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A novel titanosilicate with MWW structure
III. Highly efficient and selective production of glycidol through epoxidation of allyl alcohol with H_2O_2

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Abstract

The catalytic properties of Ti-MWW in the epoxidation of allyl alcohol (AAL) with hydrogen peroxide to glycidol (GLY) have been studied in detail by a comparison with those of TS-1 and pure silica Ti-Beta, and mechanical considerations have been given to the relation between the catalytic performance and the structural, acidic, and hydrophilic/hydrophobic nature of titanosilicates. Ti-MWW catalyzed the AAL epoxidation more actively and selectively than TS-1 and Ti-Beta in the presence of H_2O or MeCN, and exhibited a conversion of 95% for AAL and a selectivity of 99% for GLY when the AAL epoxidation was carried out at 333 K for 30 min and at 12 wt% of catalyst to substrate. Ti-MWW proved to be a reusable and sustainable catalyst as it stood up to Ti leaching and maintained the catalytic activity and the product selectivity in the reaction-regeneration cycles. The acidic character due to the boron framework was very weak, and thus contributed negligibly to the solvolysis of GLY. The AAL epoxidation proceeded mainly within the intralayer sinusoid 10-MR channels which supplied more steric fitness to the substrate molecules than the tunnel-like channels of TS-1 ad Ti-Beta. Ti-MWW was more hydrophilic than TS-1, but much more hydrophobic than Ti-Beta. The hydrophilicity of Ti-MWW was presumed to derive mainly from the defect sites due to the incomplete dehydroxylation between the layers and partially as a result of deboronation. The sinusoidal 10-MR channels serving as the reaction space for the AAL epoxidation were considered to be hydrophobic, thus rendering the Ti-MWW catalyst applicable to the substrates and solvents, both of a polar nature.

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Keywords: Ti-MWW; Allyl alcohol; Glycidol; Hydrogen peroxide; Liquid-phase epoxidation

1. Introduction

MFI-type titanosilicate, TS-1, being able to actively catalyze the liquid-phase oxidation of a variety of organic compounds to oxygenated products, has brought about a breakthrough in the field of zeolite catalysis in the past two decades [1,2]. The unique activity of TS-1 is mostly due to the isolated Ti species of tetrahedral coordination in the hydrophobic framework. The discovery of TS-1 has led to an industrialized process of hydroxylation of phenol to hydroquinone and catecol, and a promising process of cyclohexanone ammoximation to oxime. These successes imply potential applications of titanosilicates to the clean production of fine chemicals.

Nevertheless, TS-1 has a major problems in that the medium pores of a 10-membered ring (MR) limit its application to the substrates with relatively small molecular sizes and that its intrinsic activity per Ti site is still not high enough for the epoxidation of functionalized alkenes. Other titanosilicates with larger pores developed thereafter by hydrothermal synthesis or postsynthesis methods, such as Ti-Beta [3,4], Ti-MOR [5], Ti-ITQ-7 [6], and Ti-MCM-41 [7], have partially solved the problems of steric constraints encountered in the oxidation of bulky substrates. Ti-Beta especially proves to be a very attractive catalyst according to its high activity for the cyclic and branched alkenes and alkanes [3,4]. However, it seems that the above titanosilicates are intrinsically less active than TS-1 for the oxidation of small molecules and have hardly reached the level required for industrialization in terms of both catalytic activity and selectivity. Much effort has been made to pre-

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pare titanosilicates that are more applicable to the fields of fine chemicals or pharmaceuticals.

Recently, we succeeded in synthesizing a novel titanosilicate with the MWW structure, Ti-MWW [8]. Ti-MWW consists not only of the open reaction spaces of side cups and supercages but also of the medium reaction space of two independent 10-MR channels. Taking advantages of this structural diversity, Ti-MWW proves to be active for the epoxidation of linear alkenes and cyclic alkenes as well. Ti-MWW is more active in the epoxidation of linear alkenes than TS-1, the titanosilicate showing the highest intrinsic activity so far. The unusual catalytic performance of Ti-MWW suggests that it may serve as a potential catalyst for the oxidation of functionalized alkenes.

Among the oxidation of functionalized alkenes, the epoxidation of allyl alcohol (AAL) to glycidol (GLY) is probably one of the most demanded reactions. GLY is industrially produced by epoxidation of AAL with hydrogen peroxide, hypochlorous acid, or peracetic acid [9,10]. The most environmentally benign oxidant is hydrogen peroxide, which is to be catalytically activated; however, the conventional tungstate catalyst suffers from problems in activity, regeneration, and reusability. Several studies concentrated on AAL epoxidation with hydrogen peroxide on TS-1. Nevertheless, the initial reaction rate for the epoxidation of AAL was reported to be about 30 times slower than the rate of 1-butene epoxidation [11]. The selectivity to GLY was not so sufficient; only glycerol was observed when dilute H_2O_2 solution (5 wt% in water) was used [12]. The low GLY selectivity is mainly due to the consecutive hydrolysis or solvolysis of GLY on the residual acid sites of TS-1 as reported by Hutchings et al. [13]. The GLY selectivity dramatically declined from 100 to 2% when the AAL conversion increased from 3 to 100% especially in the presence of alcoholic solvents of methanol or ethanol preferred by TS-1. Control of crystal size and poisoning the acid sites with sodium cations have been attempted to improve the performance of TS-1 in AAL epoxidation [13], but the former seems to have limitations, while the latter deactivates the Ti active sites simultaneously. Therefore, TS-1 catalysts cannot maintain a favorable balance between AAL conversion and GLY selectivity.

Surveying the literature on AAL epoxidation, it seems to us that high yields of GLY depend predominantly on the intrinsic activity of titanosilicates with low acidity. What is also important is that the hydrophilicity/hydrophobicity of titanosilicates may play a significant role in the epoxidation [4,14]. Particularly, different from unfunctionalized alkenes, AAL is hydrophilic and then could exhibit different behavior. The hydrophilicity/hydrophobicity may also influence the activity and selectivity through the solvent effect [15].

In this study, we have applied Ti-MWW catalysts to the AAL epoxidation for the purpose of producing GLY efficiently and selectively. The effects of solvent and the reaction conditions on the AAL epoxidation have been investigated by comparing Ti-MWW with TS-1 and Ti-Beta. The main aim is to investigate why Ti-MWW is an excellent AAL epoxidation catalyst by considering the pore structure, acidity, and hydrophilicity/hydrophobicity.

