

Article

Influence of Impurities in a Methanol Solvent on the Epoxidation of Propylene with Hydrogen Peroxide over Titanium Silicalite-1

Gang Wang, Yue Li, Quanren Zhu, Gang Li, Chao Zhang, and Hongchen Guo *

State Key Laboratory of Fine Chemicals and School of Chemical Engineering, Dalian University of Technology, No. 2 Linggong Road, Dalian 116024, PR China; longyu5300@sina.com (G.W.); liyue871123@126.com (Y.L.); zhuquanren19871116@126.com (Q.Z.); liganghg@dlut.edu.cn (G.L.); zhangchaowo11@163.com (C.Z.)

* Correspondence: hongchengudlut@126.com; Tel./Fax: +86-411-84986120

Received: 23 November 2019; Accepted: 18 December 2019; Published: 20 December 2019

Abstract: The recycled methanol solvent of the HPPO (liquid-phase epoxidation of propylene and hydrogen peroxide to propylene oxide) process usually contains many kinds of trace impurities, such as fusel alcohol, aldehyde, ketone, ester, acetal, and amine. In this study, the influence of these impurities on the catalytic performance of titanium silicalite-1 (TS-1) in the liquid-phase epoxidation of propylene with H_2O_2 was investigated with a batch reactor and simulated methanol solvents. The results show that amine and acetone are the most hazardous impurities, as they could remarkably suppress the conversion of H_2O_2 . Furthermore, competitive adsorption experiments and IR and UV-Raman spectroscopic studies indicate that the suppression effect of impurities on the catalytic activity of TS-1 can be attributed to the competitive adsorption of the impurities on the tetra-coordination framework Ti sites. With this funding, the suppression mechanism of different impurities in a methanol solvent on the catalytic activity of TS-1 in the liquid-phase epoxidation of propylene was discussed.

Keywords: impurity; methanol solvent; TS-1; epoxidation of propylene; competitive adsorption

1. Introduction

Propylene oxide (PO) is a vital chemical intermediate, which is widely used for producing varieties of commercial and industrial products, such as polyether polyols, propylene glycol, and propylene glycol ethers [1]. Currently, chlorohydrin methods and co-oxidation methods are dominant processes for PO production. However, the chlorohydrin methods have disadvantages, such as large volumes of waste solid, waste water, and harmful byproducts, resulting in a badly contaminated environment, while co-production processes produce huge amounts of co-products that depend on market demand [2]. To eliminate these problems, great efforts have been made to develop alternative technologies.

In 1983, titanium silicalite-1 (TS-1) zeolite was first synthesized by Taramasso et al. [3]. TS-1 was primarily employed for the selective oxidation reaction using H_2O_2 as an oxidant [4]. To enhance the performance of TS-1, a great deal of research work was devoted to: (1) improving the diffusion by introducing a hierarchical pore structure or reducing the transport path [5–7]; (2) modifying the hydrophilic and/or hydrophobic properties [8–10]; (3) controlling the amount of acid sites via modification and additives [11–14]; and (4) constructing different Ti active sites [15,16]. Owing to its unique oxidation properties, TS-1 led to the HPPO (liquid-phase epoxidation of propylene and hydrogen peroxide to propylene oxide) process, which can produce PO at mild conditions with a titanium silicalite-1 (TS-1) catalyst, using H_2O_2 as an oxidant and methanol as a solvent [3,11,17–19]. Theoretically, the HPPO process only produce water as its by-product; there are no environmental

or co-product issues. In fact, due to the highest active oxygen content and the formation of water only being a by-product, the use of H_2O_2 as an oxidant is among the key aspects of modern Green Chemistry nowadays. For example, H_2O_2 has become the primary oxidant in the selective oxidations of numerous organic substances, such as imines [20], olefins [21–23], and alcohols [24].

In recent years, the HPPO process based on a TS-1 catalyst, as well as the H_2O_2 oxidant and methanol solvent, has been industrialized by BASF and Dow, Evonik and Uhde, and Sinopec Changling Refining and Chemical. Nevertheless, the HPPO process still suffers from the use of a methanol solvent. One of the problems related to the methanol solvent is that, upon recycling, it accumulates dozens of trace impurities, such as fusel alcohol, aldehyde [25,26], ketone [27], ester [26,28], acetal [27], and amine [29,30], despite successive purification measures, including distillation, hydrogenation, and adsorption being employed [27,28,31,32]. It was believed that the trace impurities carried by the recycling of the methanol solvent were responsible for the accelerated catalyst deactivation and lowered PO selectivity. So far, however, little is known about the exact influence of each kind of impurity on the catalytic performance of the TS-1 zeolite catalyst in the liquid-phase epoxidation of propylene with H_2O_2 .

Therefore, in this study, a systematic investigation was carried out to understand the influences of different impurities in a methanol solvent on the catalytic performance of TS-1. This was accomplished by using simulated methanol solvents that contained a single impurity each time they were selected from the fusel alcohol, aldehyde, ketone, ester, acetal, and amine. Competitive adsorption experiments, as well as an FT-IR (Fourier – transform infrared) and UV-Raman spectroscopic study, were also carried out to understand the fundamental aspect of the impurities' influence on the TS-1 catalyst and the propylene epoxidation.

2. Results

2.1. Liquid-Phase Epoxidation with Fresh and Recycled Methanol Solvents

As shown in Figure 1, when the propylene epoxidation is carried out in the recycled methanol solvent, the performance of TS-1 is remarkably lower than it is in the fresh methanol solvent. This is indicated by the conversion of H_2O_2 , which was below 98% when it ran for 500 h in the recycled methanol solvent. By contrast, the conversion of H_2O_2 remained higher than 98% until 700 h in the fresh methanol solvent. In addition, the selectivity of PO was still lower than 97% when the time-on-stream was extended to 500 h in the case of using a recycled methanol solvent, whereas it was already higher than 98% after 264 h when fresh methanol was used.

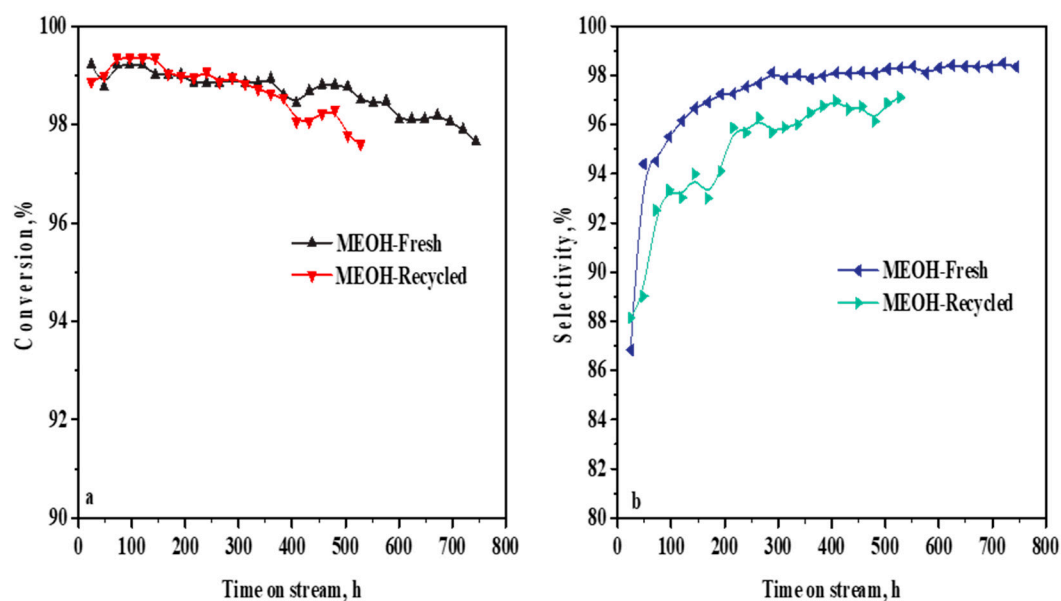


Figure 1. Comparison of the catalytic performance of titanium silicalite-1 (TS-1) in the liquid-phase epoxidation of propylene with fresh and recycled methanol solvents. (a) Fresh methanol; (b) Recycled methanol.

