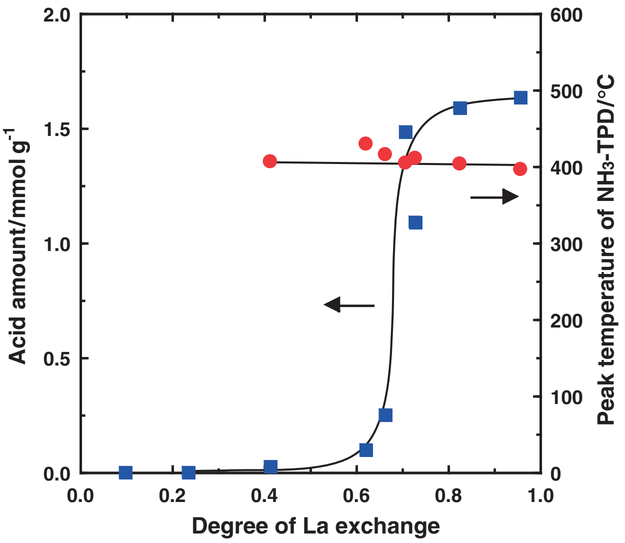


Figure 2. Effects of acid amounts and peak temperature of NH_3-TPD on La,NaMOR.

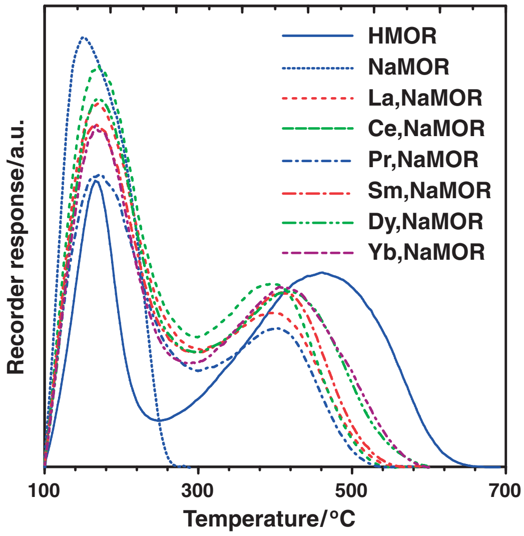
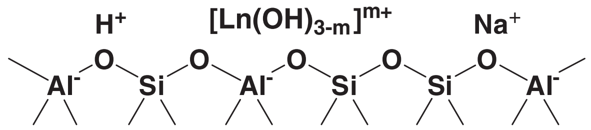


Figure 3. NH_3-TPD profiles of Ln,NaMORs.

the structures of NaMOR remained after the exchange and following calcination at 500 °C. Aluminum leaching was not significant during the exchange beccause SiO_2/Al_2O_3 ratio remained in the range of 18–20 after the exchange.

Figure 3 shows the NH_3-TPD profiles of Ln,NaMORs. NaMOR has only an *l*-peak at around 150 °C, due to physisorption of NH_3 on basic and neutral sites. However, two types of peaks, *l* and *h*, appeared after lanthanoid exchange of NaMOR. The *l*-peaks became larger by the exchange. The *h*-peaks, which are assigned to Brønsted acid sites, have almost the same peak-temperatures at around 400 °C, where unmodified HMOR has a peak at around 470 °C. These results mean that acidities of Ln,NaMORs are almost the same strength irresective of types of lanthanoid although they are weaker than that of HMOR. Ln,NaMORs also have almost the same amounts of acidic sites although they are slightly lower than the unmodified HMOR.



Scheme 1. Suggested Brønsted acidic sites on Ln,NaMORs. Ln: lanthanoid cation; $m = 1, 2, 3$.

Table 2. Catalytic Cracking of 1,3,5-TIPB and IPB over Ln,NaMOR[a)]

Mordenite	Conversion/%	
	1,3,5-TIPB	IPB
HMOR	93.1	99.4
NaMOR	0.0	0.0
La,NaMOR	18.3	64.6
Ce,NaMOR	8.7	27.0
Pr,NaMOR	29.1	67.5
Sm,NaMOR	14.9	38.7
Dy,NaMOR	15.7	43.1
Yb,NaMOR	15.5	48.1

a) Reaction conditions: catalyst, 20 mg; 1,3,5-TIPB or IPB, 0.02 µL; temperature, 450 °C; carrier gas, N_2, 0.2 MPa.

