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A novel titanosilicate with MWW structure
Catalytic properties in selective epoxidation of diallyl ether with hydrogen peroxide

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Abstract

The catalytic activity and selectivity of Ti-MWW in the epoxidation of diallyl ether (DAE) with hydrogen peroxide to allyl glycidyl ether (AGE) and diglycidyl ether (DGE) have been studied by a comparison with those of TS-1, and the issues concerning the consecutive reaction and the selective production of AGE have been considered. Ti-MWW catalyzed the DAE epoxidation in the presence of aprotic solvents such as acetonitrile or acetone, and produced only minor levels of solvolysis products. Ti-MWW proved to be a reusable catalyst standing up to the Ti leaching and maintaining the catalytic activity and the product selectivity in the reaction–regeneration cycles. Studies with different solvents, Ti contents, reaction times, temperature, and catalyst amounts confirmed that the DAE epoxidation was a typical consecutive reaction with AGE as an intermediate product and DGE as a secondary one. The reaction rate for AGE formation was much faster than that for DGE, making the selective production of AGE possible by controlling the reaction up to a DAE conversion level of ca. 30%.

Keywords: Ti-MWW; TS-1; Titanosilicate; Diallyl ether; Allyl glycidyl ether; Diglycidyl ether; Hydrogen peroxide; Liquid-phase epoxidation

1. Introduction

Titanosilicates containing tetrahedral Ti species in the framework, being capable of activating hydrogen peroxide under liquid-phase conditions, prove to be promising catalysts for the selective oxidation of a variety of organic compounds to corresponding oxygenated chemicals. The representative titanosilicate has been TS-1 of the MFI structure, which was reported two decades ago [1]. The discovery of TS-1 has led to industrialized processes such as the hydroxylation of phenol to hydroquinone and catecol, and the ammoximation of cyclohexanone to oxime. The success of these processes with water as an only by-product has a great impact on green and sustainable chemistry, and implies the potential applications of titanosilicates in clean syntheses of fine chemicals.

To solve the problems that medium pore TS-1 encounters in bulky reactions, many others titanosilicates with larger pores have also been developed thereafter by hydrothermal synthesis or postsynthesis methods, for example, Ti-Beta [2,3], Ti-ZSM-12 [4], Ti-MOR [5], Ti-ITQ-7 [6], and Ti-MCM-41 [7]. Particularly, Ti-Beta with 12-membered ring (MR) channels is a very attractive catalyst for the oxidation of cyclic and branched alkenes and alkanes [2,3]. However, they are not superior to TS-1 in the oxidation of small molecules according to the intrinsic activity per Ti site and from the viewpoint of industrialization in terms of catalytic ac-

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tivity and product selectivity. Ti-Beta and Ti-MCM-41 also have a serious weakness of Ti leaching in aqueous solutions because of the high concentration of hydrophilic silanol groups on the defect sites and the external surface.

Ti-MWW, a novel titanosilicate recently developed with the MWW structure (generally known as MCM-22), shows unique catalytic properties in the epoxidation of various alkenes with hydrogen peroxide [8]. Ti-MWW consists of 12-MR side cups and two independent interlayer and intralayer 10-MR channels, one of which contains the supercages of 7.1 × 18 Å dimension [9]. Taking advantages of this structural diversity, Ti-MWW is not only active for the epoxidation of linear alkenes but also for cyclic alkenes. Especially, Ti-MWW catalyzes the epoxidation of linear alkenes more actively and selectively than TS-1; the titanosilicate has been reported to show the highest intrinsic activity so far [8d]. The unusual catalytic performance of Ti-MWW makes it a promising catalyst for the oxidation of functionalized alkenes such as allyl alcohol (AAL), in which 95% AAL conversion and 99% selectivity to glycidol were obtained [8e].

The success in AAL epoxidation encouraged us to search for other applications of Ti-MWW in synthesizing oxygenated chemicals containing functional groups. Allyl glycidyl ether (AGE) is an active monomer with high additional value which is useful as a diluting agent in synthesizing epoxy resins and alkyd resins, also used as an important stabilization agent for resins and agrichemicals. AGE is mainly produced from the dehydrohalogenation between allyl alcohol (AAL) and epichlorohydrin which is synthesized from a stoichemical reaction of AAL and chlorine via the chlorohydrine [10]. This process lacks greenness as it coproduces a large amount of unnecessary by-products. New synthesis methods based on heterogeneous catalysts are required to replace the old ones to improve the above drawback to the AGE synthesis.

To our best knowledge, there is still no open literature reporting the synthesis of AGE from the epoxidation of DAE using titanosilicate catalysts. In this study, we have applied Ti-MWW to the DAE epoxidation for the purpose of producing AGE efficiently and selectively. The effects of solvent and the reaction conditions on the DAE epoxidation have been investigated by comparing Ti-MWW with conventional TS-1. The issue concerning the consecutive reaction involved in the DAE epoxidation has been considered, to help identify how to produce AGE selectively against diglycidyl ether.

