Extremely high *trans* selectivity of Ti-MWW in epoxidation of alkenes with hydrogen peroxide

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A novel titanosilicate with MWW topology, Ti-MWW, exhibits a behavior not observed on other titanosilicates such as TS-1, TS-2 and Ti-beta, in that it selectively epoxidizes *trans* isomers from a mixture of *cis/trans* alkenes with retention of stereochemistry.

The microporous titanosilicate TS-1 of MFI structure has attracted considerable attention of researchers since it is found to be an effective liquid-phase catalyst in the oxidation of various organic compounds using dilute hydrogen peroxide as an oxidant.[1] Ti-beta,[2,3] Ti-MOR[4] and Ti-ITQ-7[5] have also been prepared successfully with a purpose to make full use of various zeolite structures. Recently, we turned our attention to MWW zeolite (typically known as MCM-22[6]) because it has the structural diversity of supercages, 10-membered ring (MR) channels and side pockets, succeeding for the first time in preparing its titanosilicate derivative, Ti-MWW.[7]

In the epoxidation of lower olefins, Clerici *et al.* reported that TS-1 was more active for *cis*-but-2-ene than for *trans*-but-2-ene, which made TS-1 applicable to the production of epoxy derivatives with *cis*-configuration by starting from a mixture of alkenes containing *cis/trans* isomers.[8] We also observed that TS-1 was more selective for the *cis* isomers in the epoxidation of a *cis/trans* mixture of hex-2-enes.[9] The *cis*-selectivity of TS-1 is attributed to the higher reactivity of the *cis* isomer in epoxidation of various C$_4$ olefins.[1,8] However, we have discovered a totally opposite catalytic feature of Ti-MWW in the epoxidation of olefinic stereoisomers, which may bring about reconsideration of the stereoselectivity of titanosilicates in olefin epoxidation and give rise to investigation of the relationship between shape selectivity and microstructure of Ti active sites.

Ti-MWW was prepared by treating a Ti-containing lamellar precursor with MWW topology with acid solution, and subsequent calcination. The Ti-containing precursor was hydrothermally synthesized from fumed silica (Cab-o-sil M7D) and tetrabutyl orthotitanate in the presence of boric acid and using piperidine as a structure-directing agent (SDA) as reported in detail elsewhere.[7] Acid treatment with 2 M HNO$_3$ on the lamellar precursor removed extraframework Ti species together with some framework boron. The samples were then calcined in air at 803 K to burn off the organic SDA to obtain the Ti-MWW catalysts. The samples were proved to have the MWW topology by X-ray diffraction, and contain only isolated Ti species in the framework as evidenced by the predominant band at 220 nm in the UV–VIS spectrum (Fig. 1).

Other titanosilicates for control experiments, TS-1, TS-2, Ti-beta and Ti-MOR were prepared by a hydrothermal synthesis method or post-synthesis method using TiCl$_4$ vapor.[4] The liquid-phase oxidation of *cis/trans* mixtures of alkenes with hydrogen peroxide was carried out at 333 K in a round-bottom 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 alkenes, 10 mmol of hydrogen peroxide (31 wt% aqueous solution) and 10 mL of solvent was heated at a set temperature under vigorous agitation. The reaction mixture was analyzed using a gas chromatograph (Shimadzu 14 B) equipped with a 50

m OV-1 capillary column. The amount of hydrogen peroxide remaining in the reaction mixture was determined by titration with 0.1 M Ce(SO$_4$)$_2$ solution.

Table 1 shows the results of epoxidation of hex-2-ene isomers with a *cis/trans* ratio of 41:59 over various titanosilicates. The major products were 2,3-epoxyhexane with both *cis*- and *trans*-configurations. A small amount of diol product due to epoxide hydrolysis over acid sites was also obtained, especially for Ti-beta, owing to the rather strong acidity relating to the framework Al. The conversion of hex-2-enes depended greatly on the reaction conditions; Ti-MWW showed the highest specific catalytic activity in MeCN and higher efficiency in H$_2$O$_2$ utilization. What is more interesting is that Ti-MWW exhibited an extremely high selectivity for the epoxide with *trans*-configuration, while TS-1, TS-2, Ti-beta and Ti-MOR produced the *cis*-epoxide with a selectivity higher than the percentage of *cis*-isomer in the initial substrate. The selectivity of Ti-MWW for *trans*-epoxide was independent of its Ti content (entries 1–3) and the reaction time (entries 2 and 4) although the conversion increased with increase in Ti content. This unique property was not affected when using the protic solvent MeOH though the conversion was greatly decreased (entry 5). Furthermore, in the epoxidation of other olefins such as hept-2-enes, hept-3-enes and oct-2-enes all with a *cis/trans* ratio of 50:50, Ti-MWW showed a selectivity of 80, 72 and 81% for the corresponding *trans*-epoxides, respectively. All these findings allow us to draw the conclusion that Ti-MWW is a catalyst with a unique selectivity in the epoxidation of a mixture of *cis/trans* isomers.

Since the epoxidation of a mixture of *cis/trans* isomers is a competition reaction, the reaction of individual isomers would make the matter clearer. Fig. 2 compares Ti-MWW with TS-1 for the epoxidation of *cis*- and *trans*-oct-2-enes. Retention of seterochemical configuration was found for both Ti-MWW and TS-1, *i.e. cis*-oct-2-ene gave exclusively the *cis*-epoxide, and *trans*-oct-2-ene resulted in the *trans*-epoxide. This indicates no isomerization occurred during the reaction for both the substrate and epoxide. Ti-MWW exhibited the reactivity order of *trans*-oct-2-ene > *cis*-oct-2-ene, while TS-1 showed the reverse order. The higher reactivity of the *trans* isomer on Ti-MWW is
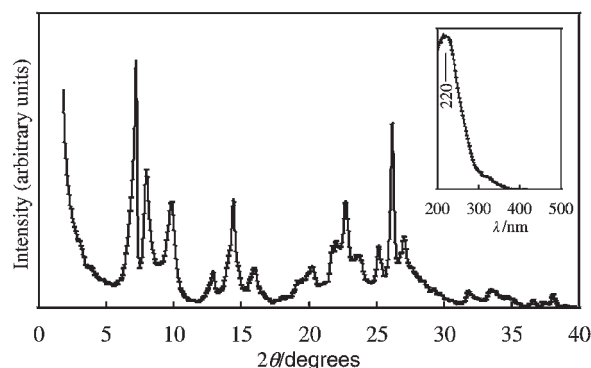

Fig. 1 X-Ray diffraction pattern and UV–VIS spectrum of Ti-MWW (Si:Ti = 64).

Table 1 Epoxidation of hex-2-ene isomers with hydrogen peroxide over various titanosilicates

Entry	Cat.	Si/Ti	Conv. (mol%)	Prod. sel. (mol%)		Epoxide distribution (mol%)[a]		H₂O₂ (mol%)	
				Epoxides	Diols	cis	trans	Conv.	Efficiency
1	Ti-MWW	146	16.4	97	3	20	80	18.4	89
2	Ti-MWW	64	37.6	99	1	17	83	39.6	95
3	Ti-MWW	46	50.8	99	1	19	81	66.1	92
4	Ti-MWW[b]	64	16.0	99	1	15	85	39.6	95
5	Ti-MWW[c]	64	9.3	98	2	18	82	9.6	97
6	TS-1	52	17.8	94	6	65	35	25.7	71
7	TS-1	42	29.1	96	4	66	34	32.5	89
8	TS-2	95	13.6	96	4	67	33	18.0	77
9	Ti-Beta	40	15.9	91	9	73	27	35.8	45
10	Ti-MOR	79	2.6	99	1	52	48	3.9	66

[a] Cat., 0.05 g; hex-2-enes (cis/trans = 41:59), 10 mmol; H₂O₂, 10 mmol; MeCN, 10 ml; temp., 333 K; time, 2 h. [b] The reaction time was 5 min. [c] MeOH used as solvent.
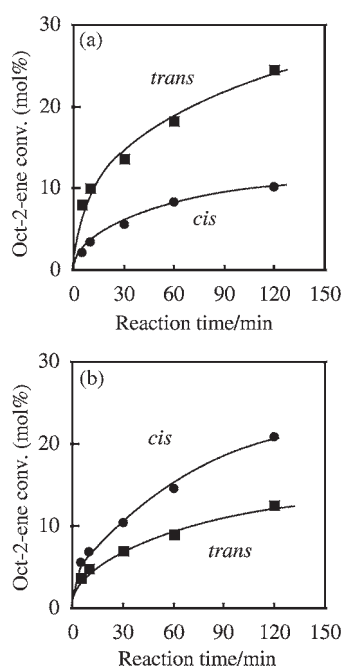
Fig. 2 Epoxidation of *cis* and *trans*-oct-2-ene over Ti-MWW (a) and TS-1 (b). Cat., 0.05 g; oct-2-ene, 10 mmol; H₂O₂, 10 mmol; MeCN, 10 mL; temp., 333 K.

thus consistent with its unique selectivity observed above in the reaction of mixtures.

Liquid-phase adsorption of a hex-2-ene mixture using the bulky solvent 1,3,5-triisopropylbenzene was carried out to investigate the different catalytic behavior between Ti-MWW and other titanosilicates. TS-1 adsorbed more selectively the *trans* isomer with smaller molecular size because of its medium pores of 10-MR. However, Ti-MWW, containing both 10-MR and 12-MR pores, exhibited similar adsorption phenomena to large-pore Ti-beta, that is, both adsorbents showed no obvious difference in the adsorption rate for the two isomers. Therefore, the high *trans* selectivity of Ti-MWW is not due to easier accommodation for the *trans* isomers.

Selective poisoning of the Ti sites in open space side pockets with 2,4-dimethylquinoline resulted in an unchanged conversion of hex-2-enes and the same *trans* selectivity for the epoxide, which indicates little contribution of the side pockets to the present epoxidation reactions. Therefore, the unique selectivity of Ti-MWW is presumed to originate mainly in its 10-MR channels and supercages, both restricted by 10-MR entrances. In particular, the 10-MR system of the MWW structure is defined by two-dimensional sinusoidal channels.[10] The unique tortuosity of the sinusoidal configuration would make the alkene molecules of *trans* configuration approach more easily to the Ti species than those of *cis* configuration, so resulting in higher *trans* selectivity. On the other hand, the channels of TS-1 and Ti-beta are suggested to favor the *cis* molecules approaching the Ti sites, owing to the characteristic tunnel-like channel structures. Further investigation in more detail is still required to clearly determine how the micro-structure of Ti active sites affects the selectivity for substrates of different configurations. Nevertheless, the uniqueness of Ti-MWW strongly suggests the importance of considering 'steric compatability' between the substrate molecules and the Ti species when investigating shape selectivity.

As a result, this study clearly shows that Ti-MWW is an unusual catalyst in the oxidation of alkene stereoisomers, revealing a new concept of shape selectivity in constrained spaces in zeolite crystals.

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