It is well known that new acidity appears by the cation exchange of sodium zeolites with multivalent cations.[1,9,15,30,31] These acidities are due to protons formed from hydrated multivalent cations. The acidities also appear in the case of lanthanoid exchange of NaMOR. The saturated species, triexchanged (Ln-3Al), have only low acidity because of valence saturation with Al species. However, stronger acidities appear through the formation of unsaturated lanthanoid cation (diexchanged (Ln-2Al) and/or monoexchanged (Ln-Al)) as shown in Scheme 1. From the scheme, the acidity highly resembles all the lanthanoids. These acidities of Ln,NaMOR are sufficient strength and amount for solid acid catalysis.

Cracking of 1,3,5-TIPB and IPB over Lanthanoid Exchanged Sodium Mordenites. Table 2 summarizes the cracking of 1,3,5-TIPB and IPB over Ln,NaMOR (Ln: La, Ce, Pr, Sm, Dy, and Yb) by pulse method. All Ln,NaMORs had low activities for the cracking of 1,3,5-TIPB, although NaMOR was inactive. However, HMOR had high activity for cracking as discussed previous papers.[15–20] Because the cracking of 1,3,5-TIPB occurs at the external acid sites because the molecule cannot enter the MOR channels, these results indicate that external acid sites of these mordenites are less active for the cracking of 1,3,5-TIPB than internal sites, and that they are lowly active for acid catalysis. On the other hand, all Ln,NaMORs were highly active for cracking of IPB although their activities are much lower than HMOR. The cracking of IPB occurs principally at the internal acid sites because IPB can enter the MOR channels. From these differences of catalytic properties toward cracking of 1,3,5-TIPB and IPB, the internal acid sites of Ln,NaMORs are active enough for the solid acid catalysis, however the external acid sites are lowly active for the catalysis.

Isopropylation of BP. Figure 4 shows the effects of lanthanum exchange on catalytic activities and selectivities for 4,4-DIPB in the isopropylation of BP. Catalytic activities

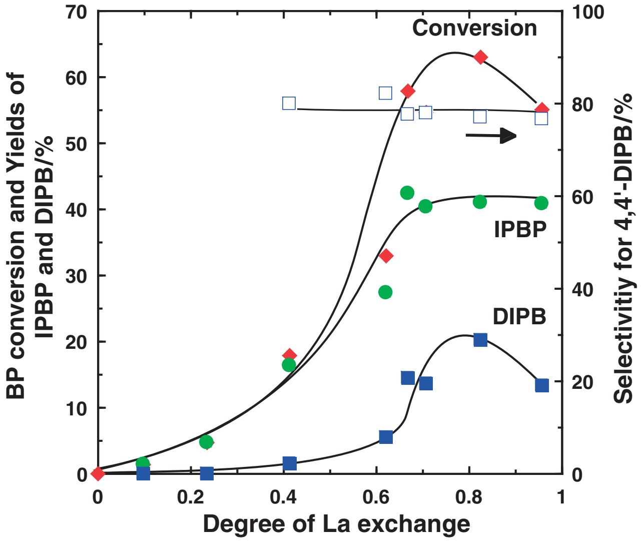


Figure 4. Effects of degree of La,NaMOR on the isopropylation of BP. Reaction conditions: BP, 100 mmol; catalyst, 0.5 g; propene, 0.8 MPa; temperature, 300 °C; period, 4 h.

