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Selective synthesis of ethylene oxide through liquid-phase epoxidation of ethylene with titanosilicate/H_2O_2 catalytic systems

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ABSTRACT

Liquid-phase epoxidation of ethylene to ethylene oxide (EO) with H_2O_2 over various titanosilicate catalysts like Ti-MWW, TS-1, Ti-MOR and Ti-Beta has been investigated. The effects of solvent, catalyst amount, reaction pressure, temperature and time on the catalytic performance of Ti-MWW have been studied in detail. Ti-MWW preferred acetonitrile as a solvent and showed the highest reactivity and EO selectivity among the titanosilicate catalysts investigated. Under optimized reaction conditions, Ti-MWW gave a EO selectivity high as 97.9% as well as a reasonable utilization efficiency of H_2O_2 of 77.7%. Ti-MWW was gradually deactivated after repeated use in ethylene epoxidation. High-temperature calcination easily recovered the catalytic activity of deactivated Ti-MWW after removing ethylene glycol (EG) and other heavy byproducts with high boiling points that were deposited inside micropores. The issues of molecular dimension and reactivity have also been considered by comparing the epoxidation of linear alkenes with different lengths (C_2 to C_6) between two representative titanosilicates Ti-MWW and TS-1. Ethylene, with the smallest dynamic diameter but containing electron-deficient C=C double bonds, was more difficult to be epoxidized than other alkenes with higher intrinsic activities.

1. Introduction

Ethylene oxide (EO), the simplest cyclic ether, is the third-largest ethylene derivative after polyethylene (PE) and polyvinyl chloride (PVC), with wide applications in the production of ethylene glycol (EG), nonionic surfactants, alcohol ether and other downstream oxygenated chemicals. The EO demand has reached 20 million metric tons in 2013 and is continually growing at an annual increasing rate of 6–7% [1]. The discovery of EO goes back to 1859 when Charles-Adolphe Wurtz conducted the reaction of 2-chloroethanol and potassium hydroxide, based on which, the chlorohydrins process was initially used to produce EO. However, suffering serious problems of equipment corrosion and environmental pollution, it was commercially replaced by greener vapor-phase oxidation process in the 1960s. The vapor-phase oxidation employs supported silver and oxygen as the catalyst and the oxidant, respectively. In comparison to chlorohydrin technique, it avoids the by-production of a massive amount of chloride salts and the discharge of chlorine-containing waste water. However, it definitely encounters a fatal disadvantage of complete burning of a part of ethylene and EO to carbon dioxide at high reaction temperatures (200–260 °C). The EO selectivity is still less than 90%, even though the Ag-based catalysts have been greatly improved in last decades, e.g. by introducing into the catalyst the promoters like Cl, Cs and Rh [2–6]. Moreover, in order to inhibit the combustion of ethylene and EO, the ethylene conversion per-pass must be maintained at a relatively low level (4–8%), that leads to a limited EO productivity and a high energy-consuming for recycling ethylene. The CO_2 emission as by-product accounts for about 3.4 million metric tons per year in this process, ranking only second to ammonia synthesis. Thus, the gas-phase oxidation process for EO production is arising big environmental concerns.

Recently, the researchers at the Center for Environmentally Beneficial Catalysis (CEBC) made a comprehensive economic and environmental assessment for the EO production by shifting the conventional vapor-phase process to a CO_2 zero emission process operated under mild liquid-phase conditions of 40 °C and 5 MPa [1,7]. The so-called CEBC process uses methyltrioxorhenium homogeneous catalyst and environmental-friendly oxidant H_2O_2, providing an excellent catalytic performance of almost 100% EO

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Table 1
Physicochemical properties of various titanosilicates.

Catalyst	Structure	Si/Ti[a]	Crystal size[b] (μm)	SA[c] ($m^2 g^{-1}$)	Ti states[d]
Ti-MWW	MWW	44	0.6 × 0.6 × 0.1	545	Tetra.
TS-1	MFI	50	0.2–0.3	527	Tetra.
Ti-MOR	MOR	51	0.2–0.4	572	Tetra.
Ti-Beta	BEA*	38	~1	614	Tetra.

[a] Molar ratio determined by ICP analysis.
[b] Evaluated by SEM.
[c] Specific surface area (Langmuir) measured by N_2 adsorption at −196 °C.
[d] Evaluated with UV–vis spectroscopy. Tetra., tetrahedral Ti species.

selectivity and H_2O_2 efficient utilization. The preliminary economic assessment on this CEBC process shows that the higher oxidant and catalyst costs can be offset by its higher EO selectivity. Nevertheless, the low abundance (10^{-7}%) of precise Re metal ($1400/1b) and the reuse of homogeneous catalyst would become the main bottlenecks for actual industrialization of bulk chemicals like EO [8]. Therefore, developing alternative process based on heterogeneous catalysts useful for the liquid-phase ethylene epoxidation with H_2O_2 is highly desirable. It may lead to a simple and eco-efficient EO process of easy separation and recycle/regeneration. Nb and W incorporated silica-based cubic mesoporous materials (W-KIT-6 and Nb-KIT-6) have been investigated as heterogeneous catalysts, showing a significant activity in the ethylene epoxidation with H_2O_2. They are barely satisfactory due to inefficient decomposition of H_2O_2 and metal leaching [9].

In view of the alkene epoxidations featured with low carbon emission and high efficient utilization of carbon source, **H**ydrogen **P**eroxide **P**ropylene **O**xide (HPPO) process has been commercialized by Dow-BASF for the production of propylene oxide (PO) [10]. The HPPO process, based on the TS-1/H_2O_2 catalytic system, gives water as the main byproduct. A small amount of alcohol ethers due to the solvolysis of PO are also produced as TS-1 prefers protic methanol as the solvent. Up to now, a large number of theoretical studies have performed on the Hydrogen Peroxide Ethylene Oxide (HPEO) process [11–14]. However, the experimental study on HPEO process has not made a substantial progress, due to the relatively low activity and selectivity achieved on conventional titanosilicates like TS-1, Ti-STT and Ti-CHA [15,16]. In early works, we once reported that Ti-MWW was superior to TS-1 in HPPO process in terms of PO selectivity and yield [17] as well as in the epoxidation of other functional groups-containing alkenes with H_2O_2 [18–24]. Its catalytic properties and possible application to HPEO process are still unknown.

