Delamination of Ti-MWW and High Efficiency in Epoxidation of Alkenes with Various Molecular Sizes

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A new titanosilicate, named Del-Ti-MWW, has been prepared by delaminating the lamellar precursor of Ti-MWW, which is postsynthesized from highly deboronated MWW zeolite with the assistance of cyclic amine. The amount of organic base used for supporting surfactant in swelling the layered structure should be controlled carefully to delaminate efficiently without the collapse of the structure. Ultrasound treatment is demonstrated to delaminate the swollen material more completely. Del-Ti-MWW materials have a large surface area, which mitigates effectively the steric restrictions imposed by conventional microporous titanosilicates to bulky molecules. Del-Ti-MWW, maintaining the fundamental structure of MWW zeolite and tetrahedral Ti species in the framework position, proves to be superior to TS-1, Ti-Beta, three-dimensional Ti-MWW and even mesoporous Ti-MCM-41 in the epoxidation of a wide range of bulky alkenes with hydrogen peroxide.

Introduction

Epoxides are industrially important intermediates produced predominantly with use of stoichiometric reactants or homogeneous catalytic systems except for ethylene oxide. These production processes cause various environmental problems by producing a range of coproducts requiring separation or poststreatment for recycle or disposal. Greener processes are expected to arise from the titanosilicate/hydrogen peroxide catalytic systems where the reactions are operated heterogeneously and only water is coproduced. TS-1,[1] Ti-Beta,[2,3] Ti-MOR,[4] Ti-ITQ-7,[5] and Ti-MWW[6] are representative titanosilicates potentially applicable to the selective oxidation of a variety of organic compounds. Nevertheless, they are suffering significant disadvantages in the oxidation of bulky substrates owing to serious steric constraint imposed by their micropores. Ti-containing mesoporous molecular sieves with much more open reaction space, e.g. Ti-MCM-41[7] and Ti–MCM-48,[8] are more efficient in the oxidation of bulky alkenes as compared with microporous titanosilicates. Unfortunately, mesoporous titanosilicates are intrinsically less active and hydrothermally unstable, and moreover are facing fatal shortcomings of easy leaching of Ti active species fundamentally owing to the amorphous and hydrophilic nature of their silica walls. Thus, to meet the demands for clean manufacture of fine chemicals and pharmaceuticals, there is a search for new titanosilicate materials with pores large enough to accommodate bulky alkene substrates and consequently bulky transition states, but simultaneously maintain the characteristics of crystalline microporous materials.

Recently, a new approach has been developed through expanding and exfoliating the lamellar precursor of zeolites that has been practicably applied to MWW first and then to ferrierite and NU-6(2) to prepare micromesoporous hybrid materials of ITQ-2,[9] ITQ-6,[10] and ITQ-18,[11] respectively. All these delaminated materials have extremely high specific surface area, and as evidenced by IR investigation, they are still characteristic of zeolites in their basic structure and catalytic properties. Aluminosilicates of ITQ-2, ITQ-6, and ITQ-18 have been prepared by direct delamination of the corresponding lamellar precursors, but a titanosilicate derivative has been reported only for ITQ-6. TiITQ-6 shows higher catalytic activity in the epoxidation of a bulky molecule, 2-norbornene, than its Ti-FER parent or large-pore Ti-Beta, but TiITQ-6 seems to be less active than TS-1 for small molecules such as 1-hexene.[10] Concerning the MWW structure, TiITQ-2 has been prepared only by secondarily grafting titanocene on the external silanol groups of pure silica ITQ-2.[12] TiITQ-2 is active for epoxidation of alkenes with organic peroxides but inactive when H_2O_2 is used as an oxidating agent.

Recently, titanosilicate with the MWW topology (Ti-MWW) has been successfully prepared by direct hydrothermal synthesis with boric acid as a crystallization-supporting agent[6] and also by postsynthesis from highly deboronated MWW and Ti precursor through a reversible structural conversion.[13] Since the MWW structure consists of two independent 10-membered-ring (MR) channels, one of which contains 12 MR supercages and the other sinusoidal tortuosity, Ti-MWW proves to be superior to conventional TS-1 in the epoxidation of both linear and cyclic alkenes with H_2O_2.[14] The outstanding catalytic properties of Ti-MWW stimulated us to prepare a new multifunctional titanosilicate catalyst through structural delamination.[15] In the present study, detailed conditions have been investigated for preparing

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such a delaminated material; thorough characterizations have been carried out to clarify its structure; and furthermore its catalytic properties have been compared in the epoxidation of various alkenes with Ti-MWW, TS-1, Ti-Beta, and Ti-MCM-41.