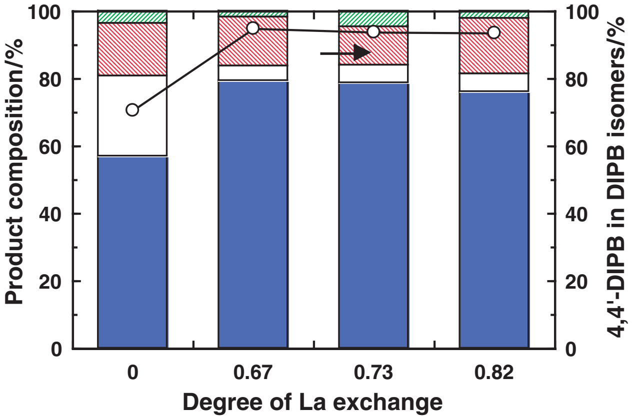


Figure 5. Effects of the isomerization of 4,4′-DIPB on degree of cation exchange of La,NaMOR. Reaction conditions: 4,4′-DIPB, 50 mmol; catalyst, 0.5 g; propene, 0.8 MPa; temperature, 300 °C; period, 4 h. Legend: ■: 4,4′-DIPB; □: 3,4′DIPB; ▧: TriIPB; ▨: IPBP.

gradually appeared at around 20%, increased with an increase in the degree of exchange, and then rapidly enhanced at around 60–70% of the exchange with the increase in acid amounts, however they were saturated at around 80% exchange, and then decreased slightly after further exchange. The catalytic activities appearing at low exchange states are due to the acidities of Ln-3Al species, which have weaker acidities than Ln-2Al and Ln-1Al species.

Principal products were IPBP isomers at lower exchanges. The formation of DIPB isomers started at around 60% exchange, saturated at around 80%, and decreased with further exchange. These features of the catalysis, particularly the formation of DIPB isomers, reflect the appearance and characteristics of Brønsted acidity of Ln-2Al and Ln-1Al species as shown in Scheme 1.

The selectivities for 4,4′-DIPB were almost constant at about 80% irrespective of the degree of lanthanum exchange. The catalysis occurs at the acidic sites in the MOR channels, and the selectivities appeared due to the shape-selective nature of the channels of La,NaMOR. These results indicate that the channels of La,NaMOR work as the sites of shape-selective catalysis as previously reported for HMOR and Ce,NaMORs.[15–18,20–25]

As shown in Figure 5, the isomerization of 4,4′-DIPB was not particularly significant over La,NaMORs with 70–80% exchange under propene pressure at 300 °C, although 4,4′-DIPB was extensively isomerized to thermodynamically stable 3,4′- and 3,3′-DIPB[32] over unmodified HMOR. The results correspond to the low activities of La,NaMOR in the cracking of 1,3,5-TIPB, and indicate that the external acid sites of La,NaMOR are lowly active for the isomerization of 4,4′-DIPB, resulting in the highly selective formation of 4,4′-DIPB in the isopropylation of BP even at temperatures as high as 300 °C.

Figure 6 shows the effects of reaction temperature on the BP conversion and the selectivity for 4,4′-DIPB over Ln,NaMORs exchanged with La^{3+}, Ce^{3+}, Pr^{3+}, Sm^{3+}, Dy^{3+}, and Yb^{3+} cations. The catalytic activities increased with the increase in temperature, and these MORs have catalytic activities at a similar level as unmodified HMOR. The principal products were IPBP isomers at lower temperatures, however the yields of DIPB increased with increasing temperature, and the formation of triisopropylbiphenyl (TriIPB) isomers accompanied in small amounts at higher temperatures (Figures S1 and S2 in Supporting Information). The selectivities for 4,4′-DIPB remained at 70–80% in the temperature range of 200 to 300 °C although the selectivity significantly decreased at 300 °C for HMOR. The selectivities for 4,4′-DIPB in encapsulated products remained at 70–80% at temperatures for all MORs (results not shown). Figure 7 shows the BP conversion and selectivities for 4,4′-DIPB at 250 and 300 °C over Ln,NaMORs. The selectivities for 4,4′-DIPB were as high as 75–80% for all mordenites including HMOR at 250 °C. The selectivities still remained at 70–75% for all Ln,NaMORs at 300 °C, although the selectivities decreased to 50% for HMOR. The decrease in selectivity for 4,4′-DIPB over HMOR is due to the isomerization of 4,4′-DIPB to thermodynamically stable DIPB isomers, particularly 3,4′-DIPB.[32] However, the external acid sites are likely deactivated, probably because of the saturation of Ln cations on aluminum moieties, resulting in prevention of the isomerization for 4,4′-DIPB.

