Available online at www.sciencedirect.com

ScienceDirect

Journal of Catalysis 246 (2007) 205–214

JOURNAL OF CATALYSIS

www.elsevier.com/locate/jcat

Highly efficient and selective production of epichlorohydrin through epoxidation of allyl chloride with hydrogen peroxide over Ti-MWW catalysts

Lingling Wang, Yueming Liu, Wei Xie, Haijiao Zhang, Haihong Wu,
Yongwen Jiang, Mingyuan He, Peng Wu *

Shanghai Key Laboratory of Green Chemistry and Chemical Processes, Department of Chemistry, East China Normal University,
North Zhongshan Rd. 3663, Shanghai 200062, PR China

Received 27 September 2006; revised 1 December 2006; accepted 1 December 2006

Abstract

The catalytic properties of Ti-MWW in the epoxidation of allyl chloride (ALC) with hydrogen peroxide to epichlorohydrin (ECH) were studied by comparing these properties with those of TS-1, Ti-MOR, and Ti-Beta. Issues concerning the stability and reuse of Ti-MWW were also considered. The investigation on various reaction parameters showed that Ti-MWW is an active and selective catalyst for ALC epoxidation. Ti-MWW prefers aprotic solvents, such as acetonitrile and acetone, over protic alcohols, which is favorable for suppressing the formation of solvolysis byproducts. ALC conversion and ECH selectivity were both as high as 99% on Ti-MWW. 3-Chloro-1,2-propanediol and other heavy byproducts with high boiling points had a negative effect on ALC conversion for both TS-1 and Ti-MWW. A novel secondary synthesis caused a structural rearrangement of the Ti-MWW framework and then improved its stability.

Keywords: Ti-MWW; TS-1; Allyl chloride; Epichlorohydrin; Hydrogen peroxide; Liquid-phase epoxidation

1. Introduction

The discovery of TS-1 titanosilicate with the MFI structure and 10-membered ring (MR) channels, being able to catalyze actively various chemicals under mild conditions using aqueous H_2O_2 as an oxidant and with water as the sole byproduct, opens up new possibilities of developing environmentally benign chemical processes [1,2]. These technologies are viable alternatives to conventional halogen-based methods for solving the problems of waste disposal, equipment corrosion, coproduction of valueless chemicals, and others. The TS-1/H_2O_2 system has found outstanding application to the liquid-phase ammoximation of cyclohexanone [3]. Furthermore, a world-scale hydrogen peroxide-to-propylene oxide (HPPO) process based on TS-1 is scheduled for commercialization in 2008 [4].

To expand further applications, it is desirable to develop more efficient titanosilicates that have good hydrophilic/hydrophobic natures as well as suitable porosity for accommodating oxidation intermediate species. It is no exaggeration to say that to date, only Ti-MWW with the MWW topology seems to be intrinsically more active than TS-1 [14–16]. The advantage of Ti-MWW is firmly related to its unique pore system consisting of two independent 10-MR channels, 12-MR side cups, and supercages [5–8]. Ti-MWW has been shown to be an efficient catalyst in the epoxidation of functional alkenes [9,10] and ammoximation of cyclohexanone [11]. These successes encourage us to investigate its application to the synthesis of valuable oxygenated chemicals containing other functional groups.

Epichlorohydrin (ECH) is an important raw material for producing epoxy resins and synthetic glycerin. The high-temperature chlorination of propylene and the method via allyl acetate are two major manufacturing routes used in current industrial processes. The key step of epoxidation in both processes depends on chlorohydrin and saponification,

---

* Corresponding author. Fax: +86 21 6223 2292.
E-mail address: pwu@chem.ecnu.edu.cn (P. Wu).

0021-9517/$ – see front matter © 2007 Elsevier Inc. All rights reserved.
doi:10.1016/j.jcat.2006.12.003

which inevitably produce a large quantity of calcium chloride byproduct and halogen-containing wastewater. Thus, alternative, greener techniques for ECH production are urgently needed. The TS-1/H_2O_2 system represents an attempt to develop environmentally benign chemical processes via direct epoxidation of allyl chloride (ALC) to ECH. But ECH is formed efficiently on TS-1 only in the presence of methanol solvent, which unavoidably leads to byproducts due to the solvolysis of ECH [12,13]. On the other hand, the heterogeneous catalytic epoxidation of ALC with molecular oxygen has been reported on TS-1 in the presence of 2-ethyl anthrahydroquinone, but the activity was extremely low [14]. Unlike simple alkenes, the electron-withdrawing chlorine group makes the C=C bond of ALC electron-deficient and then less active. A more active titanosilicate/H_2O_2 system is thus expected for the direct epoxidation of ALC.

In the present study, we applied Ti-MWW to ALC epoxidation with the aim of producing ECH efficiently and selectively. The effects of the reaction conditions on ALC epoxidation were investigated in detail by comparison with other titanosilicates. The factors governing the stability and reusability of Ti-MWW were studied. A useful method was developed for the regeneration of Ti-MWW.

2. Experimental

2.1. Catalyst preparation and characterization

Ti-MWW catalysts were hydrothermally synthesized [15] or postsynthesized [16] as described previously; these are designated Ti-MWW-HTS and Ti-MWW-PS, respectively. For control experiments, TS-1 catalysts were synthesized following conventional procedures [17]. The Si and Ti sources were tetraethyl silicate (TEOS) and tetrabutyl orthotitanate (TBOT), respectively; the structure-directing agent (SDA) was TPAOH. After burning off the organic species, TS-1 was further washed with 1 M HCl solution to remove any extra-framework Ti species and alkali ions contaminated in TPAOH solution. Other titanosilicates of Ti-MOR with the MOR structure and 12-MR channels [18] and Al-free Ti-Beta [19] were also prepared according to the literature. For both Ti-MWW and TS-1, a series of samples with different Si/Ti molar ratios have been prepared by controlling the Ti content in preparation. All of the catalysts were characterized by inductively coupled plasma (ICP, Thermo IRIS Intrepid II XSP atomic emission spectrometer), X-ray diffraction [XRD, Bruker D8 ADVANCE diffractometer ($\mathrm{Cu}K\alpha$)], N_2 adsorption (Autosorb Quancachrome 02108-KR-1), scanning electron microscopy (SEM, Hitachi 4800), TGA-DTA (METTLER TOLEDO TGA/SDTA851^e), CHN chemical analyses (Elementar Vario EL III) and UV–vis (Shimadzu UV-2400PC) and IR (Shimadzu FTIR-8100) spectroscopies.

2.2. Catalytic reactions

The epoxidation of allyl chloride with H_2O_2 was carried out in a 20-mL Teflon-lined autoclave under vigorous stirring. In a typical run, 5 mL of solvent, 10 mmol of ALC, 10 mmol of H_2O_2 (30 wt%) and a certain amount of catalyst were mixed in the autoclave without purging, and the reaction was started under agitation at desired temperatures. The autogenous pressure inside the autoclave was about 2 atm at 333 K. After the removal of catalyst powder, the analyses of organic phases were performed on a gas chromatograph (Shimadzu 14B, FID detector) equipped with a 30 m DB-1 capillary column, using toluene as an internal standard. The analyses were started by maintaining the column at 313 K for 2 min, then raising the temperature to 423 K at a rate of 10 $\mathrm{K\,min^{-1}}$. The amount of unconverted H_2O_2 was determined by a standard titration method using a 0.1 M $Ce(SO_4)_2$ solution. The solvolysis of ECH was conducted under conditions similar to those used for ALC epoxidation. The products thus formed were determined using authentic chemicals on a GC-MS (Agilent 6890 series GC system, 5937 network mass selective detector).