Experimental Section

Preparation of Catalysts and Characterization Methods. The Ti-MWW lamellar precursor was postsynthesized by treating highly siliceous MWW (Si/B > 500) with an aqueous solution of piperidine and tetrabutyl orthotitanate (TBOT) at 443 K for 7 days following previously reported procedures.[13] Resultant B-free Ti-MWW (Si/Ti = 30) was refluxed in 2 M HNO_3 solution for 18 h to remove selectively the extraframework Ti species which were located mainly on the layer surface and were less stable upon acid washing in comparison with the tetrahedral Ti species incorporated in the framework.[6] Three-dimensional material, 3D Ti-MWW, was obtained by calcining the acid-treated precursor at 823 K for 10 h. The delamination was carried out following the method for ITQ-2[9] with slight modifications. Acid-washed but uncalcined Ti-MWW precursor (1 g) was treated at 353 K for 16 h in a solution of hexadecyl trimethylammonium bromide (CTMABr) (5.6 g), 22.5 wt % of aqueous tetrapropylammonium hydroxide (TPAOH) (5.0−6.5 g), and water (12 g). The solid product was collected by centrifugation or filtration. The organic species were removed by calcination at 823 K to give delaminated samples. In some cases, the samples swollen with CTMABr were treated in an ultrasound bath (300 W, 35 kHz) for 1 h, and the pH value of the mixture was adjusted below 2 before solid collection and further calcination. The resultant product was designated as Del-Ti-MWW.

Other titanosilicates for control experiments, TS-1[16] and Al-free Ti-Beta,[17] were hydrothermally synthesized. Ti-MCM-41 was synthesized by the gel equilibrium adjustment hydrolysis method from tetraethyl orthosilicate (TEOS) and TBOT.[18]

All samples were characterized by various techniques. X-ray diffraction (XRD) patterns were collected on a MAC Science MX-Labo diffractometer (Cu Kα radiation). The chemical composition of samples was analyzed with a Shimadzu ICPS-8000E ICP atomic emission spectrometer. N_2 adsorption isotherms were measured on a BEL SORP 28SA instrument. UV−visible spectra were collected on a JASCO V-550 spectrometer. IR spectra in the region of hydroxyl stretching vibration were measured with use of self-supporting wafers on a Perkin-Elmer 1700 series FT-IR spectrometer, while the spectra in the framework vibration region were recorded by using the KBr technique. In both cases, the wafers were pretreated by evacuation in a quartz IR cell equipped with KBr windows at 773 K for 1 h. Solid-state ^{29}Si MAS NMR spectra were recorded at ambient temperature on a JEOL JNM-ECA 400 spectrometer at a frequency of 79.5 MHz. Chemical shifts were referenced to an external standard of polydimethylsilane. A spinning rate of 5.0 kHz, recycle delay time of 30.0 s, pulse widths of 7.0 μs, and 1200 to 2700 scans were adopted. High-resolution electron microscopy (HREM) images were taken on a JEOL-3010 microscope with Cs = 0.6 mm and operated at an accelerating voltage of 300 KV after the sample was dispersed in ethanol (95 vol %) by the ultrasonic method and then dropped onto a carbon microgrid.