2. Experimental

2.1. Preparation of titanosilicate catalysts

Ti-MWW catalysts were prepared in two steps according to procedures previously reported [8b]. The first step was to hydrothermally synthesize Ti-containing MWW lamellar precursors using piperidine as a structure-directing agent (SDA) and boric acid as a crystallization-supporting agent, from synthetic gels with molar compositions of 1 SiO_2: 0.01–0.05 TiO_2:0.67 B_2O_3:1.4 SDA:19 H_2O. The second step was to treat the precursors in HNO_3 or H_2SO_4 solutions under reflux for the purpose of removing the extra framework Ti species together with a part of the framework of boron. Subsequent calcination on the acid-treated sample resulted in the objective Ti-MWW catalysts.

TS-1 catalysts, with Si/Ti ratios of 100-36, were synthesized following conventional procedures [16], and were washed with 1 M HCl solution at ambient temperature to reduce the residual alkali cations contaminating the SDA solution of tetrapropylammonium hydroxide because alkali cations may partially poison the Ti active sites [17]. Titanosilicates of the BEA structure, Al-containing Ti, Al-Beta, ($Si/Ti = 40$, $Si/Al = 70$), and Al-free Ti-Beta ($Si/Ti = 42$, $Si/Al > 1000$), were synthesized according to conventional [3] and seeding methods [18], respectively.

The catalysts were characterized by inductively coupled plasma (ICP, Rigaku JY38S), X-ray diffraction (XRD, Rigaku Rint 2000), N_2 adsorption (Coulter SA 3100), and scanning electron microscopy (SEM, JEOL JSM-T220), and the spectroscopies of UV–visible (Shimadzu UV-2400PC) and IR (Shimadzu FTIR-8100). IR spectra in the region of hydroxyl stretching vibration were recorded after the self-supported disk (30 mg with 2 cm diameter) was evacuated at 773 K for 1 h. The acidic properties were measured with NH_3-TPD (BEL Japan Inc.). The sample was dehydrated under He at 773 K for 1 h and then treated with NH_3 at 373 K for 0.5 h. The TPD spectra were recorded at a heating rate of 10 $K\,min^{-1}$ using m/z of 16 to avoid the influence of any contaminating water.

2.2. Catalytic reaction

The epoxidation of allyl alcohol with hydrogen peroxide was carried out in a 20-ml glass flask with a condenser under vigorous stirring. In a typical run, 10 mmol of AAL, 5 ml of solvent, and a certain amount of catalyst were mixed in the flask and heated to desired temperatures under agitation. H_2O_2 (10 mmol, 30 wt%) was then added to the mixture to start the reaction. The products were separated by filtration and analyzed with a gas chromatograph (Shimadzu GC-14B) using a OV-1 capillary column of 50 m and an FID detector. The amount of unconverted H_2O_2 was determined by the standard titration method using a 0.1 M $Ce(SO_4)_2$ solution. The hydrolysis of glycidol and the epoxidation of 1-hexene and cyclohexene were conducted under conditions similar to AAL epoxidation.

3. Results and discussion

3.1. *Preparation and characterization of various titanosilicate catalysts*

MWW-type titanosilicate, Ti-MWW, seemed to be hardly hydrothermally synthesized up to date directly from the sources of silicon and titanium in the presence of organic structure-directing agents. Nevertheless, we recently developed new procedures to prepare this novel titanosilicate [8]. The procedures involve the hydrothermal synthesis of Ti-containing lamellar precursor with boric acid as a crystallization-supporting agent and the removal of extra framework Ti species and framework B by subsequent acid treatment of the precursor. Table 1 shows the physicochemical properties of Ti-MWW catalysts prepared by following the above procedures. Ti-containing lamellar precursors of MWW were synthesized, which proved to have Ti contents nearly stoichiometrically equivalent to those of the synthetic gels. The treatment of the precursors with HNO_3 or H_2SO_4 solutions partially removed the Ti and B species. Further calcination of the acid-treated samples resulted in Ti-MWW catalysts with Si/Ti ratios varying in a wide range. Acid-treated and subsequently calcined samples showed the XRD patterns corresponding to the MWW topology (not shown) and extremely high specific surface areas measured by N_2 adsorption, consistent with their high crystallinity.

Acid-treated Ti-MWW samples contained only isolated Ti species in the framework as evidenced by the predominant band at 220 nm in their UV–visible spectra when the Si/Ti ratio was higher than 46 (Fig. 1, a–e). However, anatase-like extra framework Ti species, although not a large amount, remained in Ti-MWW with a Si/Ti ratio of 38 (Fig. 1f); it was obtained from the precursor of Si/Ti = 20 which contained too high a concentration of octahedral Ti [8b]. The IR spectra of Ti-MWW in the framework vibration region showed the characteristic band at 960 cm^{-1} assigned to the framework Ti; the band intensity increased with increasing Ti content [8b]. Both IR and UV–visible data verified that Ti-MWW catalysts thus obtained had good quality in terms of incorporation of tetrahedral Ti coordination. The scanning electron micrographs of Ti-MWW revealed thin platelet crystals with a hexagonal morphology (0.2–0.5 µm in length and 0.05–0.1 µm in thickness). The relatively small crystal size, particularly, in thickness, is therefore considered to make Ti-MWW a highly active liquid-phase oxidation catalyst, which may place less restrictions on the diffusion of the substrates. The physicochemical properties of other titanosilicates, TS-1, Ti, Al-Beta, and Ti-Beta, matched well those given in the literature.

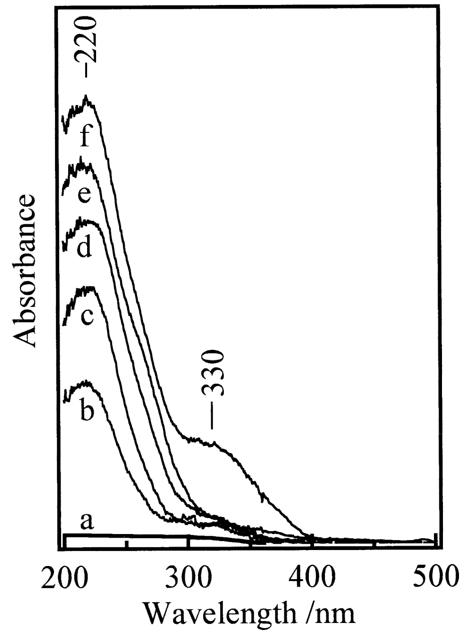


Fig. 1. UV–visible spectra of Ti-MWW with Si/Ti ratios of ∞ (a), 146 (b), 76 (c), 64 (d), 46 (e), and 38 (f).

