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Selective liquid-phase oxidation of cyclopentene over MWW type titanosilicate

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Abstract

The epoxidation of cyclopentene has been carried out over titanosilicate catalysts of Ti-Beta, TS-1 and Ti-MWW. Ti-MWW exhibited the highest cyclopentene conversion and epoxide selectivity with either H_2O_2 or *tert*-butyl hydroperoxide as an oxidizing agent. The cyclopentene conversion depended greatly on the post treatment conditions. Acid-treated but uncalcined Ti-MWW gave cyclopentene conversion twice as high as the calcined one, while the epoxide selectivity was maintained at high levels in both cases. Various techniques such as XRD, UV–vis, ^{29}Si MAS NMR, N_2 adsorption and liquid-phase adsorption, and chemical analyses have verified consistently that the acid treatment removed the organic species located between the layers of MWW sheets, which made the interlayer entrance open and easily accessible to bulky molecules. Nevertheless, a further calcination led to a complete interlayer dehydroxyaltion and made the catalyst to be more effective for the epoxidation of linear alkenes but less active for the epoxidation of cyclic ones.

Keywords: Ti-MWW; Cyclopentene; Hydrogen peroxide; Liquid-phase epoxidation; Post modification

1. Introduction

Selective oxidations are among the most important reactions in the chemical industry. Particular efforts are being made to develop sustainable heterogeneous catalytic processes to replace those homogeneous and stoichiometrical reactions suffering serious environmental problems. The application of hydrogen peroxide to the oxidation of various organic chemicals has attracted much attention in recent years from the viewpoint of environmental and economical benefits, since it gives rise to an only byproduct of water and is less expensive and more available than the other oxidants such as peracids and organic hydroperoxides.

Over the last two decades, intensive researches have verified that the catalytic system of H_2O_2/Ti-containing zeolite is highly active and selective for the liquid-phase oxidations. MFI-type titanosilicate, TS-1, has been the most active catalyst for the oxidation of small substrates [1]. However, its medium-sized pores of 10-membered ring (MR) limit the application to the oxidations of the substrates and oxidants with relatively small molecular sizes. To overcome the disadvantages of TS-1, other titanosilicates with larger pore dimensions such as Ti-Beta, Ti-MOR, Ti-ITQ-7 and Ti-containing mesoporous materials have been developed by various methods [2–5]. Ti-Beta of 12-MR pores shows a remarkable activity for the epoxidation of cyclic alkenes but a low epoxide selectivity as a result of the solvolysis contributed by a high concentration of silanol groups on the lattice defect sites [2]. Ti-MOR has been shown to be active in the hydroxylation of bulky aromatics with H_2O_2 but not effective in the oxidation of alkenes. On the other hand, Ti-containing mesoporous molecular sieves generally are facing the distinct disadvantages of low hydrothermal stability, low intrinsic activity and easy leaching of Ti species due to their amorphous pore walls and high hydrophilicity derived from abundant surface silanol groups. More effective titanosilicates are thus urgent to be developed especially for the oxidation of bulky molecules in this field.

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We have succeeded in synthesizing a novel titanosilicate with the MWW topology (typically known as MCM-22) with boric acid as a crystallization-supporting agent [6]. The three-dimensional (3D) MWW structure, formed from a lamellar precursor as a result of dehydroxylation between the layered sheets upon calcination, is expected to supply suitable spaces for incorporating highly stable and accessible Ti species and then for selective oxidations. The supercages embedded interlayers and the 12-MR side cups penetrating into the crystals from the external surface have already been demonstrated to serve as open reaction spaces in the disproportionation of toluene [7] and in the alkylation of benzene [8] in the case of MWW aluminosilicate. Owing to these unique structural properties, Ti-MWW proves to be active and selective in the epoxidation both linear and cyclic alkenes [9]; exhibits an extremely high *trans*-stereoselectivity in the epoxidation of olefinic geometrical isomers [10]; and catalyzes effectively the functionalized alkenes such as allyl alcohol and diallyl ether [11]. Despite of the catalytic effectiveness already achieved with Ti-MWW, once the 3D MWW structure is formed, the pore windows connecting to the supercages turn to be 10-MR which makes the catalytic activity not high as expected particular for bulky molecules.

