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# Highly selective 1-pentene epoxidation over Ti-MWW with modified

## micro-environment of Ti active sites

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## Abstract

The titanosilicate/H<sub>2</sub>O<sub>2</sub> catalytic system was applied to process the liquid-phase selective epoxidation of 1-pentene to 1,2-epoxypentane (EP). The effects of titanosilicate topology (MWW, MFI, MSE, MEL, MOR, and \*BEA), solvent,  $H_2O/H_2O_2$  ratio, catalyst amount, reaction temperature, pressure, and time on the EP production were investigated systematically. The Ti-MWW/H<sub>2</sub>O<sub>2</sub>/acetonitrile system exhibited the highest 1-pentene conversion of 72.9% together with high EP selectivity of 99.9% and H<sub>2</sub>O<sub>2</sub> utilization efficiency of 91.5%. Moreover, it was proved that the Ti active sites located inside the intralayer 10-membered ring sinusoidal channels catalyzed the epoxidation process primarily owing to supplying more steric fitness for 1-pentene molecules. A piperidine (PI)-assisted structural rearrangement of Ti-MWW was performed to further enhance the catalytic activity, almost doubling the turnover number value. The evolution of the micro-environment of Ti active sites in this structural rearrangement process was carefully investigated, revealing the coordination of N atoms in PI molecules to the Ti atoms. More importantly, we identified that the hexa-coordinated Ti sites with the PI molecules as ligand could significantly accelerate H<sub>2</sub>O<sub>2</sub> activation, the effect of which far exceeded the inhibition effect caused by the electronegativity increase of Ti active sites.

## 1. Introduction

1,2-Epoxypentane (EP), as one of the important oxygen-containing derivatives of 1-pentene, serves as the raw material for producing many high value-added chemical products, such as cosmetics additives, polyester fiber, and pharmaceutical intermediates. Among them, 1,2-pentanediol (PD) is now the most important downstream product of EP, which is the indispensable intermediate for propiconazole synthesis with high global consumption, expensive price currently and increasing demand year by year [1-4]. Meanwhile, a large number of  $C_5$  components are generated in the petrochemical processes. For instance, the production of ethylene from petroleum cracking in China produced 2500 kt/a C<sub>5</sub> distillates in 2015, among which the amount of 1-pentene accounted for a large proportion. However, most of these C<sub>5</sub> hydrocarbons are commonly used as additives in high-octane gasoline. Considering the comprehensive utilization of resources, it is obviously a waste to burn 1-pentene directly as fuel. Therefore, it is quite competitive to develop efficient process of 1-pentene to EP. Industrially, the chlorohydrin process, initially conducted by Wurtz for the production of propylene oxide (PO) in 1859, has been used as the main route for EP synthesis for many decades. However, it suffers serious problems of waste pollution and equipment corrosion. The peroxy organic acid oxidation method is gradually replacing the traditional chlorohydrin process [5-7]. Nevertheless, the peroxy acid oxidant is quite explosive and corrodes the equipment severely. Furthermore, the two industrialized processes both have low atomic economy.

In 1983, the first generation titanosilicate TS-1 was reported by Taramasso et al,

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which was later used as a highly effective and eco-friendly catalyst for the selective oxidation reactions with H<sub>2</sub>O<sub>2</sub> as an oxidant [8]. The TS-1/H<sub>2</sub>O<sub>2</sub> system allows the reactions operated under mild conditions, yielding only H<sub>2</sub>O as the main by-product. Subsequently, its success in developing industrial applications for manufacturing various oxygen-containing bulk chemicals, especially PO, marks an important milestone in zeolite catalysis [9-11]. With the purpose to develop highly efficient and clean selective oxidation processes using titanosilicate/H<sub>2</sub>O<sub>2</sub> catalytic system, numerous studies have been carried out in the respective of pore architecture of titanosilicates and micro-environment of Ti active sites.

The pore structure mainly affects the diffusion of substrate molecules and the accessibility of active sites. Due to the restriction of its medium 10-membered ring (MR) pores, TS-1 always exhibits a low catalytic ability in the epoxidation of bulky molecules. Therefore, other titanosilicates with larger pores were developed successively, such as Ti-MWW [12], Ti-Beta [13], Ti-ITQ-7 [14], Ti-MCM-68 [15] and Ti-MCM-41 [16]. Especially, the layered Ti-MWW, with two independent 10-MR channels, 12-MR side cups and supercages, shows high reaction activity in the epoxidation of both small and bulky substrates. In addition, introducing mesopores even macropores, changing the morphology of titanosilicate and tuning the structural hydrophilicity/hydrophobicity are also regarded as effective strategies for enhancing the catalytic activity in epoxidation reactions, especially involving the bulky substrates [17-19].

In terms of the reaction mechanism of the epoxidation reaction catalyzed by titanosilicate/ $H_2O_2$  system, it is commonly believed that the isolated Ti (IV) centers Published on 22 July 2020. Downloaded on 8/10/2020 4:09:10 AM

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firstly activate  $H_2O_2$  molecules to form the intermediates hydroperoxo (Ti- $O^{\alpha}O^{\beta}O^{\beta}H)^{\alpha}O^{\alpha}O^{\alpha}O^{\alpha}O^{\alpha}O^{\alpha}$ and peroxo (Ti- $(\eta^2-O_2)$ ) species (Scheme S1 <sup>†</sup>), and the two intermediates were interconvertible in the presence of H<sub>2</sub>O molecule [20]. Subsequently, numerous studies revealed that the Ti-O<sup> $\alpha$ </sup>-O<sup> $\beta$ </sup>-H intermediate, which interact with the protic solvent molecules of alcohols or water via hydrogen bonding, was responsible for epoxidation reaction on Ti-zeolite, rather than the Ti- $(\eta^2$ -O<sub>2</sub>) species [10, 21, 22]. Then, the electron-rich alkene substrates attack the intermediates through nucleophilic reaction to transfer the oxygen atoms into the product [23-25]. Thus, modulating the electronic environment of Ti active sites is an alternative way to improve the catalytic activity of titanosilicates. Considering the more electronegative  $O^{\alpha}$  directly coordinated to the Ti site attacks the C=C bond in the alkene epoxidation process, enhancing the electropositivity of Ti centers would accelerate the nucleophilic reaction and improve the catalytic activity. The catalytic performance of Ti-MWW was significantly enhanced by introducing fluorine atoms into the framework to create the SiO<sub>3/2</sub>F species coordinated with Ti species [26-28]. The Ti species in titanosilicate catalysts mainly exist as framework TiO<sub>4</sub> species [29], framework TiO<sub>5</sub> species [30], framework TiO<sub>6</sub> species [31], non-framework TiO<sub>6</sub> species [32] and anatase [33], among which only the framework Ti species can catalyze the epoxidation effectively. And it is commonly accepted that framework Ti species with higher coordination number exhibited the better catalytic activity in epoxidation reactions [30, 34]. For a long time, abundant efforts have been devoted to construct the highly active hexa-coordinated Ti species with  $H_2O$  as the ligand (Ti(OSi)<sub>2</sub>(OH)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>) via chemical post-modification and

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adding crystallization-supporting agent in synthesizing titanosilicates [5, 34, 35]. Recently, we communicated an organic-inorganic hybrid MWW-type titanosilicate with a two-dimensional (2D) layered structure exhibited greatly enhanced activity in the cyclopentene epoxidation reaction, which was constructed by structural arrangement of 3D Ti-MWW zeolite and possessed hexa-coordinated Ti species with piperidine (PI) as the ligand (Ti(OSi)<sub>2</sub>(OH)<sub>2</sub>(H<sub>2</sub>O)PI) besides the framework TiO<sub>4</sub> species [36]. However, the exact reason for the enhanced activity by introducing the PI ligand is still unclear.

Herein, the epoxidation of 1-pentene catalyzed by titanosilicate with H<sub>2</sub>O<sub>2</sub> have been systemically studied to produce EP selectively and efficiently. By comparison to the other five representative titanosilicates, Ti-MWW showed the highest catalytic activity with acetonitrile (MeCN) as the solvent. The effects of the reaction conditions on the 1-pentene epoxidation over Ti-MWW were investigated in detail. The activity was further enhanced by introducing PI as the ligand to construct open Ti sites. The reasons were discussed in depth for the outstanding activity of PI-modified Ti-MWW titanosilicate despite a partial blockage of micropores aroused by PI coordination.