In this work, with the purpose to develop efficient HPEO process, we have systematically studied the titanosilicate-catalyzed epoxidation of ethylene with H_2O_2. By comparing four representative titanosilicates of different topologies, Ti-MWW/H_2O_2/MeCN was confirmed as the best reaction system with high reaction activity and EO selectivity in HPEO process.

2. Experimental

2.1. Reagents and materials

Ethylene with a purity of 99.99% was procured from Shanghai Pujiang Special Gases Co., Ltd., China and hydrogen peroxide (30 wt.%) was supplied by Sinopharm Chemical Reagent Co., Ltd., China. All other analytical reagents (MeOH, MeCN, acetone, *tert*-butyl alcohol etc.) were commercially available and they are used without further purification.

Four titanosilicates with different topologies have been employed in the liquid-phase epoxidation of ethylene. Ti-MWW was prepared using boric acid as a crystallization-supporting and piperidine (PI) as a structure-directing agent (SDA) in two steps following literature method [25]. The synthetic gel with a molar composition of 1.0 SiO_2: 0.05 TiO_2: 1.4 PI: 0.67 B_2O_3: 19H_2O was hydrothermally crystallized at 170 °C for 7 days, then the powder product obtained was refluxed in a 2 M HNO_3 aqueous solution for the purpose of removing extraframework Ti species and a part of framework boron as well. TS-1 was hydrothermally synthesized using tetrapropyl hydroxide (TPAOH), tetraethyl silicate (TEOS) and tetrabutyl orthotitanate (TBOT) as SDA, Si and Ti sources, respectively [26]. To remove extraframework Ti species and residual alkali ions contaminated in TPAOH solution, the obtained TS-1 was further washed with 1 M HCl solution before calcination at 550 °C for 6 h in air. Ti-MOR was post-synthesized by the atom-planting method between highly dealuminated mordenites and $TiCl_4$ vapor at elevated temperature [27–30]. Ti-Beta has synthesized in fluoride medium according to the literature [31].

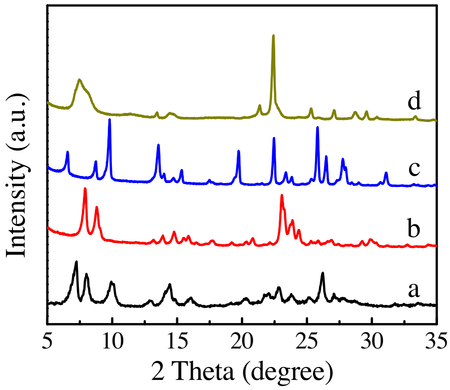


Fig. 1. XRD patterns of Ti-MWW (a), TS-1 (b), Ti-MOR (c) and Ti-Beta (d).

2.2. Characterization methods

The X-ray diffraction (XRD) patterns were recorded on a Rigaku Ultima IV diffractometer using Ni-filtered Cu Kα radiation (λ = 0.1541 nm) in a scanning range of 2θ = 5–35 to confirm the structure and crystallinity of the titanosilicates. The voltage and current were 35 kV and 25 mA, respectively. Morphologies and crystal sizes were examined by a Hitachi S-4800 scanning electron microscope. The UV–vis spectra were collected on a PerkinElmer UV–vis Lambda 35 spectrophotometer using $BaSO_4$ as a reference. The FT-IR spectra were recorded by a Nicolet Nexus 670 FT-IR spectrometer at a resolution of 2 cm^{-1} using a KBr technique. The bulk Si/Ti ratios were determined by ICP-AES on IRIS Intrepid II XSP after dissolving the titanosilicates in HF solution. The amount of acid sites was determined by temperature-programmed desorption of ammonia (NH_3-TPD) with a Micrometrics tp-5080 equipment equipped with a thermal conductivity detector (TCD). Typically, 0.1 g of sample was pretreated in helium stream (25 mL min^{-1}) at 550 °C for 1 h. The adsorption of NH_3 was carried out at 50 °C for 1 h. The sample was flushed with helium at 100 °C for 2 h to remove physisorbed NH_3 from the catalyst surface. The TPD profiles were then recorded at a heating rate of 10 °C min^{-1} from 100 °C to 550 °C. The textural properties of the titanosilicates were determined by N_2 adsorption at −196 °C using a BEL SORP instrument after the samples were degassed in vacuum at 300 °C for 6 h.

2.3. Catalytic reactions

The selective epoxidation of ethylene to EO was carried out in an autoclave reactor equipped with a 45 mL Teflon-inner. In a typical run, 150 mg titanosilicate, 10 g MeCN and 10 mmol H_2O_2 (30 wt.%) were fed into the reactor. Ethylene was charged into the autoclave to replace the air inside for three times. The pres-

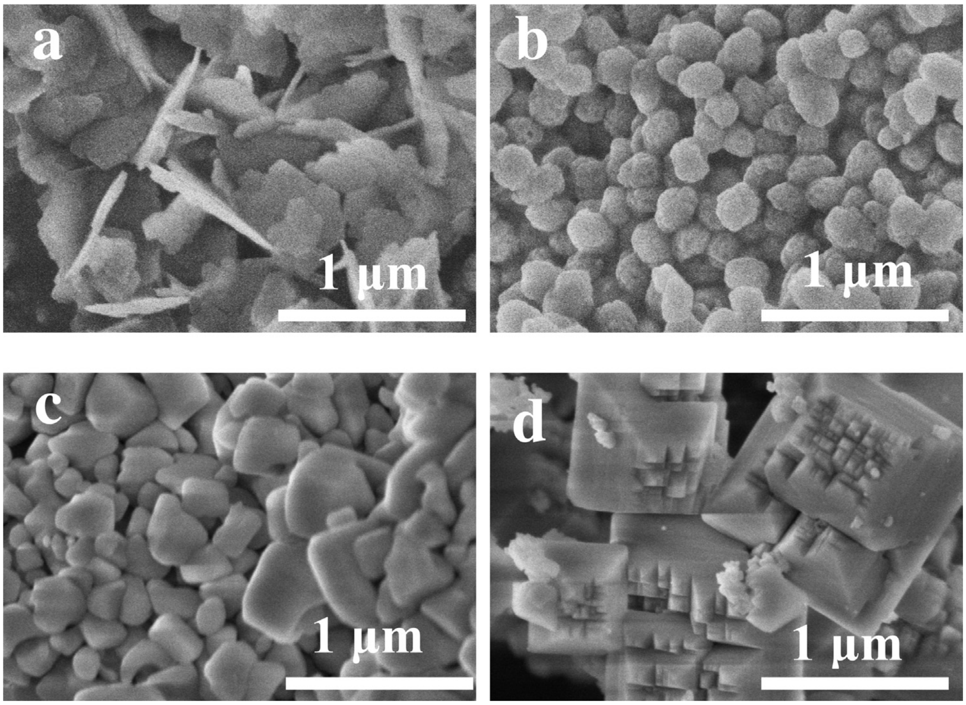


Fig. 2. SEM images of Ti-MWW (a), TS-1 (b), Ti-MOR (c) and Ti-Beta (d).

sure was then adjusted to a constant value of 2.5 MPa. After the reaction was carried out under vigorous stirring at 40 °C for 1.5 h, the reactor was cooled down by ice water and depressed slowly before opening. For other *n*-alkenes (i.e. propylene, 1-butene, 1-pentene and 1-hexene), the epoxidation was also carried out in the autocalve reactor. The reaction products were analyzed by a gas chromatograph (Shimadzu 2014, FID detector) using isopropanol as an internal standard and the remaining amount of H_2O_2 after reaction was determined by standard titration method with 0.05 M $Ce(SO_4)_2$ solution. The products formed were further confirmed by a GC–MS (Agilent 6890 series GC system, 5937 network mass selective detector).

The ring-opening reactions of EO or PO over Ti-MWW and TS-1 were operated in the abovementioned autoclave reactor at 40 °C for 1 h under N_2 pressure of 2.5 MPa. With or without adding H_2O_2, 10 mmol epoxyalkane (EO or PO) and 150 mg catalyst (Ti-MWW or TS-1) were added into 10 g different solvents (MeCN, MeOH or H_2O). The conversion of EO or PO was determined by GC analysis, which was used to evaluate the ring-opening activity.

3. Results and discussion

3.1. Characterization of titanosilicate catalysts

The XRD patterns verified that the four titanosilicates were highly crystalline materials free of impurity and possessed the topologies of MWW, MFI, MOR and BEA* structures (Fig. 1). The SEM images provided the morphologies of their crystals. Ti-MWW crystals showed a uniformly platelet-shaped morphology with a thickness of about 0.1 μm (Fig. 2a). The crystals of TS-1 and Ti-MOR both were composed of the aggregate of nanocrystals (Fig. 2b and c). Ti-Beta exhibited a morphology of truncated square bipyramid (Fig. 2d), that was in accordance with the literature [32]. As shown in UV–vis spectra (Fig. 3A), the predominant band at 220 nm was ascribed to the tetrahedrally coordinated Ti^{4+} species in the zeolite framework. Meanwhile, the band around 330 nm was nearly negligible, indicating the absence of anatase-like phase in these titanosilicates. The presence of the band at 960 cm^{-1} in IR spectra (Fig. 3B) further confirmed that the Ti species was introduced into the framework [33]. The ICP analysis showed that the Si/Ti ratios were comparable for these four titanosilicates (Table 1). Their textural properties, measured by nitrogen adsorption technique, are also summarized in Table 1. The specific surface areas (Langmuir) were in the range of 527–614 $m^2 g^{-1}$. Thus, the four titanosilicates were highly porous and crystalline materials with the isolated Ti ions in framework, and qualitatively they are considered to qualify the preconditions as the liquid-phase oxidation catalysts.

Table 2
A comparison of epoxidation of ethylene over various titanosilicates in different solvents[a].

No.	Catalyst	Products yield[b] (%)	Products distribution[c] (%)				H_2O_2 (%)	
			EO	EG	ME	others	conv.	eff.
1	Ti-MWW	44.3	98.8	1.2	–[d]	–[d]	54.4	81.4
2	TS-1	87.1	15.2	1.7	82.3	0.8	88.0	98.9
3	Ti-MOR	15.9	100.0	–[d]	–[d]	–[d]	20.4	78.3
4	Ti-Beta	1.8	94.5	5.5	–[d]	–[d]	5.9	30.9

[a] Reaction conditions: cat., 150 mg; ethylene, 2.5 MPa; H_2O_2, 10 mmol; solvent, 10 g; temp., 40 °C; time, 1.5 h. MeOH was used as the solvent for TS-1, whereas MeCN was used for the reactions on other titanosilicate catalysts.

[b] Including ethylene oxide and corresponding byproducts formed by hydrolysis or solvolysis.

[c] EO, ethylene oxide; EG, ethylene glycol; ME, methyl ether.

[d] Not determined.

3.2. Epoxidation of ethylene

3.2.1. A comparison of ethylene epoxidation over various titanosilicates

In order to choose a suitable catalyst for the HPEO process, the titanosilicates with different topologies were investigated for the epoxidation of ethylene, and the results are summarized in Table 2. As the Ti contents (or Si/Ti molar ratios) were comparable for four catalysts, the yield of oxygenated products and EO selectivity are considered to represent reliably their efficiency for this reaction.

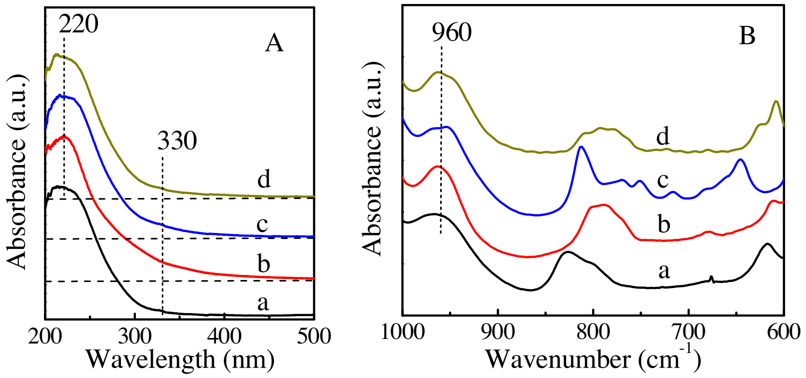


Fig. 3. UV–vis spectra (A) and FT-IR spectra (B) of Ti-MWW (a), TS-1 (b), Ti-MOR (c) and Ti-Beta (d).

MeCN was chosen as the most appropriate solvent for Ti-MWW, Ti-MOR and Ti-Beta, while MeOH was used as the most suitable one for TS-1. Table 3 compares in detail the solvent effects on the activity and EO selectivity between Ti-MWW and TS-1. Judging from the products yield and H_2O_2 conversion, the catalytic activity decreased in the order of TS-1 > Ti-MWW > Ti-MOR > Ti-Beta. Although TS-1 showed the highest H_2O_2 conversion and products yield, the solvolysis of EO in protic solvent of MeOH lowered the EO selectivity to a level of 15.2%. On the contrary, Ti-MWW gave an extremely high EO selectivity (98.8%) in aprotic solvent of MeCN. When shifting the solvent from MeOH to MeCN for TS-1, the EO selectivity was enhanced greatly to reach 99.9%, but the products yield was only 5.2% (Table 3). Thus, balancing the EO selectivity and catalytic activity (oxygenated product yield and H_2O_2), Ti-MWW is assumed to be the most effective catalyst among the investigated titanosilicates in terms of developing a selective HPEO process.

To further investigate how the solvent characters influence the EO selectivity, the hydrolysis or solvolysis of EO in various solvents was carried out over Ti-MWW and TS-1 with or without H_2O_2 (Fig. 4). The main products were ethylene glycol (EG) and methyl ether. This reaction proceeded slightly even in the absence of any catalysts and it was accelerated greatly by the presence of titanosilicate catalysts. The ring-opening of EO depends on the concentration of weak acid sites derived from Si-OH, Ti-OH or Ti- O-O-H in the titanosilicates [23]. TS-1 showed a higher EO conversion than Ti-MWW when compared in the same solvent, indicating the former may contain more or stronger acid sites. We have measured the NH_3-TPD profiles of Ti-MWW and TS-1. Ti-MWW almost did not show any chemical adsorption of ammonia, whereas TS-1 also showed a NH_3-TPD profile with an extremely low signal/noise ratio (Fig. S1). This implies that both Ti-zeolites were characteristic of very weak acidity. It was actually observed that the EO conversion decreased in the order of MeOH > H_2O > MeCN ≈ 0. The aprotic solvent molecules of MeCN with a weak basity could retard the ring-opening of EO. Moreover, the addition of H_2O_2 accelerated the hydrolysis or solvolysis of EO. This further verified that carrying out ethylene epoxidation in a favorable solvent of MeCN allows Ti-MWW to achieve a high activity along with a high EO selectivity.

Table 3
A comparison of epoxidation of ethylene over Ti-MWW and TS-1 in different solvents [a].

Catalyst	Solvent	Products yield[b] (%)	Product sel.[c] (%)				H_2O_2 (%)	
			EO	EG	ME	others	conv.	eff.
Ti-MWW	MeCN	44.3	98.8	1.2	–[d]	–[d]	54.4	81.4
	MeOH	7.0	24.1	–[d]	74.2	1.7	7.5	93.2
	Acetone	72.4	82.6	0.4	–[d]	17.0	92.4	78.4
	H_2O	48.0	72.3	13.7	–[d]	14.0	86.7	55.4
	t-BuOH	59.0	82.0	2.0	–[d]	16.0	82.7	71.4
TS-1	MeCN	5.2	99.9	0.1	–[d]	–[d]	5.2	99.2
	MeOH	87.0	15.2	1.7	82.3	0.8	88.0	98.9
	Acetone	44.7	31.1	1.4	–[d]	67.5	76.7	58.3
	H_2O	19.8	20.3	69.7	–[d]	10.0	44.1	45.0
	t-BuOH	4.4	82.1	1.9	–[d]	16.0	9.8	45.4

[a] Reaction conditions: cat., 150 mg; ethylene, 2.5 MPa; H_2O_2, 10 mmol; solvent, 10 g; temp., 40 °C; time, 1.5 h.

[b] Including ethylene oxide and corresponding byproducts formed by hydrolysis or solvolysis.

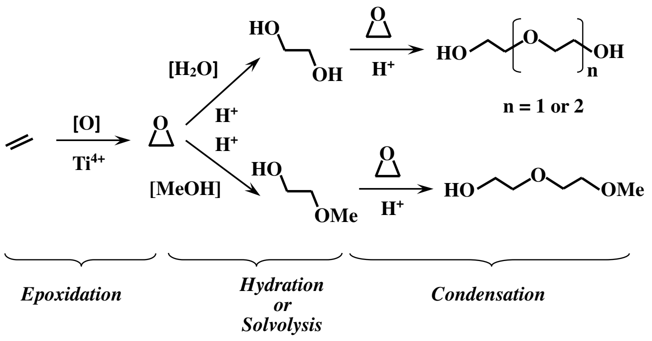
[c] EO, ethylene oxide; EG, ethylene glycol; ME, methyl ether.

[d] Not determined.

Based on the above results and the GC–MS analysis, we identified the hydrolysis and solvolysis products and confirmed the reaction pathways in HPEO process with the absence or presence of MeOH (Scheme 1). The main product was EO as a result of the epoxidation of ethylene. As the hydration of EO can proceed in the absence of any catalysts, it will occur along with the ethylene epoxidation due to the presence of H_2O from aqueous solution of H_2O_2 oxidant and its decomposition. The formed EG could further react with EO to produce the corresponding polyols. When MeOH was used as the solvent, the solvolysis of EO rather than the hydrolysis would play a dominant role in the ring-opening reaction, producing the byproducts of corresponding methyl ethers. Similar results have been reported previously for TS-1-catalyzed propylene epoxidation [34–36].

3.2.2. *Effect of solvents*

Significant solvent effects are generally involved in titanosilicate-catalyzed reactions. In this section, the solvent effects on the Ti-MWW or TS-1-catalyzed HPEO processes were investigated emphatically. The characters of solvents had a great impact on not only the catalytic activity but also the product selectivity. As shown in Table 3, Ti-MWW and TS-1 exhibited significantly different solvent effects.



Scheme 1. Reaction pathways of ethylene epoxidation and ring-opening reaction.

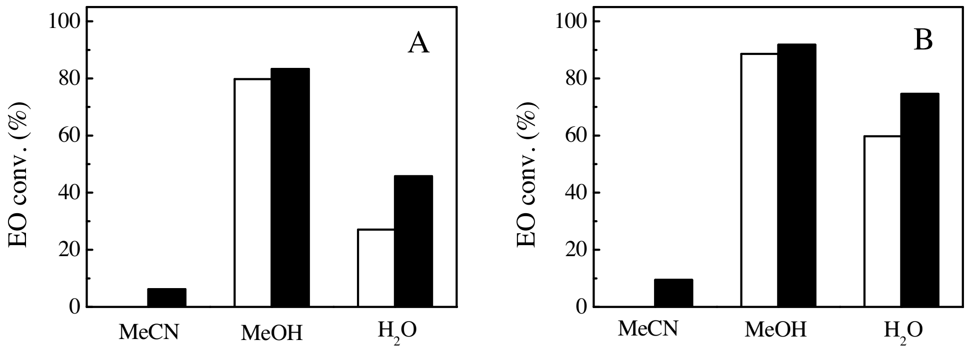


Fig. 4. Ring-opening reaction of EO in different solvents with H_2O_2 (black) or without H_2O_2 (blank) over Ti-MWW (A) or TS-1 (B). Reaction conditions: Ti-MWW or TS-1, 150 mg; EO, 10 mmol; N_2, 2.5 MPa; solvent, 10 g; H_2O_2 (if added), 10 mmol; temp., 40 °C; time, 1 h.

For both Ti-MWW and TS-1, the EO selectivity was relatively low (<90%) in the solvents other than MeCN, indicating EO is chemically unstable, tending to undergo hydration or solvolysis reactions. This is consistent with the results observed in the abovementioned ring-opening reaction of EO (Fig. 4). Hence, MeCN is presumed to be a more suitable solvent for Ti-MWW, although the H_2O_2 conversion and the products yield in MeCN were not the highest. It is of particular interests that Ti-MWW showed a higher reaction activity in water than that in MeCN, although the H_2O_2 utilization efficiency for the former was low as 55.4%. The effect of solvent is one of the most complicated issues in the catalytic system of titanosilicate/H_2O_2. It is related to the polarity of the solvent, the hydrophilic/hydrophobic character of the titanosilicate surface, the solubility of the substrates, and other factors. Ti-MWW prepared from a layered precursor contains many defect sites such as silanol groups as a result of incomplete dehydroxylation between the layers. Thus, the solvent of MeOH or H_2O molecules adsorbed on the surface silanol groups that would impose a steric hindrance on the guest molecules (solvents, substrates and H_2O_2 molecules) and limit their diffusion and approach to the Ti active site within the zeolite channels. Thus, the reactivity of Ti-MWW is higher in H_2O than that of MeOH due to the smaller diameter of the former one, although the ethylene solubility is much higher in MeOH compared to H_2O.

In the case of TS-1, MeOH was obviously the most efficient solvent from the viewpoint of catalytic activity. Aprotic but basic MeCN, a well-known unsuitable solvent for the epoxidation of simple alkenes on TS-1 catalyst, made its reaction activity somewhat low in the epoxidation of ethylene. A similar phenomenon was also observed for the solvent of *t*-BuOH.

The above results indicated that Ti-MWW may served as an appropriate and efficient catalyst for the selective formation of EO in the ethylene epoxidation when choosing MeCN as a solvent.

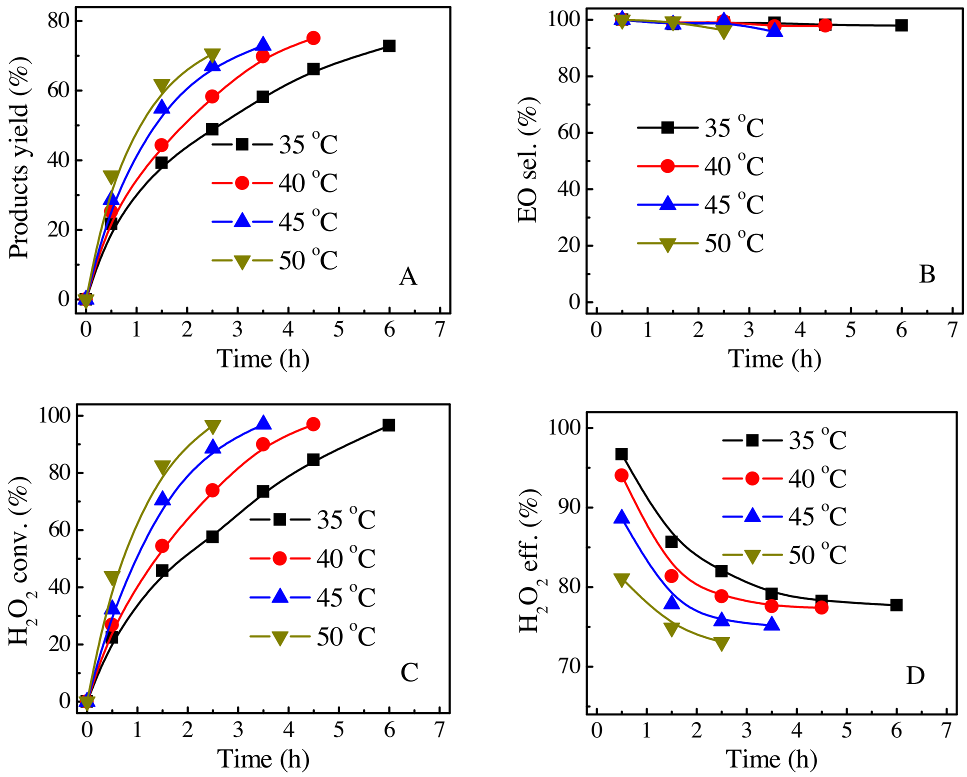


Fig. 5. Changes of products yield (A), EO selectivity (B), H_2O_2 conversion (C) and H_2O_2 utilization efficiency (D) with time on stream at different temperatures. Reaction conditions: Ti-MWW, 150 mg; ethylene, 2.5 MPa; MeCN, 10 g; H_2O_2, 10 mmol.

