CHEMCOMM
Communication
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A dramatic improvement of epoxide selectivity of [Ti,Al]-beta by ion-exchange with quaternary ammonium salts

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Received (in Cambridge, UK) 11th June 2001, Accepted 30th July 2001
First published as an Advance Article on the web 29th August 2001

Ion-exchange of [Ti,Al]-beta with quaternary ammonium acetates greatly enhances the epoxide selectivity in the oxidation of alkenes with hydrogen peroxide; this is due to the selective poisoning of the acid sites without suppressing the oxidation activity of Ti sites.

Since the first report of TS-1 by Taramasso *et al.* in 1983, titanosilicates have attracted the attention of many researchers.[1] Ti-beta zeolite has a three-dimensionally connected pore system with 12-membered-ring channels and is verified to be more active towards bulky substances such as branched and cyclic alkanes and alkenes using aqueous H_2O_2 or *tert*-butyl hydroperoxide (TBHP) as an oxidant than medium pore TS-1 because of the reduced diffusion restriction imposed by the large pores. A small amount of Al (Si/Al $<$ 200), as crystallization-promoting agent, is generally needed in the conventional hydrothermal synthesis method for Ti-beta using tetraethylammonium hydroxide (TEAOH) as a structure-directing agent (SDA).[2,3] The presence of Al leads to the formation of acid sites, which promotes the successive ring-opening solvolysis of the epoxide generated in the catalytic reactions to lower its selectivity extensively.[4] Afterwards, several novel synthesis methods for Al-free or low-Al Ti-beta were also developed, such as the seeding method,[5] cogel method,[6] fluoride method[7,8] and dry-gel conversion method;[9,10] however none of these were very efficient for enhancing epoxide selectivity in alcoholic solvents. This is probably because the very complex, severely intergrown nature of the beta structure results in high concentration of weak acid sites such as silanol groups at defect sites. Although ion-exchange with alkaline or alkaline earth metal cations inhibits the acidity of titanosilicates, it also suppresses the oxidation activity of Ti species.[11,12] We report here a new method for dramatically enhancing the yield of epoxide in the alkene oxidation reactions catalyzed by Ti-beta even in protic alcoholic solvents without losing its oxidation activity.

[Ti,Al]-beta zeolite was hydrothermally synthesized by modifying the method reported by Camblor *et al.*[2,3] Tetrabutyl orthotitanate $[Ti(OBu)_4]$ was employed as a Ti source instead of tetraethyl orthotitanate $[Ti(OEt)_4]$ and was hydrolyzed in aqueous H_2O_2 before adding to the SDA solution to suppress the formation of extraframework anatase TiO_2. The mother gel composition was $SiO_2:0.33\ TiO_2:0.005\ Al_2O_3:0.56\ TEAOH:12.5\ H_2O$. The crystallization was carried out by agitating the gel in a Teflon-lined stainless steel autoclave at 413 K for 4 days. The resultant [Ti,Al]-beta was calcined at 793 K for 10 h in a stream of O_2 (30 ml min^{-1} g-solid^{-1}) to remove the SDA. Calcined [Ti,Al]-beta was treated with 1 M aqueous solutions of various ammonium acetates (NR_4OAc, R = Me, Et, Pr and H) or 1 M aqueous potassium acetate (KOAc) solution at 353 K for 4 h and then filtered off, washed, dried and finally calcined of 473 K for 10 h. The liquid phase epoxidation of alkenes with H_2O_2 was performed in a flask.

Table 1 shows the results of epoxidation of alkenes. Calcined [Ti,Al]-beta exhibited a low selectivity to epoxide for oxidation reactions of cyclohexene and hex-2-ene (entries 1 and 2). The products were mainly diol and monomethyl glycol ether produced by the acid-catalyzed solvolysis of epoxide, together with a small amount of allylic oxidation products. The negligible formation of epoxide strongly indicates that there were a considerable amount of acid sites in [Ti,Al]-beta, which contributed to the solvolysis of epoxide.

When the catalyst ion-exchanged with tetramethylammonium acetate was employed (entries 4 and 5), the epoxide selectivity was greatly enhanced owing to the suppression of ring-opening reactions, and the selectivity to the allylic oxidation did not change significantly. The enhancement was more obvious for hex-2-ene which gave an epoxide/glycol ratio of 28. Solvent effects were also tested. It is generally known that aprotic solvents such as acetonitrile enhance the selectivity to the epoxide. Employment of the weakly basic solvent, acetoni-

Table 1 Catalytic oxidation of cyclohexene and hex-2-ene[a]

Entry	Ion-exchange	Substrate	N^+/Al	Maximum conv. (mol%)	Selectivity[b] (mol%)			H_2O_2 (mol%)	
					Epox.	Glyc.	Allyl	Conv.	Efficiency
1	No	Cyclohexene	–	76.1	0.0	97.6	2.4	83	90
2	No	Hex-2-ene[c]	–	49.5	0.2	98.0	0.0	76	64
3[d]	No	Cyclohexene	–	30.4	69.3	14.9	15.8	81	41
4	NMe_4OAc	Cyclohexene	1.8	75.2	55.1	43.2	1.8	95	79
5	NMe_4OAc	Hex-2-ene[c]	1.8	60.7	92.4	3.3	4.1	78	72
6[d]	NMe_4OAc	Cyclohexene	1.8	57.1	88.5	5.3	6.1	86	69
7	NEt_4OAc	Cyclohexene	1.8	47.2	71.6	26.5	1.9	69	67
8	NPr_4OAc	Cyclohexene	1.5	24.5	51.4	46.6	2.0	42	59
9	NH_4OAc	Cyclohexene	1.6	57.4	0.1	96.9	3.0	60	97
10	KOAc	Cyclohexene	2.2[e]	18.7	63.5	34.2	2.3	48	40

[a] *Reaction conditions*: 333 K, 3 h, 8.25 mmol of alkene, 2.5 mmol of H_2O_2 (31 wt% in water), 50 mg of catalyst (Si/Ti = 35, Si/Al = 38) and 5 ml of methanol. [b] Epox. = cyclohexene oxide or 2,3-epoxyhexane; Glyc. = cyclohexanediol or hexane-2,3-diol and their monomethyl ethers; Allyl = alcohol and ketone formed by oxidation. [c] *cis*/*trans* Isomer ratio = 41/59. [d] Acetonitrile was employed as solvent. [e] K^+/Al.