## 2. Experimental

#### 2.1 Catalyst preparation

#### 2.1.1 Synthesis of different titanosilicates

Six titanosilicates with different topologies, including Ti-MWW, TS-1, TS-2, Ti-MOR, Ti-MCM-68 and Ti-Beta, were employed to catalyze the liquid-phase 1-pentene epoxidation reaction. According to the procedures reported by previous literature [12],

Ti-MWW was hydrothermally synthesized with piperidine (PI) as the structure-

synthetic mixture gel with a molar composition of 1.0 SiO<sub>2</sub>: 0.03 TiO<sub>2</sub>: 1.4 PI: 0.67 B<sub>2</sub>O<sub>3</sub>: 19 H<sub>2</sub>O was hydrothermally crystallized at 443 K for 7 days under a rotation rate of 10 rpm. After crystallization, the product was filtered, washed with deionized water and dried at 373 K overnight, giving 2D Ti-MWW lamellar precursor denoted as P-Ti-MWW. Subsequently, P-Ti-MWW was treated by refluxing in 2.0 M HNO<sub>3</sub> at 413 K for 4 h to remove extra-framework Ti species and a part of framework B species as well. The acid-treated product was filtered, washed with deionized water, dried at 373 K overnight, and calcined at 823 K for 6 h subsequently to obtain the 3D Ti-MWW catalyst. In addition, this matrix suffered the above-mentioned acid-treatment without calcination was named as A-Ti-MWW. TS-1 was hydrothermally synthesized by classic method [8]. The as-synthesized TS-1 was treated with 1 M HCl solution to remove extra-framework Ti species before calcination. TS-2 with MEL topology was hydrothermally synthesized following the procedure reported by R. Kumar et al [37]. Ti-MOR was obtained by atom-planting method with the gas-solid reaction between deeply dealuminated mordenite and vapor TiCl<sub>4</sub> at elevated temperature [38]. The Ti-MCM-68 zeolite with MSE topology was also synthesized by performing the gas-solid reaction over the dealuminated MCM-68 zeolite [15]. Ti-Beta was synthesized in fluoride medium via the structural reconstruction method [39].

#### 2.1.2 Structural rearrangement of Ti-MWW catalyst

According to the previous report [36], the transformation of 3D Ti-MWW to 2D

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lamellar structure was carried in the solution containing PI with the molar ratio of 1.0 SiO<sub>2</sub>: 0.4 PI: 10 H<sub>2</sub>O at 443 K for 1 day under a rotation speed of 10 rpm. The resultant product was collected by filtration, washed and dried at 373 K overnight. Then, the 2D Ti-MWW containing PI molecules in the channels was obtained, which was denoted as R-Ti-MWW. As a reference, R-Ti-MWW was further calcined at 823 K for 6 h to remove the organic species, denoted as R-Ti-MWW-cal.

#### 2.2 Characterization methods

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The X-ray diffraction (XRD) patterns were collected on a Rigaku Ultima IV diffractometer using Ni-filtered CuK $\alpha$  radiation ( $\lambda = 0.1541$  nm). The voltage and current were 35 kV and 25 mA, respectively. The amount of Si and Ti were quantified by Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) on a Thermo IRIS Intrepid II XSP atomic emission spectrometer. The UV-Vis spectra were collected on a PerkinElmer UV-Vis Lambda 35 spectrophotometer using BaSO<sub>4</sub> as a reference. UV resonance Raman spectra (UVRRS) were collected on a triple spectrograph Raman system UV-Raman-100 with the excitation line at 244 nm and spectral resolution of 3 cm<sup>-1</sup>. The SEM images were taken on a Hitachi S-4800 scanning electron microscope. The FT-IR spectra were measured using the self-supported wafer by a Nicolet Nexus 670 FT-IR spectrometer at a resolution of 2 cm<sup>-1</sup>. The spectra in the framework vibration region (500 - 1300 cm<sup>-1</sup>) were measured using KBr pellet technology. In order to eliminate the influence of absorbed water, all the samples were evacuated at 723 K for 3 h before measurement. Thermogravimetric (TG) analysis was carried out in a Netzsch Sta 4049 F3 apparatus in air with a heating rate of 10 K min<sup>-1</sup>

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in the temperature range of 473-1073 K. The solid-state MAS NMR spectra Were<sup>TDOCV004788</sup> recorded on a VARIAN VNMRS-400 MB NMR spectrometer using a 7.5 mm T3HX probe and single-pulse method. The <sup>29</sup>Si MAS NMR was measured at a frequency of 100.54 MHz and spinning rate of 3 KHz with [(CH<sub>3</sub>)<sub>3</sub>SiO]<sub>8</sub>SiO<sub>12</sub> as the chemical shift reference, while the <sup>13</sup>C MAS NMR was measured at a frequency of 79.43 MHz and a spinning rate of 5 KHz and with adamantane as the chemical shift reference. The surface and pore volume of the calcined titanosilicates were determined by N<sub>2</sub> physical sorption at 77 K using a BEL SORP instrument after degassing in vacuum at 473 K for 3 h, while the textural properties of the PI-containing Ti-MWW were determined by Ar physical adsorption at 87.3 K on a Micromeritics ASAP2020 adsorption instrument after evacuation at 413 K for 3 h. The X-ray photoelectron spectroscopy (XPS) was measured on the ESCALAB 250 XI equipment. The element analysis was carried out with an Elementar Vario III analyzer.

#### 2.3 Liquid-phase epoxidation of 1-pentene

The liquid-phase 1-pentene epoxidation was carried out in an autoclave reactor equipped with a Teflon-inner. In a typical run, 50 mg catalyst, 10 mL solvent, 10 mmol 1-pentene and 10 mmol  $H_2O_2$  (30 wt.%) were added into the reactor, and the reaction pressure was then adjusted to 0.5 MPa by N<sub>2</sub>, after the air inside the autoclave was exhausted by N<sub>2</sub> exchange for 3 times. After stirring vigorously at 333 K for 2 h, the reactor was cooled down with ice water and then depressurized slowly. The products were analyzed by a Gas Chromatograph (Shimadzu 2014, FID detector) equipped with Rtx-Wax capillary column, and the generated products were confirmed by a GC-MS

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(Agilent 6890 series GC system, 5937 network mass selective detector). The remaining amount of H<sub>2</sub>O<sub>2</sub> was determined by the titration method with 0.05 M Ce(SO<sub>4</sub>)<sub>2</sub> aqueous solution.

## 3. Results and discussion

### 3.1 Characterization of various titanosilicates

The XRD patterns confirmed that the six titanosilicates synthesized by hydrothermal synthesis or post-synthesis processes all were highly crystalline materials without impurity and possessed the topologies of MSE, MWW, MFI, MEL, \*BEA, and MOR, respectively (Fig. 1). UV-Vis and FT-IR spectra were employed to investigate the coordination states of Ti species. As shown in Fig. 2A, the predominate band at 200-220 nm, assigned to the charge transfer from O<sup>2-</sup> to Ti<sup>4+</sup> in isolated Ti(OSi)<sub>4</sub> or Ti(OSi)<sub>3</sub>(OH) species, was observed for all the titanosilicates, indicating that Ti species were mainly tetrahedrally coordinated in the framework [27, 40, 41]. And negligible bands at 260 nm and 330 nm ruled out the existence of extra-framework amorphous Ti species and anatase, respectively. Consistently, all the IR spectra showed obvious characteristic bands at 960 cm<sup>-1</sup> (Fig. 2B), which was normally taken as fingerprint of the incorporation of Ti species in the zeolite framework [10, 42], although the precise attribution of this IR band is still controversial. Therefore, combining the UV-Vis and IR results, it could be concluded that Ti species in titanosilicates were mainly tetrahedrally coordinated in the frameworks. The crystal morphologies of titanosilicates were provided by the SEM images (Fig. 3). Ti-MCM-68 possessed the aggregates of nanosized cubic crystals with a particle size of 50 - 100 nm (Fig. 3a). Ti-MWW showed

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a uniform plate-shaped morphology with a thickness of ~100 nm (Fig. 3b). TS-1 possessed unique nanosized sphere crystals with a size of ~ 400 nm (Fig. 3c), while TS-2 was composed of rod-like nanocrystals (Fig. 3d). Ti-Beta was of nanosized crystalline particles with a particle size in the range of 50 - 150 nm (Fig. 3e). The irregularly shaped crystals packed closely were observed for Ti-MOR (Fig. 3f). The textural properties of these titanosilicates are listed in Table S1<sup>†</sup>. The titanosilicates possessed the Langmuir specific surface areas in the range of 514 - 615 m<sup>2</sup> g<sup>-1</sup>, and micropore volume of 0.12 -0.19 cm<sup>3</sup> g<sup>-1</sup>, respectively, indicating that they were well crystallized and characterized by microporous structures. Among them, Ti-Beta exhibited the highest surface area, while Ti-MCM-68 had the highest micropore volume, which were in good accordance with their morphologies and pore structures.

