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Synthesis of titanium silicalite (TS-1) from the TPABr system and its catalytic properties for epoxidation of propylene

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Abstract

Titanium silicalite (TS-1) was successfully synthesized by using tetra-propylammonium bromide (TPABr) and *n*-butylamine as the template and the base, respectively. XRD, IR, SEM, ^{13}C CP/MAS NMR, UV–VIS, and UV-Raman techniques were used to characterize the synthesized products. The results show that TS-1 has MFI structure with high crystallinity and large crystal size, and with two kinds of titanium species. Using epoxidation of propylene as the probe, the catalytic properties of TS-1 in the present work were investigated. The crystal size of TS-1 affects much the initial reaction rate of propylene oxide (PO) formation. The effects of reaction conditions on PO reveal that the PO formation is greatly influenced by the solvent and the solution pH value. Methanol is the most preferable solvent, and a portion of water ($<30\%$) in solution does not have much impact on the reaction. Moreover, the addition of base used to neutralize the residual acidity of the catalyst favor the reaction, the catalyst shows high activity and selectivity upon the adequate amount of base and the catalyst can be used repeatedly without regeneration. In the fixed-bed reactor, using ammonium water as the neutralizer, after 200 h of reaction, both the conversion and the utilization of H_2O_2 is about 95%, the selectivity of PO is about 90%. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: TS-1; TPABr; Epoxidation of propylene; Solvent effect; Acid–base effect; Aging test

1. Introduction

Titanium silicalite (TS-1) was first synthesized by Taramasso et al. using tetraethyl orthosilicalite (TEOS) and tetraethyl orthotitanate (TEOT) as the silicon source and titanium source, respectively, and using tetrapropylammonium hydroxide (TPAOH) as the template [1]. Because of its specifically, catalytic oxidation properties, TS-1 has received much attention of the researchers [2]. However, TPAOH is too costly for industry to make TS-1 in commercial process. The key to synthesize cheap TS-1 is the use of the inexpensive templates. Muller and Hoelderich [3] reported the synthesis of TS-1 by using TPABr as the template and $NH_3{\cdot}H_2O$ as the base in replacement of TPAOH, but the consumption of ammonia is too much. Tuel [4] adopted hexanediamine as the base to synthesize TS-1, and as a results, the synthesized zeolite has a crystal size of 7 μm × 2.5 μm × 0.5 μm. Xia and Gao [5] synthesized pure TS-1 by using binary mixtures of TEACl and TBACl as the structure directing agents, but a certain amount of good TS-1 crystalline seeds must be added, moreover, concentrated ammonia solution needs to be added. The calcined TS-1 especially shows high activity in the hydroxylation of phenol with dilute H_2O_2. To reduce the cost of TS-1, some researchers studied the synthesis by using cheap silicon source and titanium source. For example, Gontier and Tuel [6] used amorphous SiO_2 as the silicon source and TPAOH as the template to synthesize TS-1 with large crystal size (2–10 μm). The authors suggested that the nature of the silicon source has great influence on the crystal size of the TS-1. Jorda and Tuel [7] reported the

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synthesis of TS-1 by using TiF_4 as the titanium source, while Gao et al. [8] used $TiCl_3$ as the titanium source. Considering the use of TiF_4 and $TiCl_3$ as stable titanium sources favors the incorporation of titanium into the framework, another advantage of using TiF_4 and $TiCl_3$ as the titanium source is that it is possible to prepare TS-1 with commercial TPAOH solutions containing alkali cations, without formation of extra framework TiO_2 species.

We used TPABr as the template and organic amine as the base to synthesize TS-1. The effects of the template and organic amine on the synthesis of TS-1 were reported in our previous papers [9,10]. The results revealed that TS-1 has good catalytic properties for the epoxidation of propylene, as compared to that synthesized by the standard method [11,12].

There are many reports on the epoxidation of propylene by using TS-1 as the catalyst [13–16]. Recently, more reports were found in the epoxidation of propylene by using Au/TS-1 [17], Pd/TS-1 [18] and Pt–Pd/TS-1 [19], and the selectivity of propylene oxide (PO) reported is up to 95%. All TS-1 zeolites reported above were, however, synthesized by using TPAOH as the template, and we first reported the application of TS-1 prepared by TPABr system into the epoxidation of propylene. In this paper, the synthesis of TS-1 by using TPABr as the template and *n*-butylamine as the base is presented, and the catalytic properties were investigated in detail over the synthesized TS-1.

2. Experimental

2.1. TS-1 synthesis

TS-1 was prepared by using colloidal silica (30 wt.%) and tetrabutylorthotitanate (TBOT) as silicon and titanium source, respectively. TPABr was used as the template instead of TPAOH and *n*-butylamine was used as the base. A typical preparation was like: 19.36 l of silica sol were mixed at ambient temperature with 3.168 kg of TPABr dissolved in 44.24 l of deionized water. Then 2.46 l of TBOT solution were added dropwise at that temperature. After that, 4.70 l of *n*-butylamine were added under stirring. Finally, 320 g of TS-1 synthesized from TPABr were added as the seeds and the gel was placed into 100 l stainless-steel autoclaves and heated at 443 K under autogeneous pressure for 4 days. The solid obtained was filtered, washed with distilled water, dried at 373 K in static air for 12 h and calcined at 873 K for 5 h.