DOI: 10.1039/b105088p

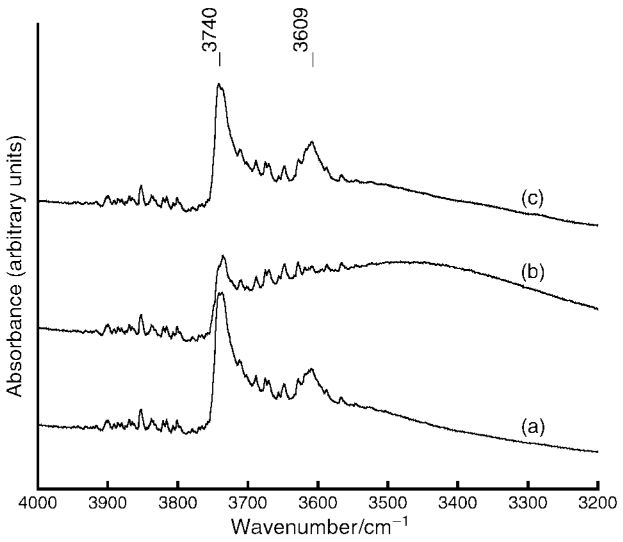

Fig. 1 FTIR spectra of Ti-beta in the OH region; (a) without ion-exchange after evacuation at 773 K, (b) ion-exchanged with NMe_4OAc and evacuated at 473 K, (c) ion-exchanged and evacuated at 773 K.

trile, further enhanced the epoxide selectivity (entries 3 and 6).

Use of larger quaternary ammonium cations led to decreased activity, probably because the bulky cations hinder the reactant molecules from approaching the Ti sites (entries 4, 7 and 8). Ammonium acetate treatment led to no enhancement of the epoxide selectivity (entry 9). FT-IR spectra of the ion-exchanged [Ti,Al]-beta taken before and after the catalytic runs indicated that NH_4^+ was oxidatively degradated while NMe_4^+ remained intact. Ion-exchange with KOAc also increased the selectivity to the epoxide; however the oxidation activity was adversely affected (entry 10). This is consistent with the observations that ion-exchange with sodium carbonate (Na_2CO_3) or sodium azide (NaN_3) on Al-containing TS-1 gave rise to a higher epoxide selectivity but a very low activity in allyl alcohol oxidation,[11] that ion-exchange with potassium carbonate severely lowered the oxidation turnover in unsaturated alcohol oxidation[12] and that TS-1 synthesized in the presence of large amounts of alkali and alkaline earth ions showed low oxidation activity.[13] Elemental analyses indicated that ion-exchanged catalyst contained NMe_4^+ cations in excess of Al, which suggests that the NMe_4^+ blocks not only all the bridging hydroxy groups but also other less acidic sites.

Calcined [Ti,Al]-beta exhibited two bands in its FTIR spectra in the OH vibration region [Fig. 1(a)]. A peak at 3609 cm^{-1} is assigned to bridged hydroxy groups [Si–(OH)–Al] and the other peak around 3740 cm^{-1} to terminal silanols (SiOH) composed of several types of silanol groups:[14] silanols of amorphous silica–alumina species (3747 cm^{-1}), silanols of amorphous silica (3745 cm^{-1}) and terminal silanols attached to the zeolite lattice (3736 cm^{-1}) After ion-exchange with NMe_4OAc followed by calcination at 473 K, the bridged hydroxy groups band disappeared and the silanol bands significantly decreased in intensity [Fig. 1(b)]. When the ion-exchanged sample was calcined at 773 K, the intensities of these bands were almost recovered [Fig. 1(c)]. The pH of aqueous NMe_4OAc used for the ion-exchange was high enough (pH ~ 9) to allow the silanol groups to be exchanged with NMe_4^+ cations since the isoelectric point of SiO_2 is 1.0–2.0. These findings indicate that a part of silanol groups with weaker acidity as well as all of the bridged hydroxy groups with strong acidity were ion-exchanged with NMe_4^+.

The pH of the NMe_4OAc solution was varied from 8 to 12 to control the ion-exchange ratio. The oxidation activity gradually increased with increasing pH. Treatment at high pH resulted in the formation of mesopores, as revealed by N_2 adsorption measurements, which could promote the diffusion of the substances. However, the catalyst ion-exchanged at high pH exhibited low selectivity for epoxide; probably the zeolite framework dissolves to form silanol groups, which would catalyze undesirable reactions.

When the ion-exchanged [Ti,Al]-beta catalyst was reused for the oxidation of cyclohexene after the catalyst was calcined at 473 K for 10 h, the epoxide selectively was retained, although the oxidation activity gradually decreased to 37% for the third run probably because of the blocking of the Ti species by unremovable reaction products such as polymers with high boiling points. Nevertheless, after re-calcination at 793 K and repeated ion-exchange of the deactivated catalyst with NMe_4OAc, both the oxidation activity and the epoxide selectivity were recovered to the initial value, which strongly indicates that the present method is effective in developing an active, selective and reusable catalyst.

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