Epoxidation of Alkenes. The liquid-phase oxidation of alkenes with H_2O_2 was carried out in a pear-shaped flask (20 mL) connected to a condenser. For a typical run, a mixture of 0.010−0.025 g of catalyst, 2.5−5.0 mmol of alkenes, H_2O_2 (31
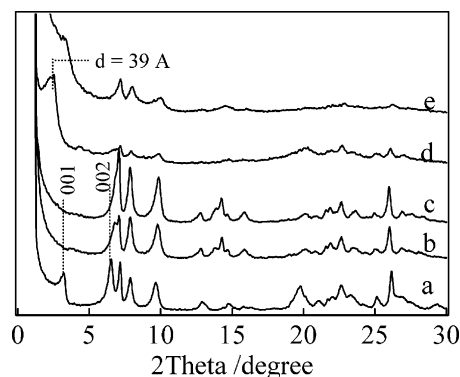

Figure 1. XRD patterns: (a) as-synthesized Ti-MWW, (b) the product from part a was refluxed with 2 M HNO_3, (c) he product from part b was calcined at 823 K, (d) he product from part b was treated with 5.6 g of CTMABr and 6.0 g of TPAOH at 353 K, and (e) he product from part d was calcined at 823 K.

wt % aqueous solution) of equal moles to alkenes, and 5−10 mL of acetonitrile solvent was agitated vigorously at a set temperature. The reaction mixture was analyzed on a gas chromatograph (Shimadzu 14 A) equipped with a 50 m OV-1 capillary column and an FID detector, and the products were quantified with cycloheptanone as an internal standard. The products were identified on a gas chromatograph−mass spectrometer (JEOL DATUM-JMS-AX500). The amount of H_2O_2 remaining in the reaction mixture was determined by titration with 0.1 M $Ce(SO_4)_2$ solution.

Results and Discussion

Preparation and Characterization of Del-Ti-MWW. The exfoliation of the lamellar zeolite structure results from a combination of expanding by surfactant and subsequent ultrasonic treatment.[9,10] The effect of surfactant on layer expansion depends greatly on the basicity during the surfactant treatment. The delamination of Ti-MWW was first carried out without ultrasonic treatment but focusing on how the amount of organic base affected the delamination degree.

The structural change during the delaminating treatment was monitored by XRD patterns; the representative data are shown in Figure 1. As-synthesized Ti-MWW showed diffraction lines at 2θ of 3.5 and 6.7 attributed to the 001 and 002 diffractions of the layers in the lamellar precursor (Figure 1a), which corresponds to a *d* spacing of 2.69 nm between the adjacent layers. Aluminosilicate ITQ-2 is generally obtained by the delamination of such a lamellar precursor.[9] One thing significantly different here is that as-synthesized Ti-MWW always contains some octahedrally coordinated Ti species distributed on the layer surface. To obtain active catalysts, these extraframework Ti species should be extracted with acid treatment first because upon calcination they finally form the catalytically inactive anatase phase, which generally accelerates the nonproductive decomposition of H_2O_2.[1,6] When the lamellar precursor was refluxed in 2 M HNO_3 and dried at 373 K, the extraframework Ti species were selectively removed as evidenced by UV−visible spectra (not shown). Simultaneously, the 001 and 002 diffractions nearly disappeared as a result of removal of organic amine species occluded between the layers (Figure 1b), which resulted in a decreased *d* spacing of 2.63 nm in comparison to that of the as-synthesized precursor. Despite the destruction of the layered structure by the acid treatment, the dehydroxylation of silanol groups between the layers still did not proceed to a large extent unless the acid-treated precursor was subjected to high-temperature calcination. In fact, the calcination completed
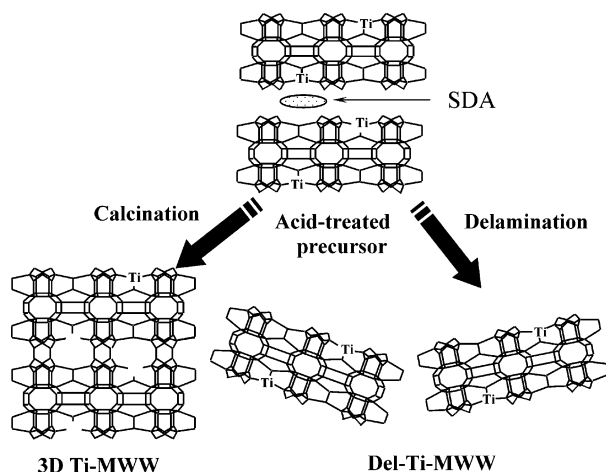
Figure 2. Possible structures of three-dimensional Ti-MWW and delaminated Ti-MWW obtained from acid-treated precursor.