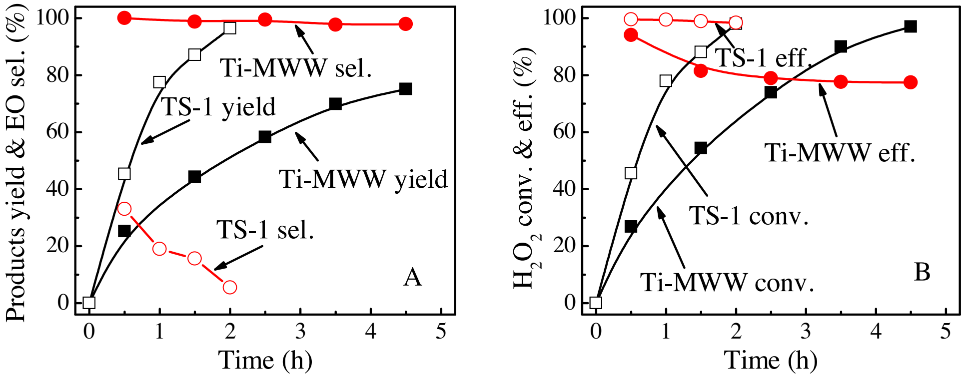


Fig. 6. Dependence of products yield and EO selectivity (A), and H_2O_2 conversion and efficiency (B) with time on stream of Ti-MWW and TS-1. Reaction conditions: Ti-MWW or TS-1, 150 mg; ethylene, 2.5 MPa; MeCN for Ti-MWW and MeOH for TS-1, 10 g; H_2O_2, 10 mmol; temp., 40 °C.

3.2.3. *Effect of reaction time at different temperatures*

The effect of reaction time on the performance of ethylene epoxidation over Ti-MWW was investigated at 35, 40, 45 and 50 °C, respectively (Fig. 5). Both the products yield and the H_2O_2 conversion increased rapidly at the beginning of epoxidation reaction (Fig. 5A and C), and then slowed down as H_2O_2 was gradually consumed with prolonging the time on stream. The H_2O_2 utilization efficiency decreased gradually with the reaction time (Fig. 5D), indicating the aggravation of non-productive decomposition of H_2O_2 because of catalysts deactivation. The EO selectivity, however, was always maintained at >95% (Fig. 5B). Fig. 5 shows that the epoxidation of ethylene favored at lower temperatures (e.g. 35 °C), where higher H_2O_2 utilization efficiency and EO selectivity were achievable when compared at a comparable H_2O_2 conversion with the reactions at higher temperature like 50 °C.

In addition, we have compared the time course of ethylene epoxidation between Ti-MWW and TS-1 with the purpose to further investigate their catalytic performances (Fig. 6). From the time-dependent courses of H_2O_2 conversion and products yield, TS-1/MeOH was obviously more active than Ti-MWW/MeCN when the reactions were conducted under the same reaction conditions except for the solvent. Most of EO was transformed to EG and methyl-ether in the catalytic system of TS-1/MeOH due to hydrolysis and solvolysis whereas the ring-opening reaction of EO was almost inert in the system of Ti-MWW/MeCN. Hence, Ti-MWW/MeCN is more suitable and selective than TS-1/MeOH for developing HPEO process.

3.2.4. *Effect of reaction pressure and catalyst amount*

The reaction pressure had a significant influence on the performance of ethylene epoxidation over Ti-MWW. As shown in Fig. 7, both H_2O_2 conversion and products yield were linearly proportional to the reaction pressure. The pressure showed a more significant effect on the ethylene expoxidation than that previously observed on the propylene expoxidation [17,35], simply because the range of the adjustable reaction pressure for ethylene is wider than that of propylene due to its higher vapor pressure. Thus, more ethylene would dissolve in the solvent (MeCN) with increasing reaction pressure, which promoted the epoxidation of ethylene. On the other hand, the EO selectivity and H_2O_2 efficiency hardly varied with the reaction pressure.

Fig. 8 shows the effect of catalyst amount on the epoxidation of ethylene with H_2O_2 in the Ti-MWW/MeCN system. The H_2O_2 conversion increased from 48.4% to 97.0% by increasing the catalyst amount from 50 mg to 150 mg and by further increasing the catalyst amount the conversion remained unchanged. The products yield increased gradually and reached the maximum at 150 mg catalyst loading. Increasing the catalyst amount tended to lower the H_2O_2 efficiency because of competition between epoxidation and H_2O_2 decomposition on the Ti active sites. Therefore, there was an optimum catalyst amount for the batchwise epoxidation of ethylene.

3.2.5. *Stability and reusability of Ti-MWW*

The stability and reusability of a heterogeneous catalyst was the essential factor for actual application in industrial processes. We have checked the catalytic cycles of Ti-MWW in the epoxidation of ethylene (Fig. 9). The used Ti-MWW catalyst was first

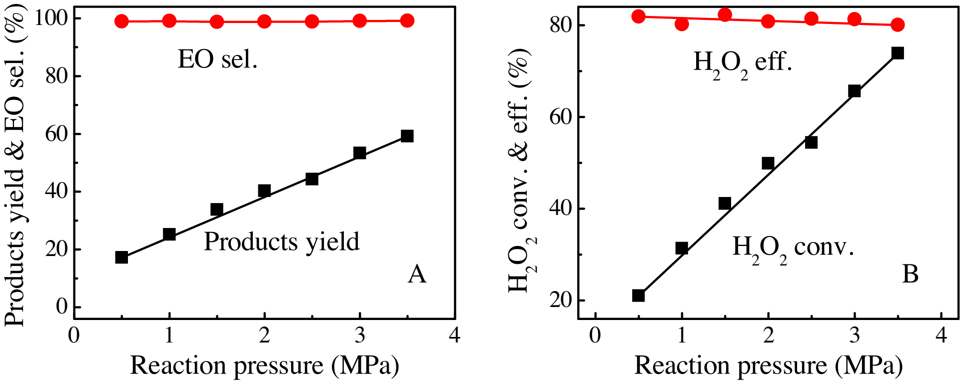


Fig. 7. Changes of products yield and EO selectivity (A), and H_2O_2 conversion and H_2O_2 efficiency (B) with the reaction pressure. Reaction conditions: Ti-MWW, 150 mg; MeCN, 10 g; H_2O_2, 10 mmol; temp., 40 °C; time, 1.5 h.