Figure 8 shows the isomerization of 4,4′-DIPB under propene pressure at 300 °C, The isomerization extensively occurred over unmodified HMOR as in the isopropylation of BP, however it was effectively prevented by lanthanoid exchange. The isomerization does not occur at the acid sites in the MOR channels, but on the external surface.[17,18,20,24] These results also correspond to the results of the cracking of 1,3,5-TIPB over Ln,NaMORs, and mean that internal Brønsted acid sites only work for the isopropylation of BP, resulting in shape-selective formation of 4,4′-DIPB.

From these results, we can summarize that the isopropylation of BP over Ln,NaMOR occurs in the channels by shape-selective catalysis, resulting in the selective formation of the least bulky 4,4′-DIPB, and that the isomerization of 4,4′-DIPB did not occur significantly because external acid sites by Ln cation exchange are inactive.

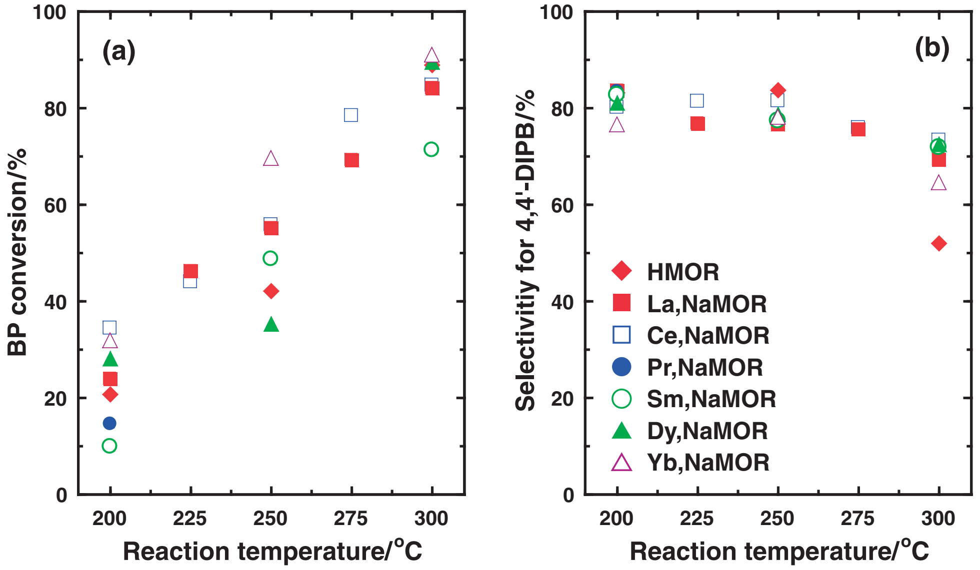


Figure 6. Effects of temperature on the isopropylation of BP over Ln,NaMORs. (a) The activities, (b) the selectivities of 4,4′-DIPB. Reaction conditions: BP, 100 mmol; catalyst, 0.5 g; propene, 0.8 MPa; temperature, 200–300 °C; period, 4 h.

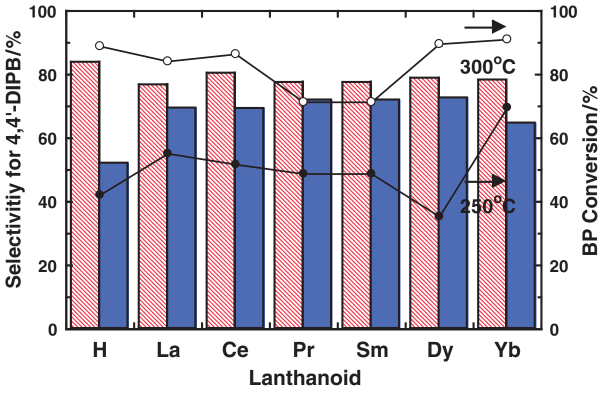


Figure 7. Effects of temperature on the isopropylation of BP over Ln,NaMORs. Reaction conditions: BP, 100 mmol; catalyst, 0.5 g; temperature, 250 and 300 °C; propene pressure, 0.8 MPa; period, 4 h. Legend: ▨: 250 °C; ■: 300 °C.