2.2. Characterization of the samples

The Si/Ti ratio of TS-1 was determined by a Bruker SRS 3400 XRF spectrometer. X-ray diffraction patterns were performed on a D/max-2400 diffractometer using the Cu Kα radiation. Framework IR spectra were recorded on an FT-5DX spectrometer. The samples used for IR were ground with KBr and pressed into thin wafers. ^{13}C solid-state CP/MAS NMR spectra were recorded on a Bruker DRX 400 spectrometer at room temperature using relaxation delay of 2 s and contact time of 2 ms and spinning frequency of 4–6 kHz. The frequency of ^{13}C was 100.577 MHz and Adamatan was used to calibrate the ^{13}C chemical shift. UV–VIS measurements were performed on a Shimadzu UV-240 by using the diffuse reflectance technique in the range of 190–490 nm, and freshly prepared silicalite was used as the reference. UV-Raman spectra were recorded on a homemade UV-DL01 UV-Raman spectrometer. The 244.0 nm line from Innova 300 FRED was used as the excitation source. The spectral resolution was estimated to be $1.0\,cm^{-1}$ and the acquisition time is 10 min.

2.3. Catalytic test

Epoxidation of propylene was carried out in a stainless-steel reactor and a continuous flow fixed-bed micro-reactor, respectively. In the autoclave reactor, the slurry is composed of 0.4 g of calcined catalyst, 2.0 ml of about 30% H_2O_2 and 31.6 ml of methanol, propylene was charged at constant pressure (0.4 MPa), the reactor is then heated at 333 K under magnetic agitation for 60∼90 min. In the fixed-bed reactor, the catalyst was prepared by spraying TS-1 (1.6 g) to the small inert ball (16 g) with a diameter of 1∼2 mm. Reaction conditions are as follows: reaction temperature 323 K, propylene pressure 3.0 MPa, C_3H_6/H_2O_2 (molar ratios) 4, the concentration of H_2O_2 0.85 mol/l, WHSV of C_3H_6 is $0.1\,h^{-1}$. Methanol was used as the solvent and ammonium water as the neutralizer.

The residual H_2O_2 was checked by iodometric titration. The product of the reaction was analyzed on a 1102 g chromatography using a flame ionization detector and a capillary column (40.0 m × 0.25 mm) containing polyethylene glycol 20 M as the stationary phase. PO was the main product, and propylene glycol (PG) and its mono-methyl ethers (MME) were the by-products. The result of the reaction was given by using the following criteria:

$$X_{H_2O_2} = \frac{n^0_{H_2O_2} - n_{H_2O_2}}{n^0_{H_2O_2}} \times 100\%,$$

$$U_{H_2O_2} = \frac{n_{PO} + n_{MME} + n_{PG}}{n^0_{H_2O_2} \times X_{H_2O_2}} \times 100\%,$$

$$S_{PO} = \frac{n_{PO}}{n_{PO} + n_{MME} + n_{PG}} \times 100\%$$

$$S_{MME} = \frac{n_{MME}}{n_{PO} + n_{MME} + n_{PG}} \times 100\%$$

$X_{H_2O_2}$, $U_{H_2O_2}$, S_{PO} and S_{MME} stand for the conversion of H_2O_2, the utilization of H_2O_2, the selectivity of PO and the selectivity of MME, respectively. The mole of PO, MME and PG, are represented by n_{PO}, n_{MME} and n_{PG}, respectively. The $n^0_{H_2O_2}$ and the $n_{H_2O_2}$ stand for the initial mole content and the final mole content of H_2O_2, respectively.

3. Results and discussion

3.1. Synthesis and characterization

TPAOH acts as the structure-directing agent and provides the alkalinity in the synthesis of TS-1. However, the high cost of TPAOH results in the costly synthesis of TS-1. An alternative way for synthesis of TS-1 is to use TPABr (usually free from alkali metal cations) and some bases instead of TPAOH, as reported by many authors [3,4]. In this paper, using $Ti(OC_4H_9)_4$ as the titanium source and TPABr as the template, TS-1 samples with different crystal size(1∼20 μm) were synthesized by adjusting the synthesis condition. The characterization of TS-1 sample synthesized in 100 l stainless-steel autoclave (sample 3 in Table 1) was first discussed.

As follows from XRD patterns shown in Fig. 1a that the calcined TS-1 sample contains an MFI phase with good crystallinity, no other diffraction peaks for contaminating crystalline zeolitic and for non-zeolitic phases were detected. ^{13}C CP/MAS NMR spectrum shows that TPA^+ is trapped in the zeolite and acts as the structure-directing agent. SEM analysis shown in Fig. 2 shows that the crystals appear in the shape of elongated prisms of about 6 μm × 2 μm × 1 μm. Generally, TS-1 synthesized by using TPAOH as the template is in the shape of small round-shaped particles of about 0.3 μm diameter, while TS-1 synthesized in this work has a prism shape. This is in agreement with the results reported by Tuel [4] and Muller and Hoelderich [3], suggesting that the large crystal size is due to the use of silica sol as the silicon source. Similar phenomenon was observed by Gontier and Tuel [6].