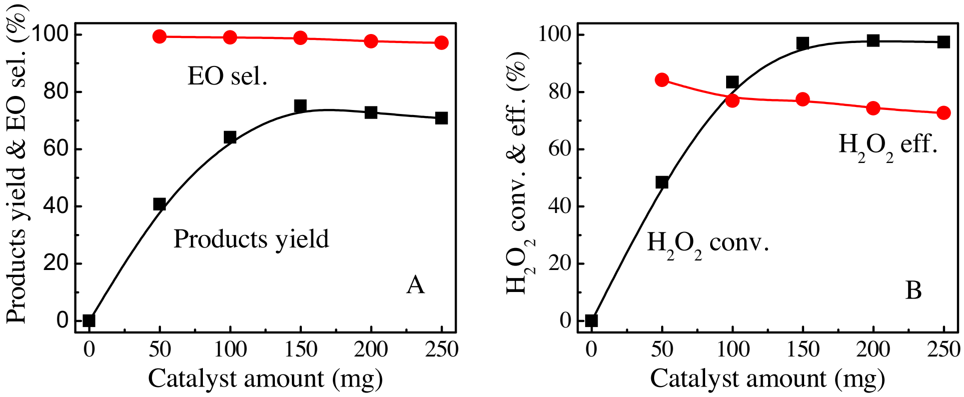


Fig. 8. Dependence of products yield and EO selectivity (A), and H_2O_2 conversion and efficiency (B) on the amount of Ti-MWW. Reaction conditions: ethylene, 2.5 MPa; MeCN, 10 g; H_2O_2, 10 mmol; temp., 40 °C; time, 4.5 h.

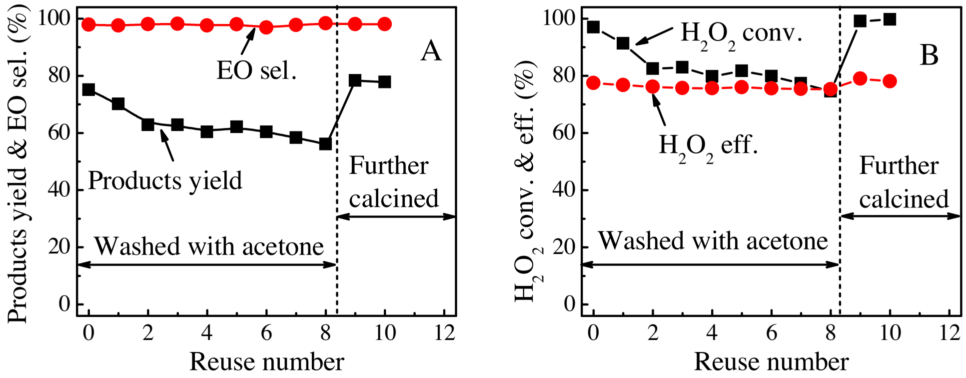


Fig. 9. Changes of products yield and EO selectivity (A), and H_2O_2 conversion and H_2O_2 utilization efficiency (B) with the reaction-regeneration cycles on Ti-MWW. Reaction conditions for the first run: Ti-MWW, 150 mg; ethylene, 2.5 MPa; MeCN, 10 g; H_2O_2, 10 mmol; temp., 40 °C; time, 4.5 h. The next catalytic runs proceed at a constant ratio of catalyst-oxidant-solvent.

recycled by centrifugation and washing with acetone, and then it was subjected to next catalytic runs. In the first three runs, both the H_2O_2 conversion and the products yield dropped largely with the reaction-regeneration cycles. The H_2O_2 conversion was maintained at a relatively high level even after nine recycles. When the reused catalyst was regenerated by washing with acetone and further calcinated at 550 °C for 6 h, the activity of Ti-MWW was almost totally recovered at the tenth run. As shown in Fig. 9B, H_2O_2 efficiency decreased slightly with the reaction-regeneration cycles due to the deactivation of the catalyst and it will be almost totally recovered at the tenth run. The Ti content of reused Ti-MWW was close to that of fresh one (Table 4), indicating that the leaching of Ti species almost did not occur in repeated catalytic runs. The high specific surface area verified that the regenerated Ti-MWW catalyst was still a highly porous material. Furthermore, no significant difference was found in the XRD patterns and UV–vis spectra between the fresh Ti-MWW and the recovered one (Fig. 10). The boron species co-existing in the framework was decreased to an extremely level

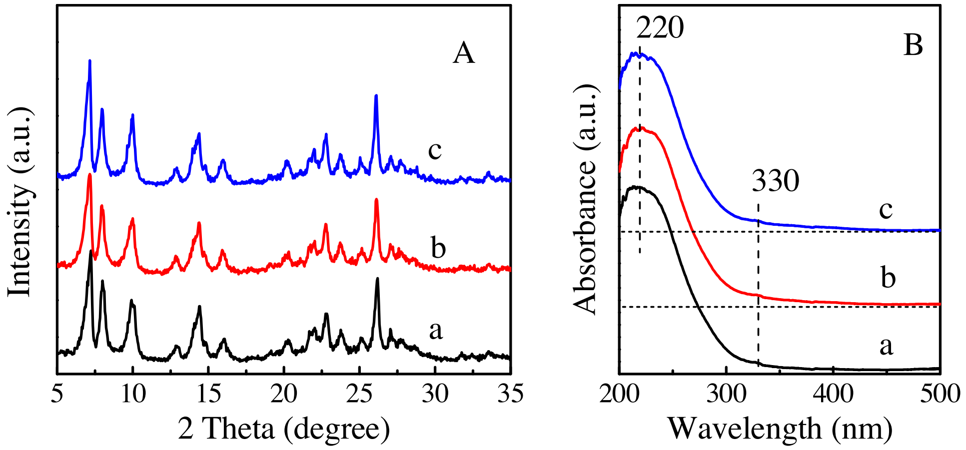


Fig. 10. XRD patterns (A) and UV–vis spectra (B) of fresh Ti-MWW (a), recovered one washed with acetone and dried (b) and further calcined at 550 °C for 6 h (c) after Ti-MWW was reused in the ethylene epoxidation for 8 times.