### 3.2 Liquid-phase epoxidation of 1-pentene over various titanosilicates

#### 3.2.1 A comparison of catalytic performance among various titanosilicates

The six titanosilicates were applied to catalyze the 1-pentene epoxidation and the catalytic results are summarized in Table 1. They all exhibited an extremely high EP selectivity (> 95%), whether in aprotic solvent of MeCN for Ti-MCM-68, Ti-MWW, Ti-Beta and Ti-MOR or in protic solvent of MeOH for TS-1 and TS-2. And no significant difference was observed in the crystallinity and the coordination state as well as the amount of Ti active center between the fresh and spent catalysts (Fig. S1-6<sup>†</sup>), indicating the excellent stability of all the Ti-zeolites. However, these titanosilicates showed different 1-pentene conversion obviously, with the order of Ti-MWW > TS-1  $\approx$  Ti-MCM-68 > Ti-Beta > TS-2 > Ti-MOR. Ti-MWW showed the

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highest 1-pentene conversion of 72.9%. Considering the different Ti contents In these titanosilicates, turnover number (TON) was calculated to compare the specific catalytic activities of these titanosilicates fairly. The TON value decreased in the order of Ti-MWW > Ti-MCM-68 > TS-1 > Ti-Beta > TS-2 > Ti-MOR. Ti-MWW exhibited the highest TON value of 390, while Ti-MOR had the lowest TON value of only 12. TON value of Ti-MCM-68 was 352, close to that of Ti-MWW (390) but much higher than that of TS-1 (183). Ti-MOR with 12-MR pores showed the worst activity for 1-pentene epoxidation. In previous reports, the catalytic activities of Ti-MOR for the epoxidation of other alkenes were also very low [43, 44], indicating Ti-MOR may be not a suitable epoxidation catalyst, although it showed excellent catalytic performance in the ammoximation reactions [45, 46]. For Ti-Beta with 3D 12-MR pores, a higher hydrophilicity aroused by the intergrowth of polymorph A and B probably induced a lower activity than TS-1. Although TS-2 possessed the 10-MR pores very similar to TS-1, its reaction activity was lower, which was consistent with previous results in catalyzing the epoxidation of other alkenes [47, 48]. It could be deduced that the pore size of Ti-zeolites is not the only parameter that determines the catalytic performance in the 1-pentene epoxidation reaction. For the three titanosilicates of TS-1, Ti-MCM-68 and Ti-MWW with outstanding catalytic activity, the solvent effects were further investigated in detail.

#### 3.2.2 Influence of solvents

The solvents generally imposed significant influence on the performance of titanosilicate in catalyzing the epoxidation reactions. The aprotic/protic nature and

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polarity of solvent, solubility of reactants and products, and the effect of diffusion are view Article Online all needed to be considered. In addition, the reactants, intermediate species or the products might have an interaction with the solvent so that the reaction pathway was also affected possibly [49].

Table 2 compared the catalytic performance of Ti-MWW, Ti-MCM-68 and TS-1 in the 1-pentene epoxidation reaction in various solvents. For Ti-MWW, all the solvents showed extremely high EP selectivity (>98%) except H<sub>2</sub>O, indicating that EP was relatively stable and not tended to suffer the ring-opening side reaction in non-aqueous solvent. Ti-MWW exhibited a superior catalytic performance in aprotic solvents of MeCN and acetone in comparison to protic solvents of MeOH, t-BuOH and H<sub>2</sub>O. And MeCN was the most favorable solvent for Ti-MWW, in which the highest 1-pentene conversion (72.9%), EP selectivity (99.9%), and H<sub>2</sub>O<sub>2</sub> utilization efficiency (91.5%) were achieved. In protic solvent system, the catalytic activity was higher in *t*-BuOH than in MeOH and H<sub>2</sub>O in despite of the larger diameter of the former one. Nevertheless, in comparison to the solvent *t*-BuOH, MeOH showed a relatively higher PD selectivity of 1.1%, and small amount of pentanediol ethers (PE) were also detected, indicating that the hydrolysis and solvolysis occurred more easily in MeOH solvent. Ti-MWW zeolite, originated from the layered precursor, inevitably contains some defect sites such as interlayer silanol groups due to the incomplete condensation of neighboring layers and intralayer hydroxyl nests [12]. The defect sites favor the adsorption of protic molecules, such as alcohol and H2O, which would impose steric hindrance and diffusion constrains. Thus, Ti-MWW exhibited a higher reaction activity in aprotic

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solvent of acetone and MeCN than in protic solvents. It was noteworthy that diol was predominately produced over Ti-MWW catalyst with H<sub>2</sub>O as the solvent, in which PD selectivity was up to 98.5%, but the 1-pentene conversion and H<sub>2</sub>O<sub>2</sub> utilization efficiency were extremely low. On the one hand, the solubility of reactants and products was much lower in H<sub>2</sub>O comparing to other investigated organic solvents. On the other hand, the generated EP and H<sub>2</sub>O solvent in the system were successively hydrolyzed to produce by-product PD, which may easily adsorb on the silanol groups to cause micropore blockage.

Similar to Ti-MWW, Ti-MCM-68 also contains some defect sites owing to the dealumination process before Ti insertion. Thus, Ti-MCM-68 could have similar solvent effects as Ti-MWW. The 1-pentene conversion decreased gradually in the order of MeCN > acetone >MeOH > t-BuOH > H<sub>2</sub>O, indicating that the aprotic solvent was more suitable for Ti-MCM-68. Meanwhile, Ti-MCM-68 exhibited the lowest EP selectivity (89%) in protic solvent MeOH, and a certain amount of PD was also detected, indicating that EP was hydrolyzed much easier over Ti-MCM-68 in the solvent of MeOH than that over Ti-MWW. Ti-MCM-68 showed a higher EP selectivity of 98.9% in solvent H<sub>2</sub>O, whereas the opposite result was observed for Ti-MWW. It might be due to the Brønsted acid sites (BAS) derived from the residual framework Al atoms in Ti-MCM-68. The BAS are effective in catalyzing the epoxide hydrolysis, but the yielding diol had a strong interaction with the BAS [50], which would cover the BAS and inhibit the further conversion of epoxide to diol.

In the case of the hydrophobic TS-1 with less defects, MeOH was the most

effective solvent from the viewpoints of reaction activity listed in Table 2. And it showed a product distribution similar to Ti-MWW and Ti-MCM-68 in the case of MeOH solvent, meaning the occurrence of solvolysis. TS-1 was almost inactive in the solvent of H<sub>2</sub>O apparently. Nevertheless, the aprotic solvent MeCN, with the 1-pentene conversion low to 8.5%, was proved unsuitable for TS-1 in catalyzing the 1-pentene epoxidation. In addition, a plenty of diols were produced in the solvent of acetone and t-BuOH, indicating the ring-opening side reaction occurred obviously over TS-1 along with the main epoxidation reaction.

Based on the above results, the reaction pathway of the 1-pentene epoxidation reaction was verified and depicted in Scheme 1. The main product of the 1-pentene epoxidation was EP, which may be hydrolyzed to form by-product PD on the Lewis acid centers provided by Ti-O-O-H in titanosilicate-H<sub>2</sub>O<sub>2</sub> system [50]. With MeOH as the solvent, EP also possibly further underwent solvolysis to produce PE by-products.