2.2. Influence of Fusel Alcohol Content in a Methanol Solvent

Figure 2 shows the influence of fusel alcohol content in a methanol solvent on the catalytic performance of TS-1. It is easy to see that the fusel alcohol, namely ethanol, 2-propanol, and 1-propanol, in the methanol solvent has no influence on the selectivity of PO, and has only a small effect on the utility of H_2O_2 . However, the fusel alcohol in the methanol solvent significantly reduced the conversion of H_2O_2 . Moreover, it can be seen that, at the same fusel alcohol content levels, the conversion and utility of H_2O_2 decreases in the order of ethanol > 2-propanol > 1-propanol, which is consistent with the results of the literature that used alcohol as the solvent [33–35]. In addition, it can be seen (Table S1) that the fusel alcohol in the methanol solvent also facilitates the formation of by-products such as acetaldehyde, propionaldehyde, acetone, and propylene glycol monoethyl ether. The amount of aldehyde and acetone by-products increases with the content of fusel alcohol in the solvent. The propylene glycol monoethyl ether only appears at a high ethanol content. Nevertheless, the fusel alcohol in the methanol solvent seems to have the effect of inhibiting the formation of 1-methoxy-2-propanol, 2-methoxy-1-propanol, and dipropylene glycol methyl ether. In any case, this effect was small.

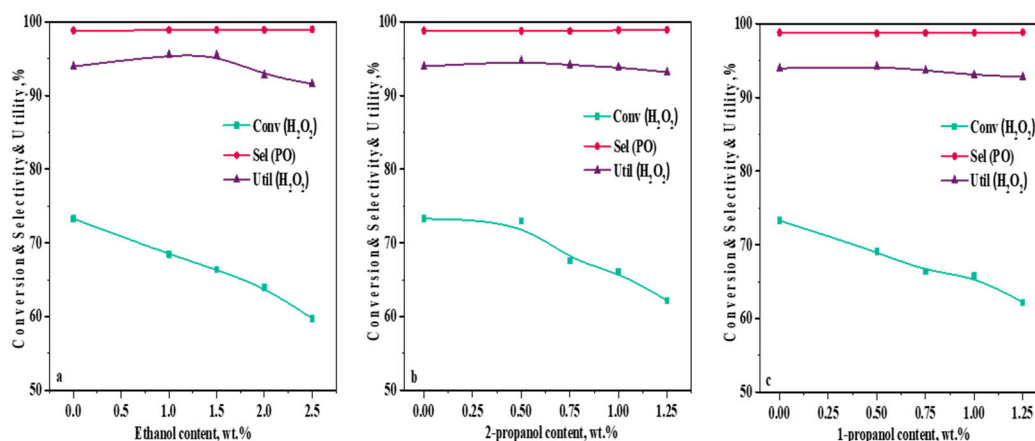


Figure 2. Influence of fusel alcohol content on the catalytic performance of TS-1 in the epoxidation of propylene with H_2O_2 . (a) Ethanol; (b) 2-propanol; (c) 1-propanol.

2.3. Influence of Ketone and Aldehyde Content in a Methanol Solvent

The reaction results of the epoxidation of propylene over TS-1 using a methanol solvent with a certain amount of acetone, acetaldehyde, and propionaldehyde were summarized, as shown in Figure 3 and Table S2. Clearly, a trace of acetaldehyde and propionaldehyde has no influence on the conversion of H_2O_2 or the selectivity of PO, and has only a slight influence on the utility of H_2O_2 and the turnover numbers, whereas acetone in a methanol solvent has a significant influence on the conversion of H_2O_2 and the utility of H_2O_2 . Additionally, acetone in methanol suppresses the formation of 1-methoxy-2-propanol, 2-methoxy-1-propanol, and dipropylene glycol methyl ether. What is more, when acetaldehyde, propionaldehyde, and acetone reached a certain amount, 1,1-dimethoxyethane, acetic acid, 1,1-dimethoxypropane, propanoic acid, and 2,2-dimethoxypropane were also detected.

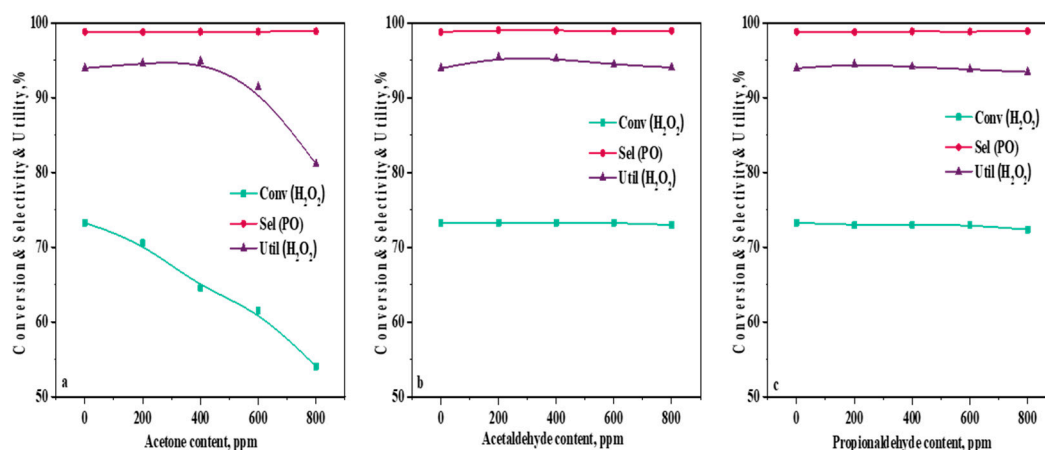


Figure 3. Influence of ketone and aldehyde content on the catalytic performance of TS-1 in the epoxidation of propylene with H₂O₂. (a) Acetone; (b) Acetaldehyde; (c) Propionaldehyde.

2.4. Influence of Ester Content in a Methanol Solvent

An overview of the influence of the ester in the methanol solvent on the catalytic performance of TS-1 is given in Figure 4 and Table S3. It was observed that, when the content of methyl formate was below 1000 ppm it had almost no effect on the conversion of H₂O₂ and the turnover numbers, whereas when the content of methyl acetate in methanol solvent was in the same range it would notably lower the conversion of H₂O₂ and the turnover numbers. The utility of H₂O₂ slightly increased first and then decreased as the methyl formate in the methanol increased, with the maximum appearing in the range 400–600 ppm. In the case of methyl acetate, the utility of H₂O₂ displays a monotonous descent curve as the methyl acetate content in the methanol solvent increases. The selectivity of PO and product distribution were not affected by methyl formate and methyl acetate in methanol.