3. Results and discussion

3.1. Characterization of various titanosilicates

The XRD patterns showed that all of the titanosilicates prepared had the objective crystalline structures and comparably high crystallinity. The samples showed in UV–vis spectra the characteristic adsorption bands at 220 nm, which is assigned to the charge transfer of O^{2-} to the Ti^{4+} species tetrahedrally coordinated in the zeolite framework [1]. Only when the Si/Ti was below 50 was a weak band observed at 330 nm due to anatase phase, particularly for TS-1, indicating the presence of a slight amount of condensed titanium oxide species. All of the samples demonstrated the 960-$\mathrm{cm^{-1}}$ band in the IR spectra, due to Si–O–Ti stretching vibration. The specific surface areas determined from N_2 adsorption at 77 K were 521–561 $\mathrm{m^2\,g^{-1}}$ for Ti-MWW, around 530 $\mathrm{m^2\,g^{-1}}$ for TS-1, 553 $\mathrm{m^2\,g^{-1}}$ for Ti-MOR, and 624 $\mathrm{m^2\,g^{-1}}$ for Ti-Beta (Table 1).

Independent of direct hydrothermal synthesis and postsynthesis, the crystals of Ti-MWW appeared to be thin platelets with a hexagonal morphology (Fig. 1a). The major difference in Ti-MWW-PS and Ti-MWW-HTS was in terms of crystal size. The former, prepared from a deboronated parent synthesized using hexamethyleneimine as an SDA, showed a slightly larger crystal size (ca. 0.6 µm long and ca. 0.1 µm thick); the latter, directly synthesized using piperidine as an SDA, showed a relatively smaller crystal size of ca. 0.3 × 0.3 × 0.1 (Table 1). Both TS-1 and Ti-Beta had a uniformly round-shaped morphology with a crystal sizes of 0.2–0.3 µm (Figs. 1b and 1c). Ti-MOR showed mainly a pillar-shaped morphology, along with some flat and prismatic shapes. The average crystal size of Ti-MOR was 0.5 × 0.5 × 2 µm, much larger than the aforementioned three titanosilicates. On the basis of the above characterization, these titanosilicates were considered to qualify the liquid-phase oxidation catalysts with H_2O_2 as an oxidant.

Table 1
Physicochemical properties of various titanosilicates

No.	Catalyst	Structure	Si/Ti[a]	Cry. size[b] (μm)	SA[c] ($m^2\ g^{-1}$)	Ti states[d]
1	Ti-MWW-PS1[e]	MWW	128	0.6 × 0.6 × 0.1	540	Tetra.
2	Ti-MWW-PS2[e]	MWW	55	0.6 × 0.6 × 0.1	550	Tetra.
3	Ti-MWW-PS3[e]	MWW	45	0.6 × 0.6 × 0.1	561	Tetra.
4	Ti-MWW-HTS[f]	MWW	37	0.3 × 0.3 × 0.1	521	Tetra.
5	TS-1-1	MFI	76	0.2–0.3	534	Tetra.
6	TS-1-2	MFI	58	0.2–0.3	525	Tetra.
7	TS-1-3	MFI	47	0.2–0.3	529	Tetra. + anatase (small)
8	Ti-Beta	BEA*	37	0.2–0.3	624	Tetra.
9	Ti-MOR[g]	MOR	90	0.5 × 0.5 × 2	553	Tetra.

[a] Molar ratio determined by ICP.
[b] Evaluated by SEM.
[c] Specific surface area (Langmuir) measured by N_2 adsorption at 77 K.
[d] Evaluated with UV–vis spectra. Tetra., tetrahedral Ti species.
[e] Postsynthesized, Si/B > 500 [16].
[f] Hydrothermally synthesized, Si/B = 39.
[g] Prepared by gas–solid reaction between $TiCl_4$ vapor and highly dealuminated mordenite (Si/Al > 300) [18].

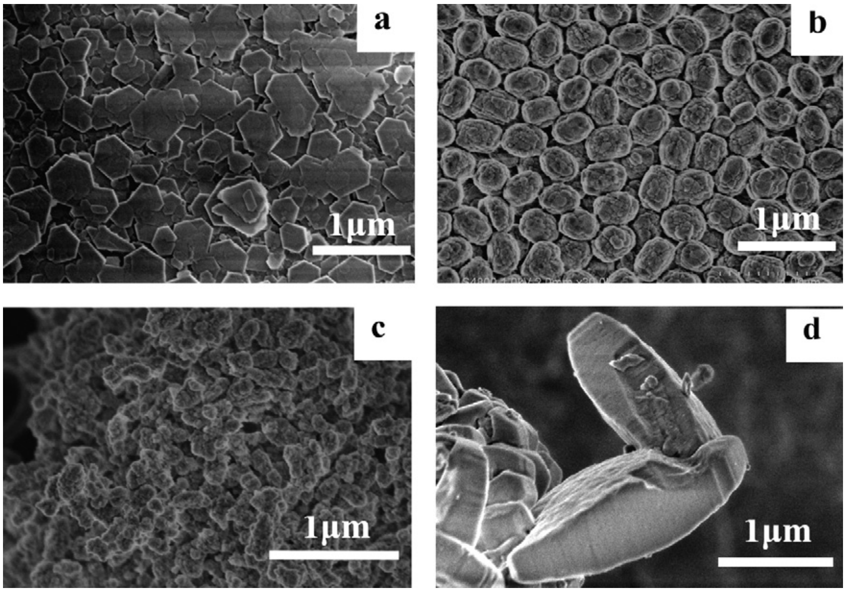


Fig. 1. Representative SEM images of Ti-MWW (a), TS-1 (b), Ti-Beta (c), and Ti-MOR (d). The samples correspond to Nos. 2, 7, 8 and 9 in Table 1, respectively.

3.2. *Oxidation of ALC in various titanosilicates*

Table 2 shows the results of ALC epoxidation with H_2O_2 over different titanosilicate catalysts. The reaction was carried out in acetonitrile for Ti-MWW, Ti-Beta, and Ti-MOR, and in methanol for TS-1. As discussed in detail later section, the most suitable solvents are acetonitrile for Ti-MWW and methanol for TS-1. Fig. 2 summarizes the reaction pathways in ALC epoxidation. The main product was ECH as a result of C=C bond oxidation. 3-Chloro-1,2-propanediol (CPDL) was co-produced due to the hydrolysis of ECH contributed by the weak acid sites, such as silanols, titanols, or Ti peroxo species (Ti–OOH). In the presence of protic solvents, such as alcohols, the successive solvolysis of ECH also led to hydroxyethers with high boiling points. Under optimal conditions (details of which are given later), Ti-MWW-PS showed an ALC conversion of 83.4% and an ECH selectivity of 99.9% (Table 2, No. 1). The absolute amount of products other than ECH was extremely small. Although slightly less active than Ti-MWW-PS, Ti-MWW-HTS also produced ECH selectively (Table 2, No. 2). Ti-MWW-HTS contained a relatively high amount of boron (corresponding to

Table 2
The results of epoxidation of ALC with H_2O_2 over different titanosilicate catalysts[a]

No.	Catalyst	Si/Ti molar ratio	Solvent	ALC conv. (mol%)	ECH sel.[b] (mol%)	TON[c]
1	Ti-MWW-PS-2	55	MeCN	83.4	99.9	275
2	Ti-MWW-HTS	37	MeCN	68.0	99.9	151
3	TS-1-3	47	MeOH	75.1	97.2	212
4	Ti-MOR	90	MeCN	1.6	98.6	9
5	Ti-Beta	76	MeCN	2.5	98.9	11

[a] Reaction conditions: catalyst 0.1 g; allyl chloride 10 mmol; H_2O_2 (30 wt%) 10 mmol; solvent 5 mL; temperature 333 K; time 2 h.
[b] Others, mainly solvolysis products together with some heavy products.
[c] TON, turnover number in mol $(\text{mol-Ti})^{-1}$.

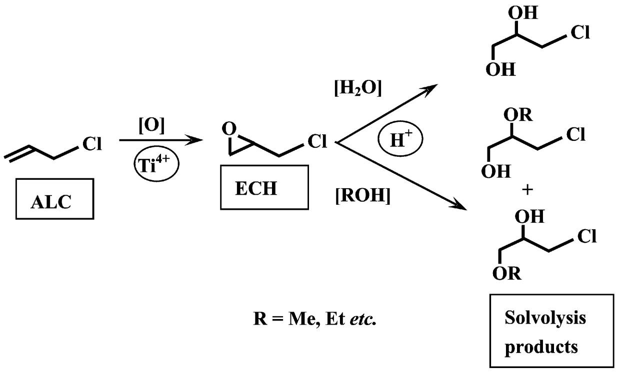


Fig. 2. Reaction pathways in the epoxidation of allyl chloride.

an Si/B ratio of 39), but the Brönsted acid sites originated from the framework boron ions were seemingly not strong enough to cause the ring opening of ECH in a basic solvent, such as acetonitrile. Thus, the ECH selectivity was comparably high on Ti-MWW-HTS (99%). The Ti species achieved by postincorporation are assumed to occupy the framework sites that are more accessible to the substrate molecules than those obtained by direct hydrothermal synthesis, leading to a higher intrinsic activity (TON) for Ti-MWW-PS [16].

Under the same reaction conditions as those adopted for Ti-MWW except for the solvent, TS-1 showed lower ALC conversion and ECH selectivity than Ti-MWW-PS in the presence of MeOH (Table 2, No. 3). On the basis of TON, TS-1 was obviously less active than Ti-MWW-PS and just slightly more active than Ti-MWW-HTS. This should not be due to the occasional case of catalyst preparation; the advantages of Ti-MWW on activity have been verified on a series of catalysts with varying Ti contents (as discussed in Section 3.3.4). The superiority of Ti-MWW to TS-1 was observed in the epoxidation of various kinds of alkenes [9,10], attributed to the unique pore system of MWW zeolite favoring the adsorption and access of substrate molecules to the Ti active sites. Ti-MOR and Ti-Beta turned out to be much less active and selective than Ti-MWW and TS-1 (Table 2, Nos. 4 and 5). Ti-Beta exhibited highly hydrophilic features due to stacking defaults, making it an unsuitable catalyst for ALC oxidation. Also unsuitable is Ti-MOR, which had overly large crystals as well as one-dimensional channels only, both of which hinder the diffusion and access of substrate molecules to Ti sites. Despite the difference in optimal reaction conditions, especially the solvent effect, the titanosilicates exhibited catalytic activity for ALC epoxidation in the following order: Ti-MWW-PS > TS-1 > Ti-MWW-HTS $\gg$ Ti-Beta > Ti-MOR.

3.3. Effects of reaction parameters on the epoxidation of ALC over Ti-MWW

3.3.1. Effect of solvents

Table 3 compares the catalytic performance of Ti-MWW and TS-1 in the epoxidation of ALC in various solvents. Both catalysts gave ECH as the main product, but they exhibited different solvent effects. The most favorable solvents for Ti-MWW were acetone and MeCN, in which higher conversion of ALC (>80%) and ECH selectivity (>99%) were obtained. In these two solvents, H_2O_2 was efficiently utilized to the oxidation of C=C bond instead of nonproductive decomposition. The epoxidation of ALC over Ti-MWW was greatly retarded in the protic solvents of alcohols, as well as in the aprotic solvent like CH_2Cl_2. The solvent effect of alcohols was once presumably related to a stabilized cyclic intermediate species of a five-membered ring (Scheme 1), presumably formed by the coordination and hydrogen-bonding of a protic molecule to a Ti-hydroperoxo complex [20]. The dimension of the intermediate species increases with increasing molecular size of ROH. This then should impose a steric hindrance on the substrate molecules by limiting their diffusion and approach to the Ti active sites within the confined channels of zeolites. It was actually observed that the ALC conversion decreased slightly in the order MeOH > EtOH > *i*-PrOH.

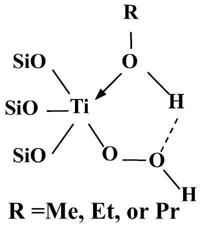
Table 3
A comparison of epoxidation of allyl chloride in various solvents between Ti-MWW and TS-1[a]

Solvent	Ti-MWW (mol%)				TS-1 (mol%)			
	Conv.	ECH sel.[b]	H_2O_2		Conv.	ECH sel.[b]	H_2O_2	
			Conv.	Eff.[c]			Conv.	Eff.[c]
MeCN	83.4	99.9	88.0	94.8	16.5	99.9	23.3	71.0
Acetone	86.1	99.9	89.5	96.1	42.4	99.9	69.9	61.0
H_2O	38.2	99.9	56.1	70.0	13.7	96.2	23.0	69.0
MeOH	42.3	98.6	63.5	67.0	75.1	97.2	87.9	85.0
EtOH	33.8	99.9	54.3	62.0	56.9	87.2	89.6	64.0
i-PrOH	28.7	98.5	56.7	50.6	31.7	96.4	54.6	58.1
CH_2Cl_2	64.4	99.6	89.0	72.0	3.5	99.9	7.6	46.0

[a] Reaction conditions: Ti-MWW-PS (Si/Ti = 55) or TS-1 (Si/Ti = 47) 0.1 g; allyl chloride 10 mmol; H_2O_2 (30 wt%) 10 mmol; solvent 5 mL; temperature 333 K; time 2 h.

[b] Others, mainly solvolysis products together with some heavy products.

[c] H_2O_2 efficiency was calculated by relating all the oxidative products to the amount of H_2O_2 converted.



Scheme 1. Five-membered ring intermediate species.

Besides influencing catalytic activity, the protic alcohols caused the opening of the oxirane ring of ALC on the acid sites, which reduced the selectivity for ECH. The solvent effects of Ti-MWW on ALC epoxidation were very similar to those previously reported on the epoxidation of allyl alcohol and diallyl ether [9,10]. Unlike hydrophobic TS-1, Ti-MWW, originating from a lamellar precursor containing interlayer silanols and intralayer defect sites like hydroxyl nests due to deboronation, is characteristic of hydrophilicity [9]. The hydroxyl groups may favor the adsorption of protic molecules such as alcohols and water, which retards the adsorption and coordination of substrates to the Ti active sites. Thus, Ti-MWW reasonably showed

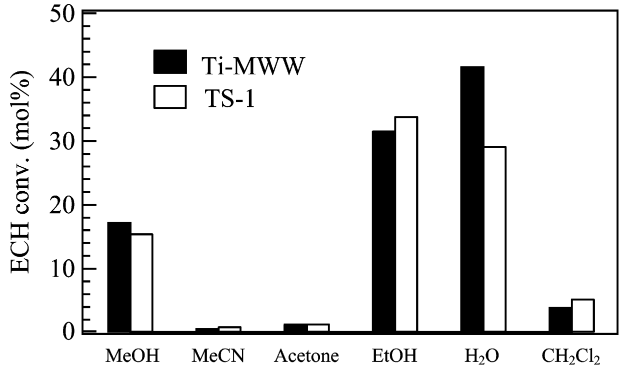


Fig. 3. A comparison of solvolysis of ECH in various solvents between Ti-MWW and TS-1. Reaction conditions: catalyst 0.1 g; ECH 10 mmol; solvent 5 mL; temperature 333 K; time 2 h.