2. Experimental

2.1. Synthesis of titanosilicate catalysts

Ti-MWW catalysts were hydrothermally synthesized using boric acid as a crystallization-supporting agent and piperidine as a structure-directing agent (SDA) according to the procedures reported previously [8b]. The synthesis was carried out at molar compositions of 1 SiO_2:0–0.05 TiO_2:0.67 B_2O_3:1.4 SDA:19 H_2O. Ti-containing MWW lamellar precursor was obtained after the gel was crystallized at 403–443 K. The precursor was then subjected to acid treatment with the purpose of removing extraframework Ti species and a part of framework boron as well. A subsequent calcination on the acid-treated sample resulted in the objective Ti-MWW catalysts of the three-dimensional crystalline structure. The detailed compositions are listed in Table 1.

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

No.	Gel		Ti-containing precursor		Ti-MWW catalysts[b]		
	Si/Ti	Si/B	Si/Ti	Si/B	Si/Ti	Si/B	SSA[c]
1	∞	0.75	∞	12	∞	102	611
2	100	0.75	120	13	146	34	628
3	70	0.75	63	12	76	41	622
4	50	0.75	51	12	64	36	624
5	30	0.75	31	11	46	49	624
6	20	0.75	21	13	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] Acid treated and calcined. Acid treatment: solid to liquid (2 M HNO_3) ratio of 1 g:20 mL; refluxed for 20 h. Calcination: at 823 K in air for 10 h.

[c] Specific surface area (Langmuir) in $m^2\ g^{-1}$.

TS-1 catalysts for control experiment were synthesized from gels with Si/Ti molar ratios of 30, 50, 70, and 100 following the conventional procedures [11]. The products were calcined to burn off organic species and further 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 poison partially the Ti active sites [12]. Acid-washed TS-1 had Si/Ti ratios of 36, 57, 83, and 116, respectively.

The zeolite structure was confirmed with X-ray diffraction (XRD) on an MAC Science MX-Labo diffractometer (Cu-K_α). The chemical analyses were carried out by inductively coupled plasma (ICP) on a Shimadzu ICPS-8000E atomic emission spectrometer. The coordination states of Ti species were characterized using UV–visible spectroscopy on a JASCO-550 spectrophotometer using Spectralon as a reference. Specific surface area was calculated using Langmuir plots from the N_2 adsorption isotherms measured on a Bel Japan BEL SORP 28 SA instrument.

2.2. Catalytic reactions

The epoxidation of diallyl ether (DAE) with hydrogen peroxide was carried out under vigorous stirring in a 20-mL glass flask connected to a condenser. In a typical run, 10 mmol of DAE, 5 mL of solvent, and a certain amount of catalyst were mixed in the flask and heated to desired temperatures under agitation. Aqueous H_2O_2 (30 wt%) was then added to the mixture to start the reaction. The products were separated by filtration and analyzed on a gas chromatograph (Shimadzu GC-14B) using an OV-1 capillary column of 50 m and an FID detector. The product amounts were calculated in reference to cycloheptanone (generally 0.2 g) which was used as a GC internal standard. 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 epoxidation of allyl glycidyl ether was conducted under conditions similar to those of DAE oxidation. The products were verified using authentic chemicals commercially available or determined on a gas chromatograph-mass spectrometer (JEOL DATUM-JMS-AX 500).

3. Results and discussion

3.1. Physicochemical properties of Ti-MWW and TS-1 catalysts

MWW-type zeolites, especially its aluminosilicates, are generally synthesized using an SDA of hexamethyleneimine (HMI) [9]. On the other hand, a borosilicate of the MWW structure, denoted as ERB-1, is synthesized possibly with piperidine (PI) as an SDA [13]. We have succeeded for the first time in preparing Ti-MWW using either PI or HMI as an SDA when a crystallization-supporting agent of boric acid coexists with Ti species in the synthetic gel [8b]. The crystal size of hexagonal palettes, however, differs greatly between PI and HMI. PI, leading to a smaller crystal size (generally 0.2–0.5 µm in length and 0.05–0.1 µm in thickness) and then a more active catalyst in comparison to HMI was thus adopted in the preparation of Ti-MWW in this study.

Ti-containing MWW precursor free of impurity and having equally intensive XRD patterns was obtained when the Si/Ti molar ratio was varied in the range of ∞–20. The Ti species added in the gel were incorporated into the precursor readily (Table 1). Nevertheless, some extraframework Ti species, presumably introduced onto the layer surface of the lamellar precursor, always coexist with tetrahedral framework Ti species, and the former was easily transformed to the anatase phase upon calcination. A selective removal of these catalytically harmful species was then necessary. Taking advantage of previous findings [8b], the extraframework Ti species were efficiently extracted by an acid treatment on the as-synthesized precursors. A part of framework boron was removed simultaneously (Table 1). After further calcining the acid-treated samples, XRD patterns indicated that Ti-MWW catalysts with a three-dimensional crystalline structure were obtained as a result of the dehydroxylation occurring between the layered sheets (XRD not shown). The high specific surface areas measured by N_2 adsorption were consistent with the XRD patterns to verify that all the Ti-MWW samples were of high crystallinity (Table 1).