Table 1
Preparation of Ti-MWW catalysts with various Ti contents[a]

No.	Gel		Ti-containing precursor			Ti-MWW catalyst			
	Si/Ti	Si/B	Si/Ti	Si/B	SA[b]	Acid treatment[c]	Si/Ti	Si/B	SA[b]
1	∞	0.75	∞	12	616	6 M HNO_3	∞	102	611
2	100	0.75	120	13	625	6 M HNO_3	170	37	–
3	100	0.75	120	13	625	2 M HNO_3	146	34	628
4	70	0.75	63	12	612	4 M H_2SO_4	107	67	–
5	70	0.75	63	12	612	1 M H_2SO_4	76	41	622
6	50	0.75	51	12	621	6 M HNO_3	94	51	–
7	50	0.75	51	12	621	2 M HNO_3	64	36	624
8	30	0.75	31	11	623	2 M H_2SO_4	49	36	–
9	30	0.75	31	11	623	2 M HNO_3	46	49	624
10	20	0.75	21	13	540	2 M HNO_3	38	54	556

[a] Crystallization: stirred at 403 K for 1 day, at 423 for 1 day, and then at 443 K for 5 days.

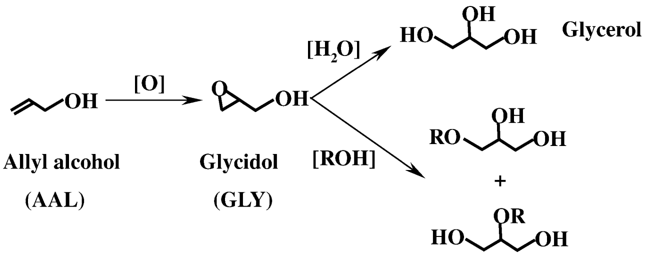
[b] Surface area (Langmuir) in $m^2 g^{-1}$.

[c] Acid treatment: ratio of acid solution to solid precursor, 20 $ml\,g^{-1}$; refluxed for 20 h.

3.2. *Effects of reaction conditions on the epoxidation of allyl alcohol*

3.2.1. *Influence of solvents*

As depicted in Scheme 1, the epoxidation of allyl alcohol produces the main product, glycidol, which may be secondarily hydrolyzed to glycerol through the ring opening reaction because aqueous H_2O_2 solution is used as an oxidant. GLY also successively undergoes solvolysis to form the by-products of glycerol ethers especially when alcohols are used as a solvent. Both the hydrolysis and the solvolysis of GLY are due to the acidic character of titanosilicates derived from the silanol groups and the additional bridging hydroxyls of trivalent cations coexisting with Ti in the

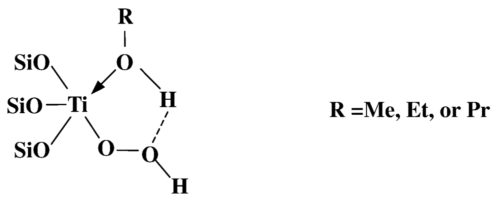


Scheme 1.

framework. The solvent, generally having a great influence on the intrinsic activity of Ti species in titanosilicates, thus also affects the product distribution in AAL epoxidation.

Table 2 compares the catalytic performance of Ti-MWW with that of conventional titanosilicates of TS-1 and Ti-Beta for AAL epoxidation in various solvents. A clear solvent effect was observed for Ti-MWW. The most favorable solvents were MeCN and H_2O, which gave comparable conversions of 82–87% for AAL, produced almost only GLY, and exhibited high efficiency for H_2O_2 utilization. The epoxidation of AAL was greatly retarded in the protic solvents of alcohols and also in the aprotic solvents of acetone and dioxane. The role of alcohol solvents in the oxidation activity of TS-1 is usually explained by assuming the formation of a stable five-membered cyclic intermediate species (Scheme 2), which is formed by the coordination of the protic molecule, ROH, to the Ti center and by the stabilization of the Ti-hydroperoxo complex through hydrogen bonding [19]. This species formed in the channels would gradually impose a steric hindrance on the substrate molecules when ROH becomes bulky. Indeed, the AAL conversion slightly decreased in the order MeOH > EtOH > 1-PrOH. Besides the influence on the catalytic activity, the protic alcohols caused the opening of the oxirane ring to reduce greatly the selectivity for GLY.

In the case of TS-1, very comparable AAL conversion was observed for the protic solvents with relatively small molecular size, H_2O and MeOH, and aprotic acetone. Aprotic but basic MeCN, a well-known unsuitable solvent for the oxidation of simple alkenes on TS-1, showed somewhat lower conversion in the epoxidation of AAL. 1-PrOH retarded greatly the reactivity of TS-1, which is simply assumed to be a result of forming bulky and sterically restricted species in Scheme 2. When the epoxidation was suppressed, nonproductive decomposition of H_2O_2 was observed to increase as reflected by the lower H_2O_2 efficiency. It is obvious that TS-1, despite higher Ti content, is much



Scheme 2.

Table 2
Epoxidation of AAL with H_2O_2 in various solvents[a]

Solvent	Ti-MWW (Si/Ti = 46) (mol%)					TS-1 (Si/Ti = 36) (mol%)					Ti-Beta (Si/Ti = 42) (mol%)				
	AAL	Product selectivity		H_2O_2		AAL	Product selectivity		H_2O_2		AAL	Product selectivity		H_2O_2	
	conversion	GLY	Others[b]	Conversion	Efficiency	conversion	GLY	Others[b]	Conversion	Efficiency	conversion	GLY	Others[b]	Conversion	Efficiency
MeCN	87.0	99.9	0.1	87.9	99.0	26.8	82.6	17.3	28.5	94.1	13.9	75.4	24.6	18.4	75.5
Water	82.3	99.9	0.1	84.3	97.6	34.6	96.0	4.0	36.6	94.5	2.8	92.6	7.4	9.6	29.2
MeOH	34.5	75.7	24.3	35.9	96.1	34.2	86.6	13.4	36.2	94.5	16.7	42.0	58.0	21.6	77.3
EtOH	32.5	91.0	9.0	33.0	98.5	24.4	94.6	5.4	29.8	81.8	15.1	59.5	40.5	28.6	52.8
1-PrOH	30.1	96.0	4.0	37.5	80.3	12.6	95.6	4.4	16.1	78.6	–	–	–	–	
Acetone	41.5	96.7	3.3	42.5	97.6	31.0	92.8	7.2	36.6	84.7	11.9	41.4	58.6	26.3	45.2
Dioxane	27.8	96.0	4.0	28.6	97.2	–	–	–	–	–	5.2	78.3	21.7	6.5	80.0

[a] Cat., 70 mg; AAL, 10 mmol; H_2O_2, 10 mmol; solvent, 5 ml; temperature, 333 K; time, 0.5 h.
[b] Solvolysis products, glycerol and alkyl glycerol ethers, etc.

less effective in epoxidizing AAL than Ti-MWW for both the activity and the selectivity to GLY.