Table 4
Influence of reaction time on the ALC conversion and ECH selectivity[a]

Time (h)	Ti-MWW (mol%)				TS-1 (mol%)			
	Conv.	ECH sel.[b]	H_2O_2		Conv.	ECH sel.[b]	H_2O_2	
			Conv.	Eff.[c]			Conv.	Eff.[c]
0.5	52.4	99.8	49.9	87.5	56.5	99.8	54.9	85.8
2	87.9	99.6	78.8	93.0	77.3	97.2	73.8	87.3
5	98.3	99.5	87.6	93.5	89.3	94.4	83.9	88.7
10	99.9	99.2	95.4	87.3	98.3	88.3	95.1	86.1

[a] Reaction conditions: catalyst 0.1 g; allyl chloride 10 mmol; H_2O_2 (30 wt%) 12 mmol; solvent (acetone for Ti-MWW and MeOH for TS-1) 5 mL; temperature 333 K.

[b] Others, mainly solvolysis products together with some heavy products.

[c] H_2O_2 efficiency was calculated by relating all the oxidative products to the amount of H_2O_2 converted.

a higher conversion in a basic solvent (e.g., MeCN) or an aprotic solvent (e.g., acetone) than in alcohols.

In the case of TS-1, MeOH was the most effective solvent, in which an ALC conversion of 75.1% was obtained. Aprotic but basic MeCN, an unsuitable solvent well known in the oxidation of simple alkenes on TS-1 [20,21], showed moderate to good lower conversion for ALC. EtOH and *i*-PrOH also retarded TS-1 activity, due predominately to the formation of bulky species with steric restrictions (Scheme 1).

Ti-MWW exhibited more advantages in product selectivity than TS-1. The solvolysis of ECH with methanol occurred readily to form 3-chloro-1,2-propanediol and ethers on TS-1. Furthermore, nonproductive decomposition of H_2O_2 was generally higher on TS-1, leading to a lower utilization efficiency of H_2O_2.

To further affirm the solvent effect and high ECH selectivity for Ti-MWW, the hydrolysis of ECH in various solvents was carried out (Fig. 3). The main products were 3-chloro-1,2-propanediol and hydroxyether, along with a few products of high boiling points. The ECH conversion was much higher in the protic solvents of alcohols and H_2O than in the aprotic solvents, such as CH_2Cl_2 and especially MeCN and acetone. ECH conversion depends on the concentration of acid sites in the titanosilicates. The acid sites of Ti-MWW derive mainly from the defect sites and residual framework boron ions. Defect-free TS-1 reasonably contains less acid sites [9]. However, from the standpoint of catalytic activity, one of the best solvents for Ti-MWW was MeCN, and one of the best for TS-1 was MeOH. The solvolysis of ECH was almost inert in MeCN, but not in MeOH. This further verified that carrying out ALC oxidation in a favorable solvent like MeCN allows Ti-MWW to achieve higher ECH selectivity. Moreover, considering a practical process based on the titanosilicate/H_2O_2 catalytic system, MeCN, with its different boiling point from water than MeOH, should avoid zeotrope in the separation step by distillation.

3.3.2. *Effect of reaction time*

Table 4 shows the time process when the epoxidation was carried out over Ti-MWW in acetone and TS-1 in MeOH. The ALC conversion increased rapidly with the reaction time at the beginning, and then slowed as H_2O_2 was consumed gradually. ALC conversion finally reached about 99% at 10 h on both catalysts. The products were predominately ECH, along with a small amount of 3-chloro-1,2-propanediol on Ti-MWW, indicating that the ring opening of ECH occurred to a negligible level and the reaction rate for ECH formation was much faster than that of ECH hydrolysis to diol. With prolonged reaction time, the ECH selectivity of Ti-MWW remained at about 99%. However, the ECH selectivity of TS-1 declined from 99.8 to 88.3% when the reaction was conducted for 10 h. The result indicates that ECH readily underwent solvolysis with MeOH on the surface acid sites of TS-1, causing a drop in ECH selectivity. On both catalysts, the conversion of H_2O_2 increased with prolonged reaction time, whereas H_2O_2 efficiency was >85%.

3.3.3. *Effect of reaction temperature*

The reaction temperature greatly affected the epoxidation of ALC over Ti-MWW. As shown in Fig. 4A, the conversion of ALC increased with increasing temperature and reached a maximum at 333 K, whereas the selectivity to ECH was maintained at >99.9%. Further increases in temperature to 373 K resulted in a rapid decrease in conversion to 47.6%. From Fig. 4B, the conversion of H_2O_2 increased, but the efficiency of H_2O_2 dropped with increasing temperature. The nonproductive decomposition of H_2O_2 occurred at temperatures above 333 K. This made the conversion of ALC decrease. The present experiment indicates that the selective epoxidation of ALC proceeds effectively at an optimal reaction temperature, such as 333 K.

3.3.4. *Effect of Ti content*

To further ensure that Ti-MWW has superiority over TS-1 in ALC epoxidation, a series of Ti-MWW and TS-1 catalysts with varying Ti contents were prepared and checked for catalytic performance (Fig. 5). To fairly compare the catalytic activity between these two titanosilicates, the reactions were carried out using the same weight ratio of catalyst to substrate but in different optimal solvents: acetone for Ti-MWW and MeOH for TS-1. The conversion of ALC increased with an increasing amount of Ti active sites for both Ti-MWW and TS-1, but Ti-MWW showed greater catalytic activity than TS-1.

3.3.5. *Effect of the amount of Ti-MWW catalyst*

Fig. 6 shows the effect of catalyst amount on ALC epoxidation over Ti-MWW. The more catalyst used, the higher the

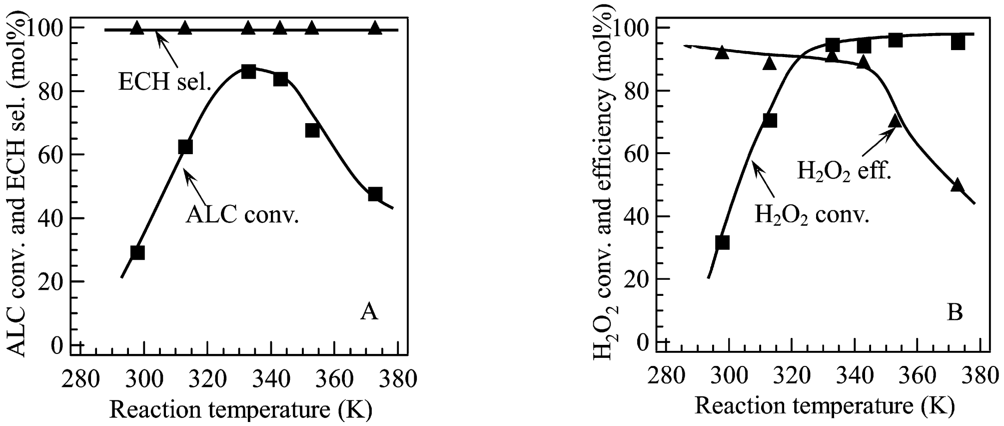


Fig. 4. Effect of reaction temperature on the ALC epoxidation over Ti-MWW. Reaction conditions: catalyst 0.1 g; ALC 10 mmol; H_2O_2 (30 wt%) 10 mmol; acetone 5 mL; time 2 h.

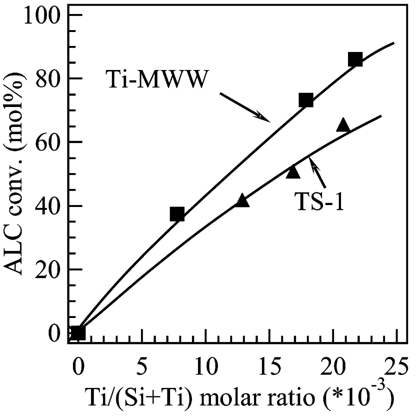


Fig. 5. Dependence of the ALC conversion on the Ti content. Reaction conditions: catalyst 0.1 g; allyl chloride 10 mmol; H_2O_2 (30 wt%) 10 mmol; solvent (acetone for Ti-MWW and MeOH for TS-1) 5 mL; temperature 333 K; time 2 h.

catalytic activity. Here 19.6 wt% of Ti-MWW relative to ALC was sufficient to convert ALC by 93% at 333 K within 2 h and to produce ECH at an H_2O_2 utilization efficiency of 96%. When the catalyst amount was <10 wt%, the nonproductive decomposition of H_2O_2 became more obvious, lowering the utilization efficiency (Fig. 6B). This means the reaction should be operated using a sufficient amount of catalyst to fasten the main reaction of C=C oxidation but suppress the decomposition of H_2O_2.

3.3.6. Effect of H_2O_2/ALC ratio

The epoxidation of ALC stoichiometrically requires equivalent amounts of ALC and H_2O_2. However, taking into account unproductive decomposition of H_2O_2, using an excess amount of H_2O_2 would be helpful for ALC conversion. The effect of H_2O_2/ALC molar ratio on the epoxidation of ALC was investigated (Fig. 7). With increasing H_2O_2/ALC ratio, the ALC conversion obviously increased. At a H_2O_2/ALC molar ratio of 0.8, the ALC conversion was only 76.3%, and the conversion of H_2O_2 reached nearly 100%. The conversion of ALC increased went up to 86.1% at a H_2O_2/ALC molar ratio of 1.0, and almost leveled off at the ratios >1.2. The efficiency of H_2O_2 utilization decreased significantly with increasing H_2O_2/ALC ratio due to nonproductive decomposition.

3.4. Stability and reusability of Ti-MWW

Ti-MWW-PS shows significantly greater catalytic activity in the oxidation of different alkenes, but its synthesis procedure is relatively complicated and troublesome [16], which may make its application difficult. However, the preparation of Ti-MWW-

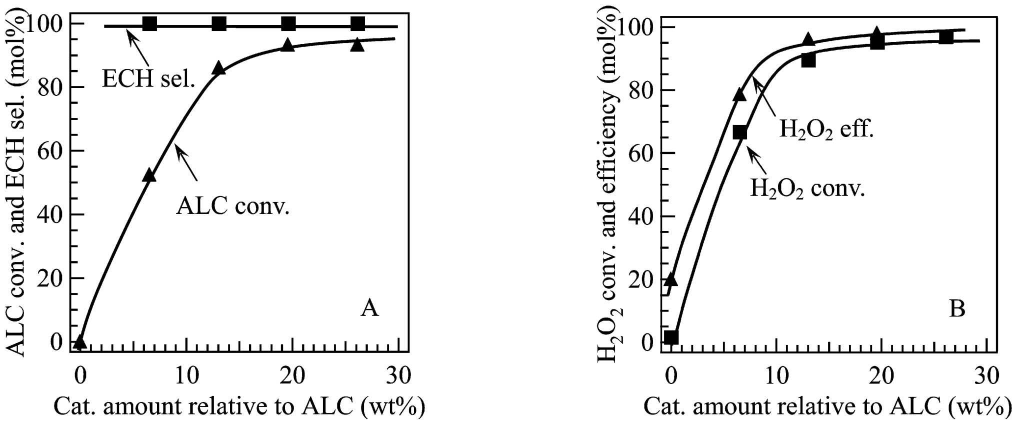


Fig. 6. Effect of catalyst amount on the epoxidation of ALC over Ti-MWW. Reaction conditions: allyl chloride 10 mmol; H_2O_2 (30 wt%) 10 mmol; acetone 5 mL; temperature 333 K; time 2 h.

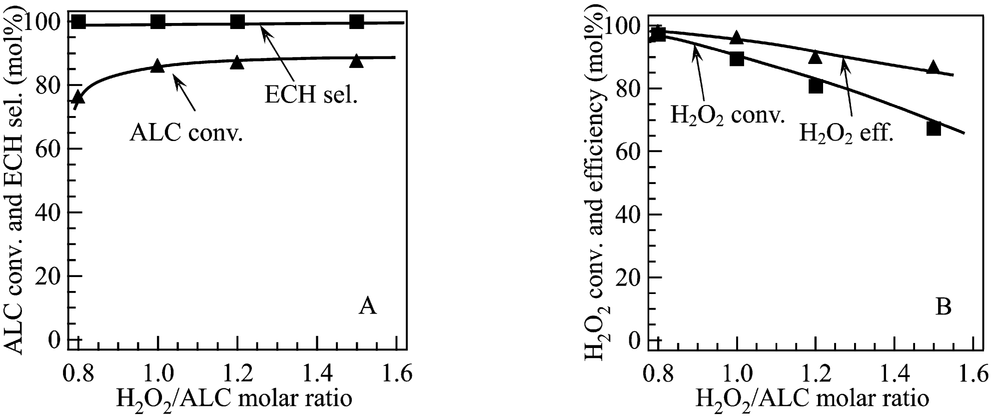


Fig. 7. Effect of H_2O_2/ALC ratio on the epoxidation of ALC over Ti-MWW. Reaction conditions: catalyst 0.1 g; allyl chloride 10 mmol; acetone 5 mL; temperature 333 K; time 2 h.

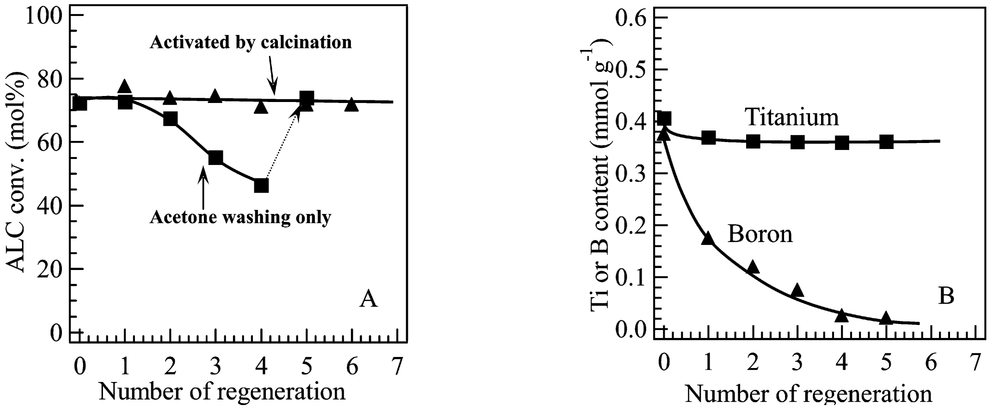


Fig. 8. Changes of ALC conversion (A), and Ti and B contents (B) with the reaction–regeneration cycles. Reaction conditions: Ti-MWW/ALC/H_2O_2/MeCN = 0.2 g/10 mmol/10 mmol/5 mL; temperature 333 K; time 2 h. Regeneration: used catalyst was washed with acetone and dried at 393 K or further calcined at 773 K in air for 4 h.