IR spectrum shows that TS-1 has a characteristic peak at about 960 cm^{-1}, which indicates that titanium has been incorporated into the framework of the zeolite [20]. UV-Raman technique can be used as a direct tool to distinguish between framework and non-framework titanium according to Li et al. [21]. UV-Raman spectrum of TS-1 (Fig. 3) exhibits a

Table 1
Epoxidation of propylene over TS-1 with different crystal sizes[a]

Samples	Crystal size (μm^3)	SiO_2/TiO_2	SiO_2/Al_2O_3	$X_{H_2O_2}$ (%)	$U_{H_2O_2}$ (%)	S_{PO} (%)	S_{MME} (%)
1[b]	0.3	34.0	8	98.7	92.5	94.8	5.2
2	1 ×1.5 × 3	32.1	627	96.5	89.8	88.2	11.8
3	1 ×2 × 6	33.7	672	94.7	91.0	92.3	7.7
4[c]	1 ×3 × 8	33.0	650	94.6	88.7	89.8	10.2
5	4 ×7 × 15	33.4	612	96.0	87.7	93.3	6.7

[a] Reaction conditions: reaction temperature 333 K, reaction time 90 min, propylene pressure 0.4 MPa, the concentration of H_2O_2 0.45 mol/l, the concentration of catalyst 12 g/l, the concentration of Na_2CO_3 6.3×10^{-4} mol/l.

[b] TS-1 was synthesized using TPAOH as the template.

[c] Reaction time 60 min.

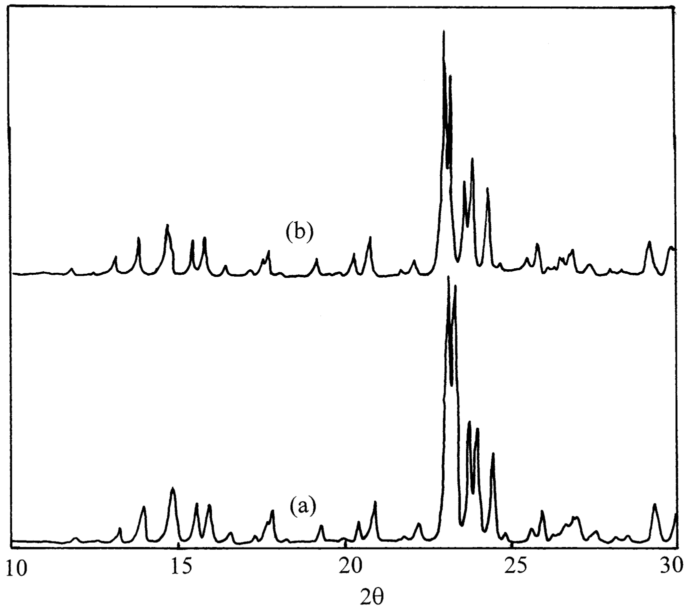

Fig. 1. XRD spectra of TS-1 with different ratios of: (a) $SiO_2/TiO_2 = 33$, synthesized in 100 l autoclave; (b) $SiO_2/TiO_2 = 8$, synthesized in 2 l autoclave.

characteristic peak at $1125\,cm^{-1}$, demonstrating that titanium has been incorporated into the framework of the zeolite. This is in line with IR spectra. However, the peak intensity is less than that of TS-1 synthesized by the standard method. This properly implies that the amount of titanium incorporated into the framework is lower than that of the TS-1 synthesized by using TPAOH as the template. UV–VIS spectrum of the calcined TS-1 shows two absorption peaks:

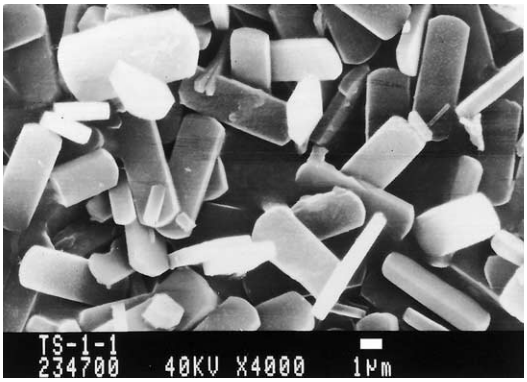

Fig. 2. SEM photograph of TS-1.

