

Catalytic Performance of [Ti,Al]-Beta in the Alkene Epoxidation Controlled by the Postsynthetic Ion Exchange

Yasuhide Goa,[†] Peng Wu,[‡] and Takashi Tatsumi^{*‡}

Department of Applied Chemistry, Graduate School of Engineering, The University of Tokyo, 7-3-1, Hongo, Bunkyo-ku, Tokyo 113-8656, Japan, and Division of Materials Science & Chemical Engineering, Graduate School of Engineering, Yokohama National University, 79-5, Tokiwadai, Hodogaya-ku, Yokohama 240-8501, Japan

Received: March 11, 2004

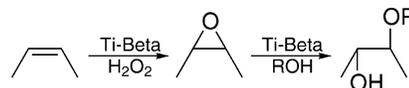
Novel methods for enhancing the epoxide selectivity in the alkene epoxidation over [Ti,Al]-Beta have been developed. When as-synthesized [Ti,Al]-Beta was treated with aqueous ammonium nitrate solution and successively calcined at low temperature, a dramatic enhancement of epoxide selectivity was attained in the liquid-phase epoxidation of cyclohexene using H₂O₂ as an oxidant in protic solvent methanol. The optimum thermal treatment temperature to achieve the maximum epoxide yield was 473 K, where the postsynthetic [Ti,Al]-Beta exhibited a catalytic activity comparable to the sample directly calcined at 793 K; nevertheless, the epoxide selectivity was as high as 63% for the former in contrast to 0% for the latter. The ion-exchange treatments with quaternary ammonium salts over calcined [Ti,Al]-Beta showed similar effects, although the treatments with alkali and alkaline earth metal ions were detrimental to the catalytic activity. It is suggested that the quaternary ammonium cations selectively blocked the acid sites deriving from the framework Al, which resulted in preventing the ring-opening hydrolysis of the epoxide, whereas the inorganic cations poisoned not only the acid sites but also the Ti active sites contributing to the catalytic epoxidation. The ion-exchanged catalyst was regenerated readily by repeated calcination and following ion exchange and thus turned out to be an active, selective, and reusable epoxidation catalyst.

1. Introduction

Because the discovery of titanium silicate-1 (TS-1) by Taramasso et al. in 1983,¹ the syntheses, characterizations, and catalytic applications of titanosilicates have attracted great attention of many researchers. TS-1 has unique catalytic properties in epoxidation of alkenes, hydroxylation of aromatics, oxidation of alkanes and alcohols, ammoximation of carbonyl compounds, etc. under mild conditions using a dilute H₂O₂ solution as an oxidant.² However, TS-1 analogous to ZSM-5 with the MFI structure exhibits low activity for bulky substrates such as cyclic or branched molecules despite the high activity for linear ones because those bulky molecules hardly penetrate into its medium pores of 10-membered rings (MR).^{3,4}

Recently developed Ti-Beta zeolite with the *BEA structure has a three-dimensionally connected pore system with 12-MR channels and is found to be more active than TS-1 for the oxidation of bulky substrates using aqueous H₂O₂ or *tert*-butyl hydroperoxide (TBHP) as an oxidant because of the less diffusion restriction imposed by the large pore system. However, the addition of a small amount of Al (SiO₂/Al₂O₃ < 200) as a crystallization-promoting agent is generally needed in the conventional hydrothermal synthesis of Ti-Beta especially when tetraethylammonium hydroxide (NEt₄OH, TEOH) is employed as a structure-directing agent (SDA).^{5,6} The presence of Al leads to the formation of strong acid sites, which promotes the successive ring-opening solvolysis of the epoxide generated in the alkene epoxidation reactions to lower its selectivity exten-

SCHEME 1: Epoxidation of Alkene and the Successive Solvolysis over Ti-Beta Catalyst



sively (Scheme 1).^{7–9} Thereupon, several novel methods for the synthesis of Al-free or low Al Ti-Beta were also developed, such as seeding method,¹⁰ Cogel method,¹¹ fluoride method,^{12,13} and dry-gel conversion method^{14–17} using TEOH as SDA. ARCO patented the synthesis of Al-free Ti-Beta using a benzyl-substituted diquaternary ammonium cation as a novel SDA.¹⁸ However, none of them were efficient enough to lead to the high epoxide selectivity in alcoholic solvents. This is probably because besides the strong acid sites originating from framework Al, the very complex, severely intergrown nature of the Beta structure results in a high concentration of silanol groups exhibiting weak acidity at defect sites. Furthermore, titanium hydroperoxide species (Ti–OOH), the oxidation active sites, are reported to show Brønsted acidity, which also catalyzes the ring-opening solvolysis.^{9,19} Solvent effects were investigated and acetonitrile proved to be a selective solvent for the epoxide production because acetonitrile is weakly basic and poisons the acid sites of titanosilicates;⁹ however, in some reaction systems acetonitrile solvent decreases the conversion of the alkene.¹⁵ Although the ion exchange with alkaline or alkaline earth metal cations eliminates the acidity of titanosilicates, it also suppresses the oxidation activity of Ti species. For example, the ion exchange with sodium carbonate (Na₂CO₃) or sodium azide (NaN₃) on Al-containing TS-1 gave rise to a higher epoxide selectivity but a decreased activity in the allyl alcohol oxidation,²⁰ whereas the ion exchange with potassium

* Corresponding author. Tel.: +81-45-339-3943. Fax: +81-45-339-3941. E-mail: ttatsumi@ynu.ac.jp.

[†] The University of Tokyo.

[‡] Yokohama National University.

carbonate severely lowered the turnover number in the oxidation of hydrocarbons,²¹ and TS-1 synthesized in the presence of large amount of alkali and alkaline earth ions showed low oxidation activity.²² While acid sites were blocked with these metal cations and acid-catalyzed solvolysis of the epoxide was suppressed to show high epoxide selectivity, these cations simultaneously poisoned the active sites for oxidation. As far as we know, however, the mechanism of the poisoning of titanosilicates by alkali cations is not clarified yet. Tatsumi et al. have suggested that Si—O—M (M: metal cation) is less covalent and more ionic than Si—O—H; the polar environment around the Ti sites makes the interaction between the catalyst and the reactant molecules having C=C double bonds weaker.²¹ We have communicated recently that ion exchange with quaternary ammonium cations dramatically enhances the epoxide selectivity of [Ti,Al]-Beta even in the protic solvent alcohols without retarding the specific activity of Ti species.²³ In this study, we have compared this postsynthetic method with the direct calcination of the as-synthesized [Ti,Al]-Beta to reveal the advantage of the postsynthesis on [Ti,Al]-Beta over the direct method. A mechanistic consideration has been given to how these methods controlled the acidity of [Ti,Al]-Beta to enhance the epoxide selectivity in the liquid-phase epoxidation of alkenes.

2. Experimental Section

2.1. Catalyst Preparation. [Ti,Al]-Beta was hydrothermally synthesized according to the literature^{5,6} by using tetraethylammonium hydroxide (TEAOH) as a structure-directing agent (SDA) with a modification to decrease the formation of extraframework anatase. Titanium tetrabutoxide (TBOT, Kanto Chemicals) was employed as a Ti source instead of ethoxide, and TBOT was hydrolyzed in the aqueous H₂O₂ (31 wt % in water, Mitsubishi Gas Chemicals) to stabilize mononuclear Ti species of peroxotitanate. H₂O₂/Ti ratio was 10. This procedure was performed in an ice bath. The resultant yellow solution of peroxotitanate was added to the TEAOH solution (35 wt % in water, Aldrich), and the mixture was continuously stirred for 1.5 h. Precipitated silica (Nipsil VN-3, SiO₂/Al₂O₃ = 457, SiO₂/Na₂O = 227) and aluminum nitrate nonahydrate (Koso, Al(NO₃)₃·9H₂O) were added to the above solution to give a mother gel with a molar composition of SiO₂·0.033TiO₂·0.005Al₂O₃·0.28TEAOH·12.5H₂O. After the gel was aged at room temperature for 2 h, hydrothermal synthesis was carried out in a PTFE-lined stainless steel autoclave with agitation under an autogenous pressure at 413 K for 4 days.

SDA cations packing the channels of as-synthesized [Ti,Al]-Beta were removed by the following two procedures: (a) as-synthesized [Ti,Al]-Beta was calcined at *T* K in the O₂ stream, where *T* was 473 and 793 K, which was designated as cal[*T*]; (b) as-synthesized [Ti,Al]-Beta was treated with 6.0 mol dm⁻³ aqueous ammonium nitrate solution twice to extract SDA, followed by the calcination at *T*, where *T* was varied in the range of 373–793 K, which was designated as ex(AN)-cal[793] (AN stands for ammonium nitrate). Acetic acid (1.0 mol dm⁻³) and hydrochloric acid were also used to extract SDA. After the treatment, the dried samples were calcined at 473 K for 10 h. These samples were designated as ex(AA)-cal[473] (AA stands for acetic acid) and ex(HCl)-cal[473], respectively. Alternatively, [Ti,Al]-Beta, calcined [Ti,Al]-Beta, cal[793], was treated with 1.0 mol dm⁻³ quaternary ammonium acetate (NR₄-OAc, R = Me, Et, Pr), ammonium acetate (NH₄OAc), or alkali or alkaline earth metal acetate solution and successively calcined at 473 K. The ion-exchange degrees were controlled by the pH of the solution. Samples prepared by the ion exchange are designated as cal[793]-ie(M)_x, where M and *x* represents the

cation of the ion-exchange reagent and the initial pH in the ion exchange. In all the cases, the final pH values of the ion-exchange ranged between 6 and 7.