Ti-Beta catalyzed the epoxidation of AAL to a certain extent in the presence of organic solvents, but was less effective even than TS-1. In agreement with the proposition that basic MeCN may poison the Brønsted acid sites of Ti, Al-Beta to suppress the ring opening of epoxide [15], the selectivity for GLY was much higher in MeCN than in the protic alcohols. Nevertheless, this positive effect of MeCN seemed to be limited since the GLY selectivity was only 75%, probably because the Beta zeolite contains too high a concentration of acidic silanol groups at structural defect sites. An important observation about Ti-Beta was that H_2O, a good solvent for both Ti-MWW and TS-1 in AAL epoxidation, appeared to be unsuitable. This proposes the importance of hydrophilic/hydrophobic features of titanosilicates. Lower activity of Ti-Beta should be ascribed to its hydrophilic character despite the Al-free form. Concerning this issue, a detailed consideration will be given in a later section.

The above investigation on the solvent effect proves that Ti-MWW is a promising catalyst for the selective formation of GLY in the AAL epoxidation if MeCN or H_2O is chosen as a solvent.

3.2.2. *Influence of Ti content*

To further ensure that Ti-MWW has superiority over TS-1 in AAL epoxidation, a series of Ti-MWW and TS-1 with various Ti contents was prepared and compared for their catalytic performance (Fig. 2). The AAL conversion reasonably increased with increasing Ti content, but Ti-MWW obviously showed much higher catalytic activity than TS-1. Ti-MWW also gave much higher GLY selectivity than TS-1; when the Ti content was more than 0.2 mmol g^{-1} corresponding to an Si/Ti ratio of ca. 80, the GLY selectivity was 99%. AAL epoxidation predominantly produced GLY, indicating that the reaction rate for GLY formation is much faster than that of the hydrolysis of GLY to glycerol. A gradual increase in GLY selectivity with increasing Ti content strongly indicates that highly efficient formation of GLY only can be achieved on those catalysts which are so active as to promote the epoxidation extensively within a short time. The consecutive hydrolysis or solvolysis can then be limited to a low level. Thus Ti-MWW proves to be an excellent catalyst.

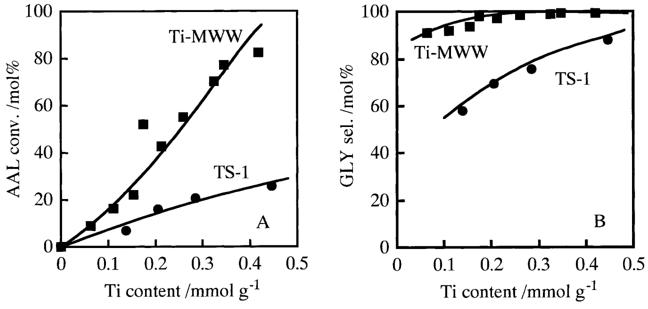


Fig. 2. Dependence of AAL conversion (A) and GLY selectivity (B) on the Ti content of Ti-MWW and TS-1. Cat., 50 mg; AAL, 10 mmol; H_2O_2, 10 mmol; MeCN, 5 ml; temperature, 333 K; time, 30 min.

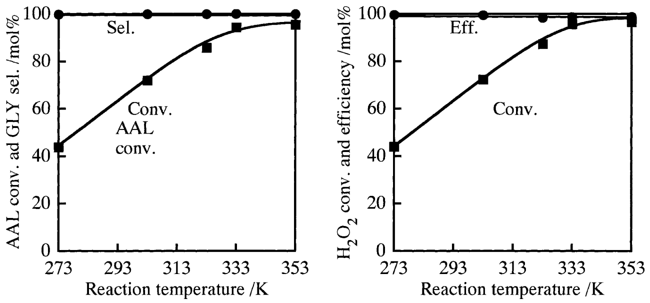


Fig. 3. Effect of reaction temperature on the AAL epoxidation over Ti-MWW. Ti-MWW (Si/Ti = 38, Si/B = 54), 70 mg; AAL, 10 mmol; H_2O_2, 10 mmol; MeCN, 5 ml; time, 60 min.

3.2.3. *Influence of reaction temperature*

The epoxidation of AAL depended greatly on the reaction temperature (Fig. 3). The AAL conversion reached about 95% with increasing temperatures up to 333 K. The GLY selectivity was always maintained above 99% irrespective of the temperature. Ti-MWW showed a significant conversion of 42% even at 273 K, indicating its high activity and usability at low temperatures.

3.2.4. *Influence of reaction time*

Fig. 4 shows the time courses for the ALL epoxidation at 333 K over Ti-MWW in the presence of H_2O and MeCN, the most suitable solvents as shown in Table 1. The AAL conversion increased rapidly with time up to 30 min and showed no further increase at 1 h because nearly all the substrate and the oxidant were consumed within 30 min. The products were predominantly GLY together with a small amount of glycerol ($<$ 1%), indicating that the ring

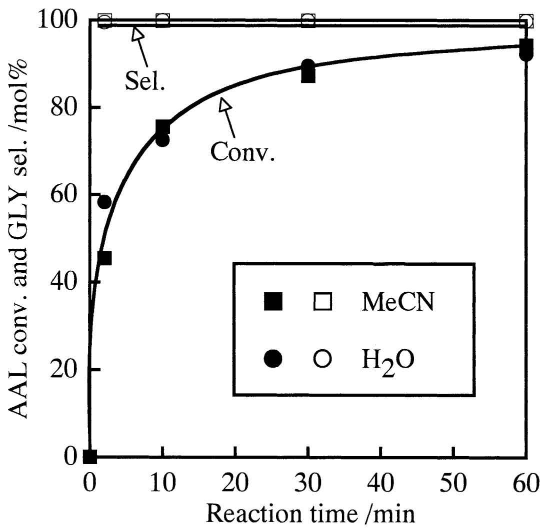


Fig. 4. Effect of reaction time on the AAL epoxidation over Ti-MWW. Ti-MWW (Si/Ti = 38, Si/B = 54), 70 mg; AAL, 10 mmol; H_2O_2, 10 mmol; MeCN or H_2O, 5 ml; temperature, 333 K.

opening of GLY occurred at a negligible level. What is more important is that no obvious difference in both the activity and the GLY selectivity was observed between H_2O and MeCN. This possibly makes Ti-MWW-catalyzed epoxidation of AAL an environmentally benign process by using H_2O as a solvent.