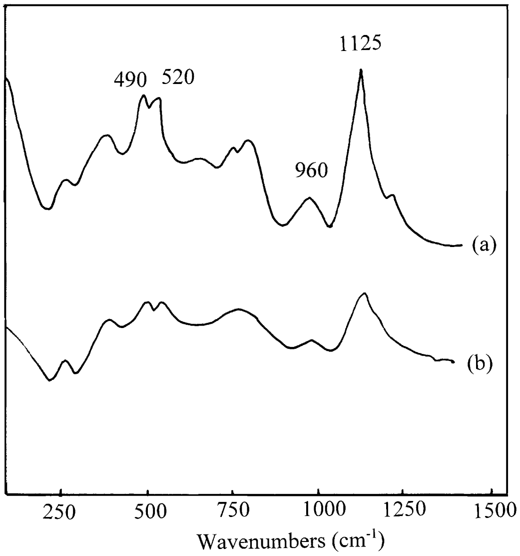

Fig. 3. UV-Raman spectra of: (a) TS-1, synthesized by standard method; (b) TS-1, synthesized using TPABr as the template in a 100 l autoclave.

one at 220 nm is attributed to tetra-coordinated titanium [22], while another at 270∼280 nm is attributed to Ti^{4+} ions in an octahedral coordination with two water molecules in the coordination sphere or small hydrated oligomeric TiO_x species [9,23]. The intensity of the peak at 270∼280 nm increases with the increase of titanium in the synthetic gel [24]. When the ratio of SiO_2/TiO_2 is up to 8, the intensity of the peak at 270∼280 nm is very strong. XRD spectrum (Fig. 1b), however, does not show the peak at $2\theta = 25.3^\circ$, which is attributed to anatase. Using TPAOH as the template, the increase of titanium in the gel will lead to the formation of anatase [25].

3.2. Catalytic properties of TS-1

3.2.1. The effect of crystal size of TS-1

Using epoxidation of propylene as the probe, the catalytic properties of TS-1 samples with different crystal sizes were investigated in an autoclave reactor and the results were presented in Fig. 4 and Table 1. It can be seen from Table 1 that, the conversion of H_2O_2 and the selectivity of PO change only little with the crystal size during 60∼90 min test. It has been reported by van der Pol et al. [26] that when TS-1 particle size is larger than 0.3 μm, diffusion limitation governs the hydroxylation rate of phenol with H_2O_2. However, in the epoxidation of propylene with H_2O_2, TS-1 samples with large crystal size still show high activity. Fig. 4 shows the conversion of H_2O_2 as a function of time of reaction. From Fig. 4, it can be seen that four TS-1 samples appear strongly different catalytic properties at the initial stage. After 1 h of reaction, there are no main differences among TS-1 samples.

Generally, the effect of crystal size on the catalytic properties can be explained by the Weisz theory. In this theory, the Weisz modulus (ϕ) and catalyst efficiency (η) are defined as:

$$\Phi = \frac{(p/6)^2 R_0}{D_{\text{eff}} C_0}, \quad \eta = \frac{\tanh\Phi}{\Phi}$$

Where p is the mean diffusion path length (m), R_0 the observed reaction rate (mol/(m^3 s)), D_{eff} the effective diffusion coefficient of substrate (m^2/s), C_0 the concentration of substrate at the outer surface of the catalyst (mol/m^3) and η is the catalyst efficiency $= R_{\text{observed}}/R_{\text{intrinsic}}$.

In the hydroxylation of phenol, the crystal size has great influence on the catalytic properties. While in the epoxidation of propylene, as for TS-1 samples synthesized with TPABr as the template, with the increase in the crystal size, the mean diffusion path length (p) increases, leading to catalyst efficiency (η) decrease. The dynamic diameter of propylene (0.5 nm) is smaller than that of phenol, so the diffusion coefficient of propylene (D_{eff}) in the pore of TS-1 is larger than that of phenol. This makes the effect of the crystal size on the epoxidation become smaller. From the effect of the concentration of H_2O_2 shown in Fig. 5, it can be seen that, when the concentration of H_2O_2 increases, TS-1 sample with small crystal size (sample 2) is still highly active, while the activity of the sample with large crystal size (sample 5) decreases. It reveals that crystal size has certain influence on the epoxidation of propylene at high concentration of H_2O_2 (>0.4 mol/l). It can be explained by partition coefficients (K) put forward by G. Langhendries et al. [27]. They found that, (1) for a given alkene, partition coefficients decrease with decreasing polarity of the alcohol solvent (e.g. $K_{\text{methanol}} > K_{\text{ethanol}} > K_{\text{1-propanol}}$). Thus the sorption is much stronger in a methanol carrier than in a less polar alcohol (1-propanol); (2) the partition coefficients

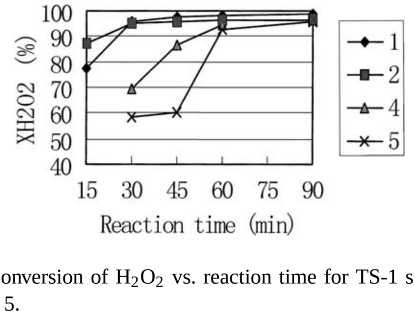

Fig. 4. Conversion of H_2O_2 vs. reaction time for TS-1 samples 1, 2, 4 and 5.

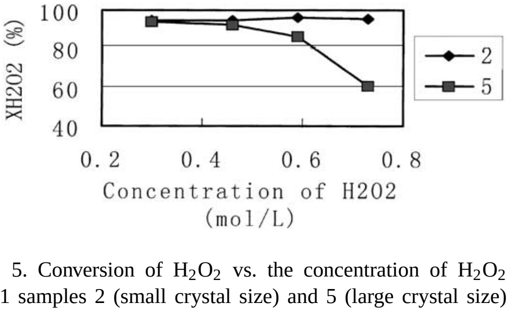

Fig. 5. Conversion of H_2O_2 vs. the concentration of H_2O_2 for TS-1 samples 2 (small crystal size) and 5 (large crystal size).