In this study, we have focused on the epoxidation of cyclopentene over the titanosilicates with different framework structures with H_2O_2 or *tert*-butyl hydroperoxide (TBHP) with the purpose to synthesize cyclopentene epoxide actively and selectively, an important chemical intermediate in pharmaceutical and fragrant industry. In particular, the effects of post treatment on the catalytic properties of Ti-MWW have been investigated. Liquid-phase adsorption experiments and active site investigation using linear and cyclic alkene substrates have revealed Ti-MWW is superior in both alkene conversion and epoxide selectivity.

2. Experimental

2.1. Preparation of catalysts

Ti-MWW was hydrothermally synthesized following the procedures reported elsewhere [6]. The preparation involves the synthesis of Ti-containing lamellar precursor (Si/Ti molar ratios of 100, 70, 50, 30, 20) with piperidine (PI) as a structure-directing agent (SDA) and using boric acid as a crystallization-supporting agent, and then the removal of extraframework Ti species by refluxing the lamellar precursor in 2.0 M HNO_3 solution for 18 h. The acid-treated sample was washed with deionized water and subsequently dried at 373 K (Ti-MWW-dry) or further calcined at 823 K (Ti-MWW-cal). Other titanosilicates for control experiments, TS-1 [12] and Al-free Ti-Beta [13] were hydrothermally synthesized as reported previously. Table 1 lists several representative Ti-MWW samples together TS-1 and Ti-Beta.

Table 1
Physicochemical properties of various titanosilicates

Number	Sample	Chemical composition			N_2 adsorption	
		Si/Ti	Si/B	Si/N[a]	A_{LANG} ($m^2 g^{-1}$)	V_P ($cm^3 g^{-1}$)
1	Ti-MWW1-dry	34	30	26	530	0.12
2	Ti-MWW1-cal	34	30	∝	659	0.15
3	Ti-MWW2-dry	66	35	22	486	0.11
4	Ti-MWW2-cal	66	35	∝	576	0.13
5	Ti-MWW3-dry	132	32	21	433	0.10
6	Ti-MWW3-cal	132	32	∝	612	0.14
7	Ti-Beta	35	–	–	621	0.14
8	TS-1	38	–	–	583	0.13

[a] Determined by CHN chemical analyses.

2.2. Characterization methods

The samples were characterized by X-ray diffraction (XRD) on a MAC Science MX-Labo diffractometer, UV–vis spectroscopy on a JASCO V-550 spectrometer, ICP elemental analysis on a Shimadzu ICPS-8000E ICP atomic emission spectrometer, N_2 adsorption on a BEL SORP 28SA instrument, CHN elemental analysis on a Perkin-Elmer 2400 series II CHNS/O analyzer, and solid-state NMR spectroscopy on a JEOL JNM-ECA 400 spectrometer. ^{29}Si MAS NMR spectra were recorded at 79.5 MHz. Chemical shifts were referenced to an external standard of polydimethylsilane. A spinning rate 5.0 kHz, recycle delay time of 30.0 s, pulse widths of 7.0 μs, and 1200–4500 scans were taken. For some samples, magnetization transfer from protons to the resonant nuclei (cross-polarization) was achieved using a single contact time of 5 ms and a repetition time of 30 s. The ^{29}Si MAS NMR spectra were deconvoluted in terms of mixed Gaussian–Lorentzian equations with a JOEL software. ^{11}B MAS NMR spectra were recorded at 128.0 MHz, by using a 1.33 μs pulse length and a 2 s repetition time. Chemical shifts are referenced to H_3BO_3 as an external standard with a chemical shift of +19.2 ppm.