Acid-treated and further calcined Ti-MWW 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. 1A). However, a small amount of anatase-like extraframework Ti species, showing a weak and broad band at 310–330 nm, remained in Ti-MWW with an Si/Ti ratio of 38. A same tendency was observed for TS-1; the sample with an Si/Ti of 36 showed a similar band due to the anatase phase (Fig. 1B), which is simply because that the amount of Ti added meets the limitation of framework incorporation [1].

3.2. Effects of reaction conditions on epoxidation of diallyl ether

3.2.1. Influence of solvents

The epoxidation of diallyl ether shows a relatively complicated product distribution as DAE contains two C=C bonds and undergoes decomposition partially during the reaction, and furthermore the solvolysis reactions depending on the solvents used are also involved in the reaction. After identifying all the products by GC MASS and using authentic chemicals, the reaction pathways were clarified as depicted in Fig. 2. The epoxidation of DAE produces the main product, allyl glycidyl ether, which can be successively oxidized to diglycidyl ether (DGE). Acid-catalyzed reactions also take place with AGE: (1) it is hydrolyzed at the ether group to form allyl alcohol and glycidol; (2) its oxirane ring undergoes the solvolysis to produce ring-opening products when water (also existing in aqueous H_2O_2 solution), alcohol, and acetone are used as solvents. The reaction paths of DAE first hydrolyzed to AAL and then oxidized to glycidol are also possible. Theoretically, glycidol can be further hy-

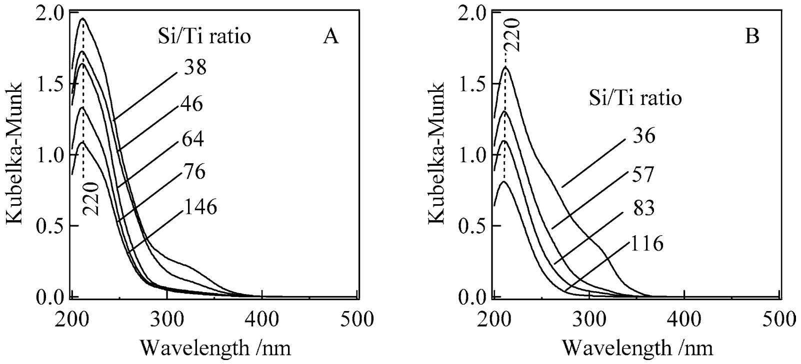


Fig. 1. UV–visible spectra of Ti-MWW (A) and TS-1 (B) both with different Si/Ti ratios.

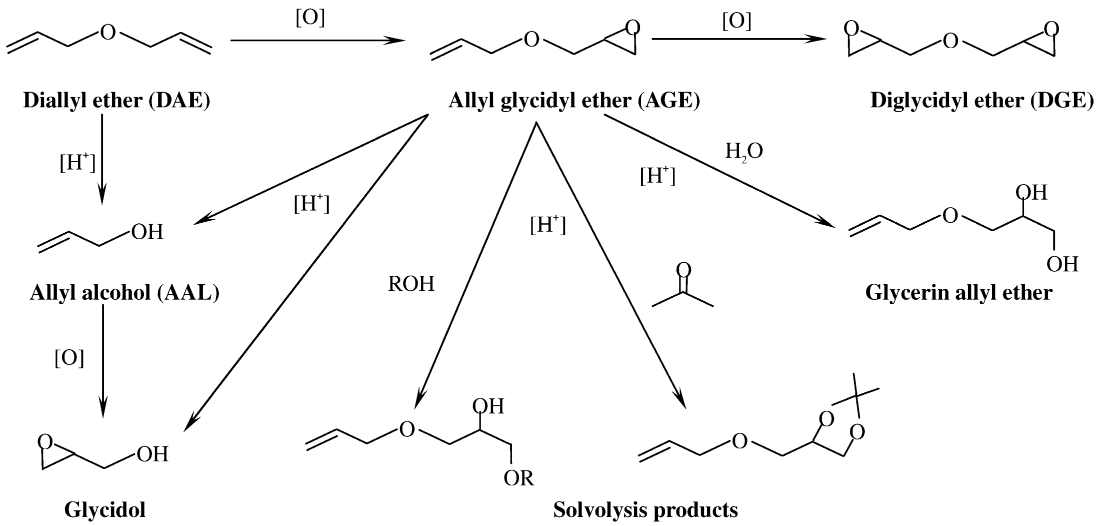


Fig. 2. Reaction pathways in the epoxidation of diallyl ether with hydrogen peroxide.