HTS is realized simply through a direct synthesis procedure [5]. In this sense, we have used Ti-MWW-HTS to check the stability and reusability, two of the most important properties of titanosilicate in an actual process, in addition to catalytic activity and product selectivity.

The loss of active sites due to Ti leaching turns to be a notable problem commonly encountered in the liquid-phase reactions, which directly determines whether a titanosilicate is really applicable and practicable. The Ti species of TS-1 are generally believed to be sufficiently stable in the liquid-phase oxidation of simple alkenes. Ti-MWW has proved to be stable against Ti leaching in the epoxidation of various alkenes [9,10]. The present ALC epoxidation gives rise to 3-chloro-1,2-propanediol, although not in a large amount. The diol may coordinate to the Ti species [22], then lower the stability of Ti-MWW to a certain extent. Thus, the stability against Ti leaching has been investigated along with the reusability in ALC epoxidation. The experiments were started at an enlarged reaction scale using 1.5 g of Ti-MWW-HTS. The used Ti-MWW catalyst was regenerated by washing with acetone or by further calcination in air at 773 K. After part of the catalyst powder was removed for the Ti and B analyses by ICP, the regenerated catalyst was subjected to repeated epoxidation of ALC at a constant ratio of catalyst–substrate solvent. The ALC conversion decreased dramatically with the reaction–regeneration cycles when the used catalyst of Ti-MWW was washed with acetone and then dried (Fig. 8A). Nevertheless, when the catalyst collected at the fourth reaction–regeneration cycle was calcined at 773 K, the ALC conversion was restored. This suggests that the deactivation of acetone-washed catalyst was due only to the deposition inside the channels of heavy organic compounds with high boiling points. The ALC conversion decreased much more slowly with the reaction–regeneration cycle when the used catalyst was activated by further calcination in air at 773 K from the very beginning (Fig. 8A).

The Ti and B contents were quantified for the used Ti-MWW catalysts (Fig. 8B). The B species were gradually leached out of the framework during the reaction, probably because of a too small ionic radius in comparison with Si. However, except for a leaching of about 5 wt% after the first use, the amount of Ti species was almost the same after five cycles of reaction-regeneration, indicating high stability.

3.5. Factors governing the stability and reusability of Ti-MWW in ALC epoxidation and the regeneration method

Structure collapse, pore jamming, active site leaching, and poisoning are the major causes of catalyst deactivation. In our experiments, the used Ti-MWW catalyst showed nearly the same XRD patterns and UV–vis spectra to the fresh one (not shown). In addition, the Ti leaching was also negligible (Fig. 8B). The reasons for the activity loss of Ti-MWW are thus hardly attributed to the degradation of crystalline structure, the leaching of active sites, and a change of Ti states. Fig. 8A showed that the catalyst was readily regenerated by calcination in air. This fact suggested us that one possible reason for deactivation may be pore jamming or active site blocking. We thus have investigated the factors affecting the activity in ALC oxidation and the regeneration method on the basis of secondary synthesis.

3.5.1. Factors for deactivation

To investigate the main reason for catalyst deactivation, ALC epoxidation was carried out on both TS-1 and Ti-MWW under the same reaction condition. Compared with the fresh sample, the ALC conversion also decreased on the used TS-1. TGA and FTIR analyses were carried out on the deactivated TS-1 and Ti-MWW samples to investigate the organic species that were occluded. IR spectra clearly showed that the bands at 2900–3000 cm^{-1} due to the stretching vibrations of CH_3 and/or CH_2 groups probably originated from the heavy organic species adsorbed on the deactivated catalyst. TGA indicated that the coke species accounted for 10–14 wt%. To identify the coke composition, the deactivated catalysts collected from the reaction were dissolved in 30 wt% hydrofluoric acid to liberate the organic species. The soluble organic compounds were extracted by dimethyl ether, whereas insoluble coke (or heavy coke) was separated by centrifugal sedimentation. The coke extractant was further concentrated by evaporating the solvent. The soluble coke components were analyzed by gas chromatography. Besides the ALC reactant, the main product of ECH, and the solvent, many other species soluble in ether were also detected on GC. One of the main species identified on GC-MS was 3-chloro-1,2-propanediol. The others, showing a complicated distribution in GC charts, were considered to be several oligomerization components with high boiling points.

We thus checked the effect of heavy byproduct on the deactivation of TS-1 and Ti-MWW using 3-chloro-1,2-propanediol, the representative coke species confirmed in the deactivated catalysts. Without coexistence of 3-chloro-1,2-propanediol, Ti-MWW and TS-1 showed an ALC conversion of 68.0 and 75.1%, respectively. With increasing amount of 3-chloro-1,2-propanediol added, ALC conversion showed a similar decreasing tendency (Fig. 9). The more 3-chloro-1,2-propanediol added, the lower the ALC conversion. This indicated that 1,3-chloro-1,2-propanediol indeed had an negative effect on ALC conversion on both TS-1 and Ti-MWW. It was thus deduced that 3-chloro-1,2-propanediol together with other heavy organic species formed during the ALC epoxidation may correspond to deactivation mainly via pore blocking and active site covering. These species with high boiling points and multi-hydroxyl groups may easily adsorb on the defect sites, such as silanols, as well as on the Ti sites. In fact, the diol product rapidly deactivates TS-1 in the epoxidation of allyl alcohol [22], whereas the triol byproducts produced in the epoxidation of crotyl alcohol could chelate the Ti sites, and even cleave the Si–O–Ti bonds [23]. Strategies to improve catalyst life would include reducing formation as well as pore deposition by heavy products.

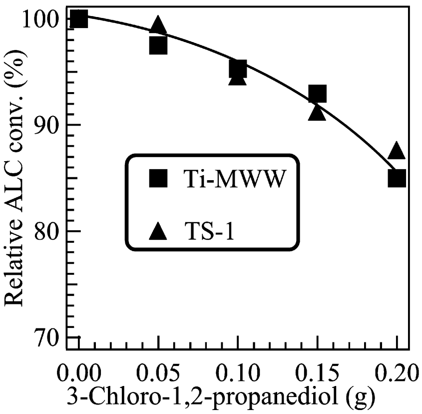


Fig. 9. Effect of 3-chloro-1,2-propanediol addition on the ALC conversion. Reaction conditions: allyl chloride 10 mmol; H_2O_2 (30 wt%) 10 mmol; solvent (acetone for Ti-MWW and MeOH for TS-1) 5 mL; temperature 333 K; time 2 h. The conversion without addition of diol (68.0% for Ti-MWW and 75.1% for TS-1) was normalized to 100%.