Table 2
Effect of reaction parameters on propylene epoxidation[a]

H_2O_2 (mol/l)	Catalyst (g/l)	$P_{propylene}$ (MPa)	T (K)	$X_{H_2O_2}$ (%)	S_{PO} (%)	S_{MME} (%)
0.233	11.9	0.6	313	95.3	91.7	8.3
0.657	23.8	0.2	313	84.0	70.9	26.7
0.451	23.8	0.6	333	96.7	8.3	85.1
0.851	11.9	0.2	333	73.1	73.2	23.3
0.233	18.0	0.2	353	87.1	43.1	53.8
0.657	6.0	0.6	353	87.8	84.8	12.8
0.451	6.0	0.2	288	31.0	100.0	0
0.851	18.0	0.6	288	44.4	87.5	11.4
0.233	6.0	0.8	333	57.4	92.8	7.2
0.657	18.0	0.4	333	97.0	65.8	32.5
0.451	18.0	0.8	313	94.5	70.5	29.5
0.851	6.0	0.4	313	42.8	98.0	2.0
0.233	23.8	0.4	288	89.7	75.5	24.5
0.657	11.9	0.8	288	53.1	100.0	0
0.451	11.9	0.4	353	88.9	61.0	37.5
0.851	23.8	0.8	353	96.5	6.8	81.6

[a] Reaction conditions: reaction time 90 min, methanol as the solvent and sample 2 as the catalyst.

for epoxides are high, particularly in methanol, and are even superior to those of the corresponding olefins. According to the results, when methanol is used as the solvent, propylene is concentrated inside TS-1 micropores, so the initial rate is fast. While large amount of epoxides formed cannot diffuse instantly from the micropore of TS-1 with large crystal size at high concentrations, which leads to the deactivation of large crystal size TS-1. From the above results, it can be seen that the effect of crystal size on the activity of catalyst correlates with reaction conditions. Hence, it is important to select optimal reaction conditions.

3.2.2. The effect of reaction conditions

Since the effects of reaction parameters (such as reaction temperature, propylene pressure, the amount of catalyst and H_2O_2) on the reaction properties may be cross-correlated, cross-experimental design was then used to arrange the experiments to study the effect of reaction conditions on the epoxidation of propylene (see Table 2). The analysis of reaction data adopts the maximum–minimum criterion (Table 3).

The pressure of propylene in the range of 0.2∼ 0.8 MPa has a little effect on the conversion of H_2O_2, while the catalyst amount and the reaction temperature

Table 3
Analysis of data in Table 2

Assess criteria		H_2O_2 (mol/l)	Catalyst (g/l)	$P_{propylene}$ (MPa)	T (K)
$X_{H_2O_2}$ (%)	Tj_1[a]	329.5	219.0	275.2	218.2
	Tj_2[a]	311.1	310.4	318.4	316.6
	Tj_3[a]	321.9	323.0	324.2	324.2
	Tj_4[a]	256.8	366.9	301.5	360.3
	Rj[b]	72.7	147.9	49.0	142.1
S_{PO} (%)	Tj_1[a]	303.1	375.6	287.2	363.0
	Tj_2[a]	239.8	325.9	300.3	331.1
	Tj_3[a]	321.5	266.9	272.3	240.1
	Tj_4[a]	265.5	161.5	270.1	195.7
	Rj[b]	81.7	214.1	30.2	167.3

[a] Tj_K ($K = 1, 2, 3, 4$) means the total of four times assess criteria when the reaction parameter is number of K value in number of j row in Table 2.

[b] $Rj = \max\{Tj_K\}$—$\min\{Tj_K\}$.

have great influence on the catalytic properties during the epoxidation of propylene. The conversion of H_2O_2 increases with the increase of the amount of catalyst and of the reaction temperature, this shows that the higher reaction rate results from the increasing of the catalyst amount and the reaction temperature. The pressure of propylene has also a little effect on the selectivity of PO, while the reaction temperature shows greatly. With an increase in reaction temperature, the selectivity of PO decreases and the selectivity of ether, however, increases, showing the easier ring-opening reaction of PO at higher temperature. Considering the reaction rate and the selectivity of PO, it is proper to carry out the epoxidation at 313∼333 K. The results also show that the negative effect of the catalyst amount on the selectivity of PO. Through the cross experiments, the appropriate operating conditions are as follows: temperature, 313∼333 K; concentration of H_2O_2, 0.451 mol/l; pressure of propylene, 0.4 MPa; amount of catalyst, 11.9 g/l.

The effect of reaction time on the catalytic properties is shown in Fig. 4. It can be seen that, in the initial stage (<30 min), the conversion of H_2O_2 increases with reaction time. However, as the reaction time extend to a longer period, both the conversion of H_2O_2 and the distribution of the product will keep constant.

3.2.3. *Effect of reaction medium*

3.2.3.1. Effect of solvent. Methanol is usually employed as the solvent in the propylene epoxidation over TS-1 zeolite. The use of a large amount of methanol in the process, however, makes the increased energy consumption of the post-treatment. Thus, the effect of diluted methanol on propylene epoxidation has been considered.

