Unique solvent effect of microporous crystalline titanosilicates in the oxidation of 1-hexene and cyclohexene

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Abstract

We investigated the influence of solvent on the activity, epoxide selectivity, and H_2O_2 efficiency of three types of zeolites—TS-1, Ti-Beta, and Ti-MWW—in the liquid-phase epoxidation of 1-hexene and cyclohexene. We found that the effect of solvent not only was related to the hydrophilicity/hydrophobicity of titanosilicates, but also was highly dependent on substrates. Acetonitrile should be the solvent of choice for the oxidation of 1-hexene over Ti-Beta and Ti-MWW, whereas methanol is preferred by TS-1. In contrast, for cyclohexene oxidation, methanol is favorable for Ti-Beta, whereas acetonitrile is the best for TS-1 and Ti-MWW. The effect of hydrophilicity/hydrophobicity is demonstrated by a series of catalytic results, but this cannot explain the solvent effect on the oxidation of cyclohexene over Ti-Beta. The H_2O_2 efficiency depends strongly on the aprotic/protic nature and polarity of solvents, as well as on the properties of titanosilicates.
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1. Introduction

Since the discovery of TS-1, titanosilicate molecular sieves have been attracting much attention, because these materials are capable of serving as highly efficient catalysts for the oxidation of various organic substrates (i.e., alkanes, alkenes, alcohols, aromatics) with H_2O_2 as an oxidant under mild conditions [1–3]. However, the nature of the active intermediate titanium species formed during the oxidation process is not yet fully understood. In addition, the factors that determine the activity and selectivity of various titanosilicates in specific reactions are not yet clear, although considerable progress toward this has been made. A full understanding of these factors will be favorable for the development of new potential catalysts and design of optimum oxidation conditions.

It has been shown that the structure of titanosilicates, synthesis methods, reaction temperature, diffusion of substrate molecules and the solvents used for oxidation strongly influence the catalytic performance [4–8]. In general, the role of solvents is to homogenize the liquid phase, thus avoiding mass-transfer problems to accelerate the interaction of reactants with catalysts. Methanol as a solvent favors the oxidation of alkanes and alkenes over TS-1, due in part to its hydrophobic character [5,9], whereas the catalytic activity of relatively hydrophilic Ti-Beta is improved in acetonitrile solvent in the oxidation of 1-hexene and cyclohexanol [5]. This is widely accepted as resulting from different active species. Species I, with a stable five-membered ring structure formed by the coordination of ROH to Ti centers and hydrogen bonding to Ti-peroxo complex, is believed to be the active intermediates in protic alcohol solvents (Scheme 1), whereas species II is assumed to contribute to the oxidation of substrates in aprotic solvents. Recently, Lamberti and co-workers found that an end-on η^2 Ti hydroperoxo complex was generated (likely by the reversible

Species I   **Species II**
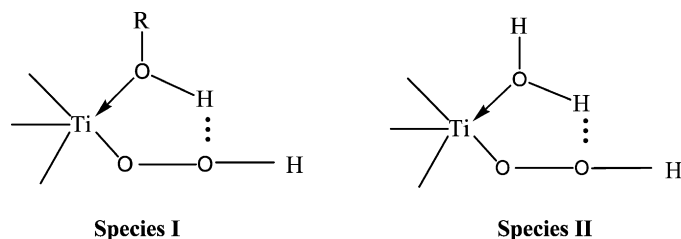
Scheme 1. Structural scheme of proposed intermediate Ti species.

rupture of Ti–O–Si bridge under anhydrous H_2O_2 conditions), and that this complex was reversibly transformed to a side-on η^2 Ti peroxo complex after addition of water, indicating that water molecules play an active role in determining the relative concentration of Ti peroxo to hydroperoxo species present on the working catalyst [10–12]. Despite such findings and interpretations, however, aprotic acetone has been reported to be the solvent of choice in terms of both activity and selectivity for the epoxidation of styrene and allyl alcohol on TS-1 [13,14]. In contrast, in the hydroxylation/oxidation of toluene, anisole, benzyl alcohol and cyclohexanol over TS-1, the catalytic activity and selectivity were significantly enhanced in water compared with in acetonitrile solvent [15], even though the reactants were in two immiscible liquids (triphasic, not biphasic, conditions).

Actually, the role of the solvent is not so simple. The aprotic/protic nature and polarity of solvents, the solubility of reactants and products in solvents, and diffusion and counterdiffusion effects also may play important roles [5,6]. In addition, the interaction of the solvent with the oxidant and/or the intermediate species possibly affects the reaction pathway [16]. Up to now, although several types of interesting titanosilicates (e.g., TS-1, TS-2, Ti-MTW, Ti-Beta and Ti-MWW) have been synthesized and found to be potential catalysts in fine chemistry, the effect of solvent on the catalytic performance remains unclear despite the reasonable explanations given to date [4,5].

In this paper, we report a comprehensive investigation into the solvent effect on the catalytic performance of three types of representative titanosilicates—TS-1, Ti-MWW, and Ti-Beta—for the oxidation of 1-hexene and cyclohexene with H_2O_2, demonstrating that the catalytic activity can be enhanced when appropriate amounts of mixed solvents are present in the oxidation system, compared with single solvent. In particular, converse results are obtained when the same titanosilicate is used for catalyzing the oxidation of 1-hexene and cyclohexene. Thus, new insight into the effect of solvent is needed.

2. Experimental

2.1. Synthesis and characterization of different titanosilicates

TS-1 was synthesized through the method reported by Thangaraj and Sivasanker [17], with modifications. Ti-Beta was synthesized with the seeding method by using fumed silica as a silica source following the procedures reported by Camblor et al. [7]. Ti-MWW was prepared by the postsynthesis

method using highly deboronated B-MWW as a silica source [18]. The as-synthesized samples were calcined at 550–600 °C for 8 h. For Ti-MWW, the as-synthesized material was first washed with 2 M HNO_3 aqueous solution at 100 °C for 24 h before calcination, whereas TS-1 was treated with 1 M HCl aqueous solution (liquid/solid = 50 mL/g) for 20 h at room temperature after calcination. Some samples (1 g) were silylated by being suspended in the boiling solution of 1,1,1,3,3,3-hexamethyldisilazane (0.2 g) and toluene (20 mL) for about 4 h.

The crystalline phase and purity of the samples were identified with a MAC Science M3X 1030 X-ray diffractometer using $CuK\alpha$ radiation. Crystal morphology and size were evaluated on a Hitachi S-5200 field-emission scanning electron microscope (FE-SEM). IR spectra in the OH stretching vibration region were measured on a Perkin-Elmer 1600 FTIR spectrometer. Before the spectra were recorded, the samples were evacuated at 500 °C for 2 h under high-vacuum conditions. The diffuse reflectance (DR) UV–vis spectra were recorded against a white halon reference standard on a Jasco V-550 UV–vis spectrophotometer equipped with an integration sphere. The chemical compositions of the calcined samples were determined by a Shimadzu ICPS-8000E inductively coupled plasma atomic emission spectrometer.

2.2. Catalytic measurements

The oxidation of 1-hexene and cyclohexene was carried out at 60 °C for 2 h under stirring condition in a 20-mL round-bottomed flask immersed in a thermostatted water bath and equipped with a condenser. The stirring was sufficiently strong to rule out the effect of external diffusion on catalytic performance for all of the batches. In a typical batch, 0.05 g of catalyst, 10 mL of solvent, 10 mmol of alkene, and 10 mmol of H_2O_2 (31% aqueous solution) were used. The product was analyzed using a Shimadzu GC-14B gas chromatograph equipped with a 50-m OV-1 capillary column and a flame ionization detector. The amount of the unconverted H_2O_2 was determined with 0.1 M $Ce(SO_4)_2$ aqueous solution using the titration method.