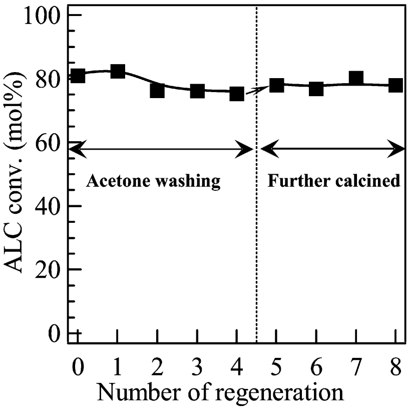


Fig. 10. Changes of ALC conversion with the reaction-regeneration cycles on structurally rearranged Ti-MWW. Reaction conditions: same as in Fig. 8. Regeneration: used catalyst was washed with acetone and dried at 393 K (Nos. 1–4), and further calcined at 773 K in air for 4 h (Nos. 5–8).

3.5.2. Secondary synthesis

To improve the stability and reusability of Ti-MWW, we performed catalyst modification by secondary synthesis. Fresh Ti-MWW catalyst was treated in an aqueous piperidine (PI) solution at 443 K for 1 day. The molar ratios of PI/SiO_2 and H_2O/SiO_2 in the mixture were 1 and 10, respectively. The treated sample was further calcined directly in air at 823 K for 5 h. The modified catalyst was subjected to the repeated reaction of ALC epoxidation (Fig. 10). Compared with the reuse of unmodified Ti-MWW (Fig. 8A), the catalyst treated with PI showed greater stability when it was regenerated by acetone washing only (Fig. 10, first to fourth reuses). Further calcination at 773 K restored its activity totally (Fig. 10, fifth to eighth reuses). This verified that the modification with PI was an effective way of prolonging lifetime when applying Ti-MWW to a continuous process of ALC epoxidation.

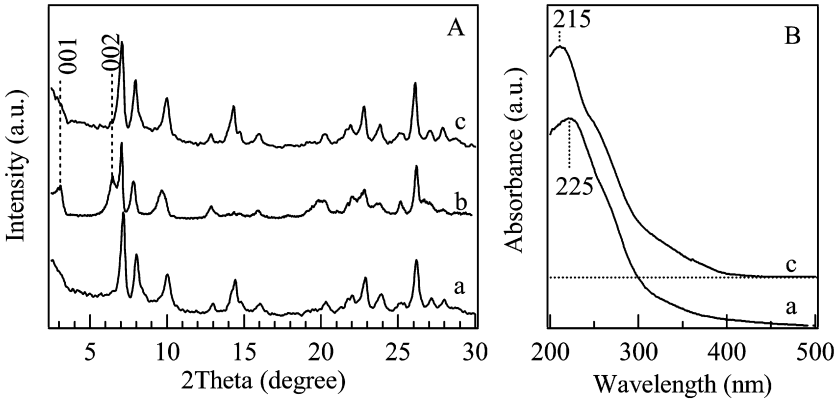


Fig. 11. XRD patterns (A) and UV–vis spectra (B) of Ti-MWW (a), piperidine-treated Ti-MWW but without calcination (b), and further calcined at 823 K for 5 h (c). Piperidine treatment was performed at a molar ratio of 1.0 SiO_2:1.0 PI:10 H_2O at 443 K for 1 day.

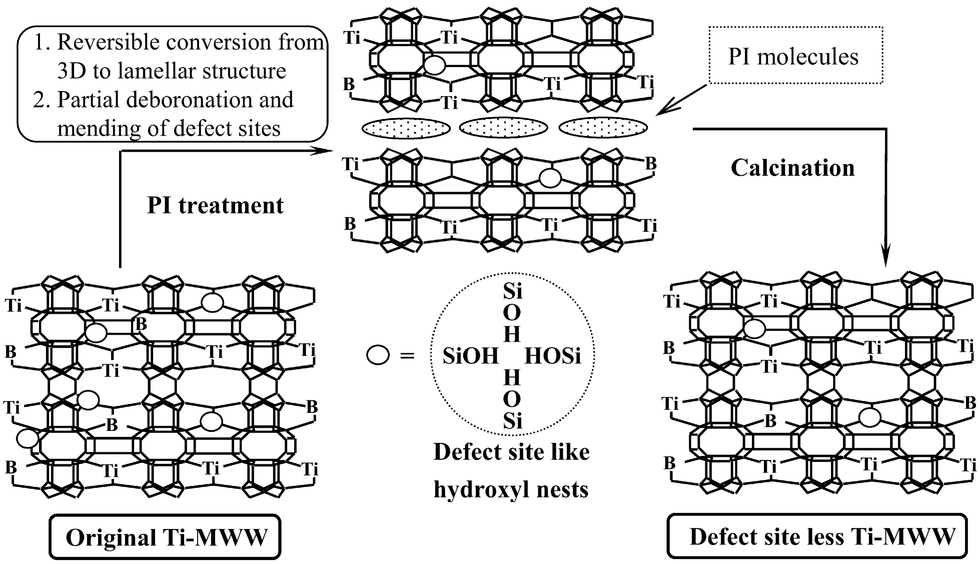


Fig. 12. A graphic description of structural change during the PI treatment of Ti-MWW.

The XRD patterns verified that the PI treatment followed by calcination caused a so-called "structural rearrangement" of MWW zeolite (Fig. 11). On PI treatment, [001] and [002] diffractions due to MWW lamellar precursor were observed (Figs. 11a and 11b). Chemical analyses indicated that 13.8 wt% of organic species with a C/N ratio of 5.3 were incorporated during the treatment (Table 5, No. 2). The structural change to lamellar precursor should be a result of interlayer insertion of PI molecules. A further calcination caused interlayer dehydroxylation, causing the diffractions due to the layered structure to disappear (Fig. 11c). A reversible structural change from 3D MWW to lamellar precursor to 3D MWW thus occurred during these treatment sequences, as shown graphically in Fig. 12. The intercalation of PI molecules was extremely important to induce interlayer expansion.

Based on the Si/Ti and Si/B ratios given by ICP analyses, the PI treatment had a negligible affect on the Ti content but deboronated slightly (Table 5, Nos. 1 and 3). After the sequence of PI treatment and calcination, the Ti active sites were still tetrahedrally isolated in the zeolite framework, as evidenced by the UV–vis spectra (Fig. 11B). A slight blue shift was observed for the UV band of Ti-MWW modified by PI treatment, likely due to decreased water adsorption on this sample with a higher hydrophobicity.

Table 5
Physicochemical properties of Ti-MWW after piperidine treatment

No.	Catalyst	Si/Ti[a]	Si/B[a]	CHN[b] (wt%)	C/N[b]	OH amount[c] (a.u.)	Ti states[d]
1	Ti-MWW-HTS	37	39	–	–	100	Tetra.
2[e]	No. 1 + PI	ND	ND[f]	13.8	5.3	ND[f]	Tetra.
3	No. 2 + calcination	38	45	–	–	65	Tetra.

[a] Given by ICP.

[b] Given by CHN analyses.

[c] The relative amount of OH groups was determined from the IR band area of OH stretchings in the region of 3900–3000 cm^{-1}.

[d] Evaluated with UV–vis spectra. Tetra., tetrahedral Ti species.

[e] The treatment of Ti-MWW with piperidine was carried out at 1.0 SiO_2: 1.0 PI:10 H_2O at 443 K for 1 day.

[f] Not determined.