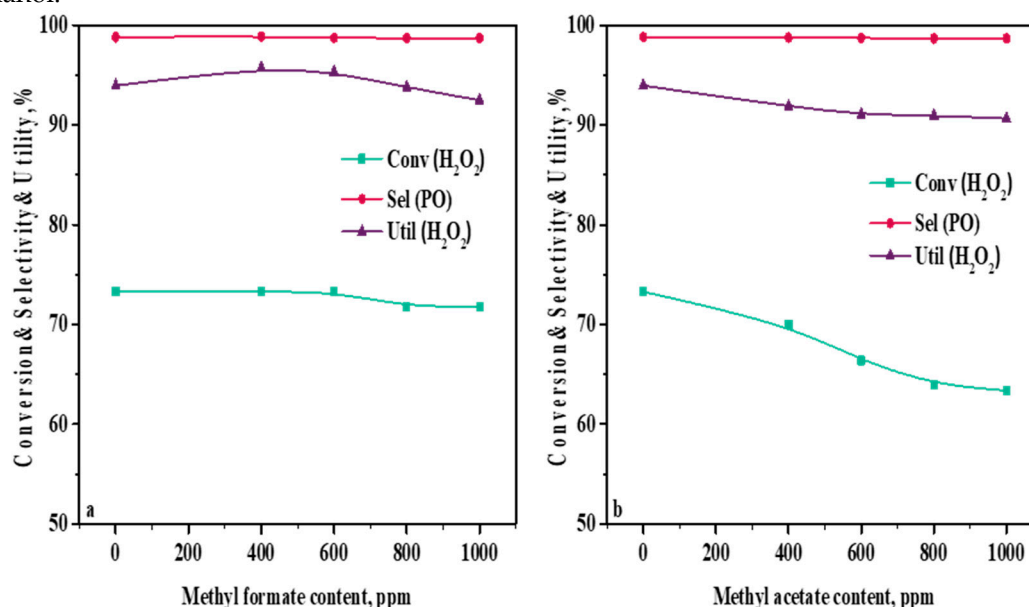


Figure 4. Influence of ester content on the catalytic performance of TS-1 in the epoxidation of propylene with H₂O₂. (a) Methyl formate; (b) Methyl acetate.

2.5. Influence of Acetal Content in a Methanol Solvent

The results of propylene epoxidation in a methanol solvent containing dimethoxymethane, 1,1-dimethoxyethane, and 1,1-dimethoxypropane are given in Figure 5 and Table S4. It can be seen that, when the acetal content is fixed, the conversion of H₂O₂ and turnover numbers decreases with the

increasing of the carbon chain length of acetal. These three kinds of acetal in the methanol solvent had no effect on the selectivity of PO and product distribution, but they had a perceptible influence on the utility of H_2O_2 .

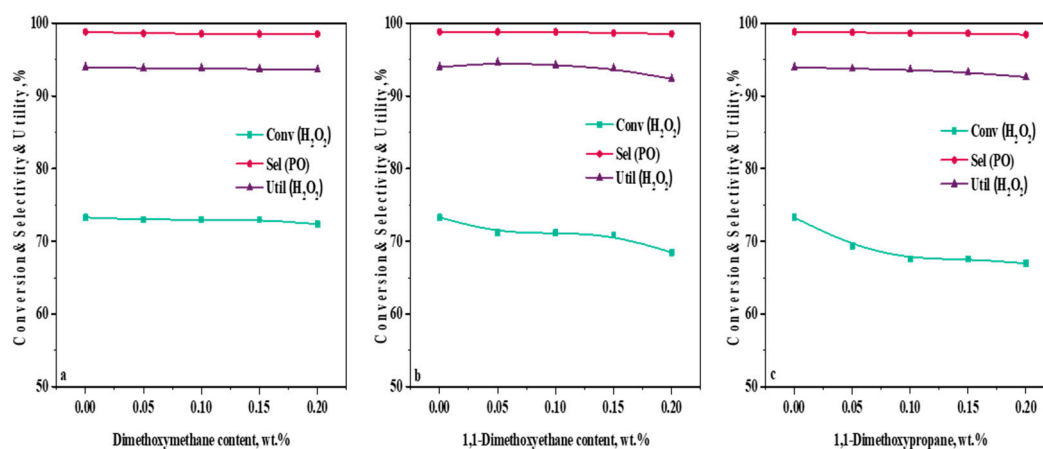


Figure 5. Influence of acetal content on the catalytic performance of TS-1 in the epoxidation of propylene with H_2O_2 . (a) Dimethoxymethane; (b) 1,1-dimethoxyethane; (c) 1,1-dimethoxypropane.

2.6. Influence of Amine Content in a Methanol Solvent

Differing from the other impurities in a methanol solvent, traces of methylamine and ethylamine in a methanol solvent would result in a significant decrease in the conversion of H_2O_2 , the utility of H_2O_2 , and turnover numbers, as shown by Figure 6 and Table S5. Interestingly, it was found that the selectivity of 1-methoxy-2-propanol declines when increasing these amines, and the selectivity of 2-methoxy-1-propanol shows a converse trend. In addition, the increased amines content in the methanol solvent also decreased the selectivity of 1,2-propanediol and dipropylene glycol methyl ether.

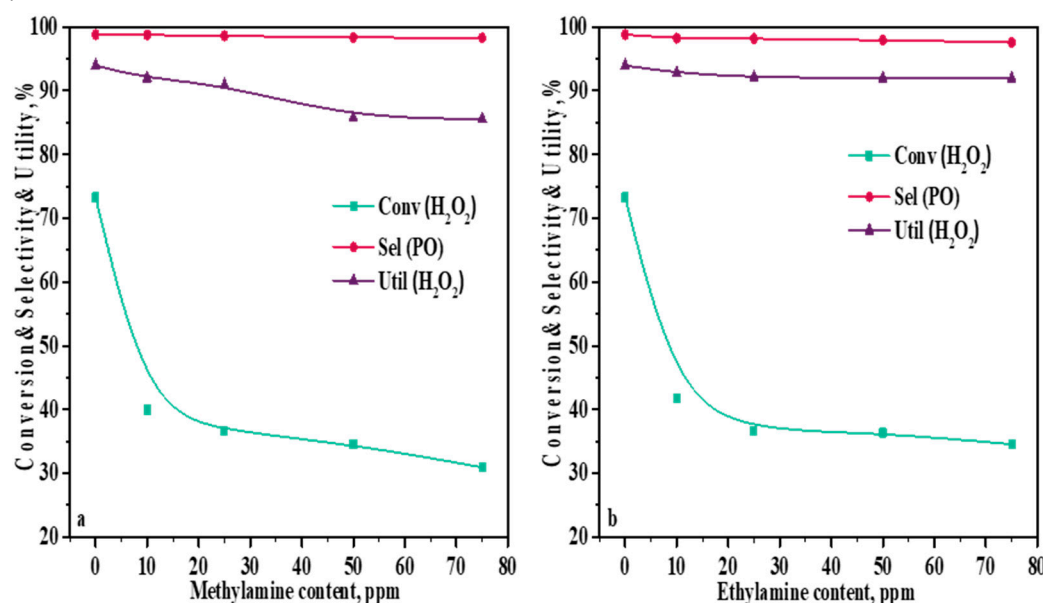


Figure 6. Influence of amine content on the catalytic performance of TS-1 in the epoxidation of propylene with H_2O_2 . (a) Methylamine; (b) Ethylamine.

3. Discussion

In this study, several typical impurities were chosen to investigate the adsorption characteristic of impurities in a methanol solvent on TS-1 and the influence mechanism of impurities in a methanol solvent on propylene epoxidation over TS-1.

As mentioned above, impurities in a methanol solvent were expected to produce competitive adsorption levels on a TS-1 catalyst with methanol. The increase in the amount (based on the concentration of impurities in the methanol solvent) of TS-1 adsorption toward the different impurities in the methanol solvent, when the solvent was in contact with TS-1, provided the proof for the competitive adsorption of the impurities on TS-1, as shown in Figure 7. In addition, it can be seen that the IR spectra obtained in Figure 8 (a–e) provide the characteristic absorption bands of not only methanol but also of five kinds of impurities. The assignments of these characteristic absorption bands are summarized in Table 1. From the spectra obtained after a vacuum desorption treatment (MEOH-x-des-80-v, x = AT (acetone), NP (1-propanol), MA (methyl acetate), DMOP (1,1-dimethoxypropane), and MEAM (methylamine)), it is easy to see that the adsorption strength of the impurities on TS-1 was in the following order: methylamine $\approx$ acetone $\approx$ methyl acetate $>$ 1-propanol $\approx$ 1,1-dimethoxypropane. Figure 8 (f) demonstrates that the influence of impurities (based on the same concentration in the methanol solvent) on the conversion of H_2O_2 decreases in the following order: acetone $>$ methylamine $>$ methyl acetate $>$ 1,1-dimethoxypropane $\approx$ 1-propanol. Roughly speaking, the competitive adsorption amount and the adsorption strength of the impurities on TS-1 were positively correlated with the activity of the propylene epoxidation. Based on this, it is supposed that the influence of the recycled methanol solvent on the epoxidation of propylene is the consequence of the competitive and relatively strong adsorption of impurities in the solvent on the epoxidation catalyst. Furthermore, from Figure 9 (a, b) it can be seen that, when the TS-1 zeolite catalyst was contacted with the methanol and the impurities (AT, NP, MA, DMOP, and MEAM), respectively, the characteristic peak of the tetra-coordinated framework Ti sites at 1125 cm^{-1} in the UV-Raman spectra [36] became weakened. Meanwhile, the infrared absorption band of the framework Ti sites at around 974 cm^{-1} was also weakened and shifted to a high wavenumber zone. These phenomena are in line with the literature [37–39], indicating that the competitive adsorption of impurities with methanol occurred on the tetra-coordinated framework Ti sites. In this way, we believe that the impurities would hamper the contact of the methanol solvent with the tetra-coordinated framework Ti sites and would therefore hinder the activation of H_2O_2 .

Table 1. Assignments of IR absorption bands.

Impurity	Band, cm^{-1}	Interpretation [40,41]	Vibration mode
methanol	3616.7	O-H	stretching
1-propanol	2880.8	CH ₂	stretching
	1395.2	CH ₃	symmetric bending
acetone	1696.1	C=O	stretching
methyl acetate	1687.6	C=O	stretching
	1308.2	C-O-C	stretching
1,1-dimethoxypropane	2992.1	unknown	--
	1391.5	CH ₃	bending
methylamine	3379.9	NH ₂	stretching
	1595.5	NH ₂	bending
	1467.5	CH ₃	asymmetric bending

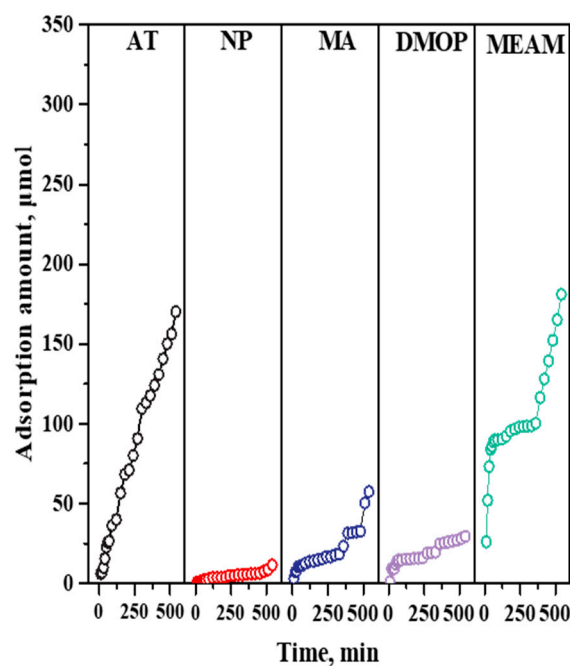


Figure 7. Competitive adsorption amount of impurities in a methanol solvent on TS-1 (NP: 1-propanol, AT: acetone, MA: methyl acetate, DMOP: 1,1-dimethoxypropane and MEAM: methylamine).

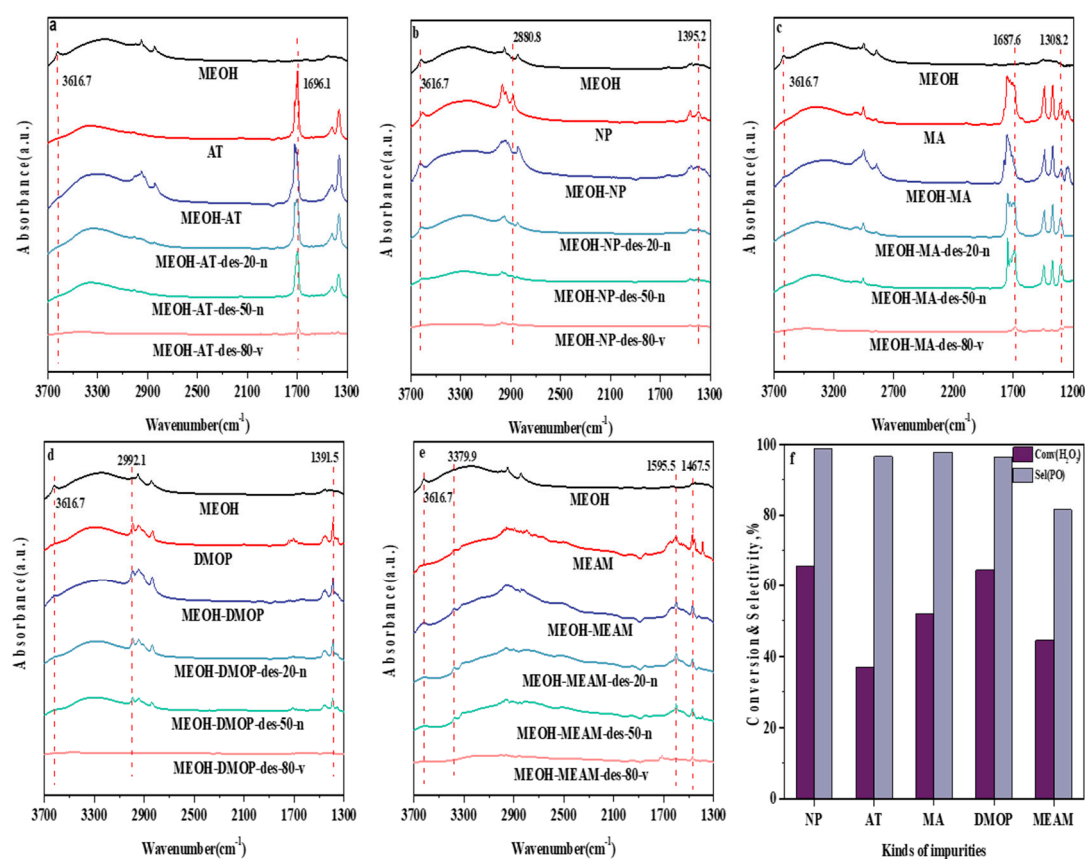


Figure 8. FT-IR spectra of adsorption and desorption of the methanol and impurities on TS-1 (a, b, c, d, e); influence of impurities in the methanol solvent on the catalytic performance of TS-1 in the epoxidation of propylene with H₂O₂ (f). (Reaction conditions: methanol solvent containing 1.0 wt.% of impurities 35.5 mL, other conditions are shown in Table S1.).