Table 2
A comparison of epoxidation of DAE between Ti-MWW and TS-1[a]

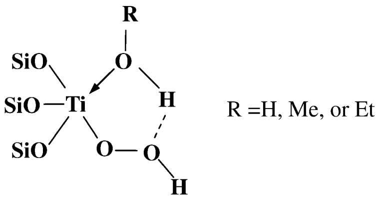
Solvent	Ti-MWW						TS-1					
	Conv.	Product selectivity (mol%)			H_2O_2 (mol%)		Conv.	Product selectivity (mol%)			H_2O_2 (mol%)	
	(mol%)	AGE	DGE	Others[b]	Conversion	Efficiency[c]	(mol%)	AGE	DGE	Others[b]	Conversion	Efficiency[c]
MeCN	39.6	71.0	28.7	0.4	99.8	95.2	19.1	77.7	15.4	6.9	42.8	48.6
Acetone	38.6	73.9	25.0	1.2	98.6	92.3	42.3	69.6	22.2	8.2	74.1	70.2
Water	25.3	52.7	40.0	7.3	78.5	86.5	6.6	60.6	13.5	25.9	38.2	18.5
MeOH	17.8	76.3	4.4	19.3	42.3	81.5	40.4	69.6	20.5	9.9	89.0	54.8
EtOH	12.1	79.8	5.7	14.5	38.7	60.5	33.9	71.7	15.4	12.9	76.7	50.2
Dioxane	18.7	79.2	19.0	1.8	46.7	93.7	23.3	88.6	6.2	5.2	44.9	52.3

[a] DAE, 10 mmol; H_2O_2/Ti-MWW (Si/Ti = 38) = 5 mmol/50 mg; H_2O_2/TS-1 (Si/Ti = 36) = 10 mmol/200 mg; solvent, 5 mL; temperature, 333 K; time, 0.5 h for Ti-MWW, 1.5 h for TS-1.
[b] Solvolysis products, etc.
[c] H_2O_2 efficiency = (AGE + 2DGE + others)/H_2O_2 converted × 100%.

drolyzed to glycerol. Nevertheless, the amount of glycerol produced was negligible because of a too low concentration of glycidol. Thus, the hydrolysis of glycidol to glycerol is omitted in Fig. 2. Both the hydrolysis and the solvolysis are assumably related to the acidic character of titanosilicates derived from the silanol groups and the additional bridging hydroxyls of trivalent cations coexisting with Ti in the framework particularly in the case of boron-containing Ti-MWW.

Significant solvent effects are generally involved in the titanosilicate-catalyzed reactions. The characters of solvents may have a great influence on the intrinsic activity of Ti species but also the product distribution. Table 2 compares the catalytic performance of Ti-MWW with that of conventional TS-1 for the DAE epoxidation in various solvents. To compare the product selectivity at a similar DAE conversion (at least at the most high conversion in the most suitable solvent), different reaction conditions were adopted between Ti-MWW and TS-1, since the former is much more active. As indicated in Table 2, higher levels of catalyst, H_2O_2, and a longer reaction time were used for TS-1.

Both Ti-MWW and TS-1 showed a clear but different solvent effect. The most favorable solvents for Ti-MWW were aprotic MeCN and acetone, in which comparable DAE conversion (38.6–39.6%), similar AGE selectivity, and extremely high efficiency for H_2O_2 utilization were observed. Although the by-products derived from the solvolysis were very low in MeCN and acetone, DGE was formed at a selectivity of 25–29%. The result that Ti-MWW favored aprotic solvent of MeCN with weak basity in the present oxidation of functionalized alkene is similar to the solvent effect on the epoxidation of simple alkene previously reported [8d]. On the other hand, the epoxidation of DAE was greatly retarded in the protic solvents of water and alcohols, and also in the aprotic solvent of dioxane. Water has been verified to be similarly efficient as MeCN for the epoxidation of ALL over Ti-MWW [8e]. The difference observed between DAE and AAL is probably due to their different solubility in water, since the former is almost immiscible with water while the later is totally soluble in water. The solvent effect involving water and alcohols was once assumed to be relative to a stabilized five-membered cyclic intermediate species (Scheme 1), formed by the coordination and hydro-



Scheme 1.

gen bonding of a protic molecule to the Ti–hydroperoxo complex [14]. The dimensions of this intermediate species would increase with increasing molecular size of ROH. This should impose a steric hindrance on the substrate molecules and limit their diffusion and approach to the Ti active sites within the zeolite channels. Thus, the DAE conversion decreased slightly in the order $H_2O > MeOH > EtOH$ as actually observed. Besides affecting the catalytic activity, the protic alcohols caused the opening of the oxirane ring on the acid sites, and gave a higher selectivity for solvolysis products than aprotic solvents. For example, in the case of DAE oxidation over Ti-MWW in MeOH, products other than AGE and DGE consisted of 80% solvolysis product of AGE by MeOH, 15% glycerin allyl ether, and 5% allyl alcohol and glycidol.