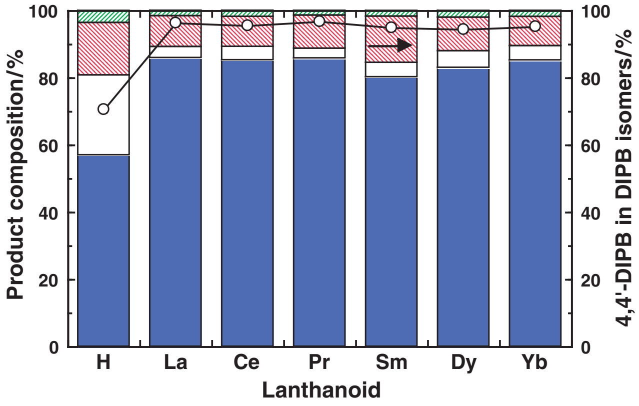


Figure 8. The isomerization of 4,4′-DIPB over Ln,NaMORs. Reaction conditions: 4,4′-DIPB, 50 mmol; catalyst, 0.5 g; temperature, 300 °C; propene pressure, 0.8 MPa; period, 4 h. Legend: the same as in Figure 5.

Mechanistic Aspects of the Catalysis over Lanthanoid Exchanged Sodium Mordenites. The characteristic acidity shown in previous chapters indicates that a new type of acid sites appears on NaMOR by lanthanoid exchange. The Brønsted acidic sites appeared by the unsaturated lanthanoid cation (mono- and/or diexchanged lanthanoid cation) near the aluminum sites. The acid sites assigned to Brønsted acidities have the quite common features of Ln,NaMOR as suggested in Scheme 1. It is well known that the appearance of acid sites shares common features of multivalent cation exchange of zeolites.[1,9,15,30,31] The results indicate the Ln,NaMORs have active acid sites in their channels strong enough for acid catalysis.

These Ln,NaMORs have high activities for the cracking of IPB at 410 °C by pulse reaction, however they are only lowly active for the cracking of 1,3,5-TIPB. The differences are due to the bulkiness of reactant molecules. External acid sites are lowly active for the cracking of IPB and 1,3,5-TIPB. Internal acid sites are only active for cracking of IPB because 1,3,5-TIPB cannot enter the MOR channels. This indicate that internal Brønsted acid sites only work for acid catalysis, and that the external acid sites are lowly active for the crackings, probably due to Ln satuation of aluminum moieties at the external surface.

Ln,NaMORs were active catalysts for the isopropylation of BP. BP predominantly yields 4-IPBP among the isomers in the first step, and 4-IPBP selectively forms 4,4′-DIPB. BP conversions were not dependent on types of lanthanoid cations, and increased with the increase in reaction temperature. These results suggest that acid sites appearing by the exchange are very similar to Brøntsted acid sites in Scheme 1 for all lanthanoids. The selectivities for 4,4′-DIPB were also around 80% for all Ln,NaMORs in the range from 200 to 300 °C; which show that the channels of Ln,NaMORs work as shape-selective catalytic sites similarly to those of unmodified HMOR. The channels can exclude the transition states of bulky DIPB isomers, resulting in the selective formation of

4,4′-DIPB by product selectivity and restricted transition state mechanisms, as proposed for the catalysis over HMOR.[17,18,20,24]

No significant decreases in the selectivity for 4,4′-DIPB were observed in the isopropylation of BP over Ln,NaMOR even at 300 °C although the extensive decrease occurred for unmodified HMOR. The differences indicate that the external acid sites of Ln,NaMOR are lowly active for the isomerization of 4,4′-DIPB, probably due to the low acidity of Ln saturation of aluminum moieties at the external surface. These results also corresponds to low activities of Ln,NaMORs in the cracking of 1,3,5-TIPB because internal Brønsted acid sites only work for the catalysis.

There are no significant differences in catalytic properties in the channels of Ln,NaMOR discussed in the isopropylation of BP and the cracking of IPB and 1,3,5-TIPB. This means that both the unmodified and lanthanoid exchanged channels work as similar reaction sites, and that there are no significant steric differences from the cationic exchange of sodium to lanthanoids.