2.2. Characterizations. Powder X-ray diffraction patterns were collected on a MAC Science MX-Labo diffractometer with an accelerating voltage and a tube current of 40 kV and 20 mA, respectively. Elemental analyses were performed on a Shimadzu ICPS-8000E photoemission spectrometer equipped with inductively coupled plasma for inorganic elements and on a Perkin-Elmer 2400 series II CHNS/O analyzer for organic elements. FT-IR spectra were collected on a Perkin-Elmer 1600 FT-IR spectrometer using a KBr pellet technique (a 2 mg sample was diluted with 100 mg of KBr and shaped into a 10 mm o.d. pellet) or a self-supporting technique (30 mg sample shaped into a 20 mm o.d. pellet). ²⁹Si- and ²⁷Al-MAS NMR spectroscopies were performed on a JEOL ECA-400 multinuclear solid-state magnetic resonance spectrometer at a magnetic field of 79.6 and 104 MHz, respectively. Nitrogen adsorption measurements were carried out on a BEL Japan BELSORP 28SA automatic gas adsorption instrument. The sample was preevacuated under a pressure of 1.33 Pa at 473 K for 3 h.

2.3. Epoxidation of Alkenes. Epoxidation of alkenes was carried out batchwise in a water-bathed 20 mL round-bottom flask equipped with a Dimroth condenser and a magnetic stirrer; 5 mL of methanol or acetonitrile as a solvent, 8.25 mmol of cyclohexene, 1-hexene, or 2-hexenes (cis/trans isomers ratio = 41/59), and 2.5 mmol of H₂O₂ (31 wt % in water) and catalyst (50 mg for cyclohexene and 100 mg for 1-hexene) were mixed and heated under vigorous stirring at 333 K. After the reaction, the reactor was quenched in an ice bath and the reaction mixture was centrifuged to separate the liquid phase from the catalyst. Quantitative analyses were performed on a Shimadzu GC-14B gas chromatograph equipped with an OV-1 50 m capillary column using cycloheptanone as the internal standard.

2.4. Ring-Opening Reaction of Epoxide. To clarify which sites catalyze the solvolysis of epoxides, the solvolysis reactions of cyclohexene oxide catalyzed by various zeolitic materials with or without the addition of peroxide were examined. The reactions were performed in a similar way to the alkene epoxidation. TS-1 (Si/Ti = 80) and three [Ti,Al]-Beta samples (cal[793], cal[793]-ie(NMe₄)9.50 and cal[793]-ie(K)8.15), Sili-calite-1, H-ZSM-5 (JRC-Z5-25H, Japan Reference Catalyst, Si/Al = 12.5), H-Beta (JRC-Z-HB25, Si/Al = 12.5) and deboronated B-Beta (Si/B > 500) were employed as catalysts. 50 mg of catalyst, 5 mL of methanol as solvent and 2.5 mmol of cyclohexene oxide were heated to 333 K in the presence or the absence of oxidant (2.5 mmol of H₂O₂ (31 wt % in water) or *tert*-butyl hydroperoxide (TBHP; (CH₃)₃COOH, 70 wt % in water)). Water was externally added when neither oxidant nor TBHP was added, to adjust the amount of H₂O to that present in the H₂O₂ added.

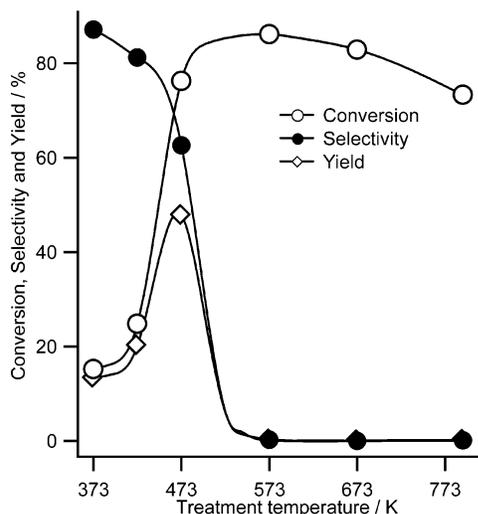
3. Results and Discussion

3.1. Effect of SDA-Extraction Treatment. Results of catalytic epoxidation of cyclohexene over directly calcined and SDA-extracted [Ti,Al]-Beta are shown in Table 1. Directly calcined [Ti,Al]-Beta (cal[793]) converted cyclohexene actively but yielded no cyclohexene oxide after 3 h (run 1). The main products were 1,2-cyclohexanediol and its monomethyl ether due to the acid-catalyzed solvolysis of cyclohexene oxide, together with small amount of allylic oxidation products. The negligible formation of cyclohexene oxide strongly indicates that there were a considerable number of acid sites in just calcined [Ti,Al]-Beta. The catalyst prepared by treating as-synthesized [Ti,Al]-Beta with ammonium nitrate followed by mild calcination at

TABLE 1: Epoxidation of Cyclohexene with H₂O₂ over Postsynthetically Treated [Ti,Al]-Beta^a

run	treatment ^b	conv/%	TON ^c	selectivity ^d /%			H ₂ O ₂ /%	
				epox	glyc	allyl	conv	select
1	cal[793]	76.6	91.3	0	98	2	83	90
2	cal[473]	17.3	20.6	82	16	2	26	66
3	ex(AN)-cal[793]	73.3	91.3	0	97	3	88	83
4	ex(AN)-cal[473]	76.2	92.9	63	35	2	82	93
5	ex(AA)-cal[473]	69.3	83.2	59	39	2	75	92
6	ex(HCl)-cal[473]	64.7	77.9	3	95	2	66	99

^a Reaction conditions: reaction temperature, 333 K; reaction time, 3 h; 5 mL of methanol; 8.25 mmol of cyclohexene; 2.5 mmol of H₂O₂ (31 wt % in water); 50 mg of catalyst. ^b AN: ammonium nitrate. AA: acetic acid. HCl: hydrochloric acid. ^c Turnover number in mol (mol of Ti)⁻¹. ^d Epox: cyclohexene oxide. Glyc: 1,2-cyclohexanediol and monomethyl glycol ether. Allyl: 2-cyclohexen-1-ol and 2-cyclohexen-1-one.

**Figure 1.** Relationships between the calcination temperature after the NH₄NO₃ treatment and the catalytic performances in the cyclohexene epoxidation. For the conditions of cyclohexene epoxidation, see Table 1.

473 K, ex(AN)-cal[473], exhibited a high epoxide selectivity of 63% without loss of activity (run 4). In contrast, ex(AN)-cal[793] showed negligible epoxide selectivity, and cal[473] showed low activity although it was fairly selective for the formation of cyclohexene oxide (runs 2 and 3), indicating that the combination of SDA extraction and thermal treatment at moderate temperature was effective for the enhancement of cyclohexene oxide selectivity while maintaining the epoxidation activity. Acids, 1.0 mol dm⁻³ acetic acid and hydrochloric acid, were also employed for the SDA extraction. Acetic acid showed an effect similar to that of ammonium nitrate (run 5); however, the catalyst treated with hydrochloric acid, ex(HCl)-cal[473] showed a very low epoxide yield (run 6).

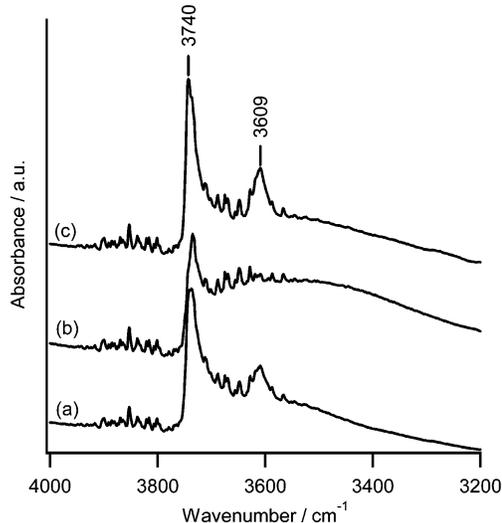
Figure 1 shows the results of oxidation over NH₄NO₃-treated [Ti,Al]-Beta calcined at various temperatures. The conversion of cyclohexene increased and the selectivity to the epoxide decreased with increasing calcination temperature. The highest epoxide yield was achieved after the thermal treatment at an optimum temperature of 473 K.