After the detail investigation of solvent effect, the three titanosilicates of Ti-MWW, TS-1, and Ti-MCM-68, were evaluated in the respective of reaction time under their most favorable solvent (Fig. S7<sup>†</sup>). Over the whole reaction time courses, Ti-MWW exhibited the highest catalytic activity, and Ti-MCM-68 was slightly inferior to it, but the former two titanosilicates were both much higher than TS-1. All the abovementioned results proved that Ti-MWW could serve as a highly efficient catalyst for the 1-pentene epoxidation in solvent of MeCN.

#### 3.2.3 Investigation of the location of the active Ti sites that catalyzed

For Ti-MWW, the active Ti sites are generally located in three different places,

near 12-MR side cups on the external surface of crystal, within the intralayer sinusoidal 10-MR channels and supercages (Scheme S2A<sup>+</sup>). To gain insight into the specific Ti location which contributed more to the catalytic activity, the selective poisoning experiment was performed over Ti-MWW. The poisoning reagent tripropylamine (TPA) with small molecule size was able to poison all the Ti sites, while the bulky 2,4,6collidine (COD) hardly entered 10-MR pores and thus selectively poisoned the Ti sites within the 12-MR side cups on the external surface of the Ti-MWW (Scheme S2B<sup>+</sup>). According to the Ti amount (0.02 mmol) in Ti-MWW catalyst that added into the reaction system, 2 mmol of the two amines was sufficient to poison the accessible Ti

reaction system, 2 mmol of the two amines was sufficient to poison the accessible Ti active sites. As listed in Table S2<sup>†</sup>, when TPA was added, the 1-pentene conversion exhibited a dramatic decrease as expected. However, the bulky COD had little impact on the catalytic activity, suggesting that most of Ti species located at the external 12-MR side cups did not involve in catalyzing the 1-pentene epoxidation. It was indicated that although the Ti sites on the external 12-MR side cups had the better accessibility, the exposed Ti sites might lack steric matching with the substrate molecules. Thus, the 1-pentene epoxidation mainly occurs in the intralayer sinusoidal 10-MR channels and supercages.

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Bearing the main reaction places of Ti-MWW in mind, the reason why Ti-MWW exhibited superior catalytic performance than TS-1 and Ti-MCM-68 could be discussed in detail. The activities of Ti-MWW and Ti-MCM-68 with 12×18 MR supercages were better than that of TS-1, indicating that the appropriately sized supercage structure might be conductive to the 1-pentene epoxidation owing to the steric restriction. It is

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worth noting that Ti-MWW, Ti-MCM-68 and TS-1 all contain 10-MR pore chained  $3^{0.7DOCY004788}$ However, the catalytic activity of Ti-MWW with 2D 10-10-MR pore structure was higher than that of TS-1 with 3D 10×10-MR pore structure and that of Ti-MCM-68 with 3D 12×10×10-MR pore structure. The different activity was speculated to be related to the pore architecture of the three titanosilicates with different topologies. The intralayer sinusoidal 10-MR channels of Ti-MWW was more restricted and elliptical (4.0×5.9 Å) than that of TS-1 (5.1×5.5 Å) and Ti-MCM-68 (5.2×5.8 Å and 5.2×5.2 Å), which might supply better steric matching between the linear 1-pentene and intermediate Ti-O-O-H complex without affecting the diffusion of substrates. This result also highlighted the significance of taking into account the relationship between the shape of substrate molecule and the topology of titanosilicate for developing a highly active titanosilicate-H<sub>2</sub>O<sub>2</sub> catalytic system.

3.3 Catalytic performance of Ti-MWW in 1-pentene epoxidation

#### 3.3.1 Influence of the $H_2O/H_2O_2$ molar ratio

 $H_2O$  was inevitably introduced into the catalytic system when aqueous  $H_2O_2$  was used as the oxidant for epoxidation reactions. Hence, the effect of  $H_2O/H_2O_2$  molar ratio on catalytic performance was investigated for Ti-MWW catalyzed 1-pentene epoxidation. As depicted in Fig. 4, both the conversions of  $H_2O_2$  and 1-pentene were linearly increased with the  $H_2O/H_2O_2$  molar ratio increased from 4.4 to 7.4, whereas no obvious effect was observed with the  $H_2O/H_2O_2$  further increasing.  $H_2O_2$  efficiency was not significantly affected by the addition of  $H_2O$  in the reaction system. However, EP selectivity was gradually decreased along the increase of  $H_2O/H_2O_2$ . Thus, in the Ti-MWW/H<sub>2</sub>O<sub>2</sub>/MeCN catalytic system, the increasing of  $H_2O/H_2O_2$  could <sup>DOI 1011029/DOCY00478B</sup> promote  $H_2O_2$  and 1-pentene conversion, while it induced negative effect on the epoxide selectivity.

#### 3.3.2 Influence of reaction temperature and time

The reaction temperature had conspicuous effect on catalytic performance of Ti-MWW in the 1-pentene epoxidation reaction. For both  $H_2O_2$  and 1-pentene conversions, higher reaction temperature favored higher conversion (Fig. 5A and C). They increased rapidly at the beginning of catalytic reaction, and then the speed gradually slowed down with further prolonging the reaction time. As shown in Fig. 5B,  $H_2O_2$  utilization efficiency decreased slowly with increase of reaction temperature, indicating higher reaction temperature promoted the non-productive decomposition of  $H_2O_2$ . Meanwhile, the EP selectivity always maintained at > 99% (Fig. 5D), which again confirmed the effective inhibition of secondary reaction of hydrolysis using MeCN as the solvent. All these results indicated the 1-pentene epoxidation should be proceeded at a relatively low reaction temperature. Considering both the  $H_2O_2$  utilization efficiency and catalytic activity, 333 K is considered to be an optimal reaction temperature.

#### 3.3.3 Influence of reaction pressure

Since 1-pentene is gas phase at the reaction temperature of 333 K, reaction pressure would have an important influence on the gas-phase involved catalytic system. As depicted in Fig. 6, when the reaction pressure increased from 0.1 to 0.5 MPa,  $H_2O_2$  and 1-pentene conversion as well as the  $H_2O_2$  utilization efficiency increased proportionally. Further increasing the pressure, the catalytic performance levelled off.

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Notably, EP selectivity was almost unaffected by the reaction pressure. Increasing the reaction pressure could improve the solubility of 1-pentene in MeCN, so as to enhance the conversion of 1-pentene.

#### 3.3.4 Influence of Ti-MWW catalyst amount

The catalyst amount was also investigated and the results were shown in Fig. 7. Reasonably, larger amount of catalyst favored the conversion of  $H_2O_2$  and 1-pentene. The  $H_2O_2$  utilization efficiency slightly increased with the increase of Ti-MWW amount, whereas the opposite result was found for EP selectivity. The  $H_2O_2$  conversion, efficiency and 1-pentene conversion reached the maximum of 94.6%, 96.3% and 91.7%, respectively, when 200 mg Ti-MWW was used. However, the EP selectivity decreased to 97.6%. Therefore, although increasing the Ti-MWW amount lead to the higher reactant conversion and oxidant utilization, the hydrolysis of epoxide was also promoted due to the introduction of more Lewis acid sites.

3.4 Ti-MWW modification by structural rearrangement with piperidine

3.4.1 A comparison of the catalytic performance of Ti-MWW and R-Ti-MWW in 1pentene epoxidation reaction

To further improve the catalytic performance, the PI-assisted structural rearrangement was performed over Ti-MWW, yielding an organic-inorganic hybrid material of R-Ti-MWW. The XRD pattern and <sup>13</sup>C MAS NMR confirmed its 2D MWW structure and the occlusion of organic PI molecules in MWW framework (Fig. S8<sup>†</sup>). The PI treatment hardly affected the Ti content and the Ti/N molar ratio was 0.25, but the TON value of R-Ti-MWW catalyst increased twice as much as that of the 3D Ti-

MWW (Table 3). Meanwhile, the  $H_2O_2$  utilization efficiency was also improved from

90.2% to 94.6%. Namely, this organic-inorganic hybrid Ti-MWW catalyst, with partially blocked pores containing PI molecules, exhibited superior catalytic activity than Ti-MWW with totally open channels in the 1-pentene epoxidation. The apparent activation energies of Ti-MWW and R-Ti-MWW were calculated by using the Arrhenius equation for 1-pentene epoxidation and they were 22.0 and 16.3 kJ mol<sup>-1</sup>, respectively (Fig. 8), indicating that the PI-assisted structural rearrangement reduced the apparent activation energy. The values of the activation energies (< 20-30 kJ mol<sup>-1</sup>) indicate that the reaction rate is controlled by the diffusion of reactants and not the chemical interaction itself [51]. Therefore, according to the results of apparent activation energies, it could be inferred that the reaction rate of R-Ti-MWW was controlled by the diffusion of reactants, which was different from that of original Ti-MWW controlled by the chemical reaction itself.

#### 3.4.2 Discussion on PI-incorporation for catalytic activity improvement

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More experiments were performed to reveal the reason for higher activity of R-Ti-MWW. When the PI-containing Ti-MWW was used as the catalyst, the products were analyzed by GC-MS and no acetamide was detected. Therefore, the contribution of Payne oxidation to the whole oxidation process could be basically excluded under this condition, even though the basic PI might favor the Payne oxidation. Once the same amount PI was added in the Ti-MWW catalyzed system, an obvious decrease of the 1pentene and  $H_2O_2$  conversion was observed (Table S3<sup>†</sup>), indicating the introduction of PI into this catalytic system directly suppressed the reaction activity. Thus, it is Published on 22 July 2020. Downloaded on 8/10/2020 4:09:10 AM

speculated that PI molecules might need to be embedded in the Ti-MWW framework

P-Ti-MWW and A-Ti-MWW, both with 2D MWW structure and PI molecules inside the framework (Fig.  $S8^{\dagger}$  and Table 4) were applied to catalyze the 1-pentene epoxidation. However, neither of them was active during the whole reaction time course (Fig. 9). P-Ti-MWW exhibited an extremely low total surface area (53 m<sup>2</sup> g<sup>-1</sup>) and micropore volume (0.001 cm<sup>3</sup> g<sup>-1</sup>), indicating its pore channels were almost fully blocked by PI. The micropore volume and total surface area of R-Ti-MWW was 0.04 cm<sup>3</sup> g<sup>-1</sup> and 187 m<sup>2</sup> g<sup>-1</sup>, which were close to those of A-Ti-MWW (0.05 cm<sup>3</sup> g<sup>-1</sup> and 217  $m^2 g^{-1}$ ), implying their pore channels were partially open. The liquid-phase 1-pentene adsorption experiment further proved that the substrate molecules could diffuse into the partially open micropores of R-Ti-MWW and A-Ti-MWW (Fig. S10<sup>†</sup>), implying the accessibility of the active sites inside A-Ti-MWW and R-Ti-MWW. Generally, the weight loss in the range of 473-1073 K was ascribed to the removal of the PI molecules in MWW zeolite. More specifically, the weight loss in the lower temperature region of 473-643 K was attributed to the decomposition of the PI molecules occluded in the interlayer space, whereas the decomposition of PI molecules in the intralayer 10-MR channels occurred in the higher temperature region of 643-1073 K [52]. The weight loss of P-Ti-MWW, A-Ti-MWW and R-Ti-MWW in the range of 473-643 K was 7.0%, 2.6% and 6.9%, respectively (Fig. S11<sup>†</sup> and Table 4). However, in the range of 643-1073 K, the weight loss value of P-Ti-MWW, A-Ti-MWW and R-Ti-MWW were 8.9%, 4.7% and 4.8%, respectively. For the 2D lamellar MWW structure, only the intralayer

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sinusoidal 10-MR pores and exterior 12-MR side pockets exist and the supercages cannot form due to the disconnection of neighboring layers (Scheme S3<sup>†</sup>). Therefore, the TG analysis indicated that the opening degree of intralayer sinusoidal 10-MR micropores of A-Ti-MWW and R-Ti-MWW was similar, which was obviously higher than that of P-Ti-MWW. The substrate diffusion in the interlayer space of P-Ti-MWW and R-Ti-MWW was more constrained than that of A-Ti-MWW.

The coordination states of Ti active sites in these PI-containing Ti-MWW zeolites were analyzed by UV-Vis, UV-Raman and XPS spectra. P-Ti-MWW displayed a main absorption band at 260 nm, attributed to the amorphous non-framework TiO<sub>6</sub> species [12], together with a weak shoulder band around at 210 nm resulting from the framework TiO<sub>4</sub> species (Fig. 10A). A-Ti-MWW sample only exhibited the band at 210 nm, indicating the non-framework  $TiO_6$  species were mostly removed via the acid washing. For R-Ti-MWW, apart from the  $TiO_4$  species, an obvious shoulder bands at 280 nm was also observed, due to the novel hexa-coordinated Ti species owing to the reinsertion of PI molecules in the structural rearrangement. The structure of this new hexahedral coordinated Ti species was verified to be the open Ti sites with PI as ligand in our previous work (Scheme S4c<sup>†</sup>) [36]. In the UV-Raman spectrum of P-Ti-MWW (Fig. 10B), the extremely strong band at 700 cm<sup>-1</sup> were assigned to the Ti-O-Ti stretching in the non-framework TiO<sub>6</sub> oligomers (Scheme S4, d and e<sup>†</sup>). Besides, a very weak band at 1108 cm<sup>-1</sup> was also observed, attributed to the symmetric vibration of the tetrahedron TiO<sub>4</sub> in the framework of titanosilicates [32]. For A-Ti-MWW, the band at 700 cm<sup>-1</sup> disappeared whereas the bands at 1108 cm<sup>-1</sup> was significantly enhanced,

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/iew Article Online demonstrating the elimination of non-framework  $TiO_6$  species upon acid treatment [53]. R-Ti-MWW showed a new weak Raman band at 724 cm<sup>-1</sup>, in addition to the band at 1108 cm<sup>-1</sup>. The Raman bands in the region of 600-800 cm<sup>-1</sup> were generally attributed to the hexahedral Ti species [32, 53]. Thus, the hexahedral Ti species in R-Ti-MWW were entirely different from those in P-Ti-MWW zeolites, which was consistent with the observation in UV-Vis spectra, indicating the formation of an unusual hexahedral Ti species in R-Ti-MWW. Furthermore, since the PI-assisted structural rearrangement process was performed in alkaline system, slight desilication inevitably occurred and resulted in the transformation of Si micro-environment, which in turn would affect the micro-structure of Ti species. The increase in Q<sup>3</sup> and the presence of additional Q<sup>2</sup> sites in R-Ti-MWW indicated that a portion of  $Q^4$  Si species was transferred to  $Q^3$  and  $Q^2$ ones (Fig. S12<sup>†</sup>) and more hydroxyl groups (Si-OH and Ti-OH) generated in the PIassisted structural rearrangement, which also implied the transformation of some close  $TiO_4$  species into the open  $TiO_6$  species (Table 4). In addition, the presence of more hydroxyl groups might also facilitate the epoxidation by promoting the enrichment of  $H_2O_2$  nearby the Ti sites to improve the activation of  $H_2O_2$  [19].

In C 1s XPS spectra, two signals with the binding energy (BE) values of 284.7 and 286.4 eV were observed for all the samples (Fig. 11A), which were ascribed to the sp<sup>2</sup> bond C and its satellite peak due to energy loss processes, respectively [54], suggesting the coordination state of carbon atom in the PI molecules was the same for the three PI-containing Ti-MWW zeolites. However, in the N 1s XPS spectra, apart from the BE value at 401.7 eV attributed to the C-N bond [55], R-Ti-MWW exhibited a new signal

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at 399.0 eV in comparison to the other two Ti-MWW zeolites (Fig. 11B), ascribed to the N atom in N-Ti-O group [56]. This indicated that R-Ti-MWW contained a new kind of coordinated N species, due to the coordination of N atoms in the PI with Ti atoms. In Ti 2p XPS spectra, the signals at 465.3 and 459.5 eV of A-Ti-MWW, corresponding to Ti  $2p_{3/2}$  and  $2p_{1/2}$ , respectively, were attributed to the framework TiO<sub>4</sub> species [57]. For P-Ti-MWW, the signals at lower BE values of 463.6 and 458.0 eV were observed due to the large amount of amorphous extra-framework Ti species. Nevertheless, for R-Ti-MWW, the BE valued of Ti  $2p_{3/2}$  and  $2p_{1/2}$  shifted from 459.5 to 459.3 eV and from 465.3 to 464.7 eV compared to A-Ti-MWW, respectively. This indicated that the density of outer electron cloud of the Ti species in R-Ti-MWW was increased in comparison with that of tetrahedral Ti species in A-Ti-MWW. Combining with the N 1s XPS spectra, this kind of more negatively charged Ti species in R-Ti-MWW was supposed to be those coordinated by N atom in the ligand PI molecules (denoted as PI-TiO<sub>6</sub> species).

Based on above characterizations of the three PI-containing Ti-MWW zeolites, P-Ti-MWW exhibited no reaction activity in 1-pentene epoxidation mainly due to the blocked pore channels and the enrichment of amorphous extra-framework TiO<sub>6</sub> species that are generally considered to play unfavorable roles in alkene epoxidation [32] (Scheme 2B). Although the Ti species of A-Ti-MWW were all tetrahedrally coordinated in the framework and had space for the diffusion of substrate molecules, A-Ti-MWW hardly catalyze the 1-pentene epoxidation. It was indicated that the residual uncoordinated PI molecules that embedded within the 10-MR pores may

poison the active centers, similar to the results of adding PI molecules directly into the reaction system (Table S3<sup>†</sup>). The 2D lamellar R-Ti-MWW, with partially blocked pore channels and micropore volume close to that of A-Ti-MWW, exhibited the superior catalytic performance than 3D Ti-MWW with totally open pore channels (Fig. 9). Thus, the fantastic catalytic performance of R-Ti-MWW was positively attributed to Ti species with unique micro-environment, through the incorporating of the organic ligand PI. A hot catalyst filtration test was also performed for R-Ti-MWW (Fig. S13<sup>+</sup>), and no Si and Ti element was detected in the filtrate, which proved the heterogeneous catalytic nature of R-Ti-MWW.

Besides, when TBHP was used as oxidant, which arouse great diffusion constrains due to the formation of bulky active intermediates of Ti alkylperoxo species, the catalytic activity of R-Ti-MWW decreased significantly (Fig. 9). It could be speculated that even if there were highly active hexahedral Ti species on the external 12-MR side cups, the epoxidation still mainly occurred in the intralayer 10-MR micropores, which further suggested that the degree of steric fitness between substrates and active centers might have the significant influence on the reaction activity. Additionally, the epoxide yield of R-Ti-MWW was slightly lower than that of Ti-MWW at the beginning of reaction, and then it started to increase more rapidly (Fig. S14<sup>†</sup>), possibly because of the diffusion constrains in R-Ti-MWW aroused by the coordinated PI molecules.

It is commonly accepted that the epoxidation process in titanosilicate-H<sub>2</sub>O<sub>2</sub> system is divided into two steps (Scheme 2Aa). One was activation of H<sub>2</sub>O<sub>2</sub> to generate the Ti- $O^{\alpha}$ -O<sup>\beta</sup>-H intermediate, which was thought to the rate determining step, and the other

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one was the effective transfer of reactive O to form epoxide. And the O<sup>P</sup>Species<sup>PDOCY004788</sup> coordinated directly with Ti sites are more electrophilic and attract the C=C in alkene, manifesting that increasing the electropositivity of the active Ti sites would be beneficial to enhance the ability of transferring reactive O. However, according to the Ti 2p XPS spectra, the BE value decreased after PI coordination (Fig. 11C), indicating the electronegativity of active Ti sites improved. Namely, taking only the reactive O transferring in account, the PI-TiO<sub>6</sub> species would decrease the activity of R-Ti-MWW in catalyzing epoxidation reaction. Therefore, the increased epoxidation activity definitely resulted from that the PI-TiO<sub>6</sub> species could significantly accelerate the step of  $H_2O_2$  activation, the effect of which far exceeded the inhibition effect caused by the increasing electronegativity of Ti active sites (Scheme 2Ab).

In addition, as a reference, the R-Ti-MWW was further calcined to remove the organic species to obtain the R-Ti-MWW-cal, during which the structure converted from 2D back to 3D and the PI-TiO<sub>6</sub> species transformed into the hexa-coordinated Ti species with  $H_2O$  as the ligand, denoted as  $H_2O$ -TiO<sub>6</sub> species (Fig. S15<sup>+</sup>).

As expected, the TON value of R-Ti-MWW-cal in 1-pentene epoxidation was 512, which was obviously higher than 329 of the Ti-MWW matrix, but lower than 663 of the R-Ti-MWW (Table 3). And the apparent energies of R-Ti-MWW-cal was 19.2 kJ mol<sup>-1</sup>, greater than 16.3 kJ mol<sup>-1</sup> of R-Ti-MWW but less than 22.0 kJ mol<sup>-1</sup> of Ti-MWW (Fig. 8). The difference in apparent energies of Ti-MWW and R-Ti-MWW-cal also implied that the rate-determining step also changed from the reaction itself to the reactants diffusion. Considering the different micro-environments of the Ti active

center, it could be inferred that the open  $TiO_6$  species constructed by structural rearrangement, including the PI-TiO<sub>6</sub> and H<sub>2</sub>O-TiO<sub>6</sub> species, were more active than the close  $TiO_4$  species, which enhanced the reaction rate and resulted in the diffusion as the rate-determining step. Moreover, the crystallinity and the coordination state as well as the amount of Ti active sites of R-Ti-MWW-cal had not changed after use (Fig. S16<sup>+</sup>). The 3D R-Ti-MWW-cal exhibited much lower activity in comparison to the 2D R-Ti-MWW, although it possessed the completely open pores. This result revealed that the micro-environment of Ti sites might be more important to the epoxidation activity than the diffusion limitation of substrates. Notably, for R-Ti-MWW-cal, the BE valued of 2p<sub>1/2</sub> shifted from 464.7 to 465.0 eV compared to R-Ti-MWW, while the BE valued of  $2p_{3/2}$  did not change, still for 459.3 eV (Fig. S17<sup>†</sup>). This meant that in comparison to PI-TiO<sub>6</sub> species, H<sub>2</sub>O-TiO<sub>6</sub> species was slightly less electronegative and thus promoted the transfer of reactive O in the epoxidation process, which should theoretically lead to a higher catalytic activity. Therefore, it indicated that the effect of PI-TiO<sub>6</sub> species on the rate-determine step of  $H_2O_2$  activation was stronger than that of  $H_2O$ -TiO<sub>6</sub> species in the 1-pentene epoxidation (Scheme 2Ac).

#### 3.4.3 Recycling tests of the modified Ti-MWW

The stability and reusability of Ti-MWW, R-Ti-MWW and R-Ti-MWW-cal were compared in the 1-pentene epoxidation (Fig. 12). To better observe the difference of stability, the initial epoxide yield of all the catalysts was controlled to  $\sim 100\%$  by adjusting the reaction conditions. The used catalysts were centrifuged, washed by MeCN and then dried before being reused in the first six cycles. After six runs, R-Ti-

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MWW still showed higher EP yield of 73.6%, while the EP yield decreased to 24.1% DOCY00478B for Ti-MWW and 37.7% for R-Ti-MWW-cal, respectively, which strongly proved an outstanding stability of R-Ti-MWW catalyst. Then, the deactivated catalysts were further washed by MeCN/H<sub>2</sub>O<sub>2</sub> at 353 K and dried to reuse. All the three catalysts regained their activity to a certain degree, signifying the promising feasibility of the insitu regeneration of deactivated catalyst by the reaction mixture after separating the main product in industry. Furthermore, in order to regenerate the three catalysts, they were calcined at 823 K to burn the organic molecules. For R-Ti-MWW, it was treated by PI aqueous solution again after calcination. As expected, all the catalysts exhibited similarly high activity to that of fresh catalysts, verifying the excellent reusability of these catalysts. It also indicated that the deactivation of Ti-MWW zeolites in 1-pentene epoxidation mainly caused by the deposition of heavy components like PD inside the micropores and further covered the active Ti sites. Moreover, no significant difference was observed in the structure, the state of active center and Ti amount among the fresh, used and regenerated R-Ti-MWW (Fig. S18<sup>†</sup>), indicating the excellent stability and recycling performance of R-Ti-MWW. In addition, the EP hydrolysis experiment was also operated on the three catalysts. The EP conversion of R-Ti-MWW with H<sub>2</sub>O<sub>2</sub> was 16.7%, far lower than 62.6% of Ti-MWW and 78.5% of R-Ti-MWW-cal (Fig. S19<sup>†</sup>). It indicated that the basic PI molecules embedded in titanosilicate could significantly suppress the Lewis acidity aroused by Ti-O-O-H in the catalytic system, and thus inhibit the EP hydrolysis and reduce the generation of heavy components.