3. Results

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

XRD and FE-SEM measurements confirmed the crystalline phase and purity of TS-1, Ti-Beta, and Ti-MWW [7,8,19–22]. The FE-SEM images showed that the crystals of TS-1 and Ti-Beta had an irregular spherical shape with diameters of about 0.15–0.2 and 0.2–0.3 µm, respectively, whereas those of Ti-MWW exhibited a habit of thin hexagonal platelets of about 0.2–0.5 µm long and 0.05–0.1 µm thick (not shown). The finding of similar crystal sizes in these three types of titanosilicate basically eliminates any effect of particle size on catalytic performance. The diffuse reflectance UV–vis spectroscopy findings demonstrated only a single band at about 205 for TS-1
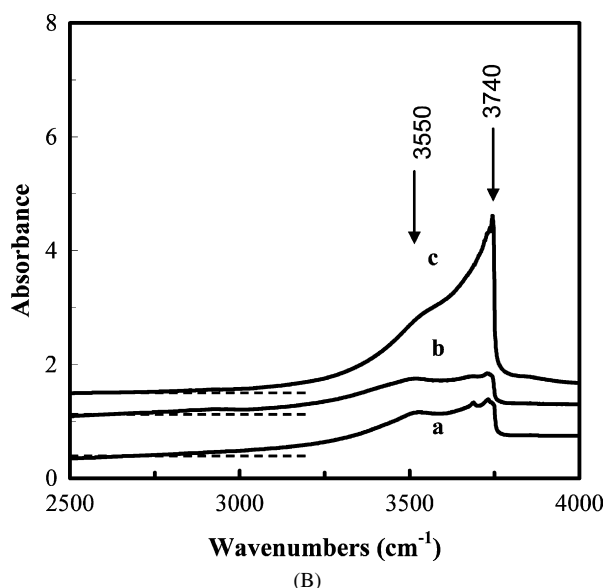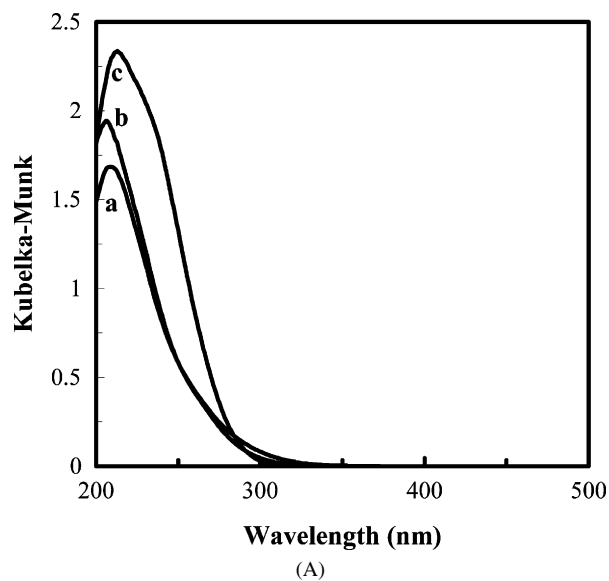
Fig. 1. (A) DR UV–vis spectra and (B) IR spectra in the OH region of (a) Ti-MWW, (b) TS-1, and (c) Ti-Beta catalysts.
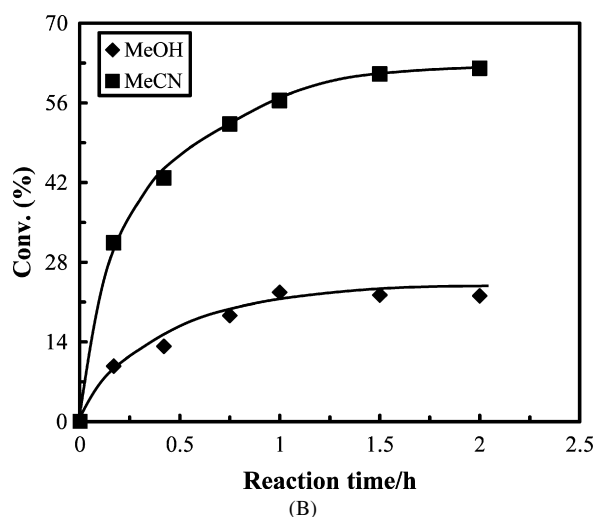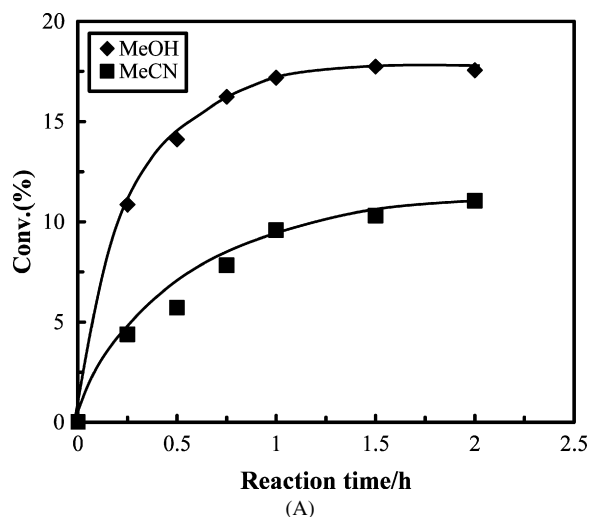

Fig. 2. Relationship of 1-hexene conversion obtained in acetonitrile and methanol solvents over TS-1 (A) and Ti-MWW (B) and reaction time. (Reaction conditions: 60 °C, 0.05 g catalyst, 10 mL solvent, 10 mmol substrate and 10 mmol H_2O_2 (30% aqueous solution).)

and at 210 nm for Ti-MWW, and one band at 215 nm with a small shoulder around 230 nm for Ti-Beta (Fig. 1A). This demonstrates that all of the Ti atoms were isolated and had a tetrahedral coordination in both TS-1 and Ti-MWW [8,21–23], whereas the Ti atoms in Ti-Beta were in a fourfold to sixfold coordination [5]. The absence of bands above 250 nm indicates that extra-framework octahedral Ti species and TiO_2 were negligible in all three materials [5,8,21–23]. The IR spectra in the OH region showed two much more intense bands at about 3740 and 3550 cm^{-1} (Fig. 1B), attributed to terminal Si–OH and hydrogen-bonded silanol groups at defect sites, respectively [22,24,25], in Ti-Beta compared with TS-1 and Ti-MWW, implying that Ti-Beta contained much more defect sites and thus was more hydrophilic. The hydrophilicity of these titanosilicates decreased in the order Ti-Beta > Ti-MWW > TS-1.

3.2. Oxidation of 1-hexene and cyclohexene over various titanosilicates in acetonitrile and methanol

Fig. 2A shows the dependence of 1-hexene conversion obtained over TS-1 on the reaction time. In agreement with the results reported in the literature [1,3,5], the use of methanol as a solvent resulted in substantially higher catalytic activity compared with the use of acetonitrile; the initial reaction rates were 0.093 mmol/min in methanol solvent and 0.036 mmol/min in acetonitrile. As expected, the difference in activity decreased with decreasing Ti content, because the number of active sites decreased (Fig. 3). However, with respect to the oxidation of cyclohexene, a converse solvent effect was observed (Fig. 4); when acetonitrile was used as the solvent, the conversion was nearly fourfold greater than that obtained with methanol as solvent. Almost no dependence of conversion on Ti content was observed at a Ti/(Si + Ti) molar ratio >0.0086, likely because the reaction occurred mainly on the external surface
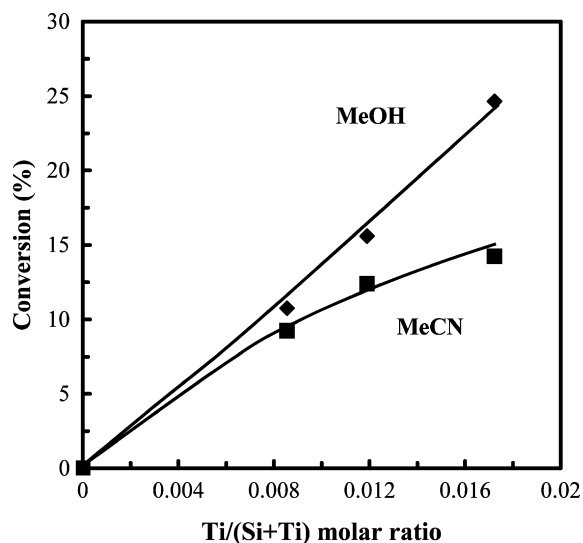
Fig. 3. Dependence of 1-hexene conversion on the Ti content of TS-1 in the oxidation of 1-hexene in methanol and acetonitrile solvents. (Reaction conditions: 60 °C, 2 h, 0.05 g catalyst, 10 mL solvent, 10 mmol substrate and 10 mmol H_2O_2 (31% aqueous solution).)