IR spectra in the region of hydroxyl stretching vibration provided more information regarding the structural rearrange-

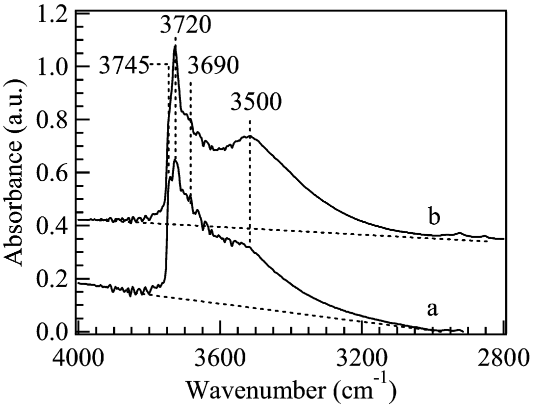


Fig. 13. IR spectra in region of hydroxyl stretching vibration of Ti-MWW before (a) and after PI treatment (b). The spectra were taken after evacuating the self-supported disk (30 mg in 20 mm diameter) at 773 K for 2 h. The spectra were normalized to the same intensity of 1880-cm^{-1} band due to the Si–O overtone of zeolite framework [27].

ment by PI treatment (Fig. 13). Ti-MWW showed a band at 3745 cm^{-1}, due to the external or terminal silanols on the crystal surface; a band at 3720 cm^{-1}, probably due to asymmetric hydroxyl-bonded silanols located in interlayers; and a band at 3690 cm^{-1} assigned to vicinal silanols and a band at 3500 cm^{-1} assigned to silanol nests, both of which were hydrogen bonded [6,24]. The internal silanols in Ti-MWW should originate from the defect sites as a result of deboronation and incomplete interlayer dehydroxylation. After the PI treatment, the OH stretching vibrations decreased in intensity, particularly at the 3690-cm^{-1} and 3500-cm^{-1} bands (Fig. 13b). In the band area integrated in the 3000–3900 cm^{-1} region, about 35% of hydroxyl groups were removed by the treatment with PI (Table 5). Thus, it can be deduced that during the reversible structural change from 3D MWW to lamellar precursor, a framework rearrangement occurred following the migration of Si into the hydroxyl nests or partial dehydroxylation of vicinal silanols to form a Si–O–Si linkage. This rearrangement, or so-called "framework recrystallization," is commonly observed in the dealumination course of zeolites by steaming [25–27]. The removal of hydroxyl nests and structural mending leads to a Ti-MWW catalyst with a defectless, more rigid, and more hydrophobic framework (Fig. 12). This would be advantageous in lowering the affinity and adsorption to the framework by the hydroxyl group-containing heavy byproducts formed in ALC epoxidation. The blocking of pores and the covering of Ti active sites are then effectively eased, leading to prolonged catalyst life.

4. Conclusion

Ti-MWW is an effective catalyst for the epoxidation of ALC to ECH with H_2O_2. Ti-MWW favors MeCN or acetone as a suitable solvent, whereas TS-1 prefers MeOH. The different solvent effects result in different behaviors in epoxide solvolysis. Ti-MWW is capable of giving conversion and selectivity both as high as 99%. One of the main heavy species, 3-chloro-1,2-propanediol, has a negative effect on the reuse of TS-1 and Ti-MWW. A secondary synthesis of piperidine treatment causes a structural rearrangement by partially removing the silanol defect sites, which enhances framework hydrophobicity and improves the stability and lifetime of Ti-MWW. This study indicates that Ti-MWW is a promising catalyst for the selective synthesis of ECH.

Acknowledgments

Financial support was provided by the Science and Technology Commission of Shanghai Municipality (05DZ22306), Program for New Century Excellent Talents in University (NCET-04-0423), Pujiang Program of Shanghai Municipality (05PJ14041), 973 Program (2006CB202508), and National Natural Science Foundation of China (20473027 and 20673038).

References

[1] G. Bellussi, M.S. Rigguto, Stud. Surf. Sci. Catal. 137 (2001) 911.
[2] B. Notari, Adv. Catal. 41 (1996) 253.
[3] H. Ichihashi, Catal. Catal. 47 (2005) 190.
[4] B. Ford, Chem. Mark. Rep. 269 (2006) 24.
[5] P. Wu, T. Tatsumi, T. Komatsu, T. Yashima, Chem. Lett. (2000) 774.
[6] P. Wu, T. Tatsumi, T. Komatsu, T. Yashima, J. Catal. 202 (2001) 245.
[7] P. Wu, T. Tatsumi, Chem. Commun. (2001) 897.
[8] M.E. Leonowicz, J.A. Lawton, S.L. Lawton, Science 264 (1994) 1910.
[9] P. Wu, T. Tatsumi, J. Catal. 214 (2003) 317.
[10] P. Wu, Y. Liu, M. He, T. Tatsumi, J. Catal. 228 (2004) 183.
[11] F. Song, Y. Liu, H. Wu, M. He, P. Wu, T. Tatsumi, J. Catal. 237 (2006) 359.
[12] H.X. Gao, W.K. Lu, Q.L. Chen, Chin. J. Catal. 23 (2002) 3.
[13] H.X. Gao, G.X. Lu, J.S. Suo, S.B. Li, Appl. Catal. A 138 (1996) 27.
[14] Q.F. Wang, Z.T. Mi, Y.Q. Wang, L. Wang, J. Mol. Catal. A 229 (2005) 71.
[15] P. Wu, T. Tatsumi, T. Komatsu, T. Yashima, J. Phys. Chem. B 105 (2001) 2897.
[16] P. Wu, T. Tatsumi, Chem. Commun. (2002) 1026.
[17] T. Taramasso, G. Perego, B. Notari, U.S. Patent 441050 (1983), to Enichem.
[18] (a) P. Wu, T. Komatsu, T. Yashima, J. Phys. Chem. 100 (1996) 10316;
(b) P. Wu, T. Komatsu, T. Yashima, J. Catal. 168 (1997) 400.
[19] T. Blasco, M.A. Camblor, A. Corma, P. Esteve, J.M. Guil, A. Martínez, J.A. Perdigón-Melón, S. Valencia, J. Phys. Chem. B 102 (1998) 75.
[20] (a) G. Bellussi, A. Carati, M.G. Clerici, G. Maddinelli, R. Millini, J. Catal. 133 (1992) 220;
(b) M.G. Clerici, P. Ingallina, J. Catal. 140 (1993) 71.
[21] W.J. Kim, T.J. Kim, W.S. Ahn, Y.J. Lee, K.B. Yoon, Catal. Lett. 91 (2003) 123.
[22] (a) G.J. Hutchings, D.F. Lee, Chem. Commun. (1994) 1095;
(b) G.J. Hutchings, D.F. Lee, A.R. Minihan, Catal. Lett. 33 (1995) 369;
(c) G.J. Hutchings, D.F. Lee, A.R. Minihan, Catal. Lett. 39 (1996) 83.
[23] (a) L. Davies, P. McMorn, D. Bethell, P.C.B. Page, F. King, F.E. Hancock, G.J. Hutchings, Chem. Commun. (2000) 1807;
(b) L. Davies, P. McMorn, D. Bethell, P.C.B. Page, F. King, F.E. Hancock, G.J. Hutchings, Phys. Chem. Chem. Phys. 3 (2001) 632.
[24] G.P. Heitmann, G. Dahlhoff, W.F. Hölderich, J. Catal. 186 (1999) 12.
[25] G.T. Kerr, J. Phys. Chem. 73 (1969) 2780.
[26] P.K. Maher, F.D. Hunter, J. Scherzer, J. Adv. Chem. Ser. 101 (1971) 266.
[27] P. Wu, T. Komatsu, T. Yashima, J. Phys. Chem. 99 (1995) 10923.