The effect of the amount of water on the epoxidation of propylene with dilute H_2O_2 was listed in Table 4, it can be seen that, when 30 vol.% of methanol was replaced by water, the conversion of H_2O_2 does not change much, but the selectivity of PO decreases. When using 50 vol.% methanol, both the conversion of H_2O_2 and the selectivity of PO decrease, when using 100 vol.% water, the selectivity of PG increases drastically. The decrease in the activity is due to the low solubility of propylene in water, while the decrease in the selectivity of PO is due to the ring-opening reaction of PO with water. When the reaction mixture is adjusted by using an Na_2CO_3 solution, the selectivity of PO can be as high as 90%, but the activity is very low.

Table 4
Effect of the amount of H_2O on the epoxidation of propylene[a]

Water content (vol.%)	$X_{H_2O_2}$ (%)	S_{PO} (%)	S_{MME} (%)	S_{PG} (%)
4.7	96.9	91.6	8.4	0
36.5	96.0	78.1	16.5	5.4
44.4	95.5	70.2	20.6	9.2
52.4	79.8	57.7	26.3	16.0
68.3	66.4	64.8	18.1	17.1
100	44.0	21.3	0	78.7
100[b]	58.2	91.3	0	8.7

[a] Reaction conditions are the same as in Table 1 and sample 2 is used as the catalyst.

[b] Increase the amount of base.

Different solvents have a dramatic influences on the propylene epoxidation as shown in Table 5. The order of reactivity is as follows: methanol > ethanol > isopropanol > *n*-propanol > acetone ∼ water. This can be explained by the following: the activity of epoxidation of propylene in dilute H_2O_2 solution depends on the solubility of propylene in solvent, the competition between solvent oxidation and epoxidation of propylene, and the stability of formed intermediate (Fig. 6). When water is used as the

Table 5
Effect of different solvent on the epoxidation of propylene[a]

Solvent	$X_{H_2O_2}$ (%)	$U_{H_2O_2}$ (%)	S_{PO} (%)	S_{MME} (%)	S_{PG} (%)
Methanol	96.9	91.9	91.6	8.4	0
Ethanol	85.7	80.3	77.3	21.1	1.6
n-Propanol	52.9	81.1	79.3	20.7	0
Iso-propanol	77.5	55.7	85.6	9.1	5.3
Acetone	45.6	98.5	90.5	9.5	0
Water	44.0		21.3	78.7	0

[a] Reaction conditions are the same as in Table 1 and sample 2 is used as the catalyst.

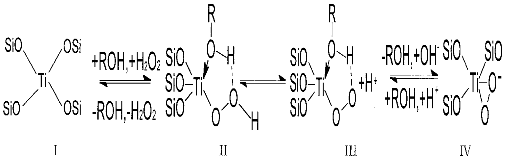

Fig. 6. Catalytic scheme of TS-1 reported by Clerici et al [14].

solvent, the disadvantages for the reaction is that the solubility of propylene in water is low (44.6 ml propylene gas per 100 ml of water at atmosphere pressure and 293 K) and, moreover, the reaction intermediate is a five-member cyclic active species structure, which is composed of a titanium hydroperoxo moiety Ti-OOH and a protic molecule ROH at Ti sites according to the proposal of Clerici et al. [14]. The stable five-member intermediate species II can activate the oxygen atom of H_2O_2, then transfer the oxygen atom to the organic substrate. When using water as the solvent, due to R=H, the active species II becomes unstable because of the poorer donor properties of the water ligand, therefore, the activity is low. When using alcohol as solvent, the solubility of propylene among them is apparently higher than that in water. The highest solution of propylene among them is methanol. It also should be kept in mind that there is a competition between epoxidation of propylene and oxidation of alcohol, the activity of oxidation of alcohol increases in the order: methanol $<$ ethanol $<$ n-propanol $<$ iso-propanol. Moreover, there is a steric effect in the five-ring active species structure. Steric crowding inside pores of 0.55 nm average diameter is strongly dependent on the nature of ROH and increases rapidly in the order: $CH_3 < C_2H_5 < n\text{-}C_3H_7 < i\text{-}C_3H_7$. Hence, species II are expected to be most stable, and therefore most easily formed with methanol ligand, as a result of small size and donor properties of the latter. Taking into consideration all these effect factors, methanol is the best solvent. When acetone is used as the solvent, the five-ring intermediate active species II will not be formed because no protic ligand is coordinated at Ti sites, so the conversion of hydrogen peroxide is also low. For the effect of alcohol solvent on the epoxidation, it also can be explained by partition coefficients [27]. Based on the sorption data measured by G. Langhendries et al., the high rates with TS-1 in methanol is due to the high intraporous propylene concentration and epoxidation by the Ti-OOH complex is faster in a methanol medium. With 1-PrOH as a solvent, the propylene concentration in TS-1 pores is lower, and consequently, epoxidation is much slower.