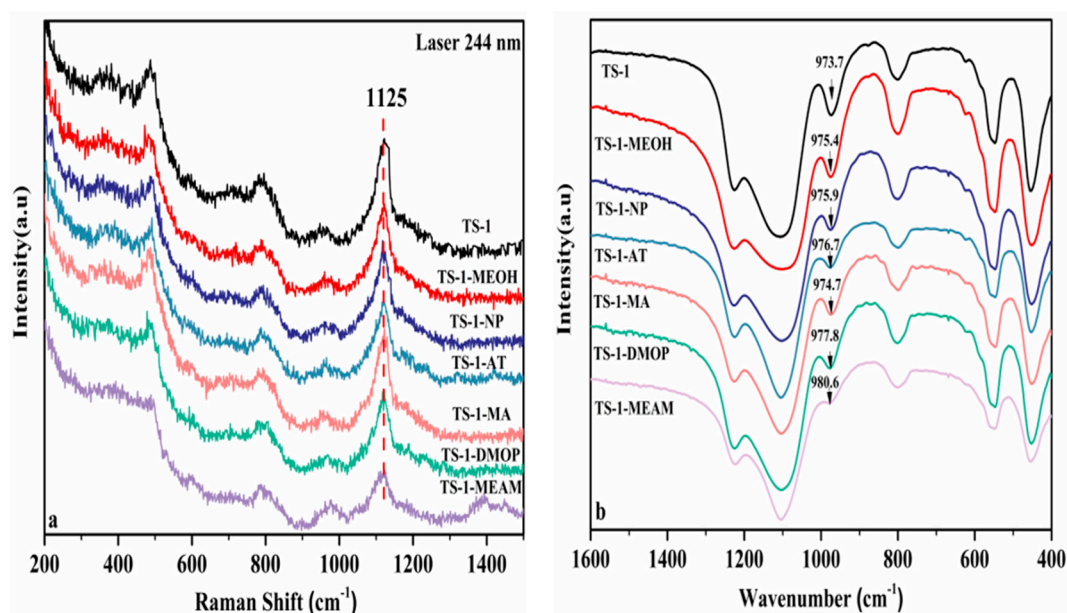
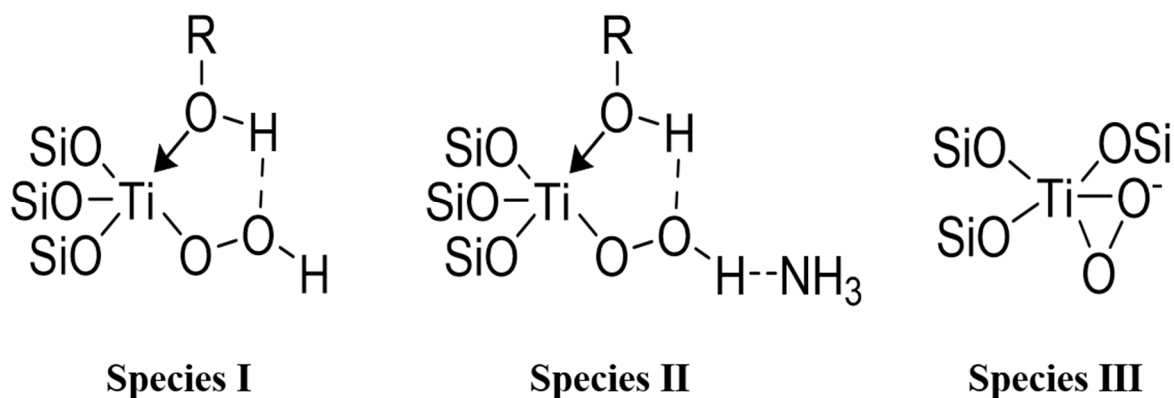
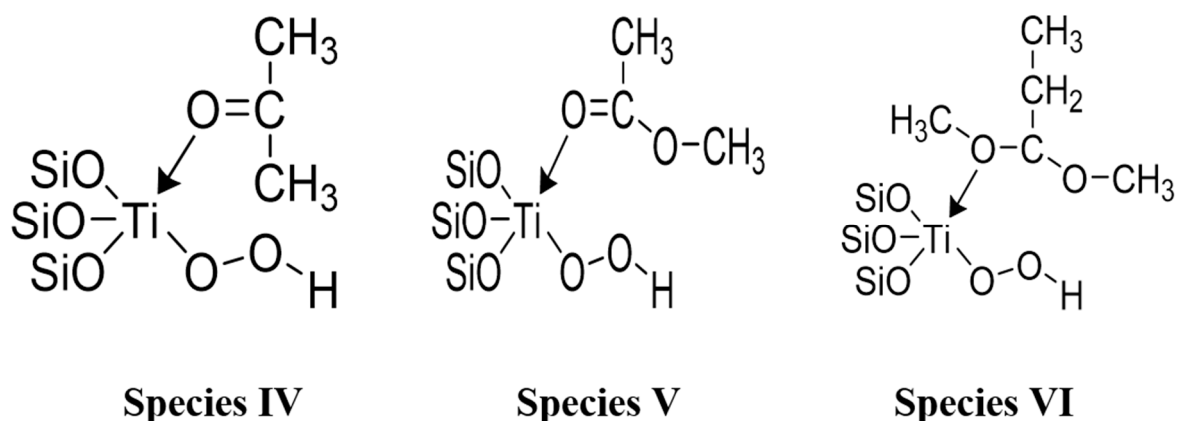


Figure 9. UV-Raman spectra (a) and skeleton IR spectra (b) of TS-1 adsorbed methanol and impurities.

It has been reported that, in the system of TS-1, H_2O_2 and alcohol (methanol, ethanol, 2-propanol, and 1-propanol), a five-membered cyclic structure (Species I from Scheme I) formed, which lowered the apparent activation energy of Ti-O-O-H and advanced the epoxidation activity [33,42–45]. However, the steric constraints of a five-membered ring intermediate increased in accordance with the following: methanol < ethanol < 2-propanol < 1-propanol [34,35], which resulted in lowering the conversion of H_2O_2 in the methanol solvent containing ethanol, 2-propanol, and 1-propanol. In addition, the activity of the epoxidation could be enhanced by forming a novel intermediate (Species II from Scheme I) that contains double hydrogen bonds, when a considerable amount of NH_3 is added [44]. However, a new Species III (Scheme I) was formed when the methanol solvent contained an excess amount of amines [34]. Since Species III with negative charge reduced its electrophilic nature, propylene oxide could not be transformed in Species III. This could explain why the activity of the propylene epoxidation in the methanol solvent containing excess amines was lowered. Furthermore, the aprotic impurities (ketone, ester, and acetal) might coordinate with framework titanium sites, as shown in Figure 9; therefore, we speculated that the aprotic impurities might form Species IV, V, and VI with TS-1 and H_2O_2 , as shown in Scheme II. Due to their inferior hydrogen-bond donor properties, the activity of the Species (IV, V, and VI) was weaker than that of Species I. Consequently, the conversion of H_2O_2 in methanol with ketone, ester, and acetal would be decreased due to the reduction in the concentration of hydrogen-bond complex Species I.



Scheme I. Reported active intermediate species in reference [33,34,42–44].



Scheme II. Speculated active intermediate species formed by different aprotic impurities

with TS-1.

4. Materials and Methods

4.1. Catalytic Reactions

4.1.1. Epoxidation with a Recycled Methanol Solvent

The recycled methanol solvent was obtained from our HPPO pilot plant in Nanjing. The recycled methanol solvent contained fusel alcohol (3.33 wt.%), aldehyde and ketone (0.01 wt.%), ester (0.02 wt.%), acetal (0.66 wt.%), total nitrogen (6 ppm), water (3.4 wt.%), and other impurities (0.25 wt.%).

The influence of the recycled methanol solvent on the catalytic performance of TS-1 in propylene epoxidation with H_2O_2 was evaluated in a fixed-bed reactor by comparing it with a fresh methanol solvent. The reaction conditions were as follows: 7.2 g of TS-1 extrudate catalyst (prepared according to the literature [46]); the concentrations of H_2O_2 and $\text{NH}_3\cdot\text{H}_2\text{O}$ in solvent (fresh methanol or recycled methanol) were 3 mol/L and 2.0 mmol/L, respectively; the ratio of $\text{C}_3\text{H}_6/\text{H}_2\text{O}_2$ was 4/1 (mol); the reaction pressure was 3.0 MPa; the reaction temperature was 35 °C; the WHSV (Weight hourly space velocity) of propylene was 0.87 h^{-1} .

4.1.2. Epoxidation with Simulated Methanol Solvents

Simulated methanol solvents were prepared with methanol (analytical reagent) and each of the 13 kinds of chemical reagents (analytical reagent or chromatographic reagent), which were classified into 6 groups (fusel alcohol (ethanol, 2-propanol and 1-propanol (Kermel, Tianjin, China)), aldehyde (acetaldehyde, propionaldehyde (Sinopharm Chemical Reagent, Shanghai, China)), ketone (acetone (Sinopharm Chemical Reagent, Shanghai, China)), ester (methyl formate and methyl acetate (Guangfu Fine Chemical Research Institute, Tianjin, China)), acetal (dimethoxymethane (Macklin, Shanghai, China)), 1,1-dimethoxyethane (Energy Chemical, Shanghai, China)), 1,1-dimethoxypropane (TCI, Shanghai, China) and amine (methylamine and ethylamine (Sinopharm Chemical Reagent, Shanghai, China)), as shown in Table S6. These chemical reagents served as a representative of impurities found in the real recycled methanol solvent. The content of each impurity in the simulated methanol solvents was determined and referred to the content of impurities in the recycled methanol solvent, as shown in Table S6.

The TS-1 powder was synthesized according to reference [46]. The Si/Ti molar ratio of the TS-1 catalyst was approximately 37. The TS-1 powder catalyst was calcined at 540 °C in air to remove the organic template in the micropores, and then it was subjected to pre-adsorption treatment by the simulated methanol solvents. The details of the pre-adsorption treatment are as follows: a certain amount of TS-1 powder catalyst was soaked in the simulated methanol solvents (in excess) at 50 °C

for 48 h under a static condition. Then, the pre-adsorbed TS-1 powder catalyst was obtained by filtration and dried at 40 °C for 12 h.

Propylene epoxidation with H₂O₂ was conducted in a batch reactor under the following reaction conditions: pre-adsorbed TS-1 powder 0.40 g, H₂O₂ (50 wt.%) 4.5 mL, NH₃·H₂O (0.32 mol/L) 0.2 mL, solvent (fresh methanol or the simulated methanol solvents) 35.5 mL, reaction temperature 50 °C, propylene pressure 0.6 MPa, and reaction time 1 h.

The residual H₂O₂ in products was analyzed by iodometric titration. The composition of the products was analyzed by gas chromatography (Shimadzu GC-2014 C), involving a flame ionization detector and a DB-WAX capillary column (30 m × 0.32 mm × 30 µm). The unknown components were identified using gas chromatography-mass spectrometry (Agilent-5975 C). The main product was propylene oxide (PO), and the by-products were propylene glycol (PG), monomethyl ether (MME, namely 1-methoxy-2-propanol and 2-methoxy-1-propanol), and other species, respectively. The conversion of H₂O₂, the selectivity of PO, and the utility of H₂O₂ were obtained using the following definitions:

$$X(\text{H}_2\text{O}_2) = \frac{n_0(\text{H}_2\text{O}_2) - n(\text{H}_2\text{O}_2)}{n_0(\text{H}_2\text{O}_2)} \times 100\%$$

$$S(\text{PO}) = \frac{n(\text{PO})}{n(\text{PO}) + n(\text{MME}) + n(\text{PG}) + n(\text{Others})} \times 100\%$$

$$U(\text{H}_2\text{O}_2) = \frac{n(\text{PO}) + n(\text{MME}) + n(\text{PG}) + n(\text{Others})}{n_0(\text{H}_2\text{O}_2) \times X(\text{H}_2\text{O}_2)} \times 100\%$$

where the $n_0(\text{H}_2\text{O}_2)$ and $n(\text{H}_2\text{O}_2)$ stand for the initial and final molar numbers of H₂O₂, respectively. The $n(\text{PO})$, $n(\text{MME})$, $n(\text{PG})$, and $n(\text{Others})$ are the molar numbers of PO, MME, PG and other by-products, respectively.

4.2. Competitive Adsorption and Desorption of Impurities on a TS-1 Catalyst

The dynamic competitive adsorption of impurities in methanol using a TS-1 catalyst was investigated with gas chromatography in the following way: a certain amount of the TS-1 catalyst was soaked at room temperature in a special methanol solution that contained an impurity (0.1 mol/L). The evolution of the impurity concentration in the methanol was monitored by gas chromatography (Shimadzu GC-2014 C, Kyoto, Japan) involving a flame ionization detector and a DB-WAX capillary column (30 m × 0.32 mm × 30 µm) or a DB-1701 (30 m × 0.32 mm × 1.0 µm) at desired time intervals.

The desorption experiments were carried out using a FT-IR spectrometer (Nicolet 6700, Waltham, MA, USA) that was operated in transmission mode. First, the TS-1 catalyst powder was pressed into a self-supporting thin wafer (approximately 15 mg) and decontaminated at 400 °C under vacuum (10^{−3} pa) for 4 h in a quartz IR cell equipped with CaF₂ windows. Next, the cell was cooled down to room temperature to record the sample background spectrum. Then, the pretreated TS-1 was exposed in the vapor of the methanol or the impurity or the methanol solvent with the impurity at room temperature for adsorption. The vapor was carried by N₂ (flow rate of 10 mL/min), and the adsorption lasted for 30 min in each experiment. Finally, the IR spectrum was collected (64 scans and a 4 cm^{−1} resolution). The adsorption spectra were denoted as MEOH, Impurity, and MEOH-Impurity, respectively.

Then, the TS-1 catalyst samples, which came into contact with the vapor of the methanol solvent containing impurity, were subjected to a desorption study. First, the samples with the methanol and the impurity were purged with nitrogen (100 mL/min) at room temperature for 20 min. This was followed by a spectrum collection. The spectra were denoted as MEOH-Impurity-des-20-n; then, the purging was resumed at a higher temperature (50 °C) for 30 min. Similarly, it was followed by a spectrum collection. The spectra were denoted as MEOH-Impurity-des-50-n; finally, the purging was replaced by an evacuation treatment (10^{−1} pa, 100 °C, 30 min). Spectra collected here were denoted by MEOH-Impurity-des-80-v.

4.3. Characterizations of the Adsorption Site of Impurities on a TS-1 Catalyst

The characterization of the adsorption site of impurities on a TS-1 catalyst was carried out with UV-Raman and skeleton vibration FT-IR. The FT-IR spectra were collected on a FT-IR spectrometer (Nicolet 6700, Waltham, MA, USA) using the KBr wafer technique. UV Raman spectra were recorded on a home-made UV Raman spectrograph (Dalian Institute of Chemical Physics, Dalian, China) using a Jobin-Yvon T64000 triple-stage spectrograph (Jobin Yvon, New York, USA) with a spectral resolution of 2 cm^{-1} . The 244 nm line was from a Coherent Innova 300 Fred laser. The power of the 244 nm line, at samples, was below 1.0 mW. The procedures used for the preparation of the TS-1 powder samples were as follows: first, the purified TS-1 was soaked in methanol (MEOH), 1-propanol (NP), acetone (AT), methyl acetate (MA), 1,1-dimethoxypropane (DMOP), and methylamine (MEAM), respectively. Then, the mixtures were stirred at room temperature for 4 h. Next, the soaked TS-1 samples were recovered by filtration and dried at $60\text{ }^{\circ}\text{C}$ for 12 h. The samples were labeled as TS-1-MEOH, TS-1-NP, TS-1-AT, TS-1-MA, TS-1-DMOP, and TS-1-MEAM, respectively.