The liquid-phase adsorption was carried out in a glass cell (5 mL) using 1,3,5-triisopropylbenzene (TIPB) as a solvent following the procedures given elsewhere [10,14]. In a typical run, 0.1 g of adsorbent was stirred continuously in 2 g of adsorbate solution (2 wt.% of cyclopentene in TIPB). The cell temperature was maintained at 273 K with an ice-water bath. A small portion of the liquid (about 0.1 μL) was taken periodically and analyzed with gas chromatography to determine the adsorption amount.

2.3. Catalytic reactions

The liquid-phase oxidation of alkenes with hydrogen peroxide was carried out in a pear shape flask (20 mL) fitted with a condenser and a magnetic stirrer. For a typical run, a mixture of 0.05 g of catalyst, 10 mmol of alkene, 10 mmol of H_2O_2 (31 wt.% aqueous solution) or 10 mmol of TBHP (70 wt.% aqueous solution), and 10 mL of solvent was heated and agitated vigorously at a desirable temperature. The reaction mixture was analyzed with GC (Shimadzu 14 A) equipped with a 50 m OV-1 capillary column and an FID detector. The products were identified on a gas chromatograph–mass spectrometer (JEOL DATUM-JMS-AX500) or with authentic samples. The amount of H_2O_2 remaining in the reaction mixture was quantified by the titration with 0.1 M $Ce(SO_4)_2$ solution.

3. Results and discussion

3.1. Physicochemical properties of Ti-MWW, TS-1 and Ti-Beta

The XRD pattern of the as-synthesized Ti-MWW (Si/Ti = 30) is consistent with that of the MWW lamellar precursor (Fig. 1a). The 001 and 002 diffraction lines are characteristic of a layered structure along the *c*-direction, which is composed of incomplete dehydroxylated MWW sheets. Other peaks are related to the crystalline sheets parallel to the *ab*-planes. When the precursor was acid-treated and dried only, the intensity of the 001 and 002 lines decreased as a result of partial disappearance of the lamellar structure (Fig. 1b). The acid treatment removed a part of boron together with some structure directing agent (SDA) of piperidine (PI) intercalating the sheets. This then would cause the formation of T–O–T linkage bonds partially between the layers. In fact, ICP and CHN analyses indicated that the as-synthesized Ti-MWW samples had an Si/B ratio of 10–13 and an Si/N ratio of ca. 11. Upon acid treatment, the ratios increased to above 30 and 21–26, respectively (Table 1, No. 1–6). More than 60% of boron and 50% of PI have been extracted out of the MWW crystals by the acid treatment. Those residual PI species are presumed to be mainly closed within the intralayer 10-MR channels embedded within the MWW sheets. Further calcination at 823 K on the acid-treated sample led to a complete removal of the organic species. Meanwhile, the 001 and 002 XRD lines disappeared while the other lines (for example, 100, 101 and 102 lines etc.) increasing in intensity (Fig. 1c). The interlayer dehydroxylation induced a structural change essentially along the *c*-axis, which resulted in a XRD pattern totally identical to the 3D MWW structure. The formation of ordered linkages between the sheets constructed the 10-MR pores connected to the supercages, which are expected to be not so accessible as uncalcined samples.

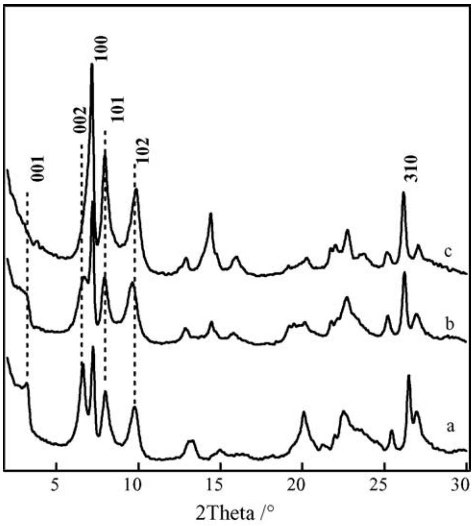


Fig. 1. XRD patterns of Ti-MWW lamellar precursor (Si/Ti = 30) (a), acid-treated precursor, Ti-MWW-dry (b), and further calcined sample, Ti-MWW-cal (c).

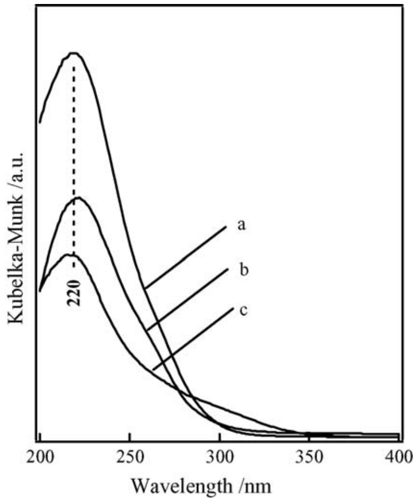


Fig. 2. UV–vis spectra of Ti-Beta (a), Ti-MWW1-cal (b) and TS-1 (c).

The specific surface area and pore volume determined by nitrogen adsorption isotherm at 77 K were in the range of 576–660 $m^2\ g^{-1}$and 0.13–0.15 $cm^3\ g^{-1}$ for Ti-MWW-cal samples, while in the range of 433–550 $m^2\ g^{-1}$ and 0.10–0.13 $cm^3\ g^{-1}$ for Ti-MWW-dry samples (Table 1). This difference is reasonable because not all of the pores in dried samples were available to N_2 adsorption. In the case of Ti-MWW-dry, the intralayer sinusoidal 10-MR channels were still occupied by residual SDA species.

The UV–vis diffuse reflection spectra showed that the Ti species in TS-1, Ti-beta, and Ti-MWW-cal exhibited only a narrow band around 220 nm (Fig. 2). The 220 nm band, resulting from the charge transfer from the excitation of an oxygen "2p" electron in the valence band to the empty "d" orbital of titanium ions, is widely found in the spectra of Ti-

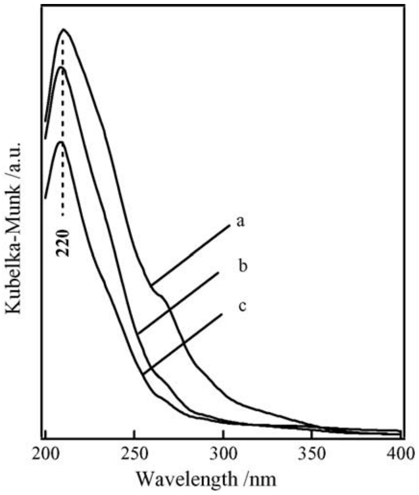


Fig. 3. UV–vis spectra of Ti-MWW-dry samples with an Si/Ti ratio of 34 (a), 66 (b) and 123 (c).

substituted zeoiltes and is characteristic of tetrahedrally coordinated Ti in the framework lattice [1]. Thus, all these titanosilicates contained mostly the tetrahedral framework Ti sites. It should be noted that the states of Ti in Ti-MWW was independent of the calcination since Fig. 3 clearly verifies that Ti-MWW-dry samples with various Ti contents showed also the band at 220 nm attributed to tetrahedral Ti.

^{29}Si and ^{11}B MAS NMR measurements of Ti-MWW have been conducted. The ^{29}Si MAS NMR spectra showed that the framework Si occupied at least 5 crystallographically nonequivalent T sites in MWW structure (Fig. 4A), which is very same as that observed in MCM-22 [15]. The lines at chemical shift of −105.1, −110.2, −113.1, −115.3 and −118.5 ppm (accuracy ± 0.3 ppm) are attributed to the Q^4 sites. Concerning the assignment of the line at −96.0 ppm, the cross-polarization (CP) experiment was performed. The intensity of the line at −96.0 ppm was enhanced by about 5 times with CP measurement, indicating an assignment to the Q^3 site [$(SiO)_3SiOH$]. Ti-MWW-dry showed a more intensive Q^3 line than Ti-MWW-cal. By deconvoluting the spectra, the amount of Q^3 of Ti-MWW-dry and Ti-MWW-cal was about 5% and 1% of total Si sites, respectively. Thus, the interlayer dehydroxylation is assumed to be incomplete in Ti-MWW-dry samples.

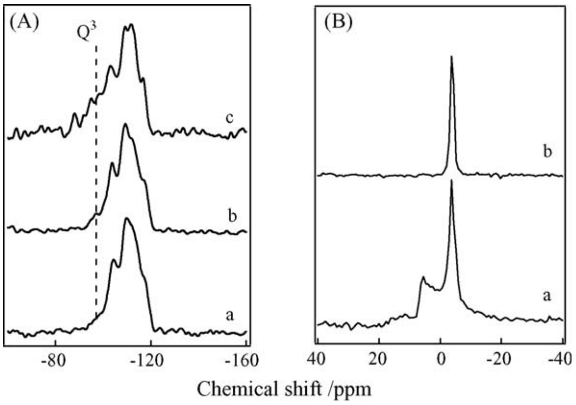


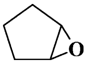
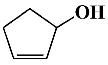
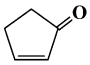
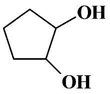
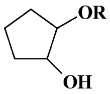
Fig. 4. ^{29}Si MAS NMR spectra (A) and ^{11}B MAS NMR spectra of Ti-MWW1-cal (a) and Ti-MWW1-dry (b) together with CP spectrum of Ti-MWW1-dry (c).

The ^{11}B MAS NMR spectra of the dried titanoborosilicate MWW samples are shown in Fig. 4B. The line at −3.6 ppm, assigned to BO_4 tetrahedra in the zeolite framework, was observed for both dried and calcined samples. The line position was the same as that in the spectrum of B-MFI [16]. In addition, the calcined Ti-MWW samples also exhibited another signal at + 5.5 ppm (Fig. 4B, b), which is attributed to trigonal boron (BO_3) [17]. The state change of boron suggests that a part of boron species were unstable because of a too small ionic radius, and then were excluded out of the framework readily by the calcination.

3.2. Epoxidation of cyclopentene over titanosilicates with H_2O_2

Cyclopentene was epoxidized over three kinds of titanosilicate catalysts by H_2O_2 in several representative solvents (Table 2). Besides cyclopentene oxide, the products due to the oxide solvolysis and the allylic oxidation were also observed. These titanosilicates exhibited greatly different solvent effects. From the viewpoint of catalytic activity, Ti-MWW favored the aprotic solvent of MeCN, while MeOH proved to be a suitable solvent for TS-1 and Ti-Beta. Taking account of oxide selectivity as well, Ti-MWW was capable of showing a selectivity of ca. 93% for oxide in MeCN, and thus it was obviously the most effective catalyst for the production of cyclopenten oxide. On Ti-Beta containing a high portion of

Table 2
Epoxidation of cyclopentene over titanosilicates with H_2O_2 as an oxidant[a]

Catalyst	Conv. (mol%)	Selectivity (mol%)				
						
CH_3CN						
Ti-Beta	9.9	61.1	8.1	20.0	10.8	0
TS-1	13.3	91.8	1.9	5.3	1.0	0
Ti-MWW-dry	25.3	92.9	3.2	1.5	2.4	0
Acetone						
Ti-Beta	9.0	63.2	8.9	18.2	9.7	0
TS-1	10.3	72.6	8.8	17.0	1.6	0
Ti-MWW-dry	17.5	91.8	4.3	2.8	1.1	0
CH_3OH						
Ti-Beta	11.9	37.3	5.7	6.5	4.0	46.1
TS-1	16.1	70.6	2.8	3.3	2.6	20.7
Ti-MWW-dry	25.4	69.2	2.7	2.6	1.8	23.7
C_2H_5OH						
Ti-Beta	11.8	35.5	2.8	4.8	33.9	23.0
TS-1	14.3	52.8	12.9	6.3	20.3	7.7
Ti-MWW-dry	12.6	91.2	1.7	5.3	1.8	0

[a] Reaction conditions: cat., 50 mg; cyclopentene, 10 mmol; H_2O_2, 10 mmol; solvent, 10 mL; temp., 313 K; time, 2 h. The Si/Ti ratio was 35 for Ti-Beta, 48 for TS-1 and 34 for Ti-MWW-dry, respectively.

hydroxyl groups in the framework, the ring opening due to the acid-catalyzed hydrolysis of oxide occurred more easily independent of the solvents adopted. In a protic solvent of MeOH, TS-1 showed a relatively high conversion for cyclopentene, but accelerated greatly the solvolysis of the oxide. Thus, we have found that the titanosilicate with the MWW structure is a catalyst of choice for the active and selective epoxidation of cyclopentene with H_2O_2.

3.3. A Comparison of reaction catalytic activity between Ti-MWW-dry and Ti-MWW-cal

Ti-MWW exhibited higher cyclopentene conversion and cyclopentene epoxide selectivity than Ti-Beta and TS-1 catalyst as shown in Table 2. It should be noted that the activity of Ti-MWW catalyst depended greatly on the post treatment conditions particularly the calcination. The catalytic activity has been compared between Ti-MWW-dry and Ti-MWW-cal by preparing a series of catalysts with various Ti contents. The conversion of cyclopentene increased reasonably with increasing Ti content for both kinds of Ti-MWW catalysts when the reaction was carried out with H_2O_2 under the same conditions (Fig. 5). Obviously Ti-MWW-dry was superior to Ti-MWW-cal at a same level of Ti content. The selectivity to cyclopentene epoxide was generally higher than 90% on both Ti-MWW catalysts.

The difference in the catalytic activity is assumed to be due to the presence of more lamellar structure and then open entrance window in Ti-MWW-dry samples, which allows the substrate with relatively bulky molecular sizes reach the Ti active sites more easily. Previous XRD patterns confirmed that the MWW lamellar structure was retained partially after the acid treatment and was almost removed by the further calcinations (Fig. 1). On the other hand, the ^{29}Si MAS NMR spectra indicated that Ti-MWW-dry sample contained more silanol groups than Ti-MWW-dry, as evidenced by a more intensive Q^3 peak in the spectrum of the former (Fig. 4A). These results verify that the interlay dehydroxylation is incomplete in Ti-MWW-dry and the interlayer pores windows have not been totally constructed to 10-MR pores.

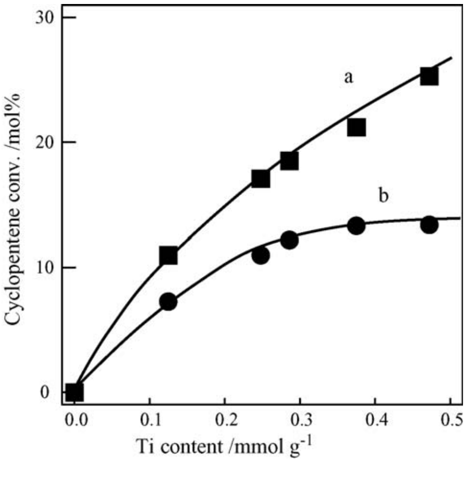


Fig. 5. Dependence of cyclopentene conversion on the Ti content of Ti-MWW-dry (a) and Ti-MWW-cal (b). Reaction conditions: solvent, MeCN; others, see Table 1.

