Characterization and catalytic activity of hydrothermally treated TS-1/SiO_2 in propylene epoxidation

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The object of this work is to study the effect of hydrothermal treatment on the TS-1/SiO_2 catalyst in propylene epoxidation in fixed bed. The TS-1/SiO_2 catalysts before and after hydrothermal treatment were characterized by means of XRD, XRF, BET, UV–Vis and EPR techniques. It was found by EPR characterization that two types of Ti(IV)-superoxide radicals, A ($g_z = 2.0271$; $g_y = 2.0074$; $g_x = 2.0010$) and B ($g_z = 2.0247$; $g_y = 2.0074$; $g_x = 2.0010$), were observed for the TS-1/SiO_2 catalyst. The superoxo species A was converted to B after the TS-1/SiO_2 catalyst was hydrothermally treated. The results show that hydrothermal treatment temperature and time have marked effects on the activity and the PO selectivity. The optimal hydrothermal treatment temperature and time are 170 and 4 h, respectively. In the long-term propylene epoxidation reaction, about 95% H_2O_2 conversion and above 94% PO selectivity are obtained over TS-1/SiO_2 catalyst hydrothermally treated at 170 °C for 4 h.

KEY WORDS: hydrothermal treatment; TS-1/SiO_2; propylene epoxidation; EPR; radical.

1. Introduction

A global research effort is under way to replace environmentally problematic liquid or halide-containing solid acids with environmentally friendly materials. Propylene oxide (PO) is an important chemical product. The conventional route for epoxidation of propylene involving the use of chlorine and lime produces much pollution. Although Halcon developed a commercial process for the manufacture of PO on the basis of the patent of Kollar [1] , a large amount of side products such as *t*-butyl alcohol or styrene were coproduced in the process accompanying PO. The invention of titanium silicalite-1 (TS-1) by Taramasso et al. [2] offers a clean and economically alternative to existing processes, therefore PO can be produced at near room temperature in the system of TS-1/ H_2O_2/CH_3OH [3]. The expensive TPAOH used in the above report makes TS-1 synthesis rather costly and therefore the synthesis of TS-1 using less expensive tetrapropylammonium bromide (TPABr) as the template has been systematically investigated [4–7]. TS-1 synthesized by using TPABr as the template also exhibits good performance in propylene epoxidation using hydrogen peroxide as the oxidant [8–10]. Industrial catalysts which are used in fixed bed must be formed using a binder into pellets or extrudates. However, the performance of the extruded catalyst is not satisfactory. Either low activity or low PO selectivity restrains its industrial application. Attempts have been made to improve selectivity of epoxides by adding neutral or acidic salts, but a lot of alkali metals such as Na^+[11], K^+[12] or Ca^+[13] result in the loss of activity. Therefore, the objective of the present work is to find a way to increase the activity of the TS-1/SiO_2 catalyst while keeping the high selectivity.

It is known that hydrothermal treatment is an effective method to tailor catalytic properties. Thus, the effect of hydrothermal treatment on the TS-1/SiO_2 catalyst is systematically studied in propylene epoxidation in fixed bed in the present paper.

2. Experimental

2.1. Preparation of the samples

TS-1 was hydrothermally synthesized using colloidal silica (26 wt%) and titanium tetrachloride dissolved in iso-propyl alcohol as silicon and titanium source, respectively. TS-1 samples crystallized from gels with the following molar composition:

$$SiO_2{-}aTiO_2{-}bC_2H_5N{-}cTPABr{-}dH_2O,$$

where $0.01 < a < 0.03$, $0.5 < b < 3.0$, $0.1 < c < 0.3$, $20 < d < 60$. TS-1 synthesized using TPABr as the template was added as the seeds at the level of 5–10% (based on SiO_2 content of the solution). The gel was transferred into the autoclave and heated for 28–40 h at 150–180 °C. The solid obtained was filtered, washed with distilled water, dried at 100 °C and calcined at 540 °C in static air. The ratio of SiO_2/TiO_2 was 45.7.

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The $TS\text{-}1/SiO_2$ catalyst was prepared through mixing TS-1 with colloidal silica as a binder ($TS\text{-}1{:}SiO_2 = 8{:}2$), extruding, drying and calcining. Hydrothermal treatment was carried out in an autoclave. In a typical processing, 15 g $TS\text{-}1/SiO_2$ catalyst and 50 mL deionized water were charged into the autoclave and sealed. Then the autoclave was heated to 170 °C and kept 4 h. After hydrothermal treatment, the catalyst was washed with deionized water, dried at 120 °C for 2 h and calcined at 540 °C for 4 h. The samples were abbreviated as HT-TS.

2.2. Characterization of the samples

X-ray diffraction patterns were obtained on a D/max-2400 diffractometer using CuKα radiation. The elemental analysis of the samples was obtained on a Bruker SRS 3400x spectrometer. BET sorption of N_2 was measured using a Quantachrome AUTOSORB-1 apparatus. UV-Vis measurements were performed on a Jasco V-550 by using the diffuse reflectance technique in the range 190–400 nm, and MgO was used as the reference. The EPR spectra of samples were recorded on a JES-FEIXG EPR spectrometer operating at X-band frequency and 100 kHz field modulation. EPR spectra of 77 K were observed using a liquid Nitrogen Dewar. The signals of g_3 and g_4 of Mn^{2+} in MgO powder (see Figure 3) were used as standard sample. For the EPR measurement, to a sample of solid $TS\text{-}1/SiO_2$ catalyst (0.2 g), 0.5 mL solvent (methanol : 30% H_2O_2(v/v) = 1 : 1) was added.

2.3. Catalytic test

Propylene epoxidation was carried out in a stainless-steel fixed-bed microreactor. The amount of catalyst used in the reaction was 6 g. The typical conditions were as follow: solvent, methanol : acetone (v/v) = 1 : 3; reaction temperature, 45 °C; the initial H_2O_2 concentration, 0.85 mol/L; propylene : H_2O_2 (molar ratio) = 3 : 1; pressure, 3.0 MPa; the WHSV of propylene, 0.5 h^{-1}. The residual H_2O_2 was checked by iodometric titration. The products of the reaction were analyzed on a 1102 gas chromatograph, using a flame ionization detector and a capillary column (30 m × 0.25 mm, polyethylene glycol 20 M). PO was the main product. Propylene glycol (PG) and its monomethyl ethers (MME) were the by-products. The result of the reaction was given using these criteria:

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

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

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

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

The experimental errors of the H_2O_2 conversion and the PO selectivity were within 1% and 2%, respectively.

3. Results and discussion

3.1. Characterization of the $TS\text{-}1/SiO_2$ catalysts before and after hydrothermal treatment

The catalytic properties of the $TS\text{-}1/SiO_2$ catalysts before and after hydrothermal treatment in the propylene epoxidation are shown in table 1. It can be seen that the catalytic activity of hydrothermally treated $TS\text{-}1/SiO_2$ catalyst is higher than that of the untreated $TS\text{-}1/SiO_2$ catalyst. Figure 1 shows XRD spectra of the $TS\text{-}1/SiO_2$ catalysts before and after hydrothermal treatment. From figure 1, it can be seen that the crystalline structure and the relative crystallinity do not change after hydrothermal treatment, which indicates that the activity increase is not due to increase of relative crystallinity. Table 2 shows the BET surface

Table 1
Performance of the $TS\text{-}1/SiO_2$ catalysts before and after hydrothermal treatment

Sample	$X_{H_2O_2}$ (%)	S_{PO} (%)	S_{MME} (%)	$U_{H_2O_2}$ (%)
HT-0	90.48	95.78	3.01	81.22
HT-170	95.99	91.83	4.97	91.35

Reaction condition: solvent, methanol : acetone(v/v) = 1 : 3; the initial H_2O_2 concentration, 0.85 mol/L; reaction temperature, 60 °C WHSV of propylene, 0.5 h^{-1}; pressure, 3.0 MPa; $n(C_3H_6)/n(H_2O_2)$ = 3/1.

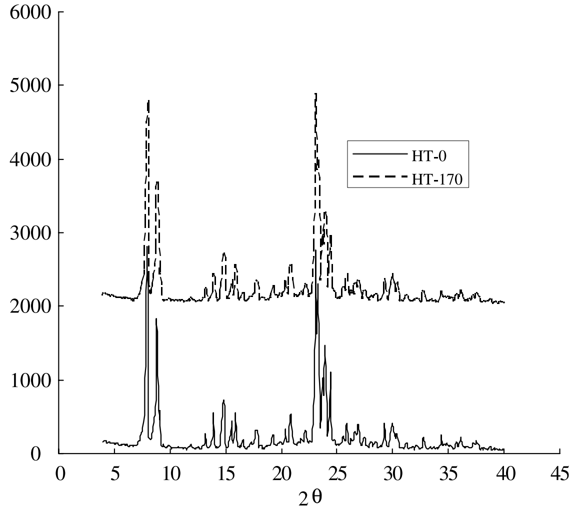

Figure 1. XRD spectra of the $TS\text{-}1/SiO_2$ catalysts before and after hydrothermal treatment.

Table 2
BET surface properties of the TS-1/SiO_2 catalysts before and after hydrothermal treatment

Sample	Surface area (m^2/g)	Total pore volume (cc/g)
HT-0	317.5	0.2682
HT-170	288.3	0.2631

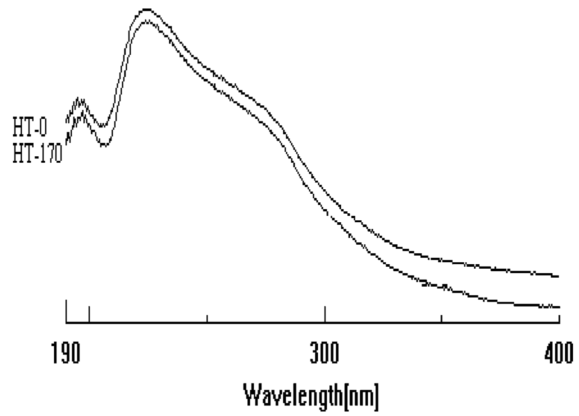

Figure 2. UV-Vis spectra of the TS-1/SiO_2 catalysts before and after hydrothermal treatment.

properties of the TS-1/SiO_2 catalysts before and after hydrothermal treatment. The surface area decreases from 317.5 to 288.3 m^2/g and total pore volume changes little after hydrothermal treatment. Moreover, there is not distinct difference in UV–Vis spectra of the TS-1/SiO_2 catalysts before and after hydrothermal treatment (figure 2), while there is little difference in elemental analysis of the TS-1/SiO_2 catalysts before and after hydrothermal treatment (table 3). So the activity increase is not due to the increase of surface area or the removal of the extra-framework Ti species.

Table 3
Elemental analysis of the TS-1/SiO_2 catalysts before and after hydrothermal treatment

Sample	Composition		
	TiO_2 (wt%)	SiO_2 (wt%)	Na_2O (wt%)
HT-0	2.45	97.26	0.29
HT-170	2.44	97.31	0.25

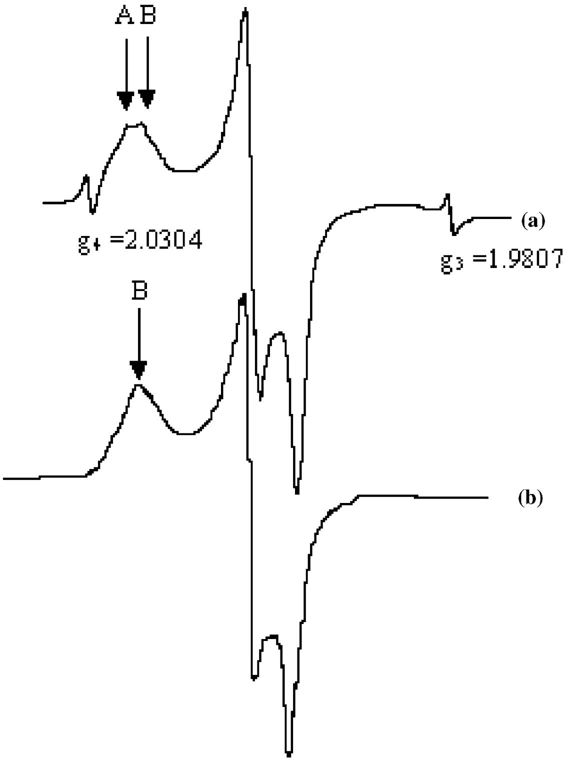

Figure 3. EPR spectra of the TS-1/SiO_2 catalysts before (a) and after hydrothermal treatment (b) after interaction with aqueous H_2O_2. (The signal of g_3(1.9807) and g_4(2.0304) wear one of Mn^{2+} in MgO powder.)

Figure 3(a) and (b) show the EPR spectra of the TS-1/SiO_2 catalyst before and after hydrothermal treatment, respectively. Activation of H_2O_2 by isolated Ti centers form three types of oxo-titanium species *viz.* Ti(IV)-peroxide, -hydroperoxide and -superoxide which are found to be active in oxidations catalyzed by titanosilicates. Among these, Ti(IV)-superoxide species is detected in EPR due to its paramagnetic nature and is also said to bring about the epoxidation reactions [14, 15]. In figure 3, there is a striking difference between the EPR spectra of these two samples. Two types of Ti(IV)-superoxide radicals: A and B (curve a) are observed for the TS-1/SiO_2 catalyst, while only one type of -superoxide radical B is observed for hydrothermally treated TS-1/SiO_2 catalyst. Species A and B differ only in g_z parameter (for A: $g_z = 2.0271$; $g_y = 2.0074$; $g_x = 2.0010$ and for species B: $g_z = 2.0247$; $g_y = 2.0074$; $g_x = 2.0010$) while in case of curve b, species A is totally absent with EPR parameters as ($g_z = 2.0271$; $g_y = 2.0074$; $g_x = 2.0010$). From the results in table 3, it can be seen that the composition of the TS-1/SiO_2 catalyst does not change after hydrothermal treatment, which indicates that Ti species are not removed from the framework. So the difference in EPR signals of the TS-1/SiO_2 catalysts before and after hydrothermal treatment could indicate that superoxo species A was converted to B. Chaudhari et al. [16] investigated the interaction of TS-1 with H_2O_2 (Figure 4). TS-1 showed no EPR signal revealing a +4 oxidation state of Ti in the silicate structures. They found three types of Ti(IV)-superoxide radical species (A, B, and C, respectively) after the interaction of TS-1 with H_2O_2 in EPR spectra (Figure 4). They concluded that Ti(IV) ions in species A and C possessing a tetrahedral geometry before the interaction with H_2O_2 expand their geometry to sixfold coordination after the interaction and the Ti sites of

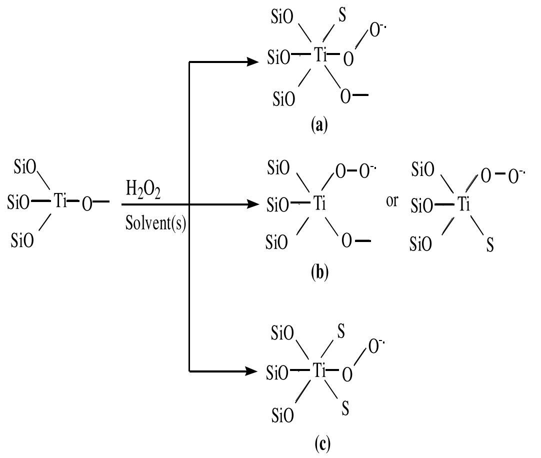

Figure 4. Tentative structure of Ti(IV) species before and after the interactions with H_2O_2[16].

species B expand their coordination geometry from tetrahedral to pentacoordination after the interaction. The species A and B were detected in our TS-1/SiO_2 catalyst. As the species B is more stable than A, pentacoordination of superoxide radical species (species B) leads to higher activity.

3.2. *Effects of hydrothermal treatment conditions*

3.2.1 *Effect of hydrothermal treatment temperature*

Table 4 shows the performance of the TS-1/SiO_2 catalyst hydrothermally treated at different temperature for 4 h in the propylene epoxidation. From table 4 it can be seen that the H_2O_2 conversion increases with increasing hydrothermal treatment temperature, while the PO selectivity changes little. When the hydrothermal treatment temperature rises up to 170 °C, the H_2O_2 conversion reaches a maximum. As the hydrothermal treatment temperature further increases, the H_2O_2 conversion does not change. More and more sixfold coordination of Ti(IV)-superoxide radical species may be converted to pentacoordination of Ti(IV)-superoxide radical species after interaction of the TS-1/SiO_2 catalyst with aqueous H_2O_2 with increase of hydrothermal treatment temperature. So the TS-1/SiO_2 catalyst hydrothermally treated at higher temperature has higher activity

Table 5
Performance of TS-1/SiO_2 hydrothermally treated at different time

Hydrothermal treatment time (h)	$X_{H_2O_2}$ (%)	S_{PO} (%)	S_{MME} (%)	$U_{H_2O_2}$ (%)
4	95.99	91.83	4.97	91.35
12	96.62	91.24	5.37	91.72
24	94.32	82.00	11.81	91.51
40	93.30	66.95	20.25	92.10

Reaction condition: solvent, methanol : acetone(v/v) = 1 : 3; the initial H_2O_2 concentration, 0.85 mol/L; reaction temperature, 60 °C WHSV of propylene, 0.5 h^{-1}; pressure, 3.0 MPa; $n(C_3H_6)/n(H_2O_2)$ = 3/1; catalyst, TS-1/SiO_2 hydrothermally treated at 170 °C.

3.2.2. *Effect of hydrothermal treatment time*

Table 5 shows the performance of the TS-1/SiO_2 catalyst hydrothermally treated at 170 C for different time in the propylene epoxidation. The performance of the TS-1/SiO_2 catalyst treated for 12 h is almost same as that of the catalyst treated for 4 h. However, hydrothermal treatment for a long time (> 12 h) leads to the drastic decrease of the PO selectivity. The presence of protic solvents with a high degree of polarity (e.g., water) generates acidity on active Ti-centers in titanium-silicate molecular sieves [17–20]. More acid sites are generated on active Ti-centers of the TS-1/SiO_2 catalyst in the presence of water as hydrothermal treatment time exceeds 12 h. More acid sites exist on the surface of the catalyst, more monomethyl ethers and glycol are produced by PO reacting with methanol and water. So the PO selectivity decreases with hydrothermal treatment time exceeding 12 h.

3.2.3. *Effect of hydrothermal treatment times*

Table 6 shows the performance of the TS-1/SiO_2 catalyst hydrothermally treated for four times in the propylene epoxidation. The performance of the TS-1/SiO_2 catalyst hydrothermally treated for four times is

Table 4
Performance of TS-1/SiO_2 hydrothermally treated at different temperature

Sample	$X_{H_2O_2}$ (%)	S_{PO} (%)	S_{MME} (%)	$U_{H_2O_2}$ (%)
HT-120	91.32	98.12	1.44	84.42
HT-140	93.02	97.99	1.78	87.33
HT-170	95.34	97.97	1.58	89.03
HT-190	95.13	98.25	1.52	88.57

Reaction condition: solvent, methanol : acetone(v/v) = 1 : 3; the initial H_2O_2 concentration, 0.85 mol/L; reaction temperature, 45 °C; WHSV of propylene, 0.5 h^{-1}; pressure, 3.0 MPa; $n(C_3H_6)/n(H_2O_2)$ = 3/1; catalyst, TS-1/SiO_2 hydrothermally treated for 4 h.

Table 6
Performance of the TS-1/SiO_2 catalyst hydrothermally treated for different times

Hydrothermal treatment times	$X_{H_2O_2}$ (%)	S_{PO} (%)	S_{MME} (%)	$U_{H_2O_2}$ (%)
1	95.34	97.97	1.58	89.03
2	95.27	97.39	1.93	86.13
3	96.51	97.34	2.09	81.33
4	95.09	96.81	2.50	86.44

Reaction condition: solvent, methanol : acetone(v/v) = 1 : 3; the initial H_2O_2 concentration, 0.85 mol/L; reaction temperature, 45 ; WHSV of propylene, 0.5 h^{-1}; pressure, 3.0 MPa; $n(C_3H_6)/n(H_2O_2)$ = 3/1;catalyst, TS-1/SiO_2 hydrothermally treated at 170 for 4 h

Table 7
Effect of space velocity of propylene

Space velocity (h^{-1})	$X_{H_2O_2}$ (%)	S_{PO} (%)	S_{MME} (%)	$U_{H_2O_2}$ (%)
0.4	95.08	98.27	1.57	90.39
0.5	95.34	97.97	1.58	89.03
0.6	92.21	98.22	1.5	88.40
0.7	87.65	98.26	1.40	93.53

Reaction condition: solvent, methanol : acetone(v/v) = 1 : 3; the initial H_2O_2 concentration, 0.85 mol/L; reaction temperature, 45 ; pressure, 3.0 MPa; $n(C_3H_6)/n(H_2O_2)$ = 3/1; catalyst, TS-1/SiO_2 hydrothermally treated at 170 for 4 h

Table 8
Effect of reaction temperature

Reaction temperature (°C)	$X_{H_2O_2}$ (%)	S_{PO} (%)	S_{MME} (%)	$U_{H_2O_2}$ (%)
40	91.23	97.98	1.38	85.88
45	95.34	97.97	1.58	89.03
50	95.62	96.81	2.35	88.06
60	95.99	91.83	4.97	91.35
65	97.61	77.63	15.89	72.05

Reaction condition: solvent, methanol : acetone(v/v) = 1 : 3; the initial H_2O_2 concentration, 0.85 mol/L; WHSV of propylene, 0.5 h^{-1}; pressure, 3.0 MPa; $n(C_3H_6)/n(H_2O_2)$ = 3/1;catalyst, TS-1/SiO_2 hydrothermally treated at 170 for 4 h.

the nearly same as that hydrothermally treated for one times. It means that hydrothermal treatment times has little effect on the performance of the TS-1/SiO_2 catalyst in the propylene epoxidation.

3.3. Effects of reaction conditions

3.3.1. Effect of space velocity of propylene

Effect of space velocity of propylene on the performance of hydrothermally treated TS-1/SiO_2 catalyst is shown in table 7. When space velocity of propylene is between 0.4 and 0.5 h^{-1}, the H_2O_2 conversion does not change. As space velocity of propylene further increases, the H_2O_2 conversion decreases gradually. So the suitable space velocity of propylene is 0.5 h^{-1}.

3.3.2. Effect of reaction temperature

Effect of reaction temperature on the performance of hydrothermally treated TS-1/SiO_2 catalyst is shown in table 8. From results in table 8, it can be seen that when reaction temperature increases from 40 to 45 °C, the H_2O_2 conversion increases from 91.23% to 95.34%. When reaction temperature is between 45 and 50 °C, the performance of the catalyst barely changes. However, as reaction temperature increases, the PO selectivity decreases. For example, the PO selectivity decreases from 97.98% to 77.63% as reaction temperature increases from 40 to 65 °C. Therefore, the suitable reaction temperature is 45 °C.

3.4. Long-term stability of hydrothermally treated TS-1/SiO_2 catalyst

Propylene epoxidation over the TS-1/SiO_2 catalyst hydrothermally treated at 170 °C for 4 h was carried out in a fixed bed reactor for a period of 300 h. The results are shown in figure 5. It can be seen that the TS-1/SiO_2 catalyst hydrothermally treated at 170 °C for 4 h exhibits very high activity and stability in propylene

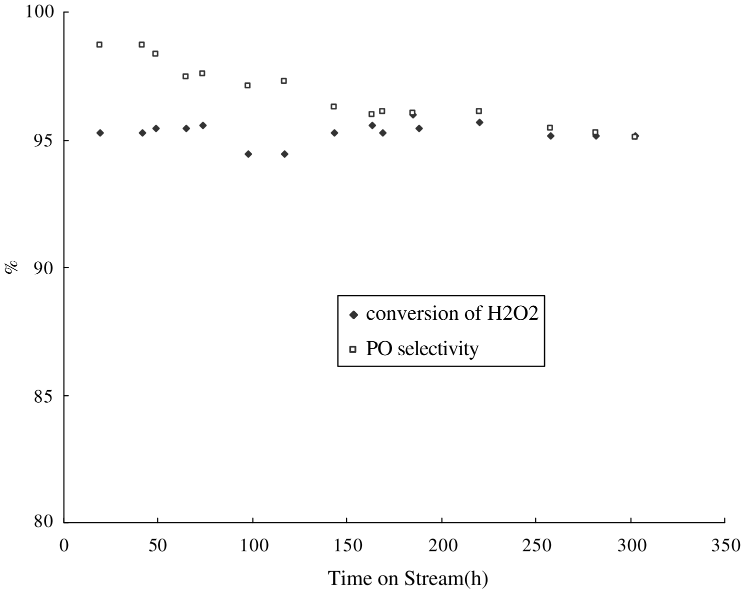

Figure 5. The stability of TS-1/SiO_2 catalyst hydrothermally treated at 170 C for 4 h in propylene epoxidation. (Reaction condition: solvent, methanol : acetone(v/v) = 1 : 3; the initial H_2O_2 concentration, 0.85 mol/L; reaction temperature, 45 C; WHSV of propylene, 0.5 h^{-1}; pressure, 3.0 MPa; $n(C_3H_6)/n(H_2O_2)$ = 3/1; catalyst, TS-1/SiO_2 hydrothermally treated at 170 C for 4 h.

epoxidation. The H_2O_2 conversion maintains about 95% during the long-term propylene epoxidation reaction. Meanwhile, the catalyst has very high initial PO selectivity and displays slightly slow decrease of the PO selectivity in the reaction course. But the PO selectivity maintains above 94% in 300 h.

4. Conclusion

Hydrothermal treatment makes the activity of TS-1/SiO_2 catalyst increase. The key factors are hydrothermal treatment temperature and time. The optimal hydrothermal treatment temperature and time are 170 °C and 4 h, respectively. Over the TS-1/SiO_2 catalyst hydrothermally treated at 170 °C for 4 h, about 95% H_2O_2 conversion and above 94% PO selectivity are obtained during the long-term propylene epoxidation reaction. An EPR study of the TS-1/SiO_2 catalysts before and after hydrothermal treatment shows the conversion of the superoxo species A ($g_z = 2.0271$; $g_y = 2.0074$; $g_x = 2.0010$) to B ($g_z = 2.0247$; $g_y = 2.0074$; $g_x = 2.0010$) leading to a higher activity of the hydrothermally treated TS-1/SiