Highly Active Delaminated Ti-MWW for Epoxidation of Bulky Cycloalkenes with Hydrogen Peroxide

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A novel titanosilicate, prepared by the partial delamination of acid-treated Ti-MWW, possesses an extremely high specific surface area and proves to be a selective and active liquid-phase oxidation catalyst for bulky alkenes.

It is a main current in the research field of titanosilicate catalysts to look for new ones with open reaction space suitable for the liquid-phase oxidation of bulky organic chemicals with an environmentally friendly oxidant of hydrogen peroxide. Recently, a novel titanosilicate with the MWW topology (typically known as MCM-22), Ti-MWW, has been successfully hydrothermally synthesized using boric acid as a crystallization-supporting agent[1] or postsynthesized from highly deboronated MWW through a reversible structural conversion.[2] Ti-MWW, having a unique crystalline structure of supercages, 12-membered ring (MR) side pockets and sinusoidal 10 MR channels, exhibits superiority to conventional TS-1 and Ti-Beta in the epoxidation of both linear and cyclic alkenes.[3] Since the three-dimensional crystalline structure of MWW originates from a lamellar precursor, pillaring and delamination techniques have been adopted to convert its aluminosilicate, i.e. MCM-22 into a micro-mesoporous hybrid and a highly accessible material, respectively.[4,5] In this study, the delamination method has been applied to Ti-MWW for the first time to prepare a highly active epoxidation catalyst for bulky alkenes.

B-free Ti-MWW was prepared by following the procedures reported previously.[2] As-synthesized Ti-MWW (Si/Ti=30) was refluxed with 2 M HNO_3 for 18 h to remove the extraframework Ti species. The acid-washed Ti-MWW (1 g) was then treated at 353 K for 16 h in a mixture of hexadodecyl trimethylammonium bromide (5.6 g), 22.5 wt% tetrapropylammonium hydroxide (TPAOH) aqueous solution (3.8-5.6 g) and water (12 g). The resulting mixture was placed in an ultrasonic bath (300 W, 35 kHz) for 1 h, and its pH was then adjusted below 2 by using 2 M HNO_3 aqueous solution. The solid product was collected by centrifugation or filtration. The organic species were removed by the calcination at 823 K to yield the modified samples, Ti-MWW-m (No. 2-5 in Table 1). ICP analyses indicated that the modification dissolved a part of Ti out of the framework with increasing TPAOH amount. Nevertheless, the tetrahedral site of Ti species survived the above treatment since UV-vis spectroscopy showed that all the samples exhibited only the 220 nm band in their spectra.

The structural change during the treatment was traced by X-ray diffraction (XRD) patterns. After the acid treatment of as-synthesized Ti-MWW partially the 001 and 002 diffraction peaks due to the layered structure disappeared as a result of the removal of the organic structure-directing agent intercalated within the layers (Figures 1a and b). Subsequent calcination caused a complete dehydroxylation condensation to lead to the 3D MWW structure (Figure 1c). The treatment of acid-washed Ti-MWW with the surfactant solution expanded its layers to give diffraction with a *d* spacing of 3.8 nm (Figure 1d). After the expanded sample was subjected to the ultrasonic treatment followed by acidification and calcination, the expanded layers almost disappeared (Figure 1e). Although the modified samples maintained the MWW structure, their specific surface area turned out to be 742-873 $m^2 g^{-1}$, extremely larger than common Ti-MWW samples, which is in agreement with the case of ITQ-2, indicating that Ti-MWW has been delaminated partially to exhibit more accessible space.[5]

Table 1 compares the results of cyclopentene epoxidation with H_2O_2 over various titanosilicates. The products were mainly cyclopentene oxide together with diol resulting from the acidic hydrolysis of epoxide, and 2-cyclopentene-1-one and 2-cyclo-

Table 1. Physicochemical and catalytic properties of various titanosilicates[a]

No.	Catalyst	Si/Ti mole ratio	A_{LANG} /$m^2 g^{-1}$	Cyclopentene epoxidation Alkene conv. /mol%	TON /mol (mol Ti)$^{-1}$	Epoxide selec. /mol%	H_2O_2 conv. /mol%	H_2O_2 selec. /mol%
1	Ti-MWW[b]	46	559	15.7	95	95	15.9	99
2	Ti-MWW-m (3.8)[c]	48	783	32.6	193	98	33.4	98
3	Ti-MWW-m (4.9)[c]	56	742	29.4	202	97	30.2	98
4	Ti-MWW-m (5.1)[c]	61	873	27.1	203	96	27.4	96
5	Ti-MWW-m (5.6)[c]	68	839	25.6	213	96	27.0	93
6	TS-1[d]	36	525	17.3	77	94	20.5	83
7	Ti-Beta[e]	35	621	9.9	43	61	11.1	89

[a]Reaction conditions: cat., 25 mg; cyclopentene, 5 mmol; H_2O_2, 5 mmol; CH_3CN, 5 mL; temp., 313 K; time, 2 h. [b]As-synthesized material was refluxed with 2 M HNO_3 and calcined subsequently. [c]The number in parentheses indicates the amount of TPAOH used for 1 g of acid-treated Ti-MWW. [d]Synthesized according to Ref. 8. [e]Synthesized according to Ref. 9.

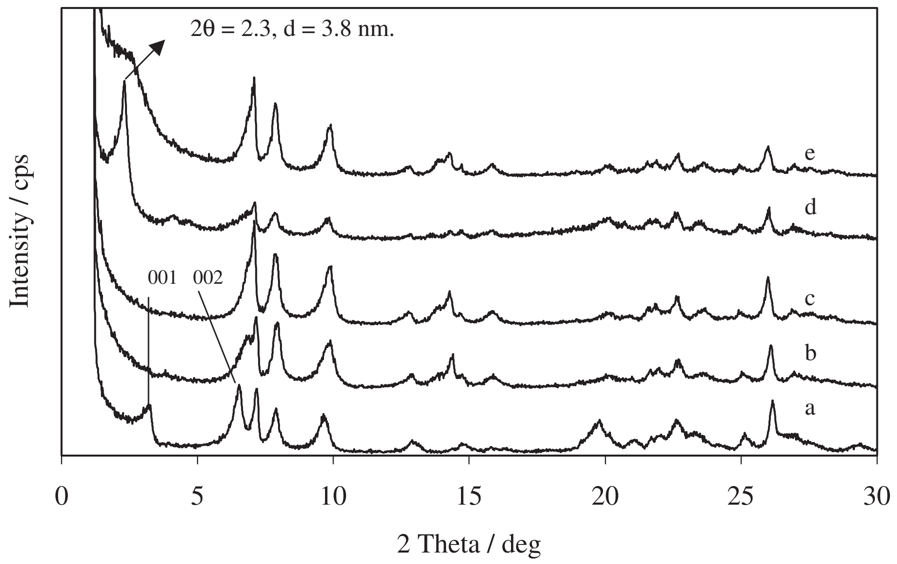

Figure 1. XRD patterns of as-synthesized Ti-MWW (a), sample a treated with 2 M HNO_3 and dried Ti-MWW (b), sample b calcined (c), sample b treated with surfactant and TPAOH solution (d), sample d subjected to ultrasound treatment and calcination (e).

pentene-1-ol produced from allylic oxidation. Ti-MWW showed higher specific activity than TS-1 and Ti-Beta, and also good selectivity to cyclopentene oxide and H_2O_2 efficiency. The inferior performance of larger pore Ti-Beta should be ascribed to its high hydrophilicity related to the hydroxyl groups on defect sites within the framework. The delamination, on the other hand, doubled the TON for cyclopentene conversion irrespective of the amount of TPAOH used (Table 1, No. 2-5). As the epoxidation of cylopentene favors the Ti active sites located in more accessible reaction space, the above results suggested that the delamination treatment has resulted in such sites. The delamination generally cleaves a part of Si-O-Si linkage to form a large amount of acidic silanol groups.[5–7] Interestingly, such silanol groups did not contribute to the hydrolysis of oxide product since the epoxide selectivity was maintained at a high level (>96 mol%).

Furthermore, the epoxidation of cyclooctene and cyclododecene were carried out to investigate the possibility of delaminated Ti-MWW catalyst for more bulky substrates (Table 2). Compared with cyclopentene epoxidation, the TON decreased sharply with increasing carbon number of cycloalkenes to 12 for both Ti-MWW and Ti-Beta, which is simply due to a more serious restriction of their pores on the diffusion of bulky molecules. Especially, Ti-Beta, without such open pores as the side pockets of Ti-MWW, was less active for cyclododecene oxidation. The activity of Ti-MWW-m was nearly two times as high as that of Ti-MWW for cyclooctene and cyclododecene. The higher activity of Ti-MWW-m proves that the delamination presents a benefit to produce more open and accessible reaction space to large molecules. A partial opening of the parts where the supercages are formed upon a normal calcination process is presumed to correspond to such space.

Table 2. Cycloalkene epoxidation with H_2O_2 over titanosilicates[a]

Catalyst	TON/mol (mol Ti)$^{-1}$	
	cyclooctene	cyclododecene
Ti-MWW	24	9
Ti-MWW-m (5.0)	37	18
Ti-Beta	23	5

[a]Reaction conditions: cat., 25 mg; cyclooctene, 5 mmol; cyclododecene, 2.5 mmol; H_2O_2, equal to alkene amount; CH_3CN, 10 mL; temp., 333 K; time, 2 h.

In conclusion, delamination modification on acid-treated Ti-MWW has provided a selective oxidation catalyst with extremely high specific surface area and improved catalytic activity for cycloalkenes with various molecular sizes.

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