In the case of TS-1, acetone and MeOH were obviously the most effective solvents from the viewpoint of DAE conversion. Nevertheless, both acetone and MeOH promoted the solvolysis to a relatively high level, resulting in the oxirane ring-opening products over 8%. 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 DAE. EtOH retarded also the reactivity of TS-1, which is simply assumed to be the result of forming bulky and sterically restricted species as shown in Scheme 1. Nonproductive decomposition of H_2O_2 was generally high on TS-1, making the utilization efficiency of H_2O_2 lower in comparison to Ti-MWW.

Considering that the epoxidation of DAE was conducted under much weaker reaction conditions for Ti-MWW, the above results prove that Ti-MWW is obviously more effective than TS-1 in catalytic activity, epoxide selectivity, and H_2O_2 efficiency when choosing MeCN or acetone as a solvent.

3.2.2. *Influence of Ti content*

A series of Ti-MWW with various Ti contents have been prepared (Table 1) and their catalytic performance has been investigated in DAE epoxidation using a suitable solvent of MeCN (Fig. 3). The DAE conversion increased reasonably with increasing Ti content, but reached a ceiling at a Ti content of 0.43 mmol g^{-1} (corresponding to $Si/Ti = 38$), which is probably due to the presence of part of the anatase phase as evidenced by UV–visible spectra (Fig. 1A). Moreover, the amount of H_2O_2 was almost consumed at such a high Ti content. Too low H_2O_2 concentration also corresponded to the leveling off of DAE conversion. The conversion of H_2O_2 simultaneously increased with Ti content, while its efficiency for epoxidation was maintained over 93%. Concerning the product selectivity, the selectivity to AGE decreased gradually from 95 to 71% with increasing Ti content while the DGE selectivity increased as a result of successively consuming AGE. The solvolysis products, however, was always lower than 2% independent of the Ti content. Thus, from the viewpoint of solvolysis, this indicates that MeCN is "inert" enough to suppress the ring opening of epoxide in comparison to aprotic solvents such as MeOH and EtOH.

3.2.3. *Influence of reaction temperature*

An obvious temperature effect on the epoxidation of DAE was observed when the reaction was carried out in MeCN (Fig. 4). Ti-MWW showed an adequate catalytic activity even around room temperature, indicating its high activity at low temperatures. The DAE conversion reached a maximum of ca. 40% with increasing temperature up to 333 K where H_2O_2 was almost consumed. The efficiency of H_2O_2 slightly decreased with increasing temperature as a result of thermal decomposition, but the value was higher than 95%. The AGE selectivity decreased while the DGE selectivity increased with increasing temperature due to a successive oxidation.

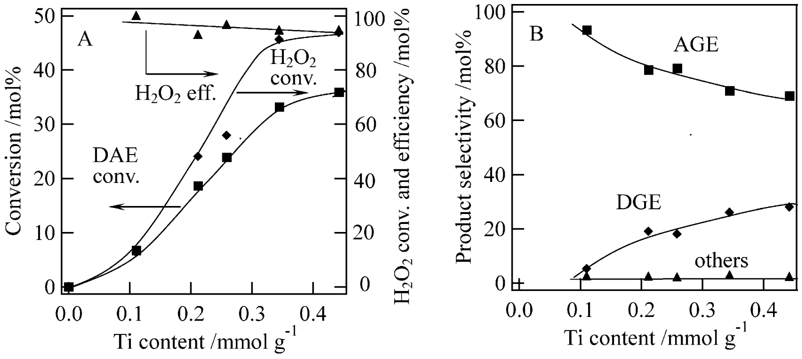


Fig. 3. Dependence of DAE conversion, H_2O_2 conversion, and efficiency (A), and product selectivity (B) on the Ti content of Ti-MWW. Reaction conditions: Ti-MWW, 50 mg; DAE, 10 mmol; H_2O_2, 5 mmol; MeCN, 5 mL; temperature, 333 K; time, 0.5 h.

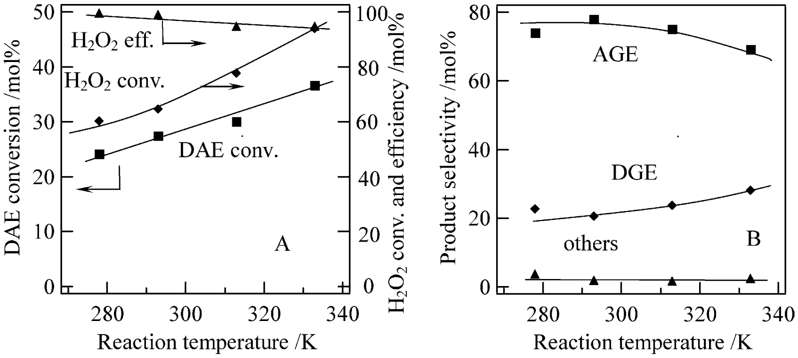


Fig. 4. Dependence of DAE conversion, H_2O_2 conversion, and efficiency (A), and product selectivity (B) on the reaction temperature. Reaction conditions: Ti-MWW (Si/Ti = 38), 50 mg; DAE, 10 mmol; H_2O_2, 5 mmol; MeCN, 5 mL; time, 0.5 h.