The identical time dependence of AAL conversion observed for these two characteristically different solvents is presumably because the AAL epoxidation in water does not suffer the heterogenization problems of reaction mixtures in the case of epoxidation of other alkene substrates since both AAL and glycidol products are soluble in water. A gradual decrease in the reaction rate with time is mainly due to the consumption of AAL and partially due to the deactivation of catalyst as shown below.

3.2.5. *Influence of amount of Ti-MWW catalyst*

The above investigations suggest that highly selective formation of GLY should be performed on the titanosilicate intrinsically active for the epoxidation of AAL. This allows the epoxidation reaction to reach an extensive level within a short reaction time, and then would suppress the consecutive solvolysis of GLY to by-products. Although it is verified that Ti-MWW is active enough to serve as such a promising catalyst, the relative amount of Ti-MWW to the substrate is an issue. As shown in Fig. 5, the AAL conversion increased rapidly with increasing amount of Ti-MWW, and 12 wt% of Ti-MWW relative to AAL was enough to convert AAL up to 92% at 333 K in 30 min, producing almost only GLY with efficiency for H_2O_2 consumption higher than 90%.

3.3. *Stability and reusability of Ti-MWW*

Besides the catalytic activity and selectivity, one of the other important properties that titanosilicate should have is its stability against Ti leaching, a notable problem commonly encountered in the liquid-phase reactions. Ti species of TS-1 are generally believed to be stable enough in the liquid-phase oxidation of simple alkenes, but Ti-Beta and Ti-MCM-41, both containing a large amount of hydrophilic silanol groups on the defect sites and the external surface, lack the stability of Ti species under hydrothermal conditions [20,21]. In fact, the reaction mixture of the AAL epoxidation over Ti-Beta changed into bright yellow due to the soluble Ti species after the removal of the catalyst, indicating leaching of Ti species out of the framework sites. Ti-MWW has proved to be stable against Ti leaching in the epoxidation of cyclohexene [8e]. However, it has been reported recently that even TS-1, especially crystallized in a short period, is not so stable to the leaching of Ti species in the epoxidation of crotyl alcohol, because the triol by-products may chelate the Ti sites, thereby cleaving easily the Si–O–Ti bonds [22]. Since the present AAL epoxidation gave rise to glycerol, although not in a large amount, and AAL itself is a highly hydrophilic substrate, the stability of Ti-MWW may be different from what was investigated previously in the epoxidation of simple alkenes.

The stability against Ti leaching of Ti-MWW has been thus investigated together with its reusability in AAL epoxidation. The experiments were conducted starting with an enlarged reaction scale using 1.2 g of Ti-MWW. The used Ti-MWW catalyst was regenerated by washing with acetone or by further calcination in air at 773 K. After taking out a part of the sample for IPC analyses, the regenerated catalyst was subjected to repeated epoxidation of AAL while keeping the catalyst-substrate-solvent composition constant. The AAL conversion decreased dramatically with the reaction-regeneration cycles if the Ti-MWW used was only washed with acetone and then dried (Fig. 6A, ■). In this case, the selectivity to GLY also declined gradually due to the suppression of epoxidation (Fig. 6B, ■). Nevertheless, when the catalyst collected after 5 reaction-regeneration cycles was calcined at 773 K, both the AAL conversion and the GLY selectivity were restored. This suggests that the decrease in the catalytic activity of acetone-washed catalyst is due only to the deposition of heavy organic compounds of high boiling points within the channels of Ti-MWW. Indeed, when the Ti-MWW used was regenerated by directly burning off residual organic species at 773 K, the AAL conversion increased during the first regeneration cycles and then maintained the level over 90% (Fig. 6A, ●); the GLY selectivity was higher than

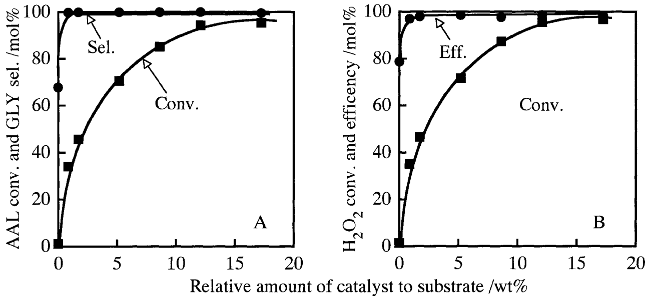


Fig. 5. Dependence of AAL conversion and GLY selectivity (A), and H_2O_2 conversion and efficiency (B) on the relative amount of Ti-MWW. Ti-MWW (Si/Ti = 38, Si/B = 54), 5–100 mg; AAL, 10 mmol; H_2O_2, 10 mmol; MeCN, 5 ml; temperature, 333 K; time, 30 min.

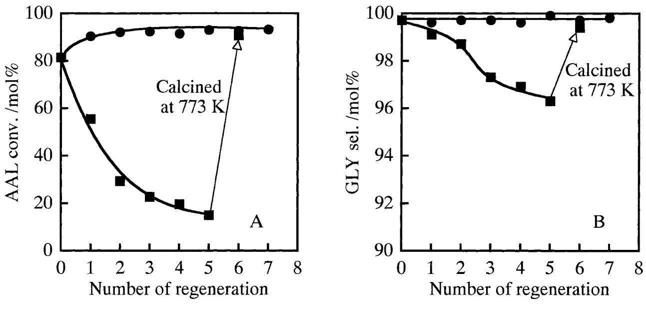


Fig. 6. Changes of AAL conversion (A) and GLY selectivity (B) with the epoxidation-regeneration cycles. AAL epoxidation conditions: Ti-MWW (Si/Ti = 49, Si/B = 36):AAL:H_2O_2:MeCN = 50 mg: 10 mmol:10 mmol:5 ml; temperature, 333 K; time, 60 min. Regeneration: used catalyst was washed with acetone and dried at 393 K (■), and further calcined at 773 K in air for 4 h (●).