3.2.3.2. Effect of the acid–base property of the reaction medium. When using silica sol as the silicon source, the trace aluminum existing in the silica sol can also be incorporated into the framework, leading to the presence of acid sites for TS-1. The acid sites will result in the ring-opening reaction of PO to form MME or PG through acid catalysis. In order to improve the selectivity of PO, a base must be used to neutralize the existing acidity in TS-1. Here, Na_2CO_3 and $NH_3 \cdot H_2O$ were used as the neutralizers. Table 6 lists the effect of the pH value of the medium on propylene epoxidation by using Na_2CO_3 as the neutralizer.

Table 6
Effect of pH of the medium on the propylene epoxidation[a]

pH before reaction	pH after reaction	$X_{H_2O_2}$ (%)	$U_{H_2O_2}$ (%)	S_{PO} (%)	S_{MME} (%)
4.42	4.66	98.5	96.4	5.1	91.9
6.60	5.28	99.3	95.4	41.9	54.7
8.56	5.61	97.6	91.2	70.8	29.2
9.66	5.92	98.4	92.6	78.2	21.8
10.29	6.56	97.9	89.1	90.7	9.3
10.66	6.78	87.8	87.0	93.9	6.1
10.72	7.12	71.8	82.1	91.4	8.6

[a] Reaction conditions are the same as in Table 1 and sample 2 is used as the catalyst.

It can be seen that the main product is MME in the acidic medium, and the addition of adequate amount of base increases the selectivity of PO. When a large amount of base was used, both the conversion and the utilization of H_2O_2 decrease. This phenomenon can be explained from the five-ring active species proposed by Clerici et al. [14]. Exchange reactions between species II with metal salts produce anionic derivatives with reduced electrophilic power. Maximum and minimum concentrations of species II are achieved in acid and basic solutions, respectively. On the other hand, the decomposition of H_2O_2 in a basic medium also leads to the low utilization of H_2O_2. Hence, in the epoxidation of propylene, it is important to control the pH value of the medium, because it has a great effect on the activity of the catalyst as well as the product distribution.

3.2.4. Aging tests

Although TS-1 can be synthesized using TPABr as the template, the cost of the TS-1 product is still quite high, so the lifetime of the catalyst is the critical to decide whether it can be used in the

Table 7
Aging tests on TS-1 catalyst with less basic additive added in every run[a]

Times	$X_{H_2O_2}$ (%)	$U_{H_2O_2}$ (%)	S_{PO}%	Na_2CO_3 content (mol/l)
1	98.0	96.4	5.1	0
2	90.0	99.8	25.3	0
3	93.9	97.9	34.5	0
4	36.0	86.0	85.8	0.042
5[b]	71.0	88.5	94.9	0
6	90.3	99.0	92.5	0
7	97.4	85.7	88.0	0
8	97.7	90.8	82.0	0
9	97.5	89.8	78.0	0
10	89.3	84.5	89.3	0.007
11	96.7	96.2	88.7	0
12	97.1	97.5	84.7	0
13	95.5	96.6	78.5	0
14	89.8	85.9	90.8	0.007
15	98.9	94.0	89.4	0.003
16	92.6	92.5	93.3	0.003
17	95.7	91.3	92.3	0.002
18	94.0	92.3	94.0	0.002
19	94.8	95.3	94.0	0.002
20	91.5	92.8	94.4	0.002
21	94.2	91.7	93.9	0

[a] Reaction conditions: reaction temperature is 60 °C, reaction time is 90 min, the concentration of H_2O_2 is 0.474 mol/l, the concentration of catalyst (sample 2) is 12.09 g/l, and methanol is used as solvent. In every run, the catalyst was centrifuged from the reaction mixture and used as the catalyst of next run directly except fifth run.

[b] The catalyst was washed with water.

Table 8
Epoxidation of propylene over TS-1[a]

Reaction times	$X_{H_2O_2}$ (%)	$U_{H_2O_2}$ (%)	S_{PO} (%)	S_{MME} (%)
1	96.4	93.1	89.0	11.0
2	45.9	83.5	93.0	7.0
3	30.8	73.9	100	0

[a] Equal amount of basic additive was added in every run, but the catalyst (sample 2), after the first use, was filtered, then used in the second run directly; after the second run, the catalyst was filtered and used in the third run directly. In the second and the third run, the catalyst was not calcined or washed with methanol before use. Reaction conditions are the same as in Table 1 except that the concentration of Na_2CO_3 is 1.25×10^{-3} mol/l.

industry. In this work, aging tests on TS-1 were carried out with the repeated batch experiments on a catalyst without regeneration. Table 7 shows the results of aging tests on TS-1. It can be seen that, after catalyst was tested repeatedly for three times without regeneration, the conversion and the utilization of H_2O_2 still remain high, the selectivity of PO, however, increases to less than 50%. After the addition of adequate amount of Na_2CO_3, the selectivity of PO increases from 34.5 to 85.8%, while the conversion and the utilization of H_2O_2 is kept constant. If the basicity is suitable, the catalyst will not be deactivated after using 20 times.