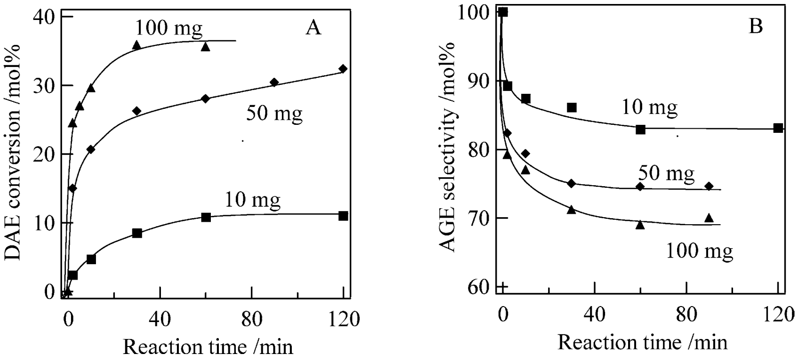


Fig. 5. Dependence of DAE conversion (A) and AGE selectivity (B) on the reaction time. Reaction conditions: Ti-MWW (Si/Ti = 38), 10–100 mg; DAE, 10 mmol; H_2O_2, 5 mmol; MeCN, 5 mL; temperature, 333 K.

3.2.4. Influence of amount of Ti-MWW catalyst and reaction time

Fig. 5 showed the time courses for the DAE epoxidation with different amounts of Ti-MWW in the solvent of MeCN. Reasonably, the more the catalyst used the higher the catalytic activity. The DAE conversion increased rapidly within 30 min and then gradually with the time. For the 100 mg Ti-MWW, no H_2O_2 was detected in the reaction mixture after the reaction for 30 min, while the H_2O_2 conversion was 30% for 10 mg sample. Thus, the decrease of reaction rate is mainly due to a result of using up H_2O_2 for the former, while it is probably due to the deactivation of pore blacking by heavy organic species for the latter since the Ti species of Ti-MWW were verified to be stable enough as shown in Section 3.3. The selectivity to AGE deceased with longer reaction times and increasing catalyst amounts (Fig. 5B) because of the secondary oxidation of AGE.

3.3. Regeneration of Ti-MWW

The stability and reusability are among the important properties of titanosilicates in addition to their catalytic activity and product selectivity. The stability against Ti leaching, a notable problem commonly encountered in the liquid-phase reactions, directly determines whether a titanosilicate is really applicable.

The reusability and regeneration of Ti-MWW in the DAE epoxidation have been investigated by starting with a larger reaction scale using 1.5 g Ti-MWW. The used Ti-MWW catalyst was gathered by filtration and washed with acetone, and then regenerated by calcination in air at 773 K for 5 h. Part of the regenerated sample was taken for chemical analyses, while the remaining catalyst was subjected to a repeated epoxidation of DAE at the same ratio of catalyst–substrate–solvent. In the second run, the used Ti-MWW catalyst showed about 70% conversion of the fresh one when the recovered sample was only acetone-washed and dried at 373 K. When the used catalyst was regenerated by the calcination at 773 K, both the DAE conversion and the product selectivity were restored and maintained for five reaction–regeneration cycles (Fig. 6A). UV–visible spectroscopy confirmed that the used catalyst after five reaction–regeneration cycles showed essentially the same band at 220 nm to the fresh one (not shown). The decrease in the catalytic activity of acetone-washed catalyst is thus assumed to be a partial blocking of Ti sites from the substrate molecules as a result of heavy organic compounds of high boiling points depositing within the zeolite channels, but not due to an irreversible deactivation such as the change of Ti species coordination states or the loss of Ti.

Chemical analyses further verified the reusability of Ti-MWW since the leaching of Ti active species was negligible during the reaction–regeneration cycles (Fig. 6B). Never-

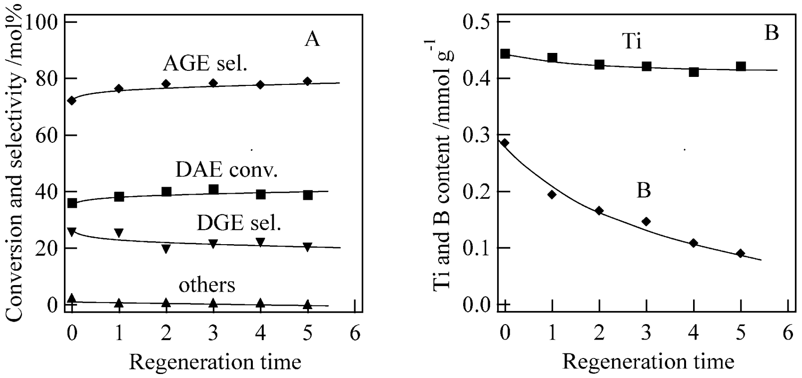


Fig. 6. Changes of DAE conversion and product selectivity (A), and Ti and B contents (B) with the reaction–regeneration cycles. Reaction conditions: Ti-MWW (Si/Ti = 38)/DAE/H_2O_2/MeCN = 50 mg/10 mmol/5 mmol/5 mL; temperature, 333 K; time, 0.5 h. Regeneration: calcination in air at 773 K for 5 h.