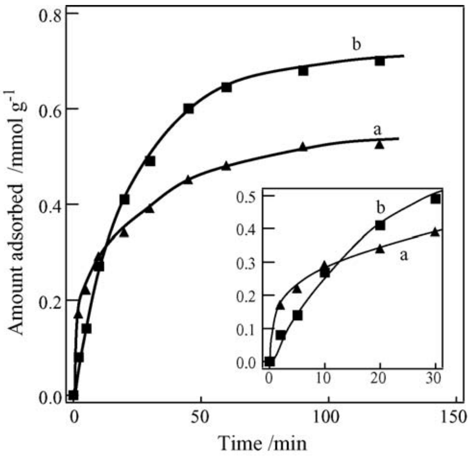


Fig. 6. Liquid-phase adsorption of cyclopentene on Ti-MWW1-dry and Ti-MWW1-cal (b). The inset shows the change of adsorption amount at the initial stage. Adsorption conditions: adsorbent, 0.1 g; 2 wt.% cyclopentene in 1,3,5-TIPB, 2 g; temp., 273 K.

This issue has been studied further by the liquid-phase adsorption. The liquid-phase adsorption of cyclopentene has been carried out in a solvent of TIPB, which is considered not to adsorb into 12-MR pores of zeolites because of a large enough molecular dimension [14]. As depicted in Fig. 6, Ti-MWW-dry sample adsorbed cyclopentene more rapidly than Ti-MWW-cal at initial stage (up to 10 min). The cyclopentene adsorption amount was leveled off within 1 h for both samples. Ti-MWW-cal showed an adsorption capacity about 1.5 times that of Ti-MWW-dry. The high saturated adsorption capacity was consistent to above N_2 adsorption which showed Ti-MWW-cal had a higher specific surface area and pore volume (Table 1), since it did not contain any organic SDA species of PI in comparison to Ti-MWW-dry. It is deduced from above results that the difference in adsorption rate should be firmly related to the pore size of titanosilicate. The acid treatment would remove effectively the extraframework Ti species together with PI molecules intercalating the MWW sheets. Meanwhile, by avoiding the dehydroxylation between the layers at high temperature, the interlayer entrance is kept open and is penetrated easily by bulky molecules such as cyclic alkenes, which subsequently makes the tetrahedral Ti active sites available to the oxidation reaction. As a result, although with a lower surface area and pore volume, Ti-MWW-dry with larger pore is superior to the calcined catalysts in the oxidation of cyclic alkenes.

The presence of large pores in Ti-MWW-dry and their importance in the oxidation involving large molecules have been investigated by the cyclopentene with H_2O_2 or TBHP as an oxidant. In comparison to H_2O_2, bulky TBHP greatly retarded the catalytic activity of Ti-MWW-cal, whereas Ti-MWW-dry showed comparable conversion for both oxidants (Table 3, No. 1–4). The catalytic performance of large pore Ti-Beta was also little affected by the molecular sizes of the oxidants, but medium pore TS-1 was much less active with bulky TBHP as it propose serious steric restriction (Table 3, No. 5–8). These results confirm that Ti-MWW-dry is characteristic of large pore zeolites.

Table 3
A comparison of cyclopentene epoxidation with H_2O_2 or TBHP over various titanosilicates[a]

Number	Catalyst	Oxidant	Conv. (mol%)	Selectivity (mol%)		
				Epoxide	Diol	Allyl[b]
1	Ti-MWW1-dry	H_2O_2	24.5	92.9	2.4	4.7
2	Ti-MWW1-cal	H_2O_2	13.4	88.7	6.0	5.3
3	Ti-MWW1-dry	TBHP	23.4	92.9	0.1	7.0
4	Ti-MWW1-cal	TBHP	5.3	88.7	1.5	9.8
5	Ti-Beta	H_2O_2	9.9	61.1	10.8	28.1
6	Ti-Beta	TBHP	9.6	57.0	0	43.0
7	TS-1	H_2O_2	13.3	91.8	1.0	6.2
8	TS-1	TBHP	3.7	32.9	0	67.1

[a] Reaction conditions: cat. 50 mg; cyclopentene, 10 mmol; oxidant, 10 mmol; MeCN, 10 mL; temp., 313 K; time 2 h.
[b] Products of allylic oxidation.