When the excess amount of Na_2CO_3 is added during the aging tests, the selectivity of PO increases a little, but the activity of TS-1 decreases dramatically as shown in Table 8. After the catalyst is collected, the activity of the catalyst cannot be reproduced completely no matter it was directly soaked into methanol, or soaked into methanol after drying, or directly calcined at 813 K (Fig. 7). In some cases, the activity of the catalyst decreases to half of that of the original. If no base was added in the reaction mixture, although the selectivity of the catalyst is low, the activity is high and the catalyst can be used for many times without regeneration. Moreover, the activity of used catalyst can be recovered by washing with dilute acid. Hence, the deactivation of the catalyst is caused by high content of Na^+ precipitating in the catalyst, resulting from adding repeatedly equivalent molar of base to the medium. Thus, the activity of the catalyst cannot be fully recovered by washing with methanol or calcinating at about 813 K.

Taking into account the disadvantage of using Na_2CO_3 as the neutralizer, epoxidation of propylene was carried out using ammonium water as the neutralizer. The tests show that even the catalyst deactivates in the excess amount of ammonium water, the activity of the used catalyst can be simply regenerated by calcinating at about 813 K. Thus, the long-run test has been carried out in fixed-bed reactor to examine the effect of ammonium water as the neutralizer. In order to eliminate the effect of heat from the reaction itself, the catalyst was prepared by spraying TS-1 on the inert small ball with diameter of about 1–2 mm. From the result shown in Fig. 8, it can be seen that, after 200 h, the selectivity of PO still keeps at about 90%, the conversion and the utilization of H_2O_2 keep at about 95%.

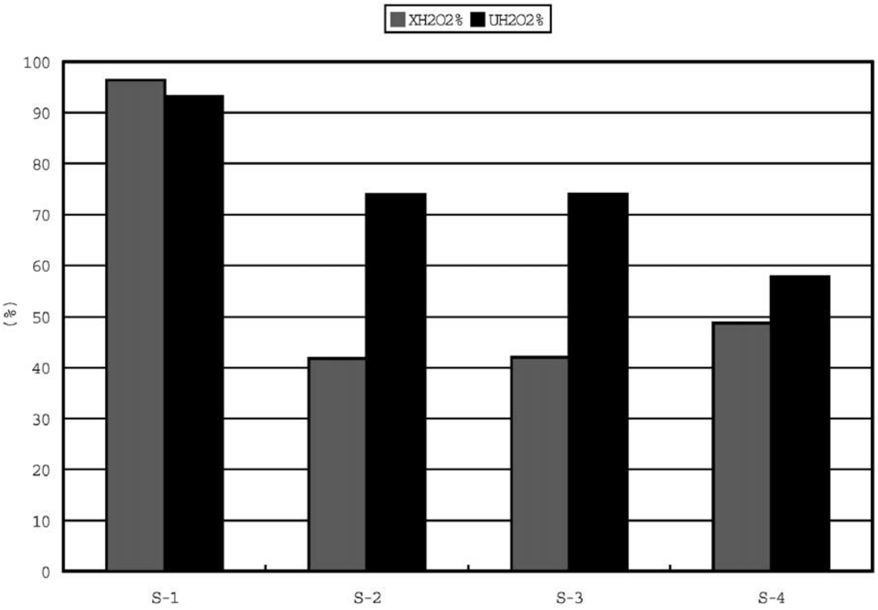

Fig. 7. Regeneration of TS-1. (1) S-1, the original catalyst; (2) S-2, the recovered catalyst was treated with methanol at room temperature for 72 h; (3) S-3, the recovered catalyst was dried and treated with methanol at 333 K for 72 h; (4) S-4, the recovered catalyst was calcined at 813 K. Reaction conditions are the same as in Table 8.

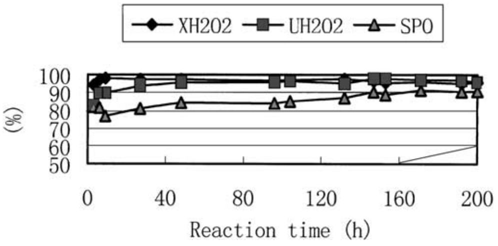

Fig. 8. Long-run test of the catalyst for epoxidation of propylene (sample 3). Reaction conditions: solvent methanol, temperature 323 K, H_2O_2 concentration 0.85 mol/l, pressure 3.0 MPa, total WHSV 0.609 h^{-1}, propylene/H_2O_2 (molar ratio) 4.17. The concentration of ammonia additive: 0∼9 h, 0.2 mM, 9∼80 h, 0.4 mM, 80∼200 h, 0.5 mM.

4. Conclusion

TS-1 has been successfully synthesized in a 100 l stainless-steel autoclave. The results of various kinds of characterization techniques show that the synthesized TS-1 has large crystal size (about 6 μm × 2 μm × 1 μm), the amount of titanium incorporated into the framework may be less than that of the TS-1 synthesized by the conventional method. However, it exhibits high activity in the epoxidation of propylene. Stirring vigorously and increasing the reaction time can decrease the effect of crystal size on the catalytic properties. Methanol is a preferable solvent, and the addition of adequate amount of water to the medium does not influence the reaction activity. The proper pH value is important for the epoxidation of propylene. The synthesized TS-1 does not deactivate after use for 20 times. In the fixed-bed reactor, the catalyst can keep high activity and selectivity when using ammonium water as the neutralizer.

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