Figure 3. XRD patterns of Del-Ti-MWW materials prepared with different weight ratios of TPAOH to acid-washed Ti-MWW precursor: (a) 5.0, (b) 5.6, (c) 6.0, (d) 6.3, and (e) 6.5.

the interlayer dehydroxylation to produce three-dimensional (3D) Ti-MWW with increased XRD intensity (Figure 1c). Subsequent treatment of the acid-treated Ti-MWW precursor in a basic solution of TPAOH and CTMABr cleaved the interlayer linkages of Si$-$O$-$Si bonds to Si$-$O$^-$ moieties and allowed the surfactant molecules to easily enter to intercalate the layers. This resulted in the formation of a swollen material with expanded layers, which exhibited a diffraction peak at lower 2θ with a corresponding d spacing of 3.90 nm (Figure 1d). The layer expansion is suggested to result from the interaction of Si$-$O$^-$ moieties with surfactant cations. After the swollen material was further calcined at 823 K to burn off any organic species, the expanded layered structure seriously collapsed, leading to a sample with extensively weakened diffractions due to the MWW structure (Figure 1e). This means a great loss of long-range order of the MWW zeolite. Nevertheless, this sample exhibited a greatly enlarged surface area in comparison to that of 3D Ti-MWW as shown later. On the basis of well-established knowledge about ITQ-2 and ITQ-6,[9,10] we have prepared the objective delaminated titanosilicate, Del-Ti-MWW, which essentially consists of thin sheets.

Based on the above XRD investigation, Figure 2 graphically illustrates the formation of 3D Ti-MWW and Del-Ti-MWW following different treatment sequences. The acid treatment removed the interlayer organic species only partially, which makes the sample characteristic of a layered structure. A subsequent calcination converts the sample completely into the 3D MWW structure. Nevertheless, it is possible to obtain thin sheet material by carrying out the delamination treatment on the uncalcined sample.

Figure 3 gives the XRD patterns of Del-Ti-MWW samples prepared by using different amounts of TPAOH but keeping other conditions the same. The diffraction peaks due to the MWW structure decreased in intensity with increasing amount of TPAOH. When the weight ratio of the aqueous TPAOH solution to acid-treated Ti-MWW was 5.6 or lower, the intensity of XRD diffraction was similar to that of 3D Ti-MWW (Figure 3, parts a and b), indicating that the 3D MWW structure was well retained. The diffractions due to MWW structure disappeared gradually with increasing amounts of TPAOH and finally were hardly observed (Figure 3c$-$e). Two possibilities are suggested to account for these phenomena. One is simply the delamination of layers into disordered thin sheets, while the other is the collapse of the structure in basic solution; partial dissolution of the solid samples is suggested since the product yield decreased from 93% to 82% when the weight ratio of
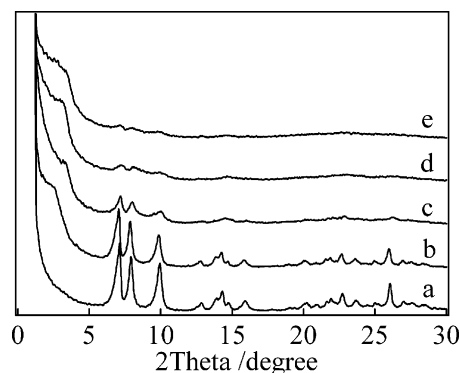
TPAOH to solid increased from 5 to 6.5. This kind of dissolution also may be controlled kinetically by treatment time and temperature, but is more dependent on the amount of base used. Nevertheless, all the Del-Ti-MWW samples had much larger specific surface area (791$-$997 m^2 g^{-1}) and external surface area (225$-$255 m^2 g^{-1}) than a 3D Ti-MWW sample (Table 1). The Si/Ti atomic ratio, on the other hand, decreased slightly with increasing amounts of TPAOH, probably because more silicon atoms than titanium atoms have been leached out of the zeolite framework in strongly basic media. SiO$_2$ is weakly acidic and TiO$_2$ is rather ampholytic as expected from the difference in electronegativity between the two elements. In fact, SiO$_2$ shows a lower isoelectonic point than TiO$_2$. Therefore, the former is more soluble in basic solution.