Table 4
Physicochemical and textural properties of fresh, used and regenerated Ti-MWW catalysts.

No.	Catalyst	SA[a] ($m^2 g^{-1}$)	Ti content[b] ($mmol g^{-1}$)	B content[b] ($mmol g^{-1}$)
1	Ti-MWW-fresh	545	0.39	0.16
2	Ti-MWW-used[c]	514	0.38	0.02
3	Ti-MWW-regeneration[d]	557	0.38	0.02

[a] Specific surface area (Langmuir) measured by N_2 adsorption at −196 °C.
[b] Ti and B contents determined by ICP analysis.
[c] Recovered one after Ti-MWW reused in the ethylene epoxidation for 8 times.
[d] Regeneration: washed with acetone and dried at 120 °C, and further calcined at 550 °C in air for 6 h.

after the reuse (Table 4). They were unstable simply because of a too small ionic radius in comparison to Si ions, which was in agreement with the previously observed in the epoxidation of various alkenes like allyl alcohol, diallyl ether and allyl chloride [20,21,23]. Considering the EG molecules, derived from the hydrolysis of EO, posses a high boiling point, a partial deactivation observed for the regenerated catalyst by only acetone washing could be ascribed to the organic compound deposition inside the channels and the covering of Ti active sites. This kind of deactivation was reversible unless the crystalline structure and the Ti sites were well maintained. Hence, burning off the organic compound efficiently restored the catalytic activity.

3.3. *Comparison of Ti-MWW and TS-1 for the epoxidation of different linear alkenes*

Ethylene is a simple alkene with the smallest molecular dimension and carbon number. It is expected that ethylene may suffer less diffusion problem in the liquid-phase epoxidation in comparison to other linear alkenes. Thus, it is desirable to know how the catalytic performance of epoxidation depends on the molecular size of alkenes, which would be helpful to understand the fundamental issues involved in developing HPEO process. Table 5 compares the catalytic behaviors in the epoxidation of different linear alkenes between Ti-MWW and TS-1. The activity of ethylene epoxidation of Ti-MWW/MeCN was inferior to TS-1/MeOH, but the EO selectivity for the former (99.6%) was almost 7 times of that for the latter (14.5%) (Table 5, No. 1). For larger alkenes (C_3=–C_6=), Ti-MWW/MeCN was superior to TS-1/MeOH not only in epoxylalkane selectivity but also in reactivity. Benefited from the electron-donating effects of the methyl groups, the electron density of the C=C bond in propylene is higher than that of ethylene, making the propylene molecules epoxidized more easily. With the substituent groups on the C=C bonds becomes longer or larger, the intrinsic reactivity of alkenes tends to be more active. Meanwhile, the diffusion problem inside zeolite micropores would emerge seriously for large substrate and product molecules. Thus, Ti-MWW and TS-1 both showed the maximum activity for propylene, and their H_2O_2 conversion and products yield dropped greatly from propylene to 1-hexene mostly due to the steric hindrance.

There was a big gap in the catalytic activity between ethylene epoxidation and propylene epoxidation on both Ti-MWW and TS-1. This result suggests that electron-deficient ethylene, although with small molecular dimension and suffering low diffusion hindrance by zeolite channels, is intrinsically inactive towards epoxidation. Thus, for developing practical HPEO process, it is desirable to adopt highly efficient titanosilicate catalysts capable of activating the alkene molecules with a low intrinsic reactivity under mild conditions and simultaneously suppressing the solvolysis or hydration of EO.

Table 5
Comparison of Ti-MWW and TS-1 for the epoxidation of various linear alkenes[a].

No.	Substrate	Ti-MWW (%)			TS-1 (%)		
		products yield[b]	H_2O_2 conv.	oxide sel.	products yield[b]	H_2O_2 conv.	oxide sel.
1	ethylene[c]	6.6	8.1	99.6	13.0	13.2	14.5
2	popylene[c]	94.9	98.9	99.5	89.3	91.6	82.8
3	1-butene[c]	64.3	68.0	99.8	48.5	52.0	92.2
4	1-pentene[d]	35.5	39.1	99.5	22.4	30.4	87.6
5	1-hexene[d]	26.9	29.1	99.3	15.6	20.2	92.4

[a] MeCN as solvent for Ti-MWW and MeOH as solvent for TS-1.
[b] Including ethylene oxide and corresponding byproducts formed by hydrolysis or solvolysis.
[c] Reaction conditions: cat., 50 mg; alkene, 0.2 MPa; H_2O_2, 15 mmol; solvent, 10 g; temp., 40 °C; time, 2 h.
[d] Reaction conditions: cat., 50 mg; alkene, 15 mmol; N_2, 0.2 MPa; H_2O_2, 15 mmol; solvent, 10 g; temp., 40 °C; time, 2 h.

4. Conclusions

Ti-MWW is an effective catalyst for the selective oxidation of ethylene with H_2O_2 to ethylene oxide. With suitable hydrophilic/hydrophobic characters favoring MeCN as solvent, Ti-MWW gives the H_2O_2 conversion and the ethylene oxide selectivity both above 95% under optimized reaction conditions. TS-1 is even more active than Ti-MWW for ethylene epoxidation, but it cannot suppress the solvolysis of ethylene oxide because of preferring MeOH solvent. Additionally, Ti-MWW proves to be superior to TS-1 in the selective oxidation of other linear alkene (from propylene to 1-hexene) with H_2O_2. No structural degradation and Ti leaching occur during the repeated use of Ti-MWW. The formation of heavy products like ethylene glycol may deactivate the Ti-MWW catalyst, which can be recovered by calcination. This study indicates that Ti-MWW is a promising catalyst for the selective synthesis of ethylene oxide and highly active titanosilicate catalyst is still desirable to develop more efficient HPEO process.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.apcata.2016.02.001.

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