Table 2 shows the results of organic elemental analyses and physicochemical properties of [Ti,Al]-Beta samples treated under various conditions. The samples treated at lower temperature exhibited a low specific surface area due to an insufficient removal of SDA. A very small Langmuir surface area of 47 m² g⁻¹ of cal[473] accounted for its low activity. The as-synthesized sample contained 5.3 NEt₄⁺ ions per unit

TABLE 2: Physicochemical Properties of Postsynthetically Treated [Ti,Al]-Beta

treatment	Si/Ti	Si/Al	N/Al	N/u.c.	C/N	A _{Lang} ^a /m ² g ⁻¹
as-synthesized	35	38	3.1	5.3	7.9	n.d. ^b
cal[793]	35	38				684
cal[473]	35	38	n.d. ^b	n.d. ^b	8.1	47
ex(AN)-cal[373]	35	38	1.8	3.4	7.8	167
ex(AN)-cal[473]	35	38	1.7	2.8	8.0	214
ex(AN)-cal[573]	35	38	1.2	2.0	8.3	n.d. ^b
ex(AN)-cal[673]	35	38	0.2	0.4	9.1	n.d. ^b
ex(AN)-cal[793]	35	38	0.0	0.0		668

^a Langmuir surface area. ^b Not determined.

**Figure 2.** FT-IR spectra in the OH vibration region of cal[793] (a), ex(AN)-cal[473] preevacuated at 473 K (b), and ex(AN)-cal[473] preevacuated at 773 K (c).

cell and each of these cations was coordinated to either bridging oxygens (Si-O⁻-Al) or terminal siloxy anions (SiO⁻) to pack the channels. The amount of SDA cations in the samples decreased after the SDA extraction and further decreased with increasing temperature of subsequent calcination. The C/N ratios were 8 at low calcination temperature up to 473 K, indicating that NEt₄⁺ cations remained intact in the zeolite channels. The ratio increased with increasing calcination temperature, suggesting that some of NEt₄⁺ cations were decomposed at a higher temperature than 573 K to form carbonaceous deposits.

Figure 2 shows the FT-IR spectra of SDA-extracted and directly calcined [Ti,Al]-Beta in the OH vibration region (3200–4000 cm⁻¹). The directly calcined sample cal[793] exhibited two intense absorption bands at 3609 and 3740 cm⁻¹ (Figure 2a), assigned to bridging hydroxyl groups and terminal silanol groups, respectively.²⁴ When the SDA-extracted sample, ex(AN)-cal[473], was preheated at 473 K in vacuo before the FT-IR measurement, only the band of terminal silanol groups remained but decreased in intensity and the band of bridging hydroxyl groups disappeared completely (Figure 2b). When the sample was further treated at 773 K, both of the bands were recovered to be as intense as in the just calcined sample (Figure 2c). These observations strongly indicate that the SDA cations compensating the terminal silanol groups were partially removed during the treatments with NH₄NO₃ in a selective manner, whereas the bridging hydroxyl groups remained blocked by the SDA cations. This leads to a decrease in surface acidity contributing to the solvolysis of epoxide and as a result the epoxide selectivity is enhanced.

Figure 3 shows the FT-IR spectra in the framework vibration region of [Ti,Al]-Beta treated under various conditions. IR

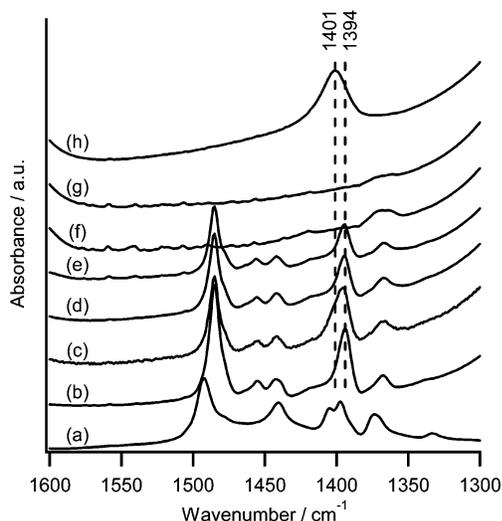
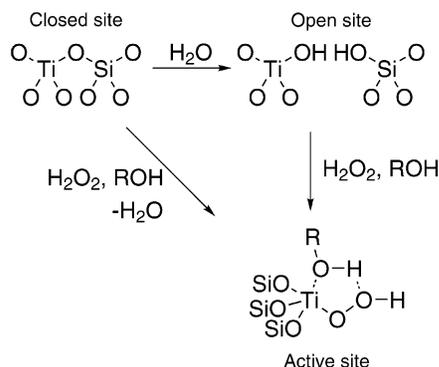


Figure 3. FT-IR spectra of bulk TEABr (a), as-synthesized [Ti,Al]-Beta (b), ex(AN)-dried (c), ex(AN)-cal[373] (d), ex(AN)-cal[473] (e), ex(AN)-cal[673] (f), ex(AN)-cal[793] (g), and NH_4NO_3 -exchanged Al-Beta (Si/Al = 50) (h).

SCHEME 2: Structure of Active Species of Titanosilicates



spectra of as-synthesized and NH_4NO_3 -treated [Ti,Al]-Beta samples were essentially identical to that of bulk TEABr (Figure 3a and b), although slight shifts were observed for several bands. The band intensity decreased gradually with increasing calcination temperature as a result of removal of SDA (Figure 3c–g). As-synthesized [Ti,Al]-Beta was treated with NH_4NO_3 and was dried at room temperature, of which the FT-IR spectrum is shown in Figure 3c. A shoulder peak was observed at 1401 cm^{-1} , which could be assigned to NH_4^+ cations. When the NH_4NO_3 -treated sample was mildly calcined at 373 K , the shoulder peak at 1401 cm^{-1} disappeared (Figure 3d). This finding proposes a mechanism of the NH_4NO_3 treatment; because NEt_4^+ cations are more weakly bound to terminal SiO^- than to bridging oxygen ($\text{Si}-\text{O}-\text{Al}$), NH_4^+ cations were exchanged with the more labile NEt_4^+ cations compensating SiO^- groups, and during the following calcination, $\text{SiO}^- \text{NH}_4^+$ was easily decomposed to form SiOH even at temperatures as low as 373 K . The selective removal of NEt_4^+ cations blocking the silanol groups but not those occupying the bridging hydroxyl sites would make the channels partially open and accessible to the reactant molecules, whereas the remaining NEt_4^+ cations make the latent strong acid sites not available to the solvolysis (Scheme 3).

In the treatment with acid solution (acetic acid and hydrochloric acid), the exchange would be dependent on the acidity. It is conceivable that the treatment with a strong acid such as HCl exchanged the NEt_4^+ cations compensating not only

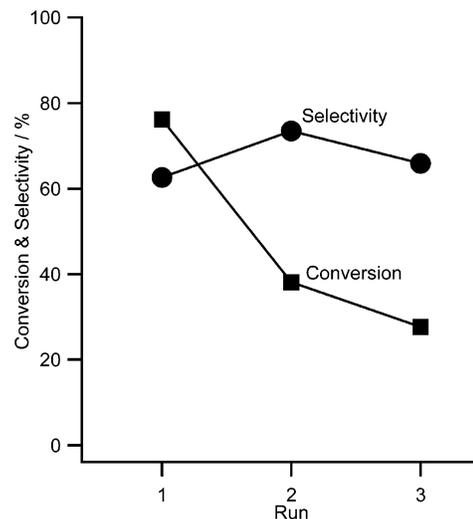
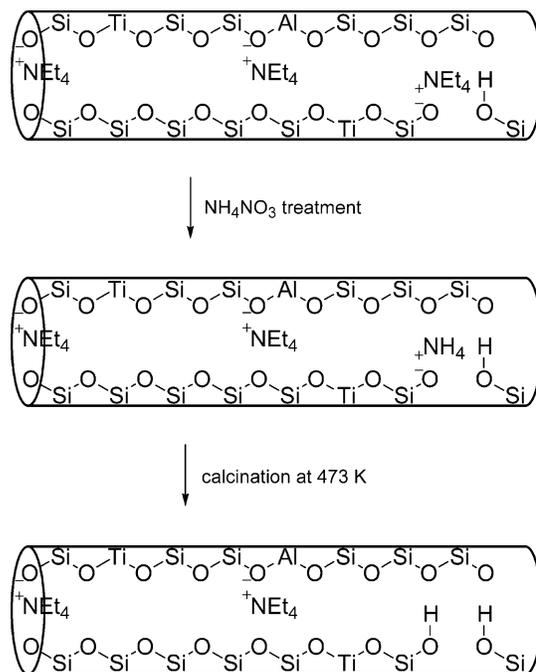


Figure 4. Results of repeated use of catalyst in the epoxidation of cyclohexene: conversion (a) and epoxide selectivity (b). For the reaction conditions, see Table 1.

SCHEME 3: Scheme of SDA Extraction by NH_4NO_3 Solution and Following Calcination at 473 K



terminal SiO^- groups but also bridging oxygens for protons to generate strong acid sites of bridging hydroxyl groups. Because acetic acid is a weaker acid than HCl , NEt_4^+ cations bound to bridging oxygen were hardly exchanged and only those on SiO^- could be exchanged with H^+ to result in a chemical environment similar to that of the NH_4NO_3 -treated catalyst, where bridging hydroxyl sites were occupied with NEt_4^+ cations and terminal silanol sites were not.