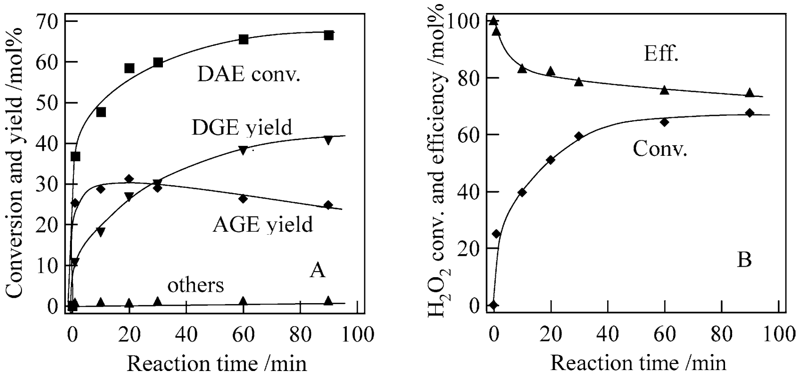


Fig. 7. Reaction time dependencies of DAE conversion and product yield (A), and H_2O_2 conversion and efficiency (B). Reaction conditions: Ti-MWW (Si/Ti = 38), 100 mg; DAE, 2 mmol; H_2O_2, 4 mmol; MeCN, 5 mL; temperature, 333 K.

theless, the boron species were gradually leached out of the framework during the reaction probably because of its small ionic radius compared with that of Si [15]. The results are very similar to those observed previously in the epoxidation of simple alkenes and allyl alcohol [8d,8e]. The loss of boron may decrease the framework electronegativity to change the electronic density in the vicinity of Ti sites, a usual phenomenon reported for Al-containing Ti-Beta [2] and Ti-MOR [5]. This may result in an increased hydrophobicity of the framework, enhancing the catalytic performance of framework Ti. In fact, the AGE conversion increased slightly after reuse (Fig. 6A).

Generally, TS-1 is believed to be stable in the liquid-phase oxidation of simple alkenes, while Ti-Beta and Ti-MCM-41 are claimed to lack the stability of Ti species under hydrothermal conditions because of a large amount of hydrophilic silanol groups on the defect sites and/or the external surface [16,17]. Even for TS-1, its Ti species are leached in the epoxidation of crotyl alcohol, as the triol by-products may chelate the Ti sites cleaving the Si–O–Ti bonds [18]. The present epoxidation of DAE also generates minor amounts of products such as AAL, glycidol, and glycerin allyl ether, etc. The stability of Ti-MWW, however, was hardly affected, suggesting Ti-MWW has a greater potential of being employed as a reusable catalyst for the DAE epoxidation unless the used catalyst is subjected to the regeneration by burning off the residual organic species.

3.4. *Investigation into the consecutive reaction and control of AGE selectivity*

The epoxidation of DAE consists of many reaction pathways among which the consecutive oxidation of AGE to DGE is the main side reaction (Table 2), which was confirmed in actual reactions (Figs. 3–5). From the viewpoint of producing selectively AGE, which is demanded in industrial and commercial applications, it is important to consider the issue of consecutive oxidation and propose some ideas for the selective production of AGE. To further confirm the issue of consecutive oxidation, the epoxidation of DAE was carried out under more extreme conditions, that is, at a higher ratio of Ti-MWW and H_2O_2 to DAE. This would allow further oxidation of DAE and AGE proceeding to a deep level. The results are shown in Fig. 7. The DAE conversion increased rapidly and reached about 65% after 90 min. The AGE yield increased and reached a maximum of 30% at 20 min, and then gradually decreased with the reaction time. The DGE yield, on the other hand, continually increased with time. The results are clearly a time course pattern of consecutive reaction, verifying that the formation of DGE is at consumption of AGE.