The effect of delamination on the catalytic performance has been investigated in the epoxidation of cycloalkenes with H$_2$O$_2$. Both cyclopentene and cyclododecene chosen here are considered to prefer the open reaction space to the intracrystalline one because of their molecular size. The delaminated catalyst showed a high turnover number (TON) for both cyclopentene and cyclododecene compared with that of conventional 3D Ti-MWW (Table 1, Nos. 1$-$4). The high activity of Del-Ti-MWW should come from the contribution of opener and accessible reaction space to large molecules produced by delamination. Among them, the Del-Ti-MWW sample prepared at a weight ratio of TPAOH to acid-treated Ti-MWW of 6 gave the best catalytic performance. However, TON tended to decrease for Del-Ti-MWW samples prepared with a larger amount of TPAOH despite increased surface area (Table 1, Nos. 5 and 6), mainly owing to severe destruction of the basic structure of the MWW zeolite. Therefore, for preparation of catalytically active delaminated catalysts, the treatment conditions, particularly the amount of base, should be controlled carefully to delaminate effectively without collapse of the zeolite framework.

The delamination cleaves part of the interlayer Si$-$O$-$Si linkage to produce a large number of acidic silanol groups.[9-11] However, such silanol groups scarcely contribute to the hydrolysis of cyclopentene oxide; the epoxide selectivity was always over 90%. Additionally, Table 1 shows that the trans-isomer of cyclododecene was selectively epoxidized when reaction was carried out over profoundly delaminated Ti-MWW catalysts, especially the one prepared by using 6.3 or 6.5 g of aqueous TPAOH solution (Table 1, Nos. 5 and 6).

The effects of ultrasonic treatment and acidification on the delamination have been investigated at the most suitable TPAOH to Ti-MWW ratio of 6. After Ti-MWW was treated in the solution of TPAOH and CTMABr, the resultant mixture was further ultrasonically treated and acidified with concentrated

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TABLE 1: Physicochemical and Catalytic Properties of 3D Ti-MWW and Del-Ti-MWW with Various Delamination Degrees[a]

| | | | surface area/m^2 g^{-1} | | TON/mol (mol Ti)$^{-1}$ | |
| | | | | | cyclopentene | cyclododecene |
no.	catalyst[b]	Si/Ti	total	external[c]	(epoxide sel./%)	(cis/trans 70/30)
1	3D Ti-MWW	46	520	163	89 (95)	9 (68/30)
2	Del-Ti-MWW (5.0)[d]	41	791	225	153 (96)	16 (57/43)
3	Del-Ti-MWW (5.6)[d]	40	839	235	160 (96)	18 (58/42)
4	Del-Ti-MWW (6.0)[d]	39	810	241	163 (97)	40 (55/45)
5	Del-Ti-MWW (6.3)[d]	35	893	255	93 (95)	34 (43/57)
6	Del-Ti-MWW (6.5)[d]	37	997	230	76 (91)	33 (40/60)
7	Del-Ti-MWW (6.0)[e]	39	885	240	174 (97)	39 (54/46)
8	Del-Ti-MWW (6.0)[f]	42	1075	421	300 (94)	57 (53/47)

[a] Reaction conditions: cat., 25 mg; cycloalkene, 2.5−5 mmol; H$_2$O$_2$, equal amount to cycloalkene; MeCN, 5−10 mL; temperature, 313 K for cyclopentene and 333 K for cyclododecene; time, 2 h. [b] The number in parentheses indicates the weight ratio of TPAOH to acid-treated Ti-MWW precursor. [c] Calculated from *t*-plot. [d] Delaminated without ultrasonic treatment and pH adjustment. [e] Delaminated with ultrasonic treatment but no pH adjustment. [f] Delaminated with ultrasonic treatment and pH adjustment.
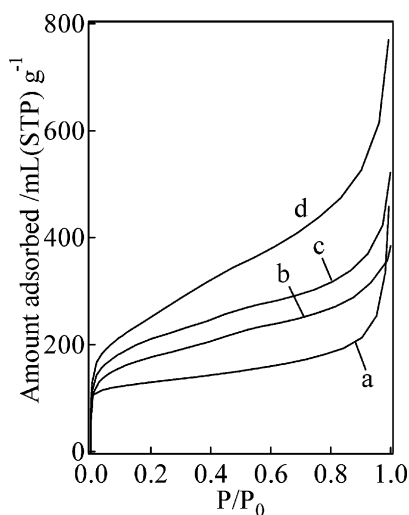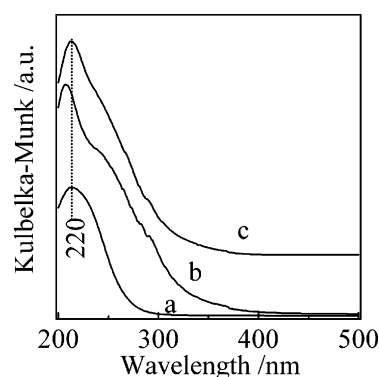