Figure 4 shows the results of repeated use of ex(AN)-cal[473]. After each reaction, the catalyst was regenerated by washing with methanol, drying at 393 K , and evacuating at 473 K overnight. Although the cyclohexene conversion decreased with repetition, the epoxide selectivity was maintained, suggesting that coordinated SDA cations endured the oxidative decomposition by H_2O_2 and stably existed after the reaction. However, the oxidation active sites of catalyst would be blocked by such compounds of high boiling point as 1,2-cyclohexanediol

TABLE 3: Results of Epoxidation Reactions over Ion-Exchanged Ti-Beta^a

run	treatment	substrate	solvent	N ⁺ /Al	conv/%	TON ^b	selectivity ^c /%			H ₂ O ₂ /%	
							epox	glyc	allyl	conv	selec
1	cal[793]	cyclohexene	methanol		76.6	91.3	0	98	2	83	90
3	ex-cal[473]	cyclohexene	methanol	1.7	76.2	92.9	63	35	2	82	93
7	cal[793]-ie(NMe ₄)9.50	cyclohexene	methanol	1.8	75.2	90.5	55	43	2	95	79
8	cal[793]-ie(NEt ₄)9.64	cyclohexene	methanol	1.8	47.2	57.0	72	26	2	69	67
9	cal[793]-ie(NPr ₄)9.41	cyclohexene	methanol	1.5	24.5	29.3	51	47	2	42	59
10	cal[793]-ie(NH ₄)9.10	cyclohexene	methanol	1.6	57.4	70.5	0	97	3	60	97
11	cal[793]-ie(K)8.15	cyclohexene	methanol	2.2 ^d	18.7	23.7	64	34	2	48	40
12	cal[793]	1-hexene	methanol		33.0	17.7	4	86	10	66	48
13	cal[793]-ie(NMe ₄)9.50	1-hexene	methanol	1.8	50.8	26.6	100	0	0	82	58
14	cal[793]-ie(NEt ₄)9.64	1-hexene	methanol	1.8	13.9	7.4	100	0	0	47	28
15	cal[793]-ie(K)8.15	1-hexene	methanol	2.2 ^d	5.6	2.8	100	0	0	30	16
16	cal[793]	2-hexenes ^e	methanol		49.5	59.0	0	100	0	76	64
17	cal[793]-ie(NMe ₄)9.50	2-hexenes ^e	methanol	1.8	60.7	72.3	92	4	4	78	72
18	cal[793]	cyclohexene	acetonitrile		30.4	44.2	69	15	16	81	41
19	cal[793]-ie(NMe ₄)9.50	cyclohexene	acetonitrile	1.8	57.1	68.3	89	5	6	86	69

^a Reaction conditions: see Table 1. A 100 mg quantity of catalyst was used in the epoxidation of 1-hexene. ^b Turnover number in mol (mol of Ti)⁻¹. ^c Epox: alkene epoxide. Glyc: solvolyzed product of the epoxide. Allyl: alcohols and ketones formed by the allylic oxidation. ^d K⁺/Al. ^e Cis/trans isomer ratio = 41/59.

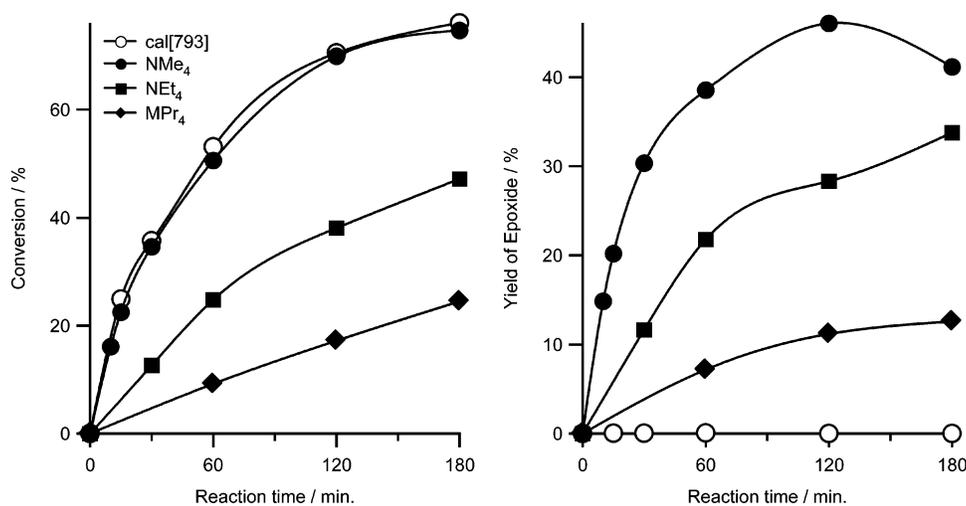


Figure 5. Dependence of conversion and epoxide yield on the reaction time in the cyclohexene epoxidation over quaternary ammonium cation-exchanged [Ti,Al]-Beta. For the reaction conditions, see Table 1.

(bp 520 K) or its oligomers generated during the reaction, leading to the decrease in the conversion. The complete reactivation of the used catalyst was achieved by calcination at high temperature; however, it reduced the selectivity to the epoxide, as shown in Figure 1.

3.2. Ion-Exchange Treatments with Quaternary Ammonium Salt. As described above, it was difficult to maintain the catalytic performance of partially SDA-extracted [Ti,Al]-Beta because of the channel blocking when it was repeatedly used. To achieve complete regeneration of activity, the used catalyst should be calcined at high temperature to burn off the organic species. However, the regeneration by high temperature calcination also restored the strong acidity to lower the epoxide selectivity. Apparently, the SDA cations suppressed the acid sites selectively without influencing the Ti active sites. Accordingly, the calcined sample (cal[793]) was ion-exchanged with various ammonium cations similar to the SDA ones to produce a chemical environment similar to that of ex(AN)-cal[473], where strong acid sites were blocked with quaternary ammonium cations.

The results of catalytic tests are summarized in Table 3. Compared with the catalyst directly calcined [Ti,Al]-Beta (cal[793], run 1), the catalyst ion-exchanged with tetramethylammonium acetate exhibited a high epoxide selectivity with a comparable activity in the cyclohexene epoxidation using

methanol as a solvent (run 7). When the quaternary ammonium cations with larger alkyl groups were employed for the ion exchange (runs 8 and 9), epoxidation activity decreased with an increase in the cation size, while the epoxide selectivity kept high values.

Figure 5 shows the reaction time courses of cyclohexene epoxidation and Figure 6 shows the relationships between the conversion and the epoxide selectivity over cal[793], NMe₄, NEt₄, and NPr₄-exchanged [Ti,Al]-Beta. The initial gradient of the curves in Figure 5a demonstrates that the oxidation rate decreased in the order NMe₄⁺ > NEt₄⁺ > NPr₄⁺. In contrast, the ion-exchange degree shown in Table 3 decreased in the order NMe₄⁺ ~ NEt₄⁺ > NPr₄⁺. The C/N ratios were 4.0, 8.1, and 12.2 for NMe₄⁺, NEt₄⁺, and NPr₄⁺, respectively, indicating that these SDA cations remained unchanged in the catalysts. Because the relative sizes of these cations are 5, 9, and 13 carbon equivalents for NMe₄⁺, NEt₄⁺, and NPr₄⁺, respectively, the packing degrees of channels estimated by multiplying the ion-exchange degrees by the relative cation size of cations are then 9.0, 16.2, and 19.5 carbon equivalents per unit cell for NMe₄⁺, NEt₄⁺, and NPr₄⁺-exchanged samples, respectively. These cations existing in the zeolite channels would limit the diffusion and access of reactant molecules to the active sites. Therefore, it is reasonable that [Ti,Al]-Beta ion-exchanged with larger quaternary ammonium cations showed lower cyclohexene conversion.

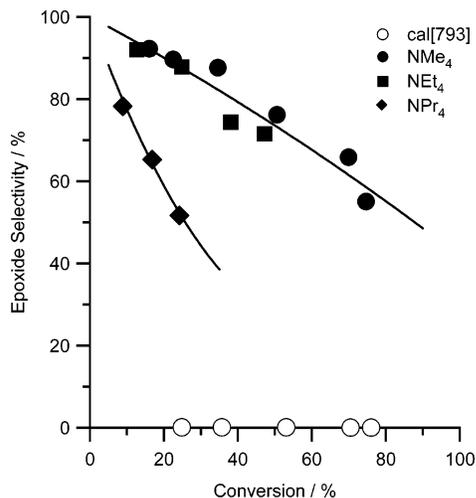


Figure 6. Relationships between cyclohexene conversion and the epoxide selectivity.