Fig. 5. Dependence of conversion on the Ti content of Ti-MWW in the oxidation of 1-hexene in methanol and acetonitrile solvents. (Reaction conditions: 60 °C, 2 h, 0.05 g catalyst, 10 mL solvent, 10 mmol substrate and 10 mmol H_2O_2 (31% aqueous solution).)

Fig. 4. Dependence of conversion on the Ti content of TS-1 in the oxidation of cyclohexene in methanol and acetonitrile solvents. (Reaction conditions: 60 °C, 4 h, 0.05 g catalyst, 10 mL solvent, 10 mmol substrate and 10 mmol H_2O_2 (31% aqueous solution).)

Fig. 6. Dependence of conversion on the Ti content of Ti-MWW in the oxidation of cyclohexene in methanol and acetonitrile solvents. (Reaction conditions: 60 °C, 2 h, 0.05 g catalyst, 10 mL solvent, 10 mmol substrate and 10 mmol H_2O_2 (31% aqueous solution).)
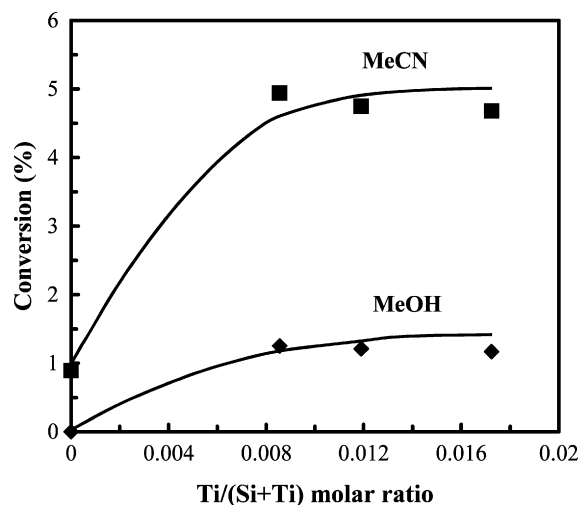
and near the pore mouth, because cyclohexene has nearly the same molecular size as cyclohexane, which hardly diffuses into the channel of MFI-type materials. The increased Ti content incorporated into the internal surface did not contribute significantly to the enhanced activity in the oxidation of cyclohexene. In contrast to TS-1, Ti-MWW exhibited much higher activity for the oxidation of 1-hexene in acetonitrile solvent than in methanol (initial reaction rate, 0.48 mmol/min vs 0.14 mmol/min) (Figs. 2B and 5), whereas it gave slightly higher conversion in the oxidation of cyclohexene in acetonitrile solvent than in methanol (Fig. 6). The conversion of 1-hexene increased almost linearly with the amount of Ti in the framework (Fig. 5), whereas a converse trend was observed in the oxidation of cyclohexene (Fig. 6). The low-content sample
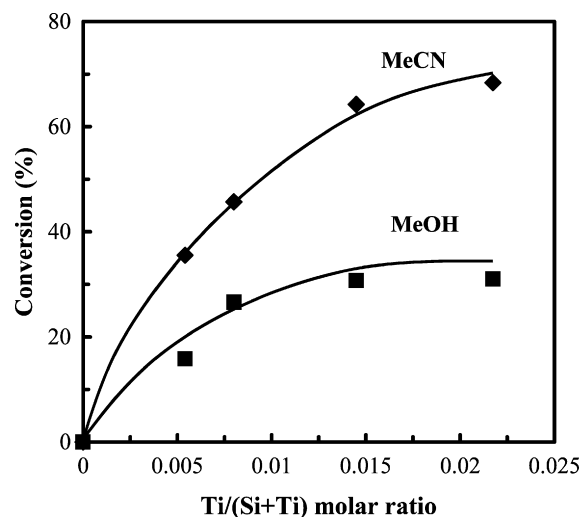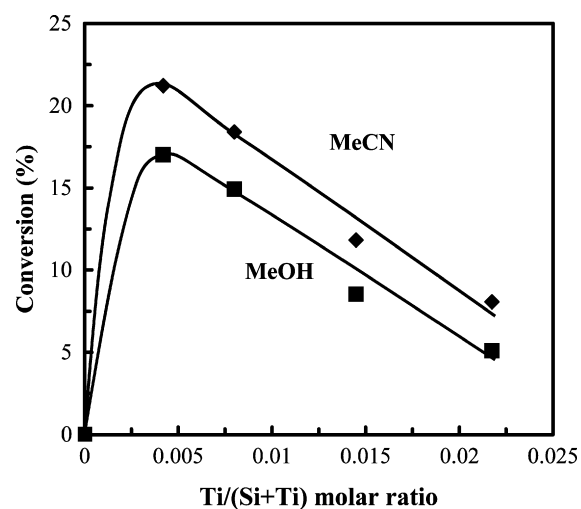
(Ti-YNU-1) had a 12 membered-ring (MR) interlayer pore-opening connected to supercages, whereas high Ti content led to the formation of a typical Ti-MWW structure with distorted 10-MR pore openings in the interlayer space [21,22]. Thus, more Ti species would be accessible to bulky substrate molecules in the low-content sample than in the high-content sample. The latter is highly active only for linear alkenes, because of the difficulty in accommodating cyclic alkenes. When 1-hexene was oxidized over Ti-Beta, the conversion in acetonitrile solvent was about twice that attained in methanol; however, for cyclohexene oxidation, methanol was clearly superior to acetonitrile as a solvent (Table 1), in conflict with the results reported by Corma et al. [5] but consistent with our previous findings [26].

Table 1
Catalytic results for the oxidation of 1-hexene and cyclohexene over various titanosilicates[a]

Entry	Titanosilicate	Si/Ti	Solvent	Substrate	Conv. (%)	TON[b]
1	TS-1	60	MeCN	1-Hexene	11.3	83.2
2	TS-1	60	MeOH	1-Hexene	18.4	135.4
3	TS-1 silylated	60	MeCN	1-Hexene	11.0	81.0
4	TS-1 silylated	60	MeOH	1-Hexene	19.2	141.3
5	TS-1 poisoned[c]	60	MeOH	1-Hexene	16.9	124.4
6	TS-1	60	MeCN	Cyclohexene	4.9	36.1
7	TS-1	60	MeOH	Cyclohexene	0.9	6.6
8	TS-1 silylated	60	MeCN	Cyclohexene	4.7	34.6
9	TS-1 silylated	60	MeOH	Cyclohexene	1.4	10.3
10	TS-1 poisoned[c]	60	MeCN	Cyclohexene	1.6	11.8
11	TS-1 poisoned[c]	60	MeOH	Cyclohexene	0.7	5.2
12	Ti-Beta	35	MeCN	1-Hexene	17.0	74.1
13	Ti-Beta	35	MeOH	1-Hexene	7.3	31.8
14	Ti-Beta silylated	35	MeCN	1-Hexene	8.7	37.9
15	Ti-Beta silylated	35	MeOH	1-Hexene	4.6	20.1
16	Ti-Beta	35	MeCN	Cyclohexene	16.5	71.9
17	Ti-Beta	35	MeOH	Cyclohexene	31.0	135.2
18	Ti-Beta silylated	35	MeCN	Cyclohexene	7.7	33.6
19	Ti-Beta silylated	35	MeOH	Cyclohexene	3.6	15.7
20	Ti-MWW	44	MeCN	1-Hexene	68.3	371.5
21	Ti-MWW	44	MeOH	1-Hexene	22.0	119.7
22	Ti-MWW silylated	44	MeCN	1-Hexene	59.4	323.1
23	Ti-MWW silylated	44	MeOH	1-Hexene	19.9	108.3
24	Ti-MWW poisoned[c]	44	MeCN	1-Hexene	60.6	332.8
25	Ti-MWW	44	MeCN	Cyclohexene	15.0	81.6
26	Ti-MWW	44	MeOH	Cyclohexene	14.9	81.1
27	Ti-MWW silylated	44	MeCN	Cyclohexene	6.1	33.2
28	Ti-MWW silylated	44	MeOH	Cyclohexene	10.6	57.7
29	Ti-MWW poisoned[c]	44	MeCN	Cyclohexene	3.4	18.5
30	Ti-MWW poisoned[c]	44	MeOH	Cyclohexene	4.2	22.8

[a] Reaction conditions: 60 °C, 2 h (4 h for TS-1 and its modified materials for the oxidation of cyclohexene), 0.05 g catalyst, 10 mL solvent, 10 mmol alkene and 10 mmol H_2O_2 (31% aqueous solution).

[b] Turnover number: the mole of substrate converted per mole of Ti present in the catalysts.

[c] The poisoning of samples was conducted by adding 1 mmol of 2,4-dimethylquinoline into the reaction mixture.

3.3. Catalytic performance of various titanosilicates after silylation and poisoning

Table 1 summarizes the catalytic results of silylated and poisoned TS-1, Ti-Beta, and Ti-MWW for the oxidation of 1-hexene and cyclohexene. Clearly, silylation of TS-1 had no significant effect on the oxidation of 1-hexene and cyclohexene regardless of the solvents used (entries 1–4, 6–9); however, the silylation of Ti-Beta drastically decreased the activity both in methanol and in acetonitrile (entries 12–19). This phenomenon also was observed in the oxidation of cyclohexene on silylated Ti-MWW, although no significant effect was produced on the oxidation of 1-hexene (entries 20–23, 25–28). On the other hand, when TS-1 and Ti-MWW were poisoned by bulky 2,4-dimethylquinoline, they were hardly active for the oxidation of cyclohexene (entries 10, 11, 29 and 30), although they still gave high conversion in the epoxidation of 1-hexene (entries 5 and 24).

In addition, the modification of titanosilicates had a marked solvent effect on H_2O_2 efficiency. In the case of TS-1, irrespective of substrates or modifications, the use of methanol as the solvent always gave higher H_2O_2 efficiency in 1-hexene oxidation compared with the use of acetonitrile (>85% vs ca. 70%).

In contrast, the H_2O_2 efficiency on Ti-MWW (>90%) and silylated Ti-MWW (ca. 80%) in acetonitrile solvent was similar to that in methanol irrespective of the alkenes oxidized. On the other hand, the poisoning by 2,4-dimethylquinoline led to a drastic decrease in H_2O_2 efficiency in the oxidation of cyclohexene. For Ti-Beta, the H_2O_2 efficiency depended on the substrates and modifications. Relatively high H_2O_2 efficiency was obtained with acetonitrile as the solvent in the oxidation of 1-hexene, whereas methanol exhibited much greater efficiency than acetonitrile in the oxidation of cyclohexene (80% vs 50%). In contrast, silylated Ti-Beta exhibited greater H_2O_2 efficiency in methanol solvent than in acetonitrile (44–55% vs <30%), regardless of the substrates.

3.4. Effects of the aprotic/protic nature and polarity of the solvents

Tables 2 and 3 give an overview of the influence of the aprotic/protic nature and polarity of different solvents on the catalytic performance of various titanosilicates for the oxidation of 1-hexene and cyclohexene, respectively. In the oxidation of 1-hexene, the activity of Ti-Beta increased with the increase in polarity for both the aprotic and protic alcohol solvents, although methanol solvent gave a lower conversion than ethanol

Table 2
Influence of the aprotic/protic nature and polarity of solvents on the catalytic performance of different titanosilicates for the oxidation of 1-hexene[a]

Solvent	Dielectric constant	TS-1 (Si/Ti = 53)					Ti-Beta (Si/Ti = 30)					Ti-MWW (Si/Ti = 44)				
		1-Hexene			H_2O_2		1-Hexene			H_2O_2		1-Hexene			H_2O_2	
		Conv. (%)	TON[b]	Selec.[c] (%)	Conv. (%)	Effi.[d] (%)	Conv. (%)	TON[b]	Selec.[c] (%)	Conv. (%)	Effi.[d] (%)	Conv. (%)	TON[b]	Selec.[c] (%)	Conv. (%)	Effi.[d] (%)
MeCN	37.5	14.5	94.5	100	22.8	63.8	17.7	66.5	100	40.6	43.6	68.3	371.5	100	69.1	97.3
MeCOMe	20.7	17.8	116.1	97.9	22.9	79.7	7.1	26.7	72.3	27.2	26.1	42.3	230.1	99.2	47.6	89.6
MeCOEt	18.5	19.1	124.5	99.2	25.6	77.6	5.0	18.8	78.9	32.5	15.6	49.4	268.7	99.7	52.9	95.1
MeOH	32.7	21.2	138.2	96.6	25.3	91.0	8.7	32.7	36.3	19.6	38.1	21.9	119.1	91.0	30.2	74.2
EtOH	24.5	17.3	112.8	81.1	19.6	90.4	11.7	44.0	34.8	22.6	53.1	16.0	87.0	92.1	21.6	75.3
t-BuOH	10.9	9.2	60.0	100	12.9	72.8	4.7	17.7	67.0	18.7	25.8	14.0	76.2	99.7	21.7	65.4

[a] Reaction conditions: 60 °C, 2 h, 0.05 g catalyst, 10 mL solvent, 10 mmol 1-hexene and 10 mmol H_2O_2 (31% aqueous solution).
[b] Turnover number: the mole of substrate converted per mole of Ti present in the catalysts.
[c] Epoxide selectivity.
[d] Efficiency.

Table 3
Influence of the aprotic/protic nature and polarity of solvents on the catalytic performance of Ti-Beta and Ti-MWW for the oxidation of cyclohexene[a]

Solvent	Dielectric constant	Ti-Beta (Si/Ti = 30)								Ti-MWW (Si/Ti = 44)							
		Conv. (%)	TON[b]	Product selectivity (%)				H_2O_2		Conv. (%)	TON[b]	Product selectivity (%)				H_2O_2	
				Epo.[c]	Diol	Ether[d]	Others	Conv. (%)	Effi.[e] (%)			Epo.[c]	Diol	Ether[d]	Others	Conv. (%)	Effi.[e] (%)
MeCN	37.5	17.7	66.5	80.0	18.8	–	1.2	36.2	52.2	15.0	81.6	70.0	20.4	–	9.6	18.4	80.8
MeCOMe	20.7	7.1	26.7	12.3	78.1	–	9.6	32.9	23.5	3.8	20.7	39.3	60.0	–	0.7	20.1	18.7
MeCOEt	18.5	11.6	43.6	3.8	94.3	–	1.9	33.8	36.3	5.3	28.8	13.7	84.4	–	1.9	21.0	25.9
MeOH	32.7	40.4	151.9	0.6	16.1	82.3	1.0	51.8	80.1	14.9	81.1	6.4	6.7	85.2	1.7	18.6	79.6
EtOH	24.5	13.0	48.9	4.3	43.2	52.6	0	22.9	89.1	9.5	51.7	11.7	42.0	43.8	2.5	15.8	88.3
t-BuOH	10.9	4.8	18.0	12.7	81.5	5.0	0.8	16.4	30.3	3.6	19.6	15.6	76.8	7.6	0	7.4	53.4

[a] Reaction conditions: 60 °C, 2 h, 0.05 g catalyst, 10 mL solvent, 10 mmol cyclohexene and 10 mmol H_2O_2 (31% aqueous solution).
[b] Turnover number: the mole of substrate converted per mole of Ti present in the catalysts.
[c] Epoxide.
[d] Monomethyl glycol ether.
[e] Efficiency.

solvent. This also held true for Ti-MWW, with the exception of lower activity in acetone solvent than in methyl ethyl ketone solvent. In contrast, the activity of TS-1 increased with decreasing polarity of the aprotic solvents, whereas the opposite effect was seen for the protic alcohol solvents. The aprotic solvents favored the formation of epoxide regardless of the titanosilicate catalysts used, whereas alcohol solvents (except t-BuOH) led to a significant reduction in epoxide selectivity, especially over Ti-Beta, where hydrolysis/solvolysis of 1-hexene epoxide occurred. In addition, compared with TS-1 and Ti-MWW, Ti-Beta also showed very low selectivity for epoxide in acetone and methyl ethyl ketone solvents. The efficiency of H_2O_2 in the oxidation of 1-hexene over TS-1 was higher in protic alcohol solvents than in aprotic solvents, whereas the opposite effect was seen for Ti-MWW. The H_2O_2 efficiency was much lower for Ti-Beta than for TS-1 and Ti-MWW. It is noteworthy that H_2O_2 efficiency generally improved with increasing 1-hexene conversion for all three materials.

For cyclohexene oxidation, because the conversion over TS-1 was very low, we focused on studying the effect of solvents on the catalytic properties of Ti-Beta and Ti-MWW. For both of these catalysts, activity decreased with decreasing solvent polarity for both the aprotic and protic alcohol series, with the exception that methyl ethyl ketone solvent gave greater conversion than acetone solvent. As the solvent polarity decreased, the epoxide selectivity decreased dramatically for the aprotic solvents but increased for the protic alcohol solvents.

3.5. Effect of water on oxidation activity

Figs. 7 and 8 depict the catalytic results of the three titanosilicates for the oxidation of 1-hexene and cyclohexene when water was added to the reaction system using acetonitrile as the solvent. The volume ratio of water to acetonitrile in the reaction mixture was kept below 13% mL/mL to avoid any serious mass-transfer problems. The activity of Ti-MWW for the oxidation of 1-hexene increased with increasing amounts of water in the system. The addition of a small amount of water also slightly promoted substrate conversion over Ti-Beta. In contrast, no positive effect was observed in the oxidation of cyclohexene over these two materials. As for TS-1, oxidation of neither 1-hexene nor cyclohexene was significantly affected by the addition of water under the present study conditions.
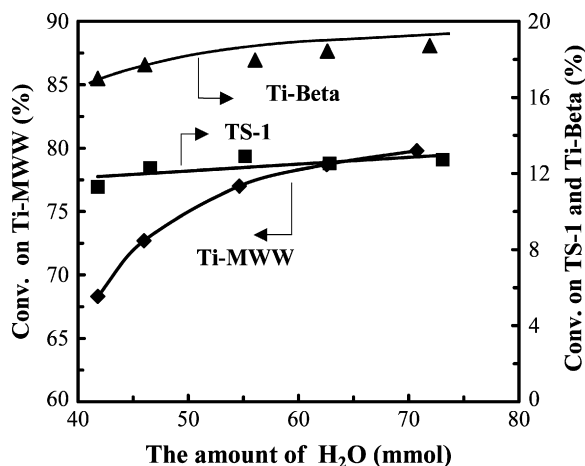
Fig. 7. Effect of the water amount, including the water contained in H_2O_2 aqueous solution, in the reaction mixture on the conversion of 1-hexene over various titanosilicates. (Reaction conditions: 60 °C, 2 h, 0.05 g catalyst, 10 mL acetonitrile, 10 mmol substrate and 10 mmol H_2O_2 (31% aqueous solution).)
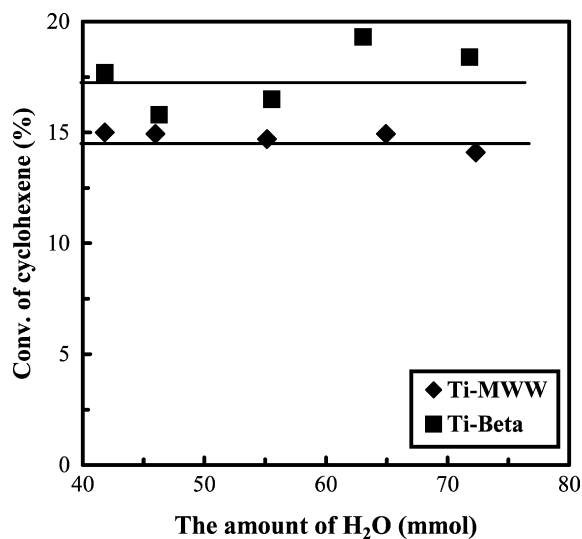

Fig. 8. Effect of the water amount, including the water contained in H_2O_2 aqueous solution, in the reaction mixture on the conversion of cyclohexene over various titanosilicates. (Reaction conditions: 60 °C, 2 h, 0.05 g catalyst, 10 mL acetonitrile, 10 mmol substrate and 10 mmol H_2O_2 (31% aqueous solution).)

Table 4
Influence of the MeCN/MeOH ratio in the solvent mixture on the catalytic property of TS-1 (Si/Ti = 53) for the oxidation of 1-hexene[a]

MeCN/MeOH (mL/mL)	Conversion of 1-hexene (%)	TON[b]	Selectivity (%)	
			Epoxide	Others
0/10	21.2	138.2	96.4	3.6
0.4/9.6	26.9	175.4	98.9	1.1
0.8/9.2	26.5	172.8	98.9	1.1
1.5/8.5	27.4	178.6	99.6	0.4
4.0/6.0	26.8	174.7	100	0
6.0/4.0	24.2	157.8	100	0
8.5/1.5	17.1	111.5	100	0
10/0	14.5	94.5	100	0

[a] Reaction conditions: 60 °C, 2 h, 0.05 g catalyst, 10 mL solvent, 10 mmol 1-hexene and 10 mmol H_2O_2 (31% aqueous solution).
[b] Turnover number: the mole of substrate converted per mole of Ti present in the catalysts.

Table 5
Influence of the MeCN/MeOH ratio in the solvent mixture on the catalytic property of Ti-Beta (Si/Ti = 30) for the oxidation of 1-hexene[a]

MeCN/MeOH (mL/mL)	Conversion of 1-hexene (%)	TON[b]	Selectivity (%)	
			Epoxide	Others
0/10	8.7	32.7	36.3	63.7
1.7/8.3	15.7	59.0	97.0	3.0
4.0/6.0	17.7	66.5	98.8	1.2
6.0/4.0	20.8	78.2	99.3	0.7
8.5/1.5	20.5	77.1	100	0
10/0	17.7	66.5	100	0

[a] Reaction conditions: 60 °C, 2 h, 0.05 g catalyst, 10 mL solvent, 10 mmol 1-hexene and 10 mmol H_2O_2 (31% aqueous solution).
[b] Turnover number: the mole of substrate converted per mole of Ti present in the catalysts.

3.6. Effect of mixed solvents on the catalytic performance of various titanosilicates

Table 4 shows the catalytic results of TS-1 for the oxidation of 1-hexene in a mixed solvent of methanol and acetonitrile with the total volume of solvent kept constant (10 mL). With increasing amounts of MeCN up to a MeCN/MeOH ratio of 1.5/8.5 (mL/mL), not only was the activity enhanced, but also the selectivity was increased to nearly 100%. But a further increase in the MeCN/MeOH (mL/mL) ratio to >6/4 produced in a significant decrease in conversion. Actually, the conversion of 1-hexene also increased when acetone or methyl ketone instead of acetonitrile was used as a mixed solvent, even though the epoxide selectivity declined. In a manner similar to that for TS-1, the activity of Ti-Beta for the oxidation of 1-hexene in a mixed acetonitrile and methanol solvent (MeCN/MeOH = 6/4–8.5/1.5 mL/mL) was greater than that obtained in a single solvent while maintaining high epoxide selectivity (Table 5). In contrast, adding a small amount of acetonitrile to methanol (e.g., MeCN/MeOH = 1.5/8.5 mL/mL) drastically lowered the conversion of cyclohexene on Ti-Beta, close to that obtained in pure acetonitrile solvent (Table 6). For the Ti-MWW catalyst, the conversion of 1-hexene was significantly reduced as increasing amounts of methanol were co-added into the acetonitrile solvent (Table 7).

3.7. Decomposition of hydrogen peroxide

The results of the decomposition of H_2O_2 over various titanosilicates at 60 °C in the absence of substrates are illustrated in Fig. 9. The figure shows that regardless of the solvents used, the Ti-Beta catalyst produced much more rapid decomposition of H_2O_2 than either TS-1 or Ti-MWW. In general, compared with methanol, MeCN solvent strongly promoted the decomposition of H_2O_2, although the difference was not apparent for TS-1.

4. Discussion

The effect of solvent on catalytic performance is a quite complicated but important area in studies of heterogeneous catalytic systems involving titanosilicate catalysts. The structure

Table 6
Influence of the MeCN/MeOH ratio in the solvent mixture on the catalytic property of Ti-Beta (Si/Ti = 30) for the oxidation of cyclohexene[a]

MeCN/MeOH (mL/mL)	Conversion of 1-hexene (%)	TON[b]	Selectivity (%)		H_2O_2	
			Epoxide	Others	Conv. (%)	Effi.[c] (%)
0/10	40.4	151.9	0.6	99.4	51.8	80.1
1.5/8.5	21.9	82.3	30.0	70.0	35.7	64.6
4.0/6.0	21.5	80.8	51.4	48.6	33.2	67.8
6.0/4.0	21.1	79.3	56.8	43.2	33.7	64.2
8.5/1.5	17.7	66.5	66.5	33.5	33.0	62.1
10/0	17.7	66.5	80.0	20.0	36.2	52.2
0/10 (HQ)[d]	36.9	138.7	1.0	99.0	41.2	93.6

[a] Reaction conditions: 60 °C, 2 h, 0.05 g catalyst, 10 mL solvent, 10 mmol cyclohexene and 10 mmol H_2O_2 (31% aqueous solution).
[b] Turnover number: the mole of substrate converted per mole of Ti present in the catalysts.
[c] Efficiency.
[d] 1 mmol of hydroquinone was added into the reaction mixture.

Table 7
Influence of the MeCN/MeOH ratio in the solvent mixture on the catalytic property of Ti-MWW (Si/Ti = 44) for the oxidation of 1-hexene[a]

MeCN/MeOH (mL/mL)	Conversion of 1-hexene (%)	TON[b]	Selectivity (%)	
			Epoxide	Others
0/10	22.0	119.7	87.6	12.4
1.5/8.5	35.4	192.6	98.8	1.2
4.0/6.0	43.9	238.8	99.4	0.6
6.0/4.0	53.2	289.4	100	0
8.5/1.5	60.5	329.1	100	0
10/0	68.3	371.5	100	0

[a] Reaction conditions: 60 °C, 2 h, 0.05 g catalyst, 10 mL solvent, 10 mmol 1-hexene and 10 mmol H_2O_2 (31% aqueous solution).
[b] Turnover number: the mole of substrate converted per mole of Ti present in the catalysts.

Fig. 9. Decomposition of H_2O_2 over different titanosilicates in methanol and acetonitrile solvents at 60 °C in the absence of substrate molecules. (Reaction conditions: 60 °C, 2 h, 0.05 g catalyst, 10 mL solvent and 10 mmol H_2O_2 (31% aqueous solution).)

and surface properties of the catalysts and the aprotic/protic nature, polarity, and basicity of solvents, along with the solubility and diffusion effects of reactants, intermediates, and products in solvents, all need to be considered when choosing a suitable solvent. It has been proposed that peroxo-compounds are formed as intermediates by the reaction of group V and VI metal oxides or metal complexes with either organic hydroperoxides or hydrogen peroxide [9]. In contrast, in the liquid-phase hydrogen peroxide oxidation of organic substrates catalyzed by titanosilicates, species I and II (Scheme 1) with a five-membered ring of hydrogen bonded structure are presumed to be the active species in alcohols and aprotic solvents, respectively [4,5].

4.1. Effect of solvent on the catalytic performance of TS-1 in the epoxidation of 1-hexene and cyclohexene

Compared with species II, species I is more likely to form on TS-1. This is believed to be due to this species' hydrophobic character [4], which allows methanol to approach Ti sites more readily than water, leading to the formation of numerous active sites of species I [4]. Therefore, when 1-hexene is oxidized on TS-1, methanol should be the solvent of choice. But because cyclohexene has a large molecule size, it is oxidized mainly on the exterior surface and/or near the pore mouth, where much more Si–OH and Ti–OH groups are present than inside the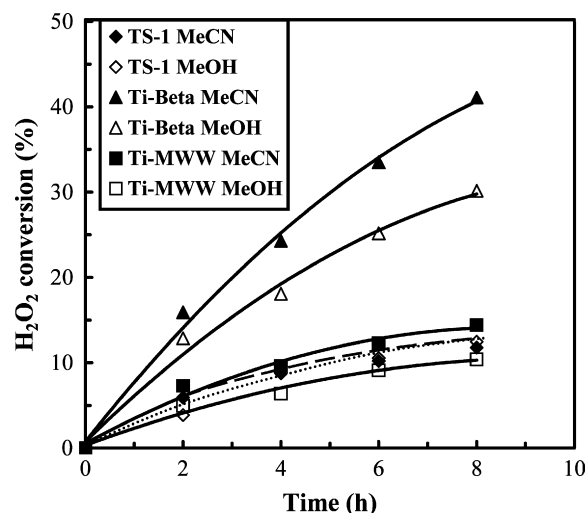 channels, making these areas relatively hydrophilic. To confirm this hypothesis, a TS-1 sample was poisoned by adding 2,4-dimethylquinoline into the reaction mixture. The conversion of cyclohexene drastically declined in acetonitrile solvent (Table 1, entry 10), whereas the conversion of 1-hexene was not significantly changed in methanol solvent (Table 1, entry 5). This finding demonstrates that the oxidation of cyclohexene was indeed catalyzed primarily by Ti sites on the exterior surface and/or near the pore mouth.

This finding is further supported by Fig. 4, which shows that the Ti content in TS-1 had no significant influence on the catalytic activity for cyclohexene oxidation; there was little difference in the numbers of Ti sites on the external surface between the low-content and high-content samples when the Ti/(Si + Ti) molar ratio in the TS-1 catalyst was >0.0086. This is probably because Ti cations did not randomly substitute Si, but instead preferably occupied T_6, T_7, T_{11}, and possibly T_{10} sites [25], the predominating defect sites in silicalite-1 [27]. Another contributing factor may be the much larger internal surface area compared with external surface area (ca. 20-fold larger). Species II should form more easily on the external surface and act as an active intermediate when acetonitrile is

used as the solvent [5]. Moreover, species II is more intrin-sically active than species I, due to its higher electrophilic character [5]. These characteristics make acetonitrile a better solvent in the oxidation of cyclohexene (which occurs mainly on the external surface of TS-1) than in the oxidation of 1-hexene over TS-1. This is supported by the finding that sily-lation slightly increased the conversion of cyclohexene over TS-1 when methanol was used as solvent (Table 1, entry 9). The selective silylation of the external surface of TS-1 by bulky 1,1,1,3,3,3-hexamethyldisilazane could increase the hydropho-bicity, favoring the formation of species I. It has been shown that the silylation of Ti-MCM-41 led to a significant increase in the Q^4/Q^3 ratio, which significantly increased its hydropho-bicity and enhanced its activity for the oxidation of 1-hexene and n-hexane [28]. Nevertheless, after silylation, considerable amounts of OH groups remained on the exterior surface of TS-1 as a result of the steric limitation due to the large molecular size of 1,1,1,3,3,3-hexamethyldisilazane. This made the exter-nal surface of TS-1 still relatively hydrophilic even after sily-lation. The preponderant methanol solvent strongly competes with water for adsorption on Ti sites, resulting in lower activity compared with that found with acetonitrile solvent.