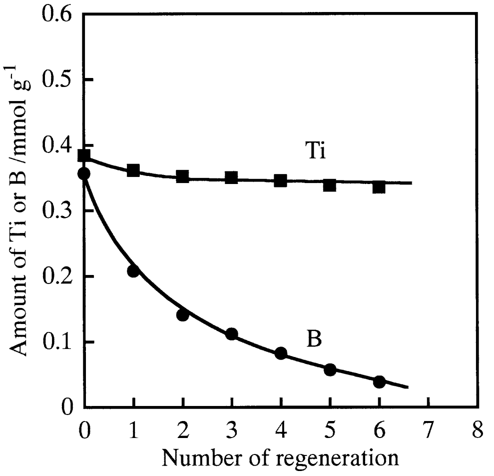


Fig. 7. Changes of the content of Ti and B during the repeated epoxidation of AAL over Ti-MWW. For epoxidation conditions, see Fig. 6.

99% (Fig. 6, ●). Therefore, it can be safely assumed that Ti-MWW can be employed as a reusable catalyst for the selective epoxidation of AAL to GLY.

This has been further confirmed by quantifying the Ti and B contents in the used Ti-MWW catalyst (Fig. 7). The B species were gradually leached out of the framework during the reaction probably because of its too small ionic radius compared with that of Si. The loss of B may decrease the framework electronegativity to vary the electronic density in the vicinity of Ti sites, a usual phenomena reported for Al-containing Ti-Beta [3] and Ti-MOR [5b], and may also increase the hydrophobicity of the framework. Thus the lose of B is presumed to account for a slight increase in the AAL conversion observed after the first reaction-regeneration cycle (Fig. 6, ●). On the other hand, the amount of Ti leached was negligible, which matches well the high conversion obtained for the catalyst regenerated by the calcination.

3.4. Factors governing the unusual catalytic activity and selectivity of Ti-MWW in AAL epoxidation

3.4.1. High activity of Ti-MWW

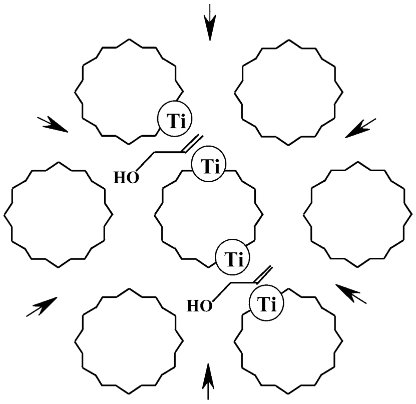
The extraordinarily high activity of Ti-MWW in the AAL epoxidation must be closely related to the unique crystalline structure of the MWW topology. The MWW structure supplies relatively complicated reaction spaces, side cups on the exterior crystal surface and two independent 10-MR channels, one of which comprises supercages [23]. Selective poisoning of the Ti active sites with amines of different molecular sizes has been carried out to determine which part of Ti sites contributes more to the AAL epoxidation (Table 3). The amount of amine (2 mmol) was about 70 times as large as the Ti amount in Ti-MWW catalysts, and thus should be sufficient to poison the Ti sites where the amine molecules diffused and approached. The poisoning reagents used were tripropylamine (TPA) and triphenylamine (TPhA) with relatively small and large molecular sizes, respectively. The former, believed to reach all the Ti sites, deactivated Ti-MWW completely as expected. The coexistence of TPhA, on the other hand, had little influence on the AAL conversion when compared to the nonpoisoning epoxidation. However, TPhA totally retarded the epoxidation of cyclohexene with *tert*-butylhydroperoxide that requires open reaction spaces (not shown). Bulky molecules of TPhA are considered to hardly penetrate the pore mouth of 10-MR channels and then selectively poison the Ti sites within the cups on the external surface. Since Ti-MWW was prepared through severe acid treatment on the lamellar precursor, the acid treatment would selectively remove the Ti species on the external surface of the layers and then deeply lower the Ti concentration within the side cups and the supercages consisting of two cups. Thus it is assumed from the above results that the extremely high activity for the AAL epoxidation mainly originates from the intralayer 10-MR channels containing no supercages.

Table 3
Poisoning epoxidation of AAL over Ti-MWW[a]

Poisoning reagent	Conversion (mol%)	Product selectivity (mol%)		H_2O_2 (mol%)	
		GLY	Glycerol	Conversion	Efficiency
None	92.6	99.5	0.5	93.7	98.8
TPA	1.3	87.7	12.3	–	–
TPhA	91.4	99.6	0.4	94.8	96.5

[a] Ti-MWW (Si/Ti = 38), 70 mg; AAL, 10 mmol; H_2O_2, 10 mmol; MeCN, 5 ml; amine, 2 mmol; temperature, 333 K; time, 0.5 h.

The intralayer 10-MR channels within the MWW structure running along the *ab* plane have a slightly restricted elliptical aperture (4.0 × 5.9 A) compared to the MFI structure, exhibiting a special tortuosity of two-dimensional sinusoidal form (Scheme 3). This kind of channel system not only is favorable for the diffusion of linear molecules but might also supply "steric fitness" between the Ti active sites and the substrate molecules. It is then proposed that the intralayer 10-MR channels of MWW structure lead to a rather high



Sinusoidal 10-MR channel system of Ti-MWW

Scheme 3.

Table 4
Hydrolysis of GLY over various titanosilicates[a]

Catalyst	H_2O_2	GLY conversion (mol%)	Product selectivity (mol%)		H_2O_2 conversion (mol%)
			Glycerol	Others	
Ti-MWW	No	3.5	100	0	–
Ti-MWW	Yes	3.4	100	0	0.4
TS-1	No	3.6	100	0	–
TS-1	Yes	3.1	100	0	2.3
Ti-Beta	No	5.7	100	0	–
Ti, Al-Beta	no	13.0	100	0	–

[a] Cat., 70 mg; GLY, 10 mmol; H_2O, 5 ml; H_2O_2, 10 mmol (if added); 333 K; time, 0.5 h.

reaction rate for functionalized alkenes not observed within the tunnel-like channels of TS-1. Indeed, taking advantage of this channel structure, Ti-MWW has been proved to oxidize more actively and selectively the *trans*-isomer from the mixture of linear *cis*/*trans* alkenes than other titanosilicates [8c,8d].