Figure 4. N$_2$ adsorption isotherms of 3D Ti-MWW and Del-Ti-MWW samples. The samples correspond to Nos. 1 (a), 4 (b), 7 (c), and 8 (d) in Table 1.

Figure 5. UV−visible diffuse reflectance spectra of 3D Ti-MWW and Del-Ti-MWW samples. The samples correspond to Nos. 1 (a), 7 (b), and 8 (c) in Table 1.

Figure 6. IR spectra in the region of hydroxyl stretching vibration after the evacuation at 773 K (A) and IR spectra in the framework vibration region taken with KBr techniques (B). The samples correspond to Nos. 1 (a) and 8 (b) in Table 1.
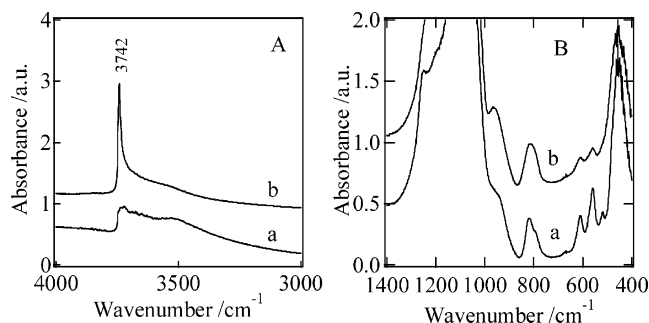
nitric acid to pH <2 (Table 1, Nos. 7 and 8). Compared with sample No. 4 in Table 1, no obvious difference was observed in XRD patterns (data not shown). However, the N$_2$ adsorption amount and hence the specific surface area increased following ultrasonic treatment and acidification (Figure 4). This suggests that ultrasonic treatment and acidification would force apart the expanded layer structure intercalated by surfactant molecules sufficiently to lead to profoundly delaminated materials. The effects of ultrasonic treatment and pH adjustment were also verified by catalytic performance. Obviously, delaminated sample thus prepared showed a superior catalytic activity for the epoxidation of both cyoclopentene and cyclododecene (Table 1, Nos. 4 and 8).

Both 3D Ti-MWW and Del-Ti-MWW showed in UV−visible spectra only an intense band around 220 nm but no obvious adsorption in the low-frequency region (Figure 5). The band below 220 nm is assigned to the monomeric tetrahedral Ti species in the zeolite framework.[1] Thus, the delamination did not disturb the microstructure of Ti species.

Del-Ti-MWW showed a greatly enhanced band at 3742 cm^{-1} in the hydroxyl stretching vibration region in comparison to that of 3D Ti-MWW (Figure 6A). The 3742-cm^{-1} band is attributed to the isolated silanol groups arising from the cleavage of Si−O−Si bonds between the layers, which is indicative of the formation of a large number of SiOH groups on the external surface of the delaminated material. In the framework vibration region (Figure 6B), 3D Ti-MWW showed an IR band around 960 cm^{-1} probably due to the framework Ti−O−Si vibration (1). On the other hand, Del-Ti-MWW showed a more intensive band at a similar position mainly due to an increase in silanol groups as a result of a phase delamination (9−11). Del-Ti-MWW still showed the fingerprint vibration due to the MWW structure in the region of 500−700 cm^{-1}, indicating the retention of basic structure of the MWW zeolite. The formation of hydroxyl groups is also consistent with ^{29}Si MAS NMR spectra where the Q^3 band at −102 ppm increased gradually in intensity with a progressive delamination (Figure 7).