## Conclusions

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Highly efficient liquid-phase 1-pentene epoxidation was successfully carried out in the titanosilicates-H<sub>2</sub>O<sub>2</sub> catalytic system. Among them, Ti-MWW catalyst possessed the superior catalytic performance in solvent MeCN due to the better steric matching between pore structure and 1-penten molecules. An organic-inorganic hybrid 2D structural Ti-MWW that possessed the framework PI-TiO<sub>6</sub> species was constructed by PI-assisted structural rearrangement. In spite of introducing diffusion constrains, the  $PI-TiO_6$  species in the framework could facilitate the formation of the intermediate Ti-O-O-H by accelerating the H<sub>2</sub>O<sub>2</sub> activation and then improve the reaction activity of Ti-MWW for the liquid-phase 1-pentene epoxidation. In addition, the basic PI molecules embedded in Ti-MWW significantly resisted the catalyst deactivation in the 1-pentene epoxidation by suppressing the formation of heavy by-products. This work shows that a suitable modification of the micro-environment of Ti centers may efficiently improve the catalytic performance, which is even superior to pore size enlargement in some cases.

## **Conflicts of interest**

There are no conflicts to declare.

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## **Figure caption**

**Fig. 1.** XRD patterns of Ti-MCM-68 (a), Ti-MWW (b), TS-1 (c), TS-2 (d), Ti-Beta (e) and Ti-MOR (f) in calcined form.

**Fig. 2.** UV-Vis spectra (A) and FT-IR spectra in framework vibration region (B) of Ti-MCM-68 (a), Ti-MWW (b), TS-1 (c), TS-2 (d), Ti-Beta (e) and Ti-MOR (f) in calcined form.

Fig. 3. SEM images of Ti-MCM-68 (a), Ti-MWW (b), TS-1 (c), TS-2 (d), Ti-Beta (e) and Ti-MOR (f).

**Fig. 4.** Dependence of  $H_2O_2$  conversion, utilization efficiency, 1-pentene conversion and EP selectivity on different  $H_2O/H_2O_2$  molar ratio in the reaction system. Reaction conditions: Ti-MWW, 50 mg; MeCN, 10 mL;  $H_2O_2$ , 10 mmol; 1-pentene, 10 mmol;  $N_2$ , 0.5 MPa; temp., 333 K; time, 2 h.

Fig. 5. Effects of reaction temperature on  $H_2O_2$  conversion (A),  $H_2O_2$  utilization efficiency (B), 1-pentene conversion (C), and EP selectivity (D) with time course for the 1-pentene epoxidation over Ti-MWW. Reaction conditions: Ti-MWW, 50 mg; MeCN, 10 mL;  $H_2O_2$  (30 wt.%), 10 mmol; 1-pentene, 10 mmol; N<sub>2</sub>, 0.5 MPa.

**Fig. 6.** Effects of reaction pressure on  $H_2O_2$  conversion,  $H_2O_2$  utilization efficiency, 1pentene conversion and EP selectivity of 1-pentene epoxidation over Ti-MWW. Reaction conditions: Ti-MWW, 50 mg; MeCN, 10 mL;  $H_2O_2$  (30 wt.%), 10 mmol; 1pentene, 10 mmol; temp., 333 K; time, 2 h. **Fig. 7.** Effects of catalyst amount on H<sub>2</sub>O<sub>2</sub> conversion, H<sub>2</sub>O<sub>2</sub> utilization efficiency, 1<sup>-</sup>/<sub>2</sub> pentene conversion and EP selectivity of 1-pentene epoxidation over Ti-MWW. Reaction conditions: catalyst, Ti-MWW; MeCN, 10 mL; H<sub>2</sub>O<sub>2</sub> (30 wt.%), 10 mmol; 1-pentene, 10 mmol; temp., 333 K; N<sub>2</sub>, 0.5 MPa, time, 2 h.

**Fig. 8.** Plots of apparent activation energy in the 1-pentene epoxidation catalyzed by Ti-MWW catalysts.

**Fig. 9.** Comparison of catalytic performance in 1-pentene epoxidation with time course over the different Ti-MWW zeolites. Reaction conditions: catalyst, 50 mg; 1-pentene, 15 mmol; oxidant, 15 mmol, wherein  $H_2O_2$  (30 wt %) was used for P-Ti-MWW (a), A-Ti-MWW (b), Ti-MWW (c) and R-Ti-MWW (d), and TBHP (70 wt.% in water) was also employed for R-Ti-MWW (e) and Ti-MWW (f); solvent MeCN, 10 mL; temp. 333 K, N<sub>2</sub>, 0.5 MPa. The EP selectivity was always >99 % for all the reactions.

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Fig. 10. UV-Vis (A) and UV-Raman (Laser 244 nm) spectra (B) of P-Ti-MWW (a), A-Ti-MWW (b) and R-Ti-MWW (c).

**Fig.11.** C 1s (A), N 1s (B), and Ti 2p (C) XPS spectra of P-Ti-MWW (a), A-Ti-MWW (b) and R-Ti-MWW (c).

**Fig. 12.** Dependence of EP yield with the reaction-regeneration cycles on Ti-MWW, R-Ti-MWW and R-Ti-MWW-cal, respectively. Reaction conditions for the first run: cat., 0.1 g; 1-pentene, 10 mmol;  $H_2O_2$  (30 wt.%), 10 mmol;  $N_2$ , 0.5 MPa; temp., 333 K; MeCN, 10 mL; time, 3 h. The condition of  $H_2O_2$ /MeCN washing:  $H_2O_2$  (2 wt%)/MeCN; liquid/solid weight ratio, 100; temp., 353 K; time, 12 h. All the catalysts were finally regeneration by calcination at 823 K for 6 h. For R-Ti-MWW, it was treated with PI Published on 22 July 2020. Downloaded on 8/10/2020 4:09:10 AM.



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**Fig. 5.** Effects of reaction temperature on  $H_2O_2$  conversion (A),  $H_2O_2$  utilization efficiency (B), 1-pentene conversion (C), and EP selectivity (D) with time course for the 1-pentene epoxidation over Ti-MWW. Reaction conditions: Ti-MWW, 50 mg; MeCN, 10 mL;  $H_2O_2$  (30 wt.%), 10 mmol; 1-pentene, 10 mmol; N<sub>2</sub>, 0.5 MPa.

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**Fig. 8.** Plots of apparent activation energy in the 1-pentene epoxidation catalyzed by Ti-MWW (a), R-Ti-MWW (b) and R-Ti-MWW-cal (c) catalysts.



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**Fig. 9.** Comparison of catalytic performance in 1-pentene epoxidation with time course over the different Ti-MWW zeolites. Reaction conditions: catalyst, 50 mg; 1-pentene, 15 mmol; oxidant, 15 mmol, wherein  $H_2O_2$  (30 wt %) was used for P-Ti-MWW (a), A-Ti-MWW (b), Ti-MWW (c) and R-Ti-MWW (d), and TBHP (70 wt.% in water) was also employed for Ti-MWW (e) and R-Ti-MWW (f); solvent MeCN, 10 mL; temp. 333 K, N<sub>2</sub>, 0.5 MPa. The EP selectivity was always >99 % for all the reactions.

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(b) and R-Ti-MWW (c).





**Fig. 12.** Dependence of EP yield on Ti-MWW, R-Ti-MWW and R-Ti-MWW-cal catalysts in the reaction-regeneration cycles. Reaction conditions for the first run: cat., 0.1 g; 1-pentene, 10 mmol;  $H_2O_2$  (30 wt.%), 10 mmol;  $N_2$ , 0.5 MPa; temp., 333 K; MeCN, 10 mL; time, 3 h. The condition of  $H_2O_2$ /MeCN washing:  $H_2O_2$  (2 wt%)/MeCN; liquid/solid weight ratio, 100; temp., 353 K; time, 12 h. All the catalysts were finally regeneration by calcination at 823 K for 6 h. For R-Ti-MWW, it was treated with PI again after calcination. The EP selectivity was always >99 % for all the reactions.



**Scheme 1.** Reaction pathways and product distribution of Ti-zeolites/H<sub>2</sub>O<sub>2</sub> catalyzed 1pentene epoxidation.



Scheme 2. The postulate reaction mechanism of 1-pentene epoxidation on close  $TiO_4$  sites, open PI-TiO<sub>6</sub> sites and open H<sub>2</sub>O-TiO<sub>6</sub> sites (A), and extra-framework  $TiO_6$  fragments (B).

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Catalyst	1-Pentene		Products	distribution	H <sub>2</sub> O <sub>2</sub> (%)			
	conv. (%)	TON <sup>b</sup>	EP	PD	PE	conv.	eff.	
Ti-MWW	72.9	390	99.9	0.1	_d	79.7	91.5	_
Ti-MCM-68	39.0	352	99.1	0.9	_d	54.0	72.2	
TS-1	39.5	183	98	1.7	0.3	46.0	85.9	

99.2

97.4

95.8

0.6

2.6

4.2

0.2

\_d

\_d

15.7

23.5

2.4

69.4

79.1

70.8

Table 1. The catalytic performance of different titanosilicates in 1-pentene epoxidation.<sup>a</sup>

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<sup>a</sup> Reaction conditions: catalyst, 50 mg; 1-pentene, 10 mmol; H <sub>2</sub> O <sub>2</sub> (30 wt.%), 10 mmol; temp., 333 K; N <sub>2</sub> , 0.5 MPa;
solvent, 10 mL; time, 2 h. MeOH was used as the solvent for TS-1 and TS-2, whereas MeCN was chosen for the
other titanosilicate catalysts.

<sup>b</sup> Turnover number (TON) of converted 1-pentene per Ti site in mol (mol-Ti)<sup>-1</sup>.

73

116

12

<sup>c</sup> EP, 1,2-epoxypentane; PD, 1,2-pentanediol; PE, pentanediol ethers.

10.9

18.6

1.7

<sup>d</sup> Not detected.

TS-2

Ti-Beta

Ti-MOR

Table 2. A comparison of 1-pentene epoxidation over Ti-MWW, TS-1 and Ti-MCM-68 in different solvents.<sup>a</sup>

Catalyst	Solvent	Dielectric	1-Pentene		Production distribution <sup>c</sup> (%)			H <sub>2</sub> O <sub>2</sub> (%)	
		constant	conv. (%)	TON <sup>b</sup>	EP	PD	PE	conv.	eff.
Ti-MWW	MeCN	37.5	72.9	390	99.9	0.1	_ d	79.7	91.5
	MeOH	31.2	16.1	85	98.4	1.1	0.5	26.0	61.9
	$\rm H_2O$	80.1	7.9	43	1.5	98.5	_ d	25.4	31.1
	Acetone	20.7	48.4	274	99.4	0.6	_ d	51.9	93.3
	t-BuOH	11.4	33.6	181	99.8	0.2	_ d	37.9	88.7
Ti-MCM-68	MeCN	37.5	39.0	352	99.1	0.9	_ d	54.0	72.2
	MeOH	31.2	25.8	238	89.0	9.6	1.4	35.4	72.9
	$\rm H_2O$	80.1	7.4	70	98.9	1.1	_d	9.7	76.3
	Acetone	20.7	34.1	316	99.8	0.2	_ d	47.0	72.6
	t-BuOH	11.4	19.5	182	99.3	0.7	_ d	31.2	62.5
TS-1	MeCN	37.5	8.5	39	99.3	0.7	_ d	22.2	38.3
	MeOH	31.2	39.5	183	98	1.7	0.3	46.0	85.9
	$H_2O$	80.1	1.8	8	3.5	96.5	_ d	13.1	13.7
	Acetone	20.7	32.5	147	64.5	35.5	_ d	35.5	91.5
	t-BuOH	11.4	18.0	80	72.3	27.7	_ d	20.6	87.4

<sup>a</sup> Reaction conditions: cat., 50 mg; 1-pentene, 10 mmol;  $H_2O_2$  (30 wt.%), 10 mmol; temp., 333K;  $N_2$ , 0.5 MPa; solvent, 10 mL; time 2 h.

<sup>b</sup> Turnover number (TON) of converted 1-pentene per Ti site in mol (mol-Ti)<sup>-1</sup>.

<sup>c</sup> EP, 1,2-epoxypentane; PD, 1,2-pentanediol; PE, pentanediol ethers.

<sup>d</sup> Not detected.

Catalyst	Structure	Si/Ti <sup>c</sup>	Ti/N <sup>d</sup>	1-Pentene		Epoxide	H <sub>2</sub> O <sub>2</sub> (%)	
	dimension <sup>b</sup>			conv. (%)	TON <sup>e</sup>	sel. (%)	conv.	eff.
Ti-MWW	3D	40	-	44.9	329	99.9	49.8	90.2
R-Ti-MWW	2D	40	0.25	91.5	663	99.9	96.7	94.6
R-Ti-MWW-cal	3D	41	-	67.7	512	99.9	72.7	93.1

 Table 3. Reaction results of 1-pentene epoxidation over Ti-MWW with structural rearrangement. a
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<sup>a</sup> Reaction conditions: catalyst, 50 mg; 1-pentene, 15 mmol; H<sub>2</sub>O<sub>2</sub> (30 wt.%), 15 mmol; solvent MeCN, 10 mL; temp., 333 K; N<sub>2</sub>, 0.5 MPa; time 2 h.

<sup>b</sup> Given by XRD patterns.

<sup>c</sup> Calculated by ICP analysis.

<sup>d</sup>Calculated by ICP, CNH and TG analysis.

<sup>e</sup> Turnover number (TON) of converted 1-pentene per Ti site in mol (mol-Ti)<sup>-1</sup>.

Table 4. The physicochemical properties of PI-containing Ti-MWW zeolites.

Catalysts	Si/Ti	C/N <sup>b</sup>	Ti	SA <sup>d</sup>		V <sub>Micro</sub> <sup>d</sup>	PI	Weight loss	e (%)	
	а		states <sup>c</sup>	(m <sup>2</sup> g	-1)	(cm <sup>3</sup> g <sup>-1</sup> )	amounts $^{\rm f}$			
				S <sub>BET</sub>	S <sub>Micro</sub>	-	(wt.%)	473-643 K	643-1073 K	
P-Ti-MWW	34	5.3	T.+H.	53	0.02	0.001	15.9	7.0	8.9	
A-Ti-MWW	39	5.1	Τ.	217	125	0.05	7.3	2.6	4.7	
R-Ti-MWW	40	5.4	T.+H.*	187	105	0.04	11.7	6.9	4.8	

<sup>a</sup> Calculated by ICP analysis.

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<sup>b</sup> Calculated by CHN analysis.

<sup>c</sup> Evaluated with UV-Vis spectra. T., tetrahedral Ti species (210 nm). H. and H.\*, hexahedral Ti species (280 nm and 260 nm, respectively).

<sup>d</sup> Measured by Ar adsorption isotherms at 87.3 K (Fig. S9<sup>†</sup>). Surface areas was calculated by BET method, and pore volume was given with t-plot method.

e Calculated by TG curves (Fig. S11<sup>†</sup>).

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## **Graphic abstract**

The performance of Ti-MWW in the 1-pentene epoxidation reaction was improved by a piperidine (PI)-assisted structural rearrangement. The hexa-coordinated Ti sites with the PI molecules as ligand significantly accelerate  $H_2O_2$  activation, the effect of which far exceeded the inhibition effect caused by the electronegativity increase of Ti active sites.



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