4.2. Effect of solvent on the catalytic performance of Ti-MWW in the epoxidation of 1-hexene and cyclohexene

In agreement with our previous results [8,18,21,22], Ti-MWW was found to be much more active in acetonitrile than in methanol in the epoxidation of 1-hexene because of its hy-drophilicity (Table 1, entries 20 and 21) [18,22]. Silylation had no marked effect on the catalytic results, because the reac-tion occurred mainly inside the channels with distorted 10-MR pore openings, hindering the silylation of internal Ti species by bulky 1,1,1,3,3,3-hexamethyldisilazane. The epoxidation of cyclohexene over Ti-MWW occurred mainly on its external surface (similar to that for TS-1), due to the slightly smaller pore openings of MWW-type materials compared with MFI-type materials [29], and the poisoning by 2,4-dimethylquinoline resulted in a drastically reduced activity for oxidation of cyclo-hexene regardless of the solvent used (Table 1, entries 29 and 30) but did not significantly affect the activity in 1-hexene epox-idation (Table 1, entry 24). The presence of numerous 12-MR side pockets on the external surface of Ti-MWW led to a cy-clohexene conversion between those obtained with TS-1 and Ti-Beta. Note that the Ti species inside the side pockets were located on the intracrystalline surface and thus had an envi-ronmental state similar to that of the Ti species in TS-1; these Ti species were relatively hydrophobic. As a result, methanol solvent gave almost the same activity as acetonitrile solvent, likely because both the hydrophilic Ti species on the exter-nal surface and hydrophobic Ti species in the side pockets could serve as active sites for the epoxidation of cyclohexene (Table 1, entries 25 and 26). On silylation with 1,1,1,3,3,3-hexamethyldisilazane, the external surface silanol groups were silylated; therefore, the sites active for the cyclohexene epoxi-dation became totally hydrophobic, making methanol the sol-vent of choice (Table 1, entry 28). But the silylation close to
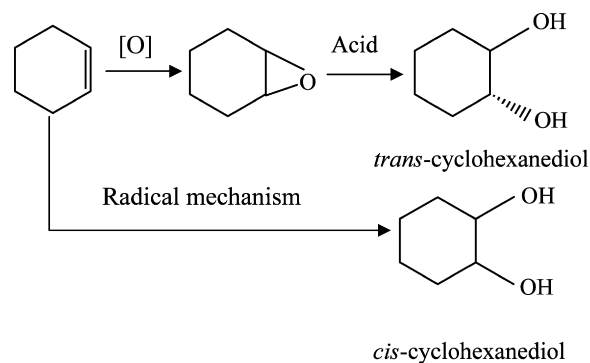
Scheme 2. Mechanistic pathway for the oxidation of cyclohexene to cyclo-hexanediol.

the entrance of side pockets with such a large-molecule agent produced a considerable steric constraint on the diffusion of substrate and product molecules into and out of these side pock-ets, giving rise to a slight decrease in activity (Table 1, entries 27 and 28).

4.3. Effect of solvent on the catalytic performance of Ti-Beta in the epoxidation of 1-hexene and cyclohexene

As suggested previously [5], in Ti-Beta the concentration of species II is higher than that of species I, due to the cat-alyst's hydrophilicity. This property may reasonably account for the positive solvent effect of acetonitrile on the oxidation of 1-hexene. However, with respect to cyclohexene oxidation, this interpretation contradicts our finding that methanol solvent gave much higher conversion than acetonitrile. The silylation of Ti-Beta caused a drastic decrease in activity for the epoxidation of alkenes, likely due to the strong influence of silylation on the pore mouth, causing narrowing or blocking of the pore open-ings. This is supported by the more profoundly decreased cy-clohexene conversion in methanol solvent; the larger molecular size of species I than species II led to a more severe geometric constraint on the diffusion of cyclohexene molecules into the channels once the intermediate species were formed near the pore mouth by the interaction of species I with cyclohexene. As a result, Ti species in the channels were less accessible to the substrate molecules when methanol was used as the solvent, re-sulting in very low conversion of cyclohexene.

The contrast in solvent effect between cyclohexene oxida-tion and 1-hexene oxidation on Ti-Beta possibly arises from different reaction mechanisms. Indeed, recently it was shown that oxidation of cyclohexene occurred in two ways over TAPO-5 (Scheme 2) [30]: trans-cyclohexanediol was produced from the acid-catalyzed ring opening of the epoxide through nucle-ophilic substitution, whereas the cis-isomer was formed via a radical mechanism. Thus, the higher conversion attained by using methanol as solvent may have resulted from the radical mechanism, because polar MeOH can stabilize the superoxo-titanium species, whereas MeCN can stabilize the hydroperoxo/peroxo-titanium species [31]. To explore this pos-sibility, we carried out cyclohexene oxidation in methanol sol-vent in the presence of 1 mmol hydroquinone (a free-radical
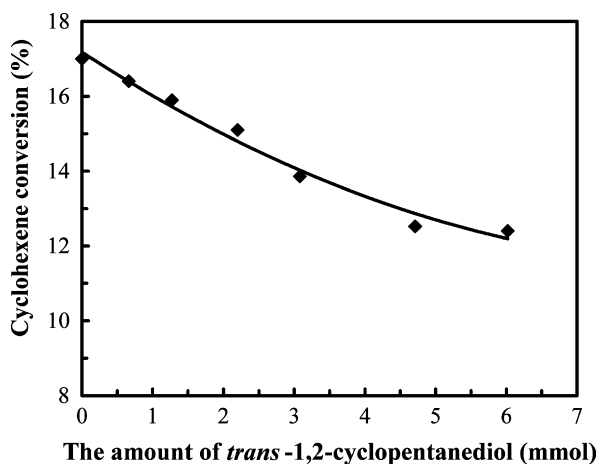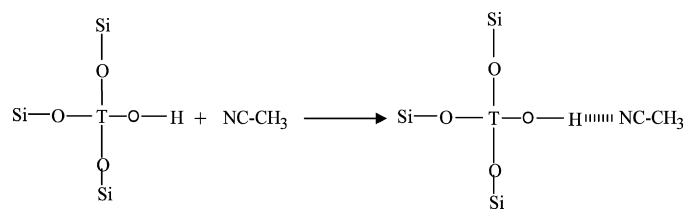
Fig. 10. Effect of *trans*-cyclopentanediol added to the reaction mixture on the conversion of cyclohexene over Ti-Beta in acetonitrile solvent. (Reaction conditions: 60 °C, 2 h, 0.05 g catalyst, 10 mL solvent, 10 mmol substrate and 10 mmol H_2O_2 (31% aqueous solution).)

Scheme 3. Interaction of MeCN with acid sites (T = Si or Ti).

Consequently, there must be a third reason why methanol is the favored solvent in the oxidation of cyclohexene over Ti-Beta. This factor is not clear at the moment; we can assume the possible existence of a synergetic effect between Ti species and acid sites resulting from defect sites in Ti-Beta when methanol solvent is used. This effect may be too subtle to enhance the rate of 1-hexene oxidation but may be strong enough to oxidize more reactive cyclohexene as an internal alkene. These contradictory results can be reasonably interpreted; the addition of a certain amount of acetonitrile poisoned some of the acid sites (as shown in Scheme 3) [5], leading to a drastic diminution of the synergetic effect and thus a marked reduction in activity. The poisoning of acid sites by acetonitrile is strongly supported by the increased epoxide selectivity with an increasing amount of acetonitrile in the mixed solvents.