Combustion of Coke Deposit in MOR Channels. Figure 9 summarizes TG profiles of Ln,NaMORs after using for catalysis. A peak appeared at around 600 °C for unmodified HMOR. The peak from coke combustion for Ln,NaMORs appeared at lower temperatures more than 100 °C. Thus, the peak appeared at around 380 °C for Ce,NaMOR, and at around 430 °C for the other lanthanoids. These results indicate that lanthanoid species, formed by the exchange, work as oxidation catalysts for coke combustion. Particularly, cerium species, dispersed in MOR channels work as effective catalysts for combustion of coke-deposit inside the channels. Hashimoto et al. also found cerium oxide dispersed in MOR channels was active for the oxidation of *p*-xylene.[33] The coke combustion at low temperatures below 400 °C indicates the advantages to prevent the collapse of zeolite structure during the regeneration of the spent catalysts.

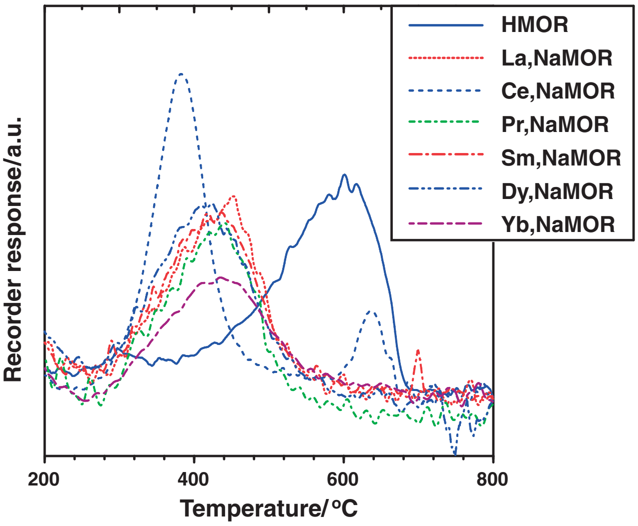


Figure 9. TG profiles of Ln,NaMORs used for the isopropylation of BP. Reaction conditions: BP, 100 mmol; temperature, 250 °C; propene pressure, 0.8 MPa; period, 4 h. TG measurement: sample, 10 mg; temperature programmed rate, 10 °C min^{-1} in an air stream.

Conclusion

The lanthanoid exchange was applied to sodium mordenite (NaMOR) using aqueous lanthanoid nitrate solution. The acidities of La,NaMOR appear gradually at 60–70% exchange based on La/3Al ratio. Similar acidities were also observed for other lanthanoid exchanged sodium mordenites, Ln,NaMOR (Ln: Ce, Pr, Sm, Dy, and Yb). The acidic properties have features in common with Brønsted acidities, which appear due to unsaturated lanthanoid cations on aluminum moieties.

The liquid-phase isopropylation of BP with propene was studied to elucidate the acidic properties appearing by lanthanoid exchange of NaMOR. Shape-selective formation of 4,4′-diisopropylbiphenyl (4,4′-DIPB) occurred over Ln,NaMORs. Ln,NaMORs afforded almost the same level of selectivities for HMOR with similar SiO_2/Al_2O_3 ratios. These results indicate that the catalyses occurred inside the channels on the Brønsted acidic sites appearing from unsaturated lanthanoid species on aluminum sites. Ln,NaMORs remained highly selective for 4,4′-DIPB at temperatures as high as 300 °C although the selectivities decreased over HMOR with the isomerization of 4,4′-DIPB. The results in this paper show that the shape-selective catalysis arises from MOR channels, and not from the acidities of the zeolites.

The combustion of coke-deposits of used catalysts for the catalysis occurred at lower temperatures over Ln,NaMORs because the lanthanoids work as oxidation catalysts. This is ascribed to the fact that finely dispersed lanthanoid species work for the catalysis of combustion of coke inside the channels. It should be noted that the low temperature coke-combustion can prevent the collapse of zeolite structure during the regeneration of the spent catalysts.

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Supporting Information

Figure S1: The isopropylation of BP over HMOR. Figure S2: The isopropylation of BP over Ln,NaMOR (Ln: La, Ce, Pr, Sm, Dy, and Yb). These materials are available free of charge on the Web at: http://www.csj.jp/journals/bcsj/.

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