3.4.2. High GLY selectivity of Ti-MWW

High GLY selectivity of Ti-MWW may be due to its outstanding oxidation activity which makes the epoxidation progress to a high level within a short time before significant solvolysis occurs. Alternatively, Ti-MWW may contribute little to the acid-catalyzed solvolysis. Concerning this issue, the hydrolysis of GLY has been carried out (Table 4), and the acidity of Ti-MWW together with TS-1, Ti-Beta and Ti,Al-Beta has been characterized with NH_3-TPD measurements (Fig. 8). Both TS-1 and Ti-MWW showed comparably low conversion of GLY to glycerol, irrespective of whether H_2O_2 is present or not, suggesting the Ti hydroperoxo intermediate (Scheme 2), proposed to act as a kind of weak acid site [17], does not promote the ring opening of GLY under our reaction conditions. The GLY conversion was slightly high for Ti-Beta and further for Ti,Al-Beta owing to high concentration of acid sites.

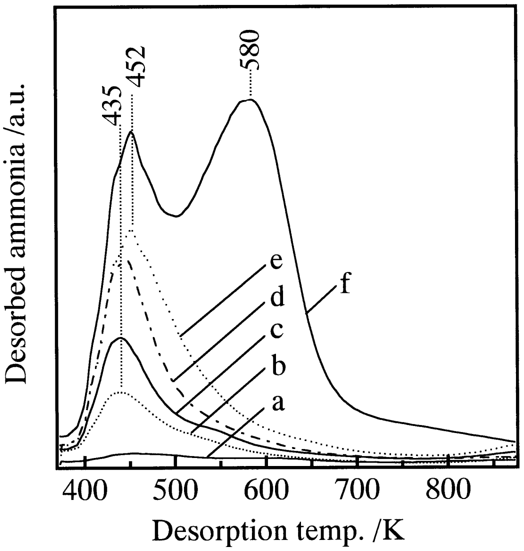


Fig. 8. NH_3-TPD profiles of TS-1 (a), reused Ti-MWW after 4 reaction-regeneration cycles in AAL epoxidation (Si/Ti = 39, Si/B = 149) (b), fresh Ti-MWW (Si/Ti = 38, Si/B = 54) (c), directly calcined precursor (Si/Ti = 21, Si/B = 13) (d), Ti-Beta (Si/Ti = 42, Si/Al > 1000) (e), and Ti, Al-Beta (Si/Ti = 40, Si/Al = 70) (f).

Nearly defect-free TS-1 reasonably contained no acid sites (Fig. 8a), while Ti,Al-Beta had both weak and strong acid sites as evidenced by the desorption peaks at 452 and 580 K (Fig. 8f). These two kinds of acid sites are presumably attributed to the silanols at defect sites and the framework Si(OH)Al groups, respectively. The high-temperature peak disappeared for pure silica Ti-Beta, but the low one still remained, although the intensity was slightly reduced (Fig. 8e). Ti-MWW contained some acid sites, weaker in strength and lesser in amount than Ti-Beta (Figs. 8b–d). The acid sites of Ti-MWW are mainly related to the framework B since the amount decreased from the directly calcined precursor to acid-treated sample, and further to the catalyst repeatedly used in the actual AAL epoxidation.

Combining the results of Table 3 and Fig. 8, it is concluded that the acid sites of Ti-MWW are too weak to promote the hydrolysis or solvolysis of GLY effectively to yield corresponding glycerol and its derivatives. It is possible to remove completely the acidity related to B by repeated acid treatment on Ti-MWW [8b], but it seems not necessary for AAL epoxidation.

3.4.3. Hydrophilic/hydrophobic properties of Ti-MWW

Besides the dimensional suitability between the substrates and the zeolite channels, the polarity and solubility of reactants and products, and the diffusion problems, the hydrophilicity/hydrophobicity of titanosilicates may play an important role in the liquid-phase oxidation especially in the case of AAL, which is protic and hydrophilic unlike simple alkenes. We investigated this subject by comparing the epoxidation of AAL with that of simple alkenes. As shown in Table 5, Ti-MWW showed the highest conversion for 1-hexene, while Ti-Beta, less effective than Ti-MWW and TS-1 in

Table 5
Epoxidation of simple alkenes with H_2O_2 over various titanosilicates[a]

Catalyst	Substrate	Conversion (mol%)	Product selectivity (mol%)		H_2O_2 (mol%)	
			Epoxide	Others[b]	Conv.	Eff.
Ti-MWW	1-Hexene	44.8	99	1	48.2	93.0
Ti-MWW	Cyclohexene	7.1	63	37	15.0	95.0
TS-1	1-Hexene	9.7	98	2	11.5	84.2
TS-1	Cyclohexene	0.8	78	12	–	–
Ti-Beta	1-Hexene	8.5	96	4	9.1	63.7
Ti-Beta	Cyclohexene	16.2	52	48	35.8	75.4
Ti-Beta[c]	Cyclohexene	24.7	0	100	58.3	86.0

[a] Cat., 50 mg; alkene, 10 mmol; MeCN, 10 ml; H_2O_2, 10 mmol for 1-hexene and 5 mmol for cyclohexene; 333 K; time, 2 h.

[b] Glycols, monomethyl glycol ether, 2-cyclohexen-1-ol, and 2-cyclohexen-1-one.

[c] MeOH was used as a solvent.

AAL epoxidation (Table 2), catalyzed the epoxidation of 1-hexene and simultaneously showed the highest activity in cyclohexene epoxidation. The more effective Ti-Beta for the bulky substrates is simply owing to its large pores imposing less steric restriction than those of Ti-MWW and TS-1. Considering the extremely low activity of Ti-Beta in AAL epoxidation especially in the presence of H_2O (Table 2) and in the epoxidation of 1-hexene compared to Ti-MWW and TS-1 (Table 5), the issue of hydrophilicity/hydrophobicity is raised. Beta zeolite generally contains high concentration of hydrophilic silanol groups at the defect sites formed within the complex and severely intergrown crystallites. High hydrophilicity thereafter originating from the silanols would favor the adsorption of protic molecules of solvent and substrate, which could make these molecules hardly accessible to the Ti sites. This probably accounts for the low specific activity per Ti site in Ti-Beta. This then raises the question of the hydrophilicity/hydrophobicity of Ti-MWW.