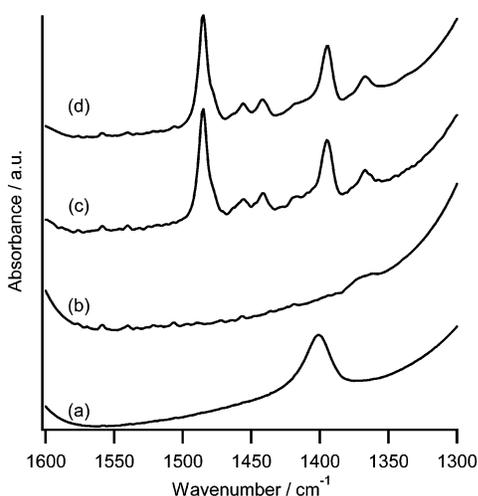


Figure 7. FT-IR spectra of NH_4 -exchanged [Ti,Al]-Beta (a), (b) and NEt_4 -exchanged [Ti,Al]-Beta (c), (d) before (a), (c) and after (b), (d) the cyclohexene epoxidation.

In Figure 6, the cyclohexene conversion was changed by varying the reaction time. Just calcined [Ti,Al]-Beta (cal[793]) showed negligible formation of cyclohexene oxide even for the low conversions, which indicates that the reaction rate of the solvolysis is much higher than that of the epoxidation. NMe_4 - and NEt_4 -exchanged [Ti,Al]-Beta catalysts were similar in the tendency for the epoxide selectivity to decrease with increasing conversion. NPr_4 -exchanged catalyst showed quite lower selectivity as compared to the epoxide at the same conversions, which would be probably accounted for the observations that ion-exchange degrees of NMe_4^+ and NEt_4^+ were comparable but that of NPr_4^+ was lower. A lower ion-exchange degree should result in higher acidity and therefore lower epoxide selectivity.

The ion-exchange treatments with ammonium acetate and potassium acetate were also investigated. The ammonium acetate treatment was not effective in improving the epoxide selectivity (Table 3, run 10). To investigate the difference between the ion exchange with quaternary ammonium and simple ammonium, FT-IR measurements have been conducted. FT-IR spectra of the NEt_4 -treated catalyst before and after the reaction were almost identical (Figure 7c and d), indicating that quaternary ammonium cations remained intact during the reaction. However, the peak assigned to NH_4^+ disappeared completely after the reaction (Figure 7a,b), probably because

NH_4^+ was oxidatively decomposed in the presence of H_2O_2 . Therefore, the lack of stability of NH_4^+ in the epoxidation presumably interprets its less effectiveness in the enhancement of the epoxide selectivity.

Although potassium treatment resulted in a great improvement of selectivity to the epoxide, the oxidation was adversely affected (Table 3, run 11). This is consistent with the observations by Hutchings et al.,^{20,25} Tatsumi et al.,²¹ and Khouw and Davis²² that the Ti active sites of TS-1 are poisoned by alkali cations simultaneously with the deactivation of the solvolysis of the epoxide.

The enhancement of the epoxide selectivity was more obvious for 1-hexene and 2-hexene epoxidation, which gave particularly high epoxide selectivity over 90% (Table 3, runs 12, 13, 16, and 17). Cyclohexene oxide is sterically more unstable than 1-hexene oxide and is more easily solvolysed to decrease the epoxide selectivity. Interestingly, the conversion of the substrate was higher after the ion exchange with NMe_4OAc than before the ion exchange in the epoxidation of 1-hexene and 2-hexene, whereas the conversion of cyclohexene over unexchanged and exchanged catalyst was comparable. The enhancement of the conversion was more remarkable in the epoxidation of 1-hexene (ca. 1.5 times) than that of 2-hexene (ca. 1.2 times). These might be explained by the steric effect of the substrate and the hydrophobicity/hydrophilicity of the catalysts. The NMe_4 -exchanged catalyst could be more hydrophobic than the unexchanged catalyst due to the substitution of organic ammonium species for protons, which could attract olefinic substrate to give higher conversion of the substrate. However, multisubstituted bulkier alkenes such as 2-hexenes and cyclohexene are sterically less favored in the channels of the catalyst owing to the presence of bulky ammonium cations, and the conversion of these bulky alkenes were less or not enhanced by the NMe_4 exchange. This is also evidenced by a smaller decrease in the 1-hexene conversion than the cyclohexene conversion when the ion-exchange agent was changed from NMe_4OAc to NEt_4OAc .

Solvolysis of 1-hexene oxide hardly occurred, whereas 2-hexene oxides were slightly solvolysed to give the selectivity to the glycol and its monomethyl ether of 3.3%. One reason could be the lower alkene conversion and another reason might be explained by the mechanism of the solvolysis. The acid-catalyzed ring-opening solvolysis of the epoxide proceeds in a mixed mechanism of $\text{S}_{\text{N}}1$ and $\text{S}_{\text{N}}2$. The dissociation of the oxirane C–O bond and the bond formation between C of oxirane and O of either water or the alcohol molecule occur in a single step; however, the former exceeds the latter a little bit, because the oxirane C–O bond is already weak due to the angle strain, the leaving group (weakly basic alcoholic hydroxyl) is good, and the nucleophile (water or alcohol) is poor. Thus the $\text{S}_{\text{N}}1$ mechanism is predominant over the $\text{S}_{\text{N}}2$ mechanism. This drives a water or alcohol molecule to attack the C atom of the oxirane ring with more substituting groups. 2-Hexene oxides have more substituted C atoms and would be more favorably solvolysed than 1-hexene oxide.

Solvent effects on the cyclohexene oxidation were also examined (Table 3, runs 18 and 19). It is generally known that aprotic solvent enhances the selectivity to the epoxide.⁹ When the aprotic and weakly basic solvent, acetonitrile, was employed as a solvent, the epoxide selectivity over cal[793]-ie(NMe_4)9.50 was enhanced from 55% to 89%.

Figure 8 shows the FT-IR spectra of the [Ti,Al]-Beta samples before and after the ion-exchange treatments with NMe_4OAc . Before the ion exchange, two absorption bands assigned to terminal silanols and bridging hydroxyl groups were clearly

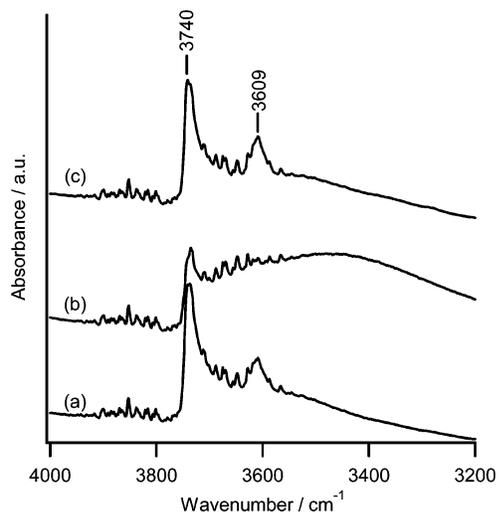
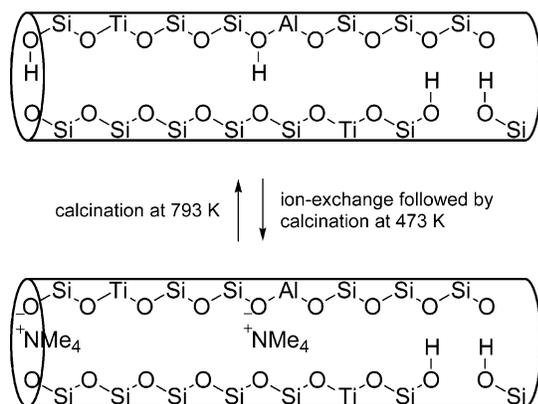


Figure 8. FT-IR spectra in the OH vibration region of just calcined [Ti,Al]-Beta (a), NMe₄-exchanged [Ti,Al]-Beta preevacuated at 473 K (b), and NMe₄-exchanged [Ti,Al]-Beta preevacuated at 773 K (c).

SCHEME 4: Reversible Ion-Exchange Scheme with Tetramethylammonium Salt



observed (Figure 8a). After the ion exchange with NMe₄⁺, the band assigned to bridging hydroxyl groups completely disappeared and that assigned to terminal silanol groups decreased in intensity when the sample was preevacuated at 473 K (Figure 8b). The pH of aqueous NMe₄OAc used for the ion exchange was high enough to allow the silanol groups to be exchanged with NMe₄⁺ cations because the isoelectric point of SiO₂ is 1.0–2.5.²⁶ These findings indicate that a part of terminal silanol groups with weak acidity as well as all of the bridging hydroxyl groups with strong acidity and were blocked by NMe₄⁺ for the ion-exchanged [Ti,Al]-Beta even after the calcination at 473 K as shown in Scheme 4. Thus, the reversal approach through ion-exchanging the calcined [Ti,Al]-Beta with quaternary ammonium cations can also remove the strong acidity selectively, suppressing the ring-opening reaction. When the NMe₄⁺-exchanged sample was evacuated at 773 K, the intensities of these bands were almost recovered (Figure 8c), indicating that ion exchange and calcination caused the reversible interconversion (Scheme 4).