5. Conclusions

This study indicates that, during the liquid-phase epoxidation of propylene and H_2O_2 , the influence of impurities in a methanol solvent on the conversion of H_2O_2 is significant, but the influence on the selectivity of PO and the utility of H_2O_2 is unremarkable. Among the impurities, the influence of acetone and amines (methylamine and ethylamine) on the conversion of H_2O_2 was the most striking. In general, the content of methylamine, ethylamine, acetone, methyl acetate, 1,1-dimethoxypropane, and 1-propanol in a methanol solvent should be strictly controlled. In addition, the influence mechanism of impurities in a methanol solvent on the liquid-phase epoxidation of propylene and H_2O_2 has been preliminarily studied. It was found that impurities competitively adsorbed on tetra-coordinated framework titanium sites of TS-1, and that they consequently hindered the contact of methanol with the tetra-coordinated framework Ti sites, which might account for the negative influence of impurities in methanol solvent on the epoxidation. For example, Species III might have been formed on TS-1 when the methanol solvent with excess amines (methylamine and ethylamine) was used. This species could not take part in the epoxidation of propylene. In the case of the methanol solvent, contained aprotic impurities (acetone, methyl acetate, and 1,1-dimethoxypropane) were used. A decrease in the concentration of Species I, which would slow down the conversion of H_2O_2 , is a possible consequence of this. Our future research will be focused on a solution to reduce the influence of these impurities on the liquid-phase epoxidation of propylene and H_2O_2 .

Supplementary Materials: The following are available online at www.mdpi.com/xxx/s1, Table S1: Influence of fusel alcohol content on the product distribution and turnover numbers in epoxidation of propylene with H_2O_2 , Table S2: Influence of ketone and aldehyde content on the product distribution and turnover numbers in epoxidation of propylene with H_2O_2 , Table S3: Influence of ester content on the product distribution and turnover numbers in epoxidation of propylene with H_2O_2 , Table S4: Influence of acetal content on the product distribution and turnover numbers in epoxidation of propylene with H_2O_2 , Table S5: Influence of amine content on the product distribution and turnover numbers in epoxidation of propylene with H_2O_2 , Table S6: Contents of impurities in simulated methanol solvents.

Author Contributions: Conceptualization, G.W. and H.G.; Investigation, G.W.; Validation, Y.L., Q.Z. and C.Z.; Writing—original draft preparation, G.W. and H.G.; Writing—review and editing, H.G. and G.L.; Supervision, H.G. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Russo, V.; Tesser, R.; Santacesaria, E.; Serio, M.D. Chemical and Technical Aspects of Propene Oxide Production via Hydrogen Peroxide (HPPO Process). *Ind. Eng. Chem. Res.* **2013**, *52*, 1168–1178.
2. Schmidt, F.; Bernhard, M.; Pascaly, M. HPPO Process Technology a Novel Route to Propylene Oxide without Coproducts. *Chim. Oggi* **2014**, *32*, 31–35.
3. Taramasso, M.; Perego, G.; Notari, B. Preparation of Porous Crystalline Synthetic Material Comprised of Silicon and Titanium Oxides. U.S. Patent 4410501, 18 October 1983.
4. Perera, A.S.; Coppens, M.O. Titano-Silicates: Highlights on Development, Evolution and Application in Oxidative Catalysis. *Catalysis* **2016**, *28*, 119–143.
5. Xin, H.C.; Zhao, J.; Xu, S.T.; Li, J.P.; Zhang, W.P.; Guo, X.W.; Hensen, E.J.M.; Yang, Q.H.; Li, C. Enhanced Catalytic Oxidation by Hierarchically Structured TS-1 Zeolite. *J. Phys. Chem. C* **2010**, *114*, 6553–6559.
6. Chen, L.H.; Li, X.Y.; Tian, G.; Li, Y.; Rooke, J.C.; Zhu, G.S.; Qiu, S.L.; Yang, X.Y.; Su, B.L. Highly Stable and Reusable Multimodal Zeolite TS-1 Based Catalysts with Hierarchically Interconnected Three-Level Micro-Meso-Macroporous Structure. *Angew. Chem. Int. Ed.* **2011**, *50*, 11156–11161.
7. Zuo, Y.; Wang, X.S.; Guo, X.W. Synthesis of Titanium Silicalite-1 with Small Crystal Size by Using Mother Liquid of Titanium Silicalite-1 as Seed. *Ind. Eng. Chem. Res.* **2011**, *50*, 8485–8491.
8. Na, K.; Jo, C.; Kim, J.; Ahn, W.S.; Ryoo, R. MFI Titanosilicate Nanosheets with Single-Unit-Cell Thickness as an Oxidation Catalyst Using Peroxides. *ACS Catal.* **2011**, *1*, 901–907.
9. Wang, L.L.; Liu, Y.M.; Xie, W.; Wu, H.H.; Li, X.H.; He, M.; Wu, P. Improving the Hydrophobicity and Oxidation Activity of Ti-MWW by Reversible Structural Rearrangement. *J. Phys. Chem. C* **2008**, *112*, 6132–6138.
10. Wang, L.; Sun, J.; Meng, X.J.; Zhang, W.P.; Zhang, J.; Pan, S.X.; Shen, Z.; Xiao, F.S. A Significant Enhancement of Catalytic Activities in Oxidation with H₂O₂ over the TS-1 Zeolite by Adjusting the Catalyst Wettability. *Chem. Commun.* **2014**, *50*, 2012–2014.
11. Wu, L.Z.; Zhao, S.F.; Lin, L.F.; Fang, X.Q.; Liu, Y.M.; He, M.Y. In-depth Understanding of Acid Catalysis of Solvolysis of Propene Oxide over Titanosilicates and Titanosilicate/H₂O₂ Systems. *J. Catal.* **2016**, *337*, 248–259.
12. Li, G.; Wang, X.S.; Yan, H.S.; Chen, Y.Y.; Su, Q.S. Effect of Sodium Ions on Propylene Epoxidation Catalyzed by Titanium Silicalite. *Appl. Catal. A Gen.* **2001**, *218*, 31–38.
13. Arca, V.; Furlan, P.; Buzzoni, R. Process for the Preparation of Olefinic Epoxides. Eur. Patent 0930308B1, 3 March 2004.
14. Paparatto, G.; Forlin, A.; De Alberti, G.; D'Aloisio, R.; Tegen, P. Integrated Process for the Preparation of Olefin Oxides. U.S. Patent 6888013 B2, 3 May 2005.
15. Signorile, M.; Crocellà, V.; Damin, A.; Rossi, B.; Lamberti, C.; Bonino, F.; Bordiga, S. Effect of Ti Speciation on Catalytic Performance of TS-1 in the Hydrogen Peroxide to Propylene Oxide Reaction. *J. Phys. Chem. C* **2018**, *122*, 9021–9034.
16. Wu, L.Z.; Deng, X.J.; Zhao, S.F.; Yin, H.M.; Zhuo, Z.X.; Fang, X.Q.; Liu, Y.M.; He, M.Y. Synthesis of a Highly Active Oxidation Catalyst with Improved Distribution of Titanium Coordination States. *Chem. Commun.* **2016**, *52*, 8679–8682.
17. Notari, B. Titanium Silicalites. *Catal. Today* **1993**, *18*, 163–172.
18. Lin, M.; Xia, C.J.; Zhu, B.; Li, H.; Shu, X.T. Green and Efficient Epoxidation of Propylene with Hydrogen Peroxide (HPPO Process) Catalyzed by Hollow TS-1 Zeolite: A 1.0 kt/a Pilot-scale Study. *Chem. Eng. J.* **2016**, *295*, 370–375.
19. Clerici, M.G.; Kholdeeva, O.A. *Liquid Phase Oxidation via Heterogeneous Catalysis: Organic Synthesis and Industrial Applications*; John Wiley & Sons, Inc.: Hoboken, NJ, USA, 2013; pp. 474–494.
20. Kraïem, J.; Ghedira, D.; Ollevier, T. Hydrogen Peroxide/Dimethyl Carbonate: A Green System for Epoxidation of N-alkylimines and N-sulfonylimines. One-pot Synthesis of N-alkyloxaziridines from N-alkylamines and (hetero) Aromatic Aldehydes. *Green Chem.* **2016**, *18*, 4859–4864.
21. Grigoropoulou, G.; Clark, J.H.; Elings, J.A. Recent Developments on the Epoxidation of Alkenes Using Hydrogen Peroxide as an Oxidant. *Green Chem.* **2003**, *5*, 1–7.
22. Matsumoto, K.; Oguma, T.; Katsuki, T. Highly Enantioselective Epoxidation of Styrenes Catalyzed by Proline-Derived C₁-Symmetric Titanium (Salan) Complexes. *Angew. Chem. Int. Ed.* **2009**, *48*, 7432–7435.
23. Ballistreri, F.P.; Gangemi, C.M.A.; Pappalardo, A.; Tomaselli, G.A.; Toscano, R.M.; Sfrazzetto, G.T. (Salen) Mn(III) Catalyzed Asymmetric Epoxidation Reactions by Hydrogen Peroxide in Water: A Green Protocol. *Int. J. Mol. Sci.* **2016**, *17*, 1112.