The delamination was further characterized by HRTEM. In the case of 3D Ti-MWW, the images viewed along the *c* axis showed the stacking of MWW sheets with a thickness from 100 to 200 nm, corresponding to the thickness of platelet crystals (not shown). TEM images of Del-Ti-MWW along the *ab* plane (Figure 8) exhibited the crystalline materials consisting of
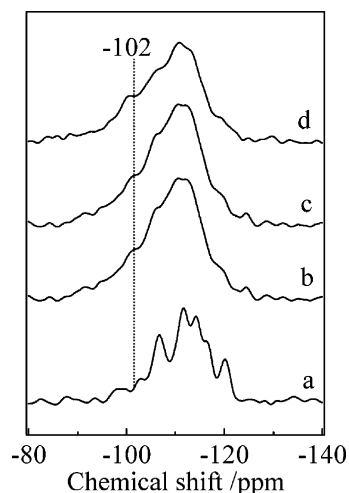
Figure 7. ^{29}Si MAS NMR spectra of 3D Ti-MWW and Del-Ti-MWW samples. The samples correspond to Nos. 1 (a), 4 (b), 7 (c), and 8 (d) in Table 1.

extremely fewer sheets than 3D Ti-MWW, even of single sheet (Figure 8A). All the samples prepared with different TPAOH amounts showed similar images of sheets forced apart to different levels. This is very similar to what has been reported on aluminosilicate form ITQ-1 (9). Therefore, HRTEM, IR, and ^{29}Si MAS NMR spectra verified consistently that the delamination really occurred to form a material with extremely high surface area accessible to bulky molecules and having the structure depicted in Figure 2.

A Comparison between Del-Ti-MWW and Various Titanosilicates in Alkene Epoxidation. The catalytic properties of Del-Ti-MWW have been compared with those of other titanosilicates in the epoxidation of alkenes with H_2O_2 (Table 2), where the alkene substrates chosen varied greatly in molecular size. The titanosilicates used here differed in structure, surface area, and crystalline nature. All these samples contained only tetrahedral Ti species as detected by UV−visible spectroscopy. With changing from linear alkenes to cycloalkenes and increasing molecular size of cycloalkenes, the TON decreased sharply for TS-1, Ti-Beta, and 3D Ti-MWW. This is due to a serious steric constraint of their pores, which made diffusion of the bulky substrate molecules difficult within the channels or even impossible into the channels. Ti-MCM-41 with mesoporous pores showed higher TON for cyclooctene and cyclododecene than the three titanosilicate zeolites, although it was nearly inactive for 1-hexene and 2-hexenes because of the amorphous and highly hydrophilic nature of the walls. This implies that the reaction space is extremely important for the reactions of bulky molecules. The delamination of Ti-MWW increased the TON greatly for both linear alkenes and cycloalkenes. Especially, the catalytic activity of the Del-Ti-MWW1 sample was about 6 times as high as that of 3D Ti-MWW in the case of cyclooctene and cyclododecene. Del-Ti-MWW samples turned out to be even superior to Ti-MCM-41 in the epoxidation of bulky substrates. When the epoxidation of cyclooctene was carried out under the same conditions but by adding 1 mmol of 2,4-dimethylqunoline (the amount is about 80 times that of Ti, being enough to poison all the Ti active sites), the reaction was greatly suppressed; the TON turned out to be 10 and 4 mol (mol of Ti)$^{-1}$ for Del-Ti-MWW1 and 3D-Ti-MWW, respectively. Since 2,4-dimethylqunoline with a relatively large molecule size is considered to poison selectively the Ti sites on the external surface, the poisoning experiment verified that the reactions involving bulky molecules need open reaction space, and emphasized the importance of increasing external surface for reactions of bulky molecules. Thus, the
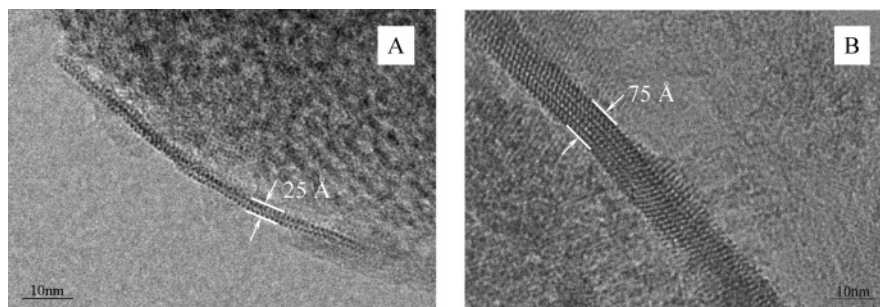
Figure 8. HRTEM images of single sheet (A) and three sheets (B) in Del-Ti-MWW. The sample corresponds to No. 6 in Table 1.