The catalytic properties of the dried and calcined Ti-MWW catalyst have been further compared in the oxidation of other alkene substrates (Table 4). In comparison to cyclopentene, the conversion of Ti-MWW-dry was slightly decreased in the case of cyclohexene which caused the problem of diffusion restriction because of a larger molecular size. This phenomenon was more obvious for Ti-MWW-cal with narrow interlayer entrance, since it showed a conversion of cyclohexene only half of the cyclopentene conversion. In contrast, for the linear chain alkenes with both terminal and internal C=C bonds, Ti-MWW-cal catalyst showed a much higher conversion than the dried one. This is because all of the Ti sites even those located in the intralayer sinusoidal 10-MR channels in the calcined catalyst could serve as active sites to the terminal and internal straight chain alkenes. The linear alkenes free of the severe restriction proposed by the zeolite channels are assumed to diffuse into all the channels of 3D Ti-MWW-cal. On the other hand, although having open interlayer entrance, the 10-MR channels of Ti-MWW-dry was partially closed by the presence of residual PI species and not accessible to linear alkene molecules, which results in a lower catalytic activity. Concerning the improvement of catalytic performance for bulky substrates, it is an effective way to keep the interlay open by acid treatment but without further calcinations.

The reuse and stability of Ti-MWW-dry have been checked in the oxidation of cyclopentene. The reaction was begun with an enlarged scale, and the used catalyst was subjected to ICP analyses and repeated reactions under the same conditions. As shown in Table 5, No obvious Ti leaching occurred after the repeated reaction while the content of boron was gradually decreased because of the low stability related to its too small ionic radius. The used catalyst showed similar XRD pattern to the fresh one, that is, the 001 and 002 diffraction peaks due to lamellar structure remained, indicating no obvious structural changes such as peeling off layers occurred. The catalyst maintained almost the catalytic activity and the selectivity to oxide after being reused for three times. A slight decrease in conversion is probably due to a partial deposition of by products with high boiling temperature within the channels of Ti-MWW catalyst. Nevertheless, Ti-MWW-dry has proved to serve as a stable catalyst for the epoxidation of bulky alkenes.

Table 4
Epoxidation of various alkenes over Ti-MWW[a]

Substrates	Alkene conversion (mol%)	
	Ti-MWW1-dry	Ti-MWW1-cal
Cyclopentene	24.5	16.9
Cyclohexene	18.8	7.8
1-Hexene	26.2	53.7
2-Hexene	40.6	66.2

[a] Reaction conditions: cat. 50 mg; alkene, 10 mmol; H_2O_2 10 mmol; temp., 313 K; time, 2 h.

Table 5
Reuse of Ti-MWW-dry in the epoxidation of cyclopentene with H_2O_2[a]

Reused times	Si/Ti	Si/B	Conv (mol%)	TON (mol (mol Ti)$^{-1}$)	Selectivity (mol%)		
					Epoxide	Diol	Allyl[b]
Fresh	42	38	24.4	127	97.9	0	2.1
1	45	55	21.8	129	95.9	0	4.1
3	48	70	20.5	123	95.7	0	4.3

[a] Reaction conditions: cat. 50 mg.; cyclopentene, 10 mmol; H_2O_2, 10 mmol; MeCN, 10 mL; temp. 313 K; time 2 h.
[b] Products of allylic oxidation.

4. Conclusion

Ti-MWW proves to be a more effective catalyst than Ti-Beta and TS-1 for the epoxidation of cyclopentene. The catalytic performance of Ti-MWW for bulky substrates can be greatly improved by avoiding the interlayer dehydroxylation and then maintaining open pore windows. Acid treatment of Ti-MWW lamellar precursor is a useful way for preparing such an oxidation catalyst, which is stable and reusable.

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