Interestingly, the SDA-extracted catalyst (ex(AN)-cal[473], Table 1, run 4) exhibited higher conversion of cyclohexene than the NEt₄-exchanged catalyst (cal[793]-ie(NEt₄)9.64, Table 3, run 8) despite the comparable N/Al ratios. This would be due to the difference in the distribution of the NEt₄⁺ cations in the zeolitic crystals. SDA extraction of as-synthesized materials and NEt₄ exchange of calcined materials should preferentially occur from the pore openings. The diffusion of bulky cyclohexene in

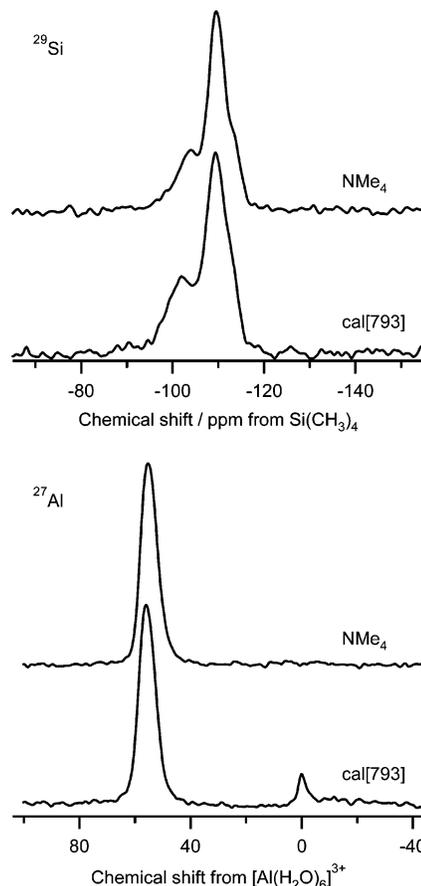


Figure 9. ²⁹Si- and ²⁷Al-MAS NMR spectra of calcined and NMe₄-exchanged [Ti,Al]-Beta.

the NEt₄-exchanged catalyst could be interfered by the pore blockage with NEt₄⁺ cations near the pore openings, whereas that in SDA-extracted catalyst would be fast because of the less pore blockage near the pore openings. Thus, the difference in the intracrystalline diffusion rate between the two catalysts could have caused different catalytic performances.

Figure 9 shows ²⁹Si- and ²⁷Al-MAS NMR spectra of [Ti,Al]-Beta samples before and after the ion-exchange treatment with NMe₄OAc. In ²⁹Si-MAS NMR spectra, the peak at -102 ppm decreased in intensity and the position of the peak top shifted to -106 ppm. This peak can be assigned to the combination of the Si environments at Q⁴(1Al), Q³, and possibly Q⁴(1Ti). Because Q³ should be observed at the lowest magnetic field among these three chemical environments, the spectral change observed after the NMe₄ exchange would indicate the decrease in the Q³ species by the ion exchange to Si-ONMe₄. It would be reasonable to speculate that the low charge gradient of SiO⁻-NMe₄⁺ decreased the degree of the magnetic shielding around Si atoms, resulting in the appearance of the NMR signal assigned to the Si-ONMe₄ environment at high magnetic field near the Q⁴ species. This observation also agrees with the speculated scheme of the ion exchange in Scheme 4.

In ²⁷Al-MAS NMR spectra, a peak at 0 ppm, which is assigned to the extraframework octahedral Al species, disappeared after the ion exchange. It is indicated that extraframework Al species in calcined [Ti,Al]-Beta sample were reinserted into the framework during the treatment with an aqueous solution of aqueous ammonium acetate because the amount of Al in the catalyst was unchanged.²⁷ It has been reported that extraframework Al species interact with intraframework Al, resulting in the enhanced acidity;²⁸ however, it would be reasonable to

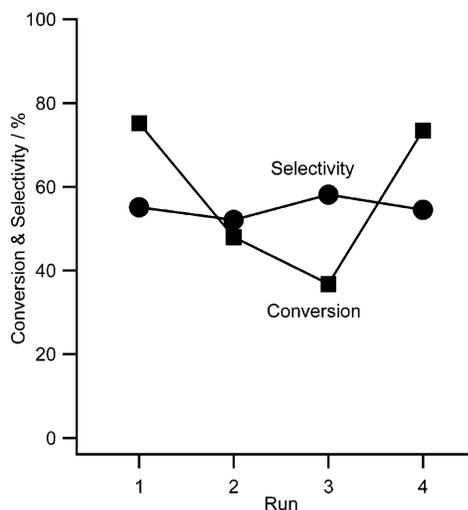


Figure 10. Catalytic results in the repeated use of NMe_4^+ -exchanged catalyst. The catalyst was regenerated by evacuating at 473 K after the first and second run, and by the calcination at 773 K and ion exchange after the third run.

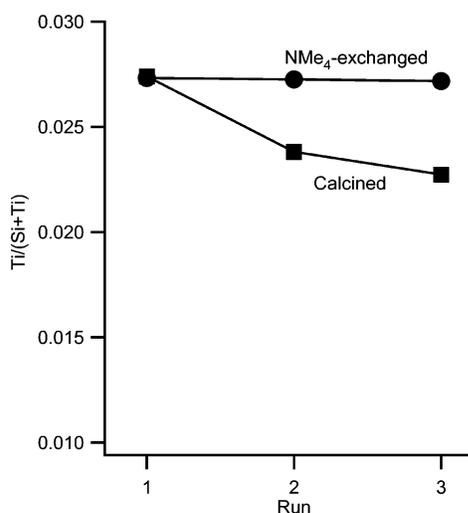


Figure 11. Variation of the Ti content during repeated epoxidation reaction in the catalyst for unexchanged (●) and ion-exchanged [Ti,Al]-Beta (●) with NMe_4^+ .

consider that the influence of the extraframework Al species on the whole acidity of calcined [Ti,Al]-Beta is small because the amount of extraframework Al is small compared to the intraframework Al species.

This reversibility suggests that the catalyst could be regenerated by recalcination—re-ion-exchange treatment. The results of repeated use of the NMe_4^+ -exchanged catalysts are shown in Figure 10. In a manner similar to what has been observed for SDA-extracted [Ti,Al]-Beta as shown in Figure 4, the oxidation activity of ion-exchanged catalyst decreased gradually as the recovered catalyst was repeatedly used after just evacuating at 473 K overnight. The oxidation activity in the third run was almost half as high as that in the first run, whereas the selectivity to epoxide was constant. Then, the catalyst was calcined and ion-exchanged again. The oxidation activity was completely recovered in the fourth run, which indicates that the catalyst ion-exchanged with quaternary ammonium cation is easily regenerated by repeated calcination and ion exchange.

Figure 11 shows the changes of Ti content on the catalyst with the repeated use. NMe_4^+ ion-exchanged catalyst was regenerated by just evacuating at 473 K overnight and unexchanged catalyst was regenerated by calcination at 793 K.

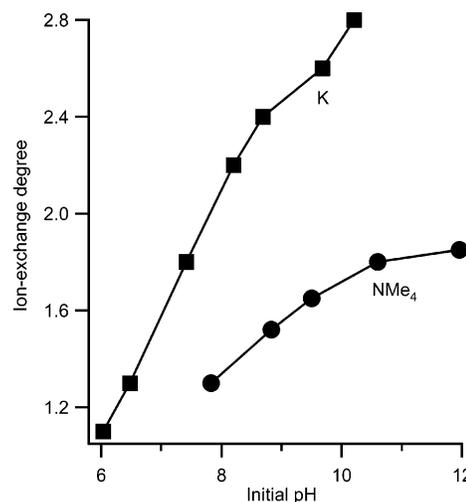
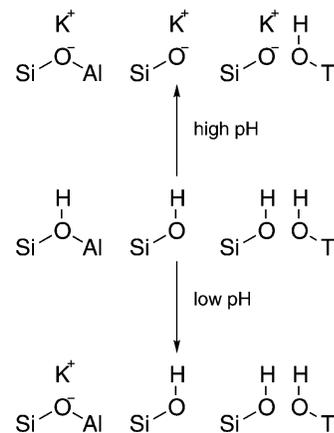


Figure 12. Dependence of the ion-exchange degree on the initial pH in the treatment.

SCHEME 5: Scheme of the Selective Ion Exchange of the Bridging Hydroxyl Groups with Stronger Acidity by Controlling the pH in the Ion Exchange



Although the Ti content on the unexchanged sample decreased as the catalyst was repeatedly used, that on the ion-exchanged sample hardly changed even after the third run. This indicates that NMe_4^+ cations present on the catalyst suppressed the leaching of framework Ti and enhanced its stability, probably because of the increased hydrophobicity resulting from the substitution of NMe_4^+ for proton.

3.3. Variation of Ion-Exchange Degree. The effects of ion-exchange degree were also investigated. [Ti,Al]-Beta zeolite possesses three types of ion-exchange sites; bridging hydroxyl groups are strong acid sites and ion-exchangeable at lower pH and terminal silanols and open active sites containing Ti are weak in acidity and need higher pH to be ion-exchanged. We suppose that terminal silanols and open sites could be ion-exchanged simultaneously (Scheme 5). If the bridging hydroxyl groups are selectively ion-exchanged with alkali cations without causing ion exchange of open sites, it is likely that the solvolysis of the epoxide is suppressed without the deactivation of the epoxidation. Accordingly, we aimed at the selective poisoning of bridging hydroxyls with K^+ . The initial pH of the ion-exchange solution, 1 mol dm^{-3} aqueous KOAc and NMe_4OAc , was varied in the range of 6–12 by adding AcOH, and either KOH or NMe_4OH , respectively. After the ion exchange, the pH values of the mixture were in the range 6.0–6.5 in all the cases.