TABLE 2: Alkene Epoxidation with H_2O_2 over Various Titanosilicates[a]

			alkene epoxidation[b]									
			1-hexene		2-hexenes		cyclopentene		cyclooctene		cyclododecenes	
catalyst	Si/Ti	surface area/ m^2 g^{-1}	conv.	TON	conv.	TON (trans/cis 61/39)	conv.	TON	conv.	TON	conv.	TON (cis/trans 70/30)
Del-Ti-MWW1[c]	42	1075	51.8	1390	89.5	2352 (81/19)	58.9	306	28.2	147	20.7	57 (53/47)
Del-Ti-MWW2[d]	39	810	24.8	863	53.7	1305 (84/16)	34.7	163	14.4	76	16.4	40 (55/45)
3D Ti-MWW	46	520	29.3	934	40.5	1053 (83/17)	5.7	89	4.3	24	3.3	9 (68/32)
TS-1	34	525	12.0	49	24.5	105 (36/64)	16.3	69	1.6	7	1.2	3 (50/50)
Ti−Beta	35	621	6.0	26	9.2	40 (35/65)	9.9	4.3	4.6	20	1.9	4 (56/44)
Ti−MCM-41	46	1144	0.5	3	2.3	13 (67/33)	3.5	20	5.1	29	4.1	12 (63/37)

[a] Reaction conditions: cat., 10−25 mg; alkene, 2.5−10 mmol; H_2O_2, equal to the alkene amount; CH$_3$CN, 5−10 mL; temperature, 313 K for cyclopentene and 333 K for other substrates; time, 2 h. [b] Conv. in mol %; TON in mol (mol Ti)$^{-1}$, which was calculated by dividing the amount of alkene converted with the amount of Ti used. [c] Delaminated with ultrasonic treatment and pH adjustment. [d] Delaminated without ultrasonic treatment and pH adjustment.

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increase in activity after the delamination should be the benefit of high accessibility of Ti active sites in Del-Ti-MWW.

It should be noted that Del-Ti-MWW showed a much higher activity than 3D Ti-MWW but a comparably high trans selectivity in the epoxidation of 2-hexene isomers. The activity enhancement as a result of delamination was assumed to be the change in crystal size. Scanning electron micrographs showed that the delamination treatment in basic media partially destroyed the crystals to smaller ones. This would shorten the length of 10-ring channels, make the diffusion of substrates and products in the channels more rapid, and lead to high activity. This unique geometric selectivity has been reported to be possessed only by the MWW structure composed of sinusoidal 10MR channels.[14b] It is deduced from these results that Del-Ti-MWW retains the characteristics of basic structure, i.e., thin layer sheets of MWW zeolite, despite a great change of the bulk structure.

Conclusion

A new titanosilicate, Del-Ti-MWW, is successfully prepared by delaminating the Ti-MWW precursor. Del-Ti-MWW exhibits dual catalytic properties of micro- and mesoporous titanosilicates. The delamination leads to greatly improved TON for the epoxidation of bulky alkene molecules such as cyclooctene and cyclododecene, as well as linear alkenes, as a result of the preservation of zeolitic structure unit but enlarged accessible surface area. The outstanding catalytic properties applicable to a wide range of alkene substrates make Del-Ti-MWW a potential catalyst for the green synthesis of fine chemicals.

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