4.4. Effect of the protic/aprotic nature of solvent on the catalytic performance of titanosilicates

As reported previously, with respect to the protic alcohol solvents, the activity of TS-1 for the epoxidation of 1-hexene decreased in the order MeOH > EtOH > *t*-BuOH due to diminishing electrophilicity and increasing steric constraints [9]. Basically similar trends also were found for Ti-Beta and Ti-MWW, but with small differences, possibly due to the larger pores of Ti-Beta compared with TS-1 and the presence of side pockets on the exterior surface of Ti-MWW. The increased epoxide selectivity in the order MeOH < EtOH < *t*-BuOH can be attributed to the increased steric hindrance to the alcoholysis of epoxide with increasing alcohol molecular size; this was more evident for cyclohexene oxidation, even though the epoxide selectivity was not high (Table 3). When 1-hexene was oxidized in aprotic solvents, the activity of Ti-Beta decreased with decreasing polarity, in agreement with results reported by Corma et al. [5], in contrast with the trend in oxidation over TS-1. This difference may be attributed to the strong organophilicity of TS-1, which hinders formation of species II in strongly polar aprotic solvents. Ti-MWW behaves like Ti-Beta and unlike TS-1.

If species II were indeed the active intermediate, as hypothesized previously for the oxidation of organics in aprotic solvents [5], then it would be reasonable to conclude that the number of species II would increase with increasing water content in the reaction mixture until saturation is reached. Ti-MWW showed much higher activity in the oxidation of linear alkenes in MeCN solvent than in MeOH solvent, suggesting that Ti-MWW was rather hydrophilic. Thus, it is not unexpected that Ti-MWW gave a higher conversion of 1-hexene with in-

scavenger), and found that the conversion indeed declined (Table 6), but only slightly. This demonstrates that the higher activity obtained in methanol solvent itself does not demonstrate the presence of the radical mechanism.

The competition of alcohol substrates with protic alcohol solvents for adsorption on the Ti sites of titanosilicates can be extended to the competition of the water molecules with alcohol substrates on hydrophilic Ti-Beta with the use of aprotic solvents, as supported by the decreasing activity for the oxidation of cyclohexanol on Ti-Beta with decreasing polarity of aprotic solvents [5]. This suggests that another possible reason may be that the formed diol competed with water present in the added H_2O_2 aqueous solution for readsorption on Ti sites, leading to the decreased activity with the MeCN solvent due to the very small amount of water in the reaction system. In contrast, in methanol solvent, because diol and monomethyl glycol ether were formed in much smaller amounts than the methanol, and because the molecular sizes of these two products are much larger than that of methanol, they might not be easy to coordinate to the Ti center to form the five-membered cycle. Consequently, their effect on the oxidation of cyclohexene would be negligible. To further confirm this point, we added different amounts of *trans*-cyclopentanediol to the cyclohexene oxidation system with acetonitrile solvent. As expected, the conversion of cyclohexene decreased as the amount of cyclopentanediol increased (Fig. 10). This suggests that the adsorption of product cyclohexanediol on Ti sites indeed may be a factor in the low conversion of cyclohexene in acetonitrile solvent. But the reduction was not significant enough to account for the remarkable difference in solvent effect; the cyclohexene conversion in methanol solvent was twice that in acetonitrile solvent even after subtracting the effect of radical-based oxidation. Moreover, this finding is not in agreement with the previous finding that addition of small amounts of acetonitrile into the methanol solvent (e.g., MeCN/MeOH = 1.5/8.5 mL/mL) resulted in a drastic decrease in activity similar to that obtained in pure MeCN solvent.

creasing water content in the reaction mixture. Corma et al. reported that the higher the water content, the greater the oxidation activity of Ti-Beta for the epoxidation of 1-hexene [5]. Our result is consistent with that observation, although the activity increase was greater for Ti-MWW than for Ti-Beta. Because TS-1 is organophilic, water in less than large amounts did not affect the types and amounts of active species. Irrespective of the titanosilicates, due to the stronger nucleophilicity of alcohol compared with water, protic alcohol solvents generally gave a lower epoxide selectivity compared with aprotic solvents (except for *t*-butyl alcohol, which demonstrated a very high epoxide selectivity as a result of serious steric constraints).

Compared with a single solvent of methanol or acetonitrile, mixed solvents composed of appropriate amounts of these two agents enhanced the oxidation of 1-hexene over TS-1 and Ti-Beta. This finding can be explained by assuming that although TS-1 is basically hydrophobic, a certain amount of hydrophilic sites originate from defect sites and surface silanol groups; therefore, Ti sites located at these positions would give much higher activity in acetonitrile than in methanol. As a result, a suitable mixture of solvents makes all Ti sites form active species, leading to the increase in activity. In contrast, Ti-Beta is essentially hydrophilic, due to the presence of numerous defect sites; however, some of the Ti sites are in hydrophobic lattice sites, which favor methanol as a solvent. With respect to Ti-MWW, the decreased activity with increasing amount of methanol in the oxidation of 1-hexene possibly can be attributed to the presence of lamellar structure and/or many defect sites arising from deboronation, making almost all of the Ti sites relatively hydrophilic.

The conversion of hydrogen peroxide occurs by two routes: the effective oxidation of substrate and simple decomposition. Generally, the decomposition rate was lower in methanol than in acetonitrile, although this was not evident for TS-1. This is in agreement with previous findings [5] and may be ascribed to the different active species; species II is more active than species I for the decomposition of H_2O_2 [5]. In addition, the decomposition of H_2O_2 also was seen to be related to the structure of the titanosilicates. Ti-Beta promoted significantly greater decomposition of H_2O_2 compared with Ti-MWW and TS-1. The efficiency of H_2O_2 is a combined result of substrate oxidation and decomposition; the lower the decomposition, the more the amount consumed for substrate oxidation, and hence the higher the efficiency. This property can account for the much higher efficiency obtained in aprotic solvents (e.g., MeCN) compared with protic alcohol solvents in the oxidation of alkenes conducted on Ti-MWW. In contrast, TS-1 showed higher H_2O_2 efficiency in methanol than in acetonitrile, as a result of the high activity and low decomposition rate. Although MeCN solvent gave higher H_2O_2 selectivity on Ti-Beta than MeOH solvent, the efficiency of H_2O_2 on Ti-Beta was still much lower than that on Ti-MWW and TS-1, due to its intrinsic properties. In summary, regardless of the solvent used, high oxidation activity led to high H_2O_2 efficiency.

5. Conclusion

Our findings demonstrate that the activity and selectivity of titanosilicates for the epoxidation of alkenes depend on the substrate as well as the nature and polarity of solvents. In contrast to TS-1, both Ti-MWW and Ti-Beta exhibited much higher activity and selectivity in acetonitrile than in methanol for the oxidation of 1-hexene. The addition of water to the reaction mixture increased the catalytic activity of Ti-MWW and Ti-Beta for the oxidation of 1-hexene, whereas the mixed solvents of methanol and acetonitrile were superior to an optimum single solvent for TS-1 and Ti-Beta. The differences in these titanosilicates can be accounted for by their hydrophilicity/hydrophobicity (except for the result of the oxidation of cyclohexene over Ti-Beta). Acetonitrile solvent was more suitable for the epoxidation of cyclohexene on TS-1 than methanol, because the reaction occurred mainly on the hydrophilic external surface. Except for TS-1 in aprotic solvents, the titanosilicates demonstrated increased catalytic activity with increasing solvent polarity. Acetonitrile solvent favored the formation of epoxide. H_2O_2 efficiency was affected by the solvent and the catalyst structure; Ti-Beta exhibited much lower H_2O_2 efficiency than TS-1 and Ti-MWW regardless of the solvent used.

Acknowledgments

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