As shown in Figure 12, an ion-exchange degree as high as $\text{K}/\text{Al} = 2.8$ was achieved in the ion exchange with K^+ , whereas

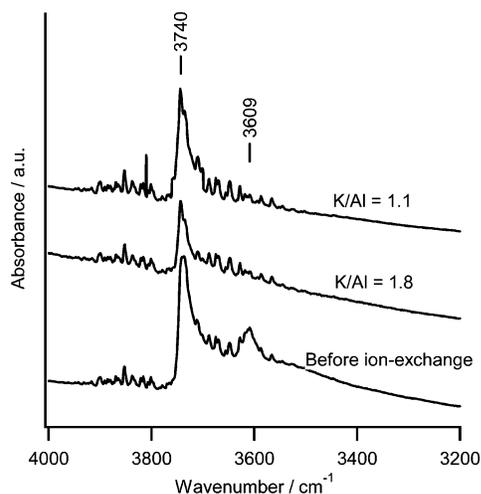


Figure 13. FT-IR spectra of K-exchanged [Ti,Al]-Beta with controlled ion-exchange degree.

NMe_4^+ -exchanged [Ti,Al]-Beta showed a lower ion-exchange degree of $\text{NMe}_4/\text{Al} = 1.9$ at its maximum, probably because of the large size of NMe_4^+ cations. FT-IR spectra of the K-exchanged [Ti,Al]-Beta in the OH vibration region are shown in Figure 13. At the K/Al ratio of 1.1, the peak assigned to bridging hydroxyls at 3609 cm^{-1} disappeared and the peak assigned to terminal silanols at 3740 cm^{-1} was comparable to that of unexchanged [Ti,Al]-Beta. This observation indicates that bridging hydroxyl groups with stronger acidity were selectively ion-exchanged with K. The results of the cyclohexene epoxidation are shown in Figure 14. When potassium acetate was employed as an ion-exchange reagent, the higher K^+ content resulted in the higher epoxide selectivity at the expense of oxidation activity because of the poisoning effect of alkali cations (Figure 14a). On the other hand, when $\text{NMe}_4\text{-OAc}$ was employed, increasing the NMe_4/Al ratio up to 1.6 caused the enhancement of the epoxide selectivity, together with a slight increase in activity (Figure 14b) presumably due to the increased hydrophobicity around the active sites for the epoxidation. The catalysts with a higher NMe_4/Al ratio than 1.6 exhibited inversely lower selectivity. In both cases of K^+ and NMe_4^+ , even when the ion-exchange degree was 1.1 and bridging hydroxyl groups should be completely poisoned, no epoxide was formed, suggesting that the solvolysis of cyclohexene oxide is catalyzed by other acid sites than bridging hydroxyl groups.

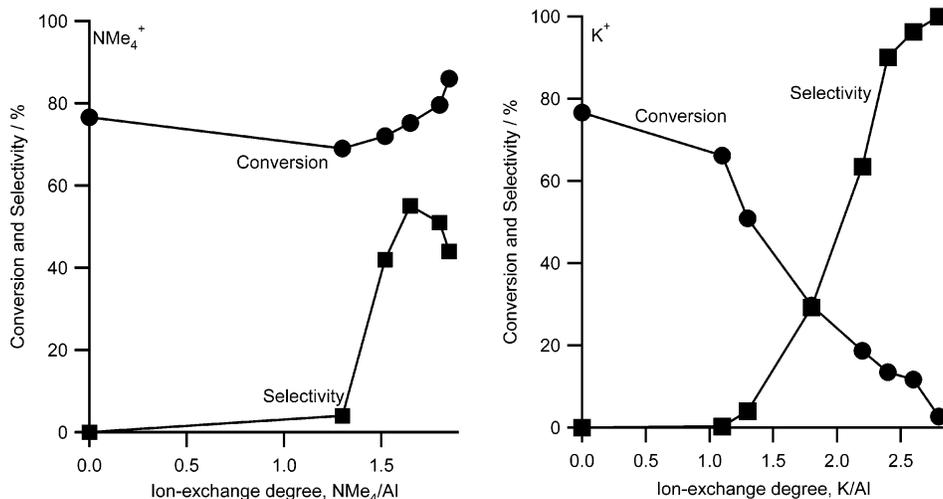


Figure 14. Effects of ion-exchange degree on the catalytic performances of ion-exchanged [Ti,Al]-Beta with NMe_4^+ and K^+ .

Figure 15 shows the pore size distribution of the catalyst ion-exchanged at the pH of 12, calculated by the Dollimore–Heal (D–H) method from the adsorption branch of the nitrogen adsorption isotherm at 77 K. Obviously, mesopores with a diameter of ca. 20 nm were created in the ion exchange at high pH. Tatsumi et al. have reported that the diameter of primary particles of Ti-Beta synthesized by the dry-gel conversion method is 20–40 nm.¹⁶ It was confirmed that the particle size of the present [Ti,Al]-Beta was 150–200 nm by scanning electron micrography. It is suggested that hydrothermally synthesized [Ti,Al]-Beta nucleates to form primary particles 20 nm in diameter and then these primary particles aggregate into larger particles 150–200 nm in diameter. When the catalyst is treated at high pH, the silica framework of [Ti,Al]-Beta would be partly dissolved and some of primary particles attached to the aggregate would be released to form the mesopores. These mesopores would promote the intraparticle diffusion of molecules to enhance the oxidation activity; however, the surface silanols in the mesopores generated as a result of silica dissolution contributed to the undesirable solvolysis reactions of epoxide.

3.4. Solvolysis of Cyclohexene Oxide. As mentioned above, the catalyst, of which bridging hydroxyl groups were completely and selectively poisoned, exhibited negligible selectivity to the epoxide. Bellussi et al. showed that the solvolysis of 2,3-epoxybutanes over TS-1 were promoted in the presence of hydrogen peroxide in the reaction system.¹⁹ We also examined the acidity of various catalysts in the presence or the absence of oxidant. The results are shown in Table 4. Addition of H_2O_2 to the system of three non-titanosilicates (H-ZSM-5, silicalite-1, and deboronated B-Beta) produced no enhancement effect in the solvolysis of cyclohexene oxide. In contrast, the coexistence of H_2O_2 with calcined [Ti,Al]-Beta catalyst (cal[793]) promoted the solvolysis of cyclohexene oxide; however, the solvolysis was not promoted in the presence of *tert*-butyl hydroperoxide. This is because the existence of H_2O_2 caused the formation of acidic protons in silanol groups hydrogen-bonding to titanium hydroperoxide species (Scheme 6, species 1'), whereas *tert*-butyl hydroperoxide did not produce such species but instead *tert*-butyl peroxide species (Scheme 6, species 1''). It is conceivable that SiO-H is ion-exchanged with NMe_4^+ cations in preference to TiO-H because the isoelectric point of SiO_2 and TiO_2 is 1.0–2.5 and 4.7–6.7, respectively.²⁶ The ion exchange with NMe_4^+ cations of cal[793] marred the solvolysis enhancement effect. When cal[793]-ie(NMe_4)9.50 was exposed to hydrogen peroxide, acidic protons did not form,

SCHEME 6: Mechanisms of the Suppression of the Acidity of the Oxidation Active Sites

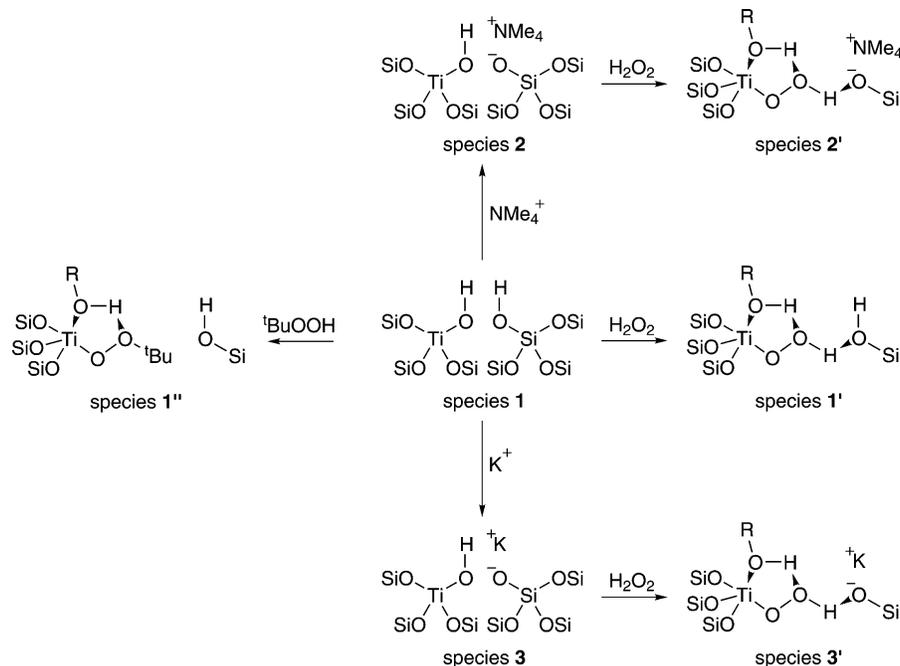


TABLE 4: Results of the Solvolysis of Cyclohexene Oxide in the Presence and the Absence of Oxidant^a

run	treatment	conversion/%		
		none	H ₂ O ₂	TBHP
20	H-ZSM-5	85	83	
21	deboronated B-Beta	15	15	
22	silicalite-1	1.2	1.3	
23	cal[793]	65	100	69
24	cal[793]-ie(NMe ₄)9.50	14	17	15
25	cal[793]-ie(K)8.15	7.5	7.6	7.2