Table 3
Epoxidation of DAE and AGE on Ti-MWW[a]

Substrate	Catalyst	Conversion	TON	Product selectivity (mol%)			H_2O_2 (mol%)	
	(mg)	(mol%)	mol $(\text{mol-Ti})^{-1}$	AGE	DGE	Others[b]	Conversion	Efficiency
GAE	10	8.5	213	86.1	10.5	3.5	18.7	95.4
GAE	100	35.9	111	69.0	28.0	2.4	93.9	94.6
AGE	10	1.6	35	n.a.[c]	99.9	0.1	3.4	85.5
AGE	100	14.4	33	n.a.[c]	98.9	1.1	31.5	78.6

[a] Catalyst, Ti-MWW (Si/Ti = 38); substrate, 10 mmol; H_2O_2, 5 mmol; MeCN, 5 mL; temperature, 333 K; time, 0.5 h.
[b] Solvolysis products, etc.
[c] Not available.

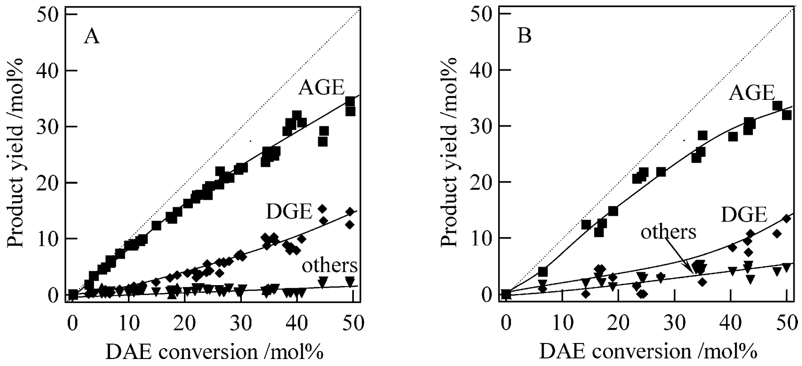


Fig. 8. Dependence of product yields on the DAE conversion on Ti-MWW (A) and TS-1 (B) at 333 K. Representative reaction conditions: 50 mg and 0.5 h for Ti-MWW; 200 mg and 1.5 h for TS-1.

To investigate the possibility of producing AGE selectively, the DAE oxidation was compared with the AGE oxidation using different amounts of Ti-MWW (Table 3). The AGE oxidation resulted in mainly DGE together with a small amount of solvolysis by-products. Although the conversion and turnover number (TON) were dependent on the catalyst amount, it is obvious that the oxidation of DAE proceeds at a much higher reaction rate than AGE oxidation. The higher reaction rate of DAE assumably derives from its two C=C bonds having a higher percentage reached by the Ti active sites in comparison to AGE. The difference in hydrophilicity/hydrophobicity between DAE and AGE could also be a reason. As Ti-MWW containing hydroxyl defect sites is relatively a hydrophilic catalyst [8e], the higher epoxidation rate for DAE conversion relative to AGE conversion could be because DAE is more hydrophobic and once it is adsorbed in the catalyst the subsequent epoxidation occurs just as quickly. Whereas for the less hydrophobic AGE the rate is limited by adsorption onto to catalyst. This big difference in oxidation rate between DAE and AGE would make the selective production of AGE possible.

Fig. 8 summarizes the dependence of product yield on the DAE conversion when the DAE epoxidation was carried out over Ti-MWW and TS-1. All the data were gathered using the most suitable solvents, that is, in MeCN and acetone for Ti-MWW and in MeOH and acetone for TS-1, while the Ti content and reaction temperature were varied. It should be noted that the amount of TS-1 was four times that of Ti-MWW, and the reaction time was 2 h for TS-1 and 0.5 h for Ti-MWW. The dotted line indicates the formation of AGE at a selectivity of 100%. At a given DAE conversion, more by-products were produced on TS-1 because it preferred solvents not so “inert” to the solvolysis. Both Ti-MWW and TS-1 showed similar profiles for the formation of AGE and DGE; i.e., the AGE selectivity gradually decreased when the reaction proceeded to a high level, due to the consecutive oxidation of AGE to DGE. The results suggest that it is necessary to control the reaction level from the viewpoint of producing AGE selectively on both Ti-MWW and TS-1. Nevertheless, Ti-MWW is obviously superior to TS-1 because Ti-MWW produces less solvolysis products and requires less harsh reaction conditions such as lower catalyst amounts and shorter reaction times.

4. Conclusion

Ti-MWW catalyzes the epoxidation of DAE to AGE and DGE with aqueous hydrogen peroxide more actively than TS-1. Ti-MWW favors MeCN or acetone as a suitable solvent while TS-1 prefers acetone and MeOH. The difference in solvent effect results in less solvolysis products being formed on Ti-MWW. Ti-MWW which is stable enough to endure the Ti leaching proves to a regeneratable catalyst for DAE epoxidation. The investigation under many reaction conditions, such as Ti content, reaction time and temperature, catalyst amount, indicates that the DAE oxidation is a typical consecutive reaction in which the reaction rate for AGE formation is much faster than that for DGE. It is possible to produce valuable AGE selectively on both Ti-MWW and TS-1 by controlling the reaction level carefully, but Ti-MWW exhibits more benefits in catalytic activity using less harsh reaction conditions.

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