IR spectra of hydroxyl stretching vibration have been measured to investigate the hydrophilicity of titanosilicates. It has been verified that this indirect method is useful for Ti-Beta synthesized by the dry-gel conversion method [4c]. Fig. 9 shows the IR spectra of various titanosilicates. The band at 3740 cm^{-1} is due to the surface silanols, while the broad one around 3550 cm^{-1} is attributed to the defect site silanols of a hydrogen-bonded nature [4c,5a]. The band area or intensity in 3200–3800 cm^{-1} corresponds to the total amount of silanols that possibly adsorb water molecules, and consequently can be taken as a measure for evaluating the hydrophilicity. Obviously, TS-1 and Ti-Beta contained the lowest and the highest concentration of silanol groups, respectively (Figs. 9a and e), which are consistent with the well-known fact that TS-1 is much more hydrophobic than Ti-Beta. Careful consideration then should be taken for Ti-MWW because it was prepared by the acid treatment of a lamellar precursor. The removal of B and Ti during the acid treatment would produce hydroxyl nests at the framework vacancy of tetrahedral cation, as shown in Scheme 4 for the removal of B. Actually, directly calcined lamellar precursors already had relatively high concentrations of silanols probably due to the formation of defect sites between the layers when the interlayer dehydroxylation upon calcination is incomplete (Fig. 9b). Silanols increased further in concentration for the acid-treated and calcined Ti-MWW as a result of deboronation (Fig. 9c). Nevertheless, the amount of silanols on MWW samples was not as large as that on the hydrophilic Ti-Beta. The band intensity for Ti-MWW decreased after the reaction-regeneration cycles (Fig. 9d), despite a progressive deboronation in the AAL epoxidation as shown earlier (Fig. 7). The silanols on Ti-MWW, unlike those on Ti-Beta formed in the crystallization, were therefore presumed to be in the pseudo-stable states and partially disappeared probably through the dehydroxylation to form Si–O–Si bridging bonds, or by the migration of Si into the vacancy at elevated temperatures (Scheme 4). This rearrangement or so-called framework recrystallization is commonly observed in the dealuminaion of zeolites [24–26], and may explain why Ti-MWW is more hydrophobic than Ti-Beta although it is slightly hydrophilic compared to TS-1. Considering Ti-MWW without deboronation contained a certain amount of defect sites between the layers, the amount of silanols, consequently the hydrophilicity, is conceivably not so high within the sinusoidal 10-MR channels, i.e., the main reaction space for the AAL epoxidation (see above). The hydrophobicity of the intralayer 10 MR channels of Ti-MWW would allow the protic molecules of AAL to diffuse and reach the Ti active sites to cause epoxidation even in H_2O solvent. In contrast, AAL and H_2O molecules prefer to be adsorbed on the silanols within the hydrophilic channels

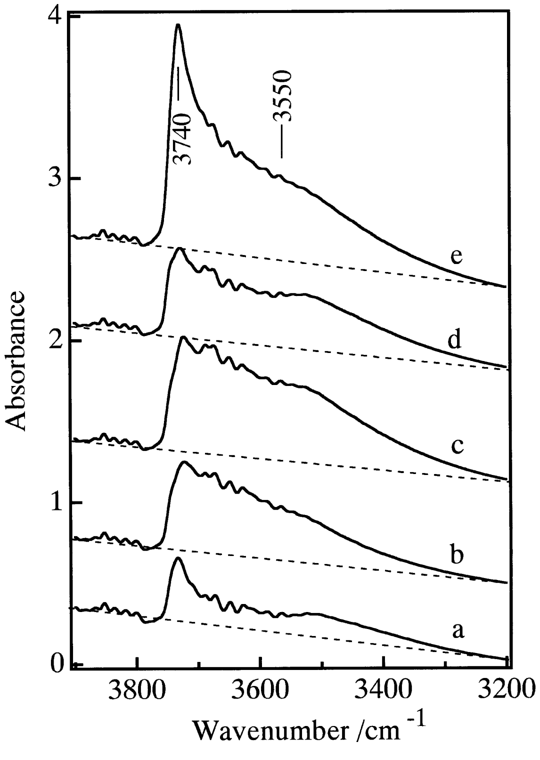
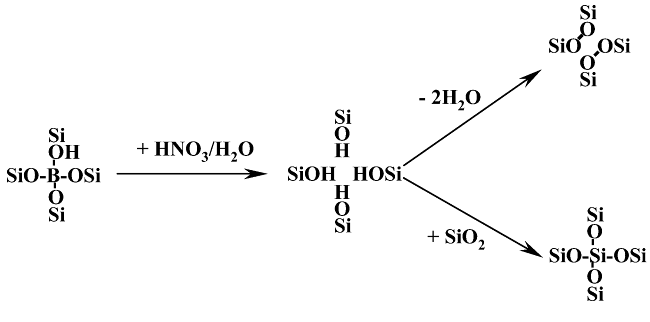


Fig. 9. IR spectra in the region of hydroxyl stretching vibration for TS-1 (a), directly calcined precursor (Si/Ti = 21, Si/B = 13) (b), fresh Ti-MWW (Si/Ti = 38, Si/B = 54) (c), reused Ti-MWW after 4 reaction-regeneration cycles in AAL epoxidation (Si/Ti = 39, Si/B = 149) (d), and Ti-Beta (Si/Ti = 42, Si/Al > 1000) (e). The spectra were recorded at room temperature after the evacuation at 773 K for 1 h.



Scheme 4.

of Ti-Beta, which makes AAL hardly accessible to Ti sites, retarding the epoxidation.

4. Conclusion

Ti-MWW catalyzes the epoxidation of AAL to GLY more effectively and selectively than TS-1 and Ti-Beta in the solvents of H_2O or MeCN. It is conceivable that the unique tortuosity makes the sinusoidal 10-MR channels of Ti-MWW more suitable for molecular diffusion, and also allows the Ti sites to be more accessible to the carbon–carbon double bonds of substrate molecules than those in the tunnel-like channels of TS-1. This explains the higher intrinsic activity of Ti-MWW when compared to TS-1. Ti-MWW is more hydrophilic than TS-1 due to the silanols on the exterior surface and on the defect sites formed between the layers, but the space within the sinusoidal 10-MR channels where the AAL epoxidation may mainly occur is essentially hydrophobic. The present study shows that the steric fitness between the substrate molecules and the Ti active sites and the hydrophobic environment of Ti sites is simultaneously important for a titanosilicate when it is employed as a catalyst for the liquid-phase oxidation of hydrophilic substrates especially in solvents of a protic nature.

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