^a Reaction conditions: temp, 333 K; time, 2 h; 2.5 mmol of cyclohexene oxide; 2.5 mmol of H₂O₂ (31 wt % in water) or *tert*-butyl hydroperoxide (TBHP, 70 wt %); 50 mg of catalyst; 5 mL of methanol.

ion-exchange degree of NMe₄-exchanged catalyst is N/(Al+Ti) = 0.86 (Si/Ti = 35, Si/Al = 38, N/Al = 1.8). The solvolysis over cal[793]-ie(K)8.69 was also suppressed. (K/(Al+Ti) = 1.0).

On cal[793], the ring-opening solvolysis is considered to occur mainly on strong acid sites of bridging hydroxyl groups; however, the contribution of the acid sites generated by the contact of Ti sites with H₂O₂ is also significant. The ion-exchange treatment of cal[793] with NMe₄OAc poisoned silanol groups at the open sites of Ti as well as bridging hydroxyl groups, resulting in the suppression of the acidity of both bridging hydroxyl groups and Ti hydroperoxo species at active sites for oxidation.

4. Conclusions

The catalytic performance of [Ti,Al]-Beta is dramatically improved by two novel methods. SDA-extracted [Ti,Al]-Beta, obtained by treating as-synthesized [Ti,Al]-Beta with aqueous ammonium nitrate and then calcining at an optimum temperature of 473 K, gives a very high cyclohexene oxide yield of 48% even in the protic solvent of methanol. This is because the combination of SDA extraction and mild calcination selectively removes the SDA cations attaching to the silanol groups to open the reaction space but makes the unremoved SDA block the acid sites in [Ti,Al]-Beta to suppress the ring-opening solvolysis.

[Ti,Al]-Beta ion-exchanged with quaternary ammonium acetate followed by mild calcination shows similarly high epoxide selectivity. Tetramethylammonium acetate is the best modifier, resulting in almost no loss of epoxidation activity. High acidity is reduced by blocking the acid sites such as bridging hydroxyl groups and surface silanol groups with quaternary ammonium cations, which results in a similar chemical environment to SDA-extracted catalyst. Regeneration of the ion-exchanged catalyst is achieved by the repeated calcination and ion-exchange treatments, making the catalyst reusable. The pH in the ion-exchange treatment strongly influences the catalytic performance. The optimum pH of the treatments is ca. 10. High pH treatments causes the partial dissolution of [Ti,Al]-Beta frameworks to increase the activity but decrease the epoxide selectivity.

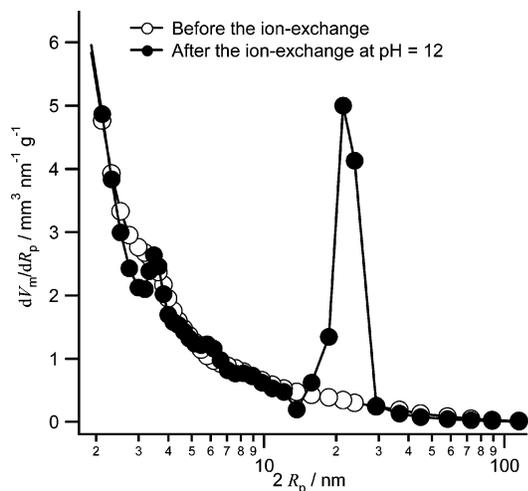


Figure 15. Pore size distribution curves of before and after ion exchange with NMe₄⁺ at pH 12.

probably because the silanol protons were exchanged with NMe₄⁺ cations and the polarity of TiOO-H could be decreased via the hydrogen bonds to the oxygen atom of SiO⁻-NMe₄⁺ (Scheme 6, species 2'). The small enhancement of the solvolysis could be due to the remaining species 1, considering that the

The acidity of the active oxidation sites of titanium hydroperoxy species was also reduced by the ion exchange with NMe_4^+ or K^+ . Although alkali cations severely poisoned the epoxidation active sites, quaternary ammonium cations enhanced the epoxidation activity.

Thus we have devised the novel postsynthetic methods to precisely control the [Ti,Al]-Beta catalyst to obtain active, selective, and reusable catalyst for the epoxidation of alkenes.

References and Notes

- (1) Taramasso, M.; Perego, G.; Notari, B. *US. Pat.* **1983**, 4410501.
- (2) Notari, B. *Adv. Catal.* **1996**, *41*, 253.
- (3) Tatsumi, T.; Nakamura, M.; Yuasa, K.; Tominaga, H. *Chem. Lett.* **1990**, 297.
- (4) Tatsumi, T.; Nakamura, M.; Negishi, S.; Tominaga, H. *J. Chem. Soc., Chem. Commun.* **1990**, 476.
- (5) Cambor, M. A.; Corma, A.; Martínez, A.; Pérez-Pariente, J. *J. Chem. Soc., Chem. Commun.* **1992**, 589.
- (6) Cambor, M. A.; Corma, A.; Pérez-Pariente, J. *Zeolites* **1993**, *13*, 82.
- (7) Corma, A.; Cambor, M. A.; Esteve, P.; Martínez, A.; Pérez-Pariente, J. *J. Catal.* **1994**, *145*, 151.
- (8) Corma, A.; Esteve, P.; Martínez, A.; Valencia, S. *J. Catal.* **1995**, *152*, 18.
- (9) Corma, A.; Esteve, P.; Martínez, A. *J. Catal.* **1996**, *161*, 11.
- (10) Cambor, M. A.; Constantini, M.; Corma, A.; Gilbert, L.; Esteve, P.; Martínez, A.; Valencia, S. *Chem. Commun.* **1996**, 1339.
- (11) Cambor, M. A.; Constantini, M.; Corma, A.; Esteve, P.; Gilbert, L.; Martínez, A.; Valencia, S. *Appl. Catal.* **1995**, *133*, L185.
- (12) Blasco, T.; Cambor, M. A.; Corma, A.; Esteve, P.; Martínez, A.; Prieto, C.; Valencia, S. *Chem. Commun.* **1996**, 2367.
- (13) Blasco, T.; Cambor, M. A.; Corma, A.; Esteve, P.; Guil, J. M.; Martínez, A.; Perdigón-Melón, J. A.; Valencia, S. *J. Phys. Chem. B* **1998**, *102*, 75.
- (14) Tatsumi, T.; Xia, Q.; Jappar, N. *Chem. Lett.* **1997**, 677.
- (15) Jappar, N.; Xia, Q.; Tatsumi, T. *J. Catal.* **1998**, *180*, 132.
- (16) Tatsumi, T.; Jappar, N. *J. Phys. Chem. B* **1998**, *102*, 7126.
- (17) Ogura, M.; Nakata, S.; Kikuchi, E.; Matsukata, M. *J. Catal.* **2001**, *199*, 41.
- (18) Saxton, R. J.; Grocco, G. L.; Zajacek, J. G.; Wijesekera, K. S. *Eur. Pat.* **1994**, 0659685.
- (19) Bellussi, G.; Carati, A.; Glerici, M. G.; Maddinelli, G.; Millini, R. *J. Catal.* **1992**, *133*, 220.
- (20) Hutchings, G. J.; Lee, D. F.; Minihan, A. R. *Catal. Lett.* **1996**, 83.
- (21) Tatsumi, T.; Koyano, K. A.; Shimizu, Y. *Appl. Catal. A* **2000**, *200*, 125.
- (22) Khouw, C. B.; Davis, M. E. *J. Catal.* **1995**, *151*, 77.
- (23) Goa, Y.; Wu, P.; Tatsumi, T. *Chem. Commun.* **2001**, 1714.
- (24) Janin, A.; Maache, M.; Lavalley, J. C.; Joly, J. F.; Raatz, F.; Szydłowski, N. *Zeolites* **1991**, *11*, 391.
- (25) Hutchings, G. J.; Lee, D. F. *J. Chem. Soc. Chem. Commun.* **1994**, 1095.
- (26) Parks, G. A. *Chem. Rev.* **1965**, *65*, 177.
- (27) Oumi, Y.; Mizuno, R.; Azuma, K.; Nawata, S.; Fukushima, T.; Uozumi, T.; Sano, T. *Microporous Mesoporous Mater.* **2001**, *49*, 103.
- (28) Corma, A.; Martínez, A.; Martínez, C. *Appl. Catal. A* **1996**, *134*, 169.