24. Zahedi-Niaki, M.H.; Kapoor, M.P.; Kaliaguine, S. H_2O_2 Oxidation and Epoxidation of Hydrocarbons and Alcohols over Titanium Aluminophosphates TAPO-5, TAPO-11, and TAPO-36. *J. Catal.* **1998**, *177*, 231–239.
25. Rueter, M.A. Propylene Oxide Purification. PCT. Patent WO 99/07690, 18 February 1999.
26. Göbbel, H.G.; Bassler, P.; Teles, J.H.; Rudolf, P.; Müller, U.; Forlin, A.; Schulz, M.; Weidenbach, M. A Process for Epoxidizing Propene. PCT. Patent WO 2007/074101 A1, 5 July 2007.
27. Berges, J.; Brasse, C.; Eickhoff, H.; Haas, T.; Hofen, W.; Kampeis, P.; Moroff, G.; Pohl, W.; Stochniol, G.; Thiele, G.; et al. Process for the Epoxidation of Olefins. PCT. Patent WO 03/093255 A1, 13 November 2003.
28. Teles, J.H.; Rehfinger, A.; Bassler, P.; Wenzel, A.; Rieber, N.; Rudolf, P. Method for the Production of Propylene Oxide. U.S. Patent 2003/0146080 A1, 7 August 2003.
29. Haas, T.; Hofen, W.; Wöll, W.; Brasse, C.; Stochniol, G.; Ullrich, N. Process for the Epoxidation of Olefins. PCT. Patent WO 2004/048354 A1, 10 June 2004.
30. Wang, Z.J.; Pascaly, M.; Bernhard, M. Process for the Epoxidation of Propene. PCT. Patent WO 2018/205244 A1, 15 November 2018.
31. Hofen, W.; Thiele, G.; Moller, A. Process for the Epoxidation of Olefins. U.S. Patent 2003/0114694 A1, 19 June 2003.
32. Rueter, M.A.; Jubin, J.C., Jr. Separation of Methanol and Propylene Oxide from a Reaction Mixture. U.S. Patent 5849938, 15 December 1998.
33. Clerici, M.G.; Ingallina, P. Epoxidation of Lower Olefins with Hydrogen Peroxide and Titanium Silicalite. *J. Catal.* **1993**, *140*, 71–83.
34. Li, G.; Meng, J.W.; Wang, X.S.; Guo, X.W. Effect of Solvents on Propene Epoxidation Catalyzed by Titanium Silicalite. *React. Kinet. Catal. Lett.* **2004**, *82*, 73–80.
35. Liu, X.W.; Wang, X.S.; Guo, X.W.; Li, G. Effect of Solvent on the Propylene Epoxidation Over TS-1 Catalyst. *Catal. Today* **2004**, *93*, 505–509.
36. Li, C.; Xiong, G.; Xin, Q.; Liu, J.K.; Ying, P.L.; Feng, Z.C.; Li, J.; Yang, W.B.; Wang, Y.Z.; Wang, G.R.; et al. UV Resonance Raman Spectroscopic Identification of Titanium Atoms in the Framework of TS-1 Zeolite. *Angew. Chem. Int. Ed.* **1999**, *38*, 2220–2222.
37. Bolis, V.; Bordiga, S.; Lamberti, C.; Zecchina, A.; Carati, A.; Rivetti, F.; Spanò, G.; Petrini, G. A Calorimetric, IR, XANES and EXAFS Study of the Adsorption of NH_3 on Ti-Silicalite as a Function of the Sample Pre-treatment. *Microporous Mesoporous Mater.* **1999**, *30*, 67–76.
38. Bordiga, S.; Coluccia, S.; Lamberti, C.; Marchese, L.; Zecchina, A. XAFS Study of Ti-Silicalite: Structure of Framework Ti (IV) in the Presence and Absence of Reactive Molecules (H_2O , NH_3) and Comparison with Ultraviolet-Visible and IR Results. *J. Phys. Chem.* **1994**, *98*, 4125–4132.
39. Scarano, D.; Zecchina, A.; Bordiga, S.; Geobaldo, F.; Spoto, G. Fourier-transform Infrared and Raman Spectra of Pure and Al-, B-, Ti- and Fe-substituted Silicalites: Stretching-mode Region. *J. Chem. Soc. Faraday Trans.* **1993**, *89*, 4123–4130.
40. Pretsch, E.; Bühlmann, P.; Badertscher, M. *Structure Determination of Organic Compounds: Tables of Spectral Data*; Springer: Berlin/Heidelberg, Germany, 2009; pp. 287–335.
41. Field, L.D.; Sternhell, S.; Kalman, J.R. *Organic Structures from Spectra*; John Wiley & Sons, Ltd.: West Sussex, WI, USA, 2013; pp. 15–17.
42. Bellussi, G.; Carati, A.; Clerici, M.G.; Maddinelli, G.; Millini, R. Reactions of Titanium Silicalite with Protic Molecules and Hydrogen Peroxide. *J. Catal.* **1992**, *133*, 220–230.
43. Clerici, M.G.; Ingallina, P. Oxidation Reactions with in Situ Generated Oxidants. *Catal. Today* **1998**, *41*, 351–364.
44. Deng, X.J.; Zhang, S.; Wang, B.S.; Wang, Y.N.; Wu, H.H.; Liu, Y.M.; He, M.Y. Enhanced Catalytic Activity of Titanosilicates Controlled by Hydrogen-Bonding Interactions. *Chem. Commun.* **2013**, *49*, 7504–7506.
45. Sever, R.R.; Root, T.W. DFT Study of Solvent Coordination Effects on Titanium-Based Epoxidation Catalysts. Part One: Formation of the Titanium Hydroperoxo Intermediate. *J. Phys. Chem. B* **2003**, *107*, 4080–4089.
46. Song, W.C.; Xiong, G.; Long, H.Y.; Jin, F.Y.; Liu, L.P.; Wang, X.S. Effect of Treatment with Different Bases on the Catalytic Properties of TS-1/ SiO_2 Extrudates in Propylene Epoxidation. *Microporous Mesoporous Mater.* **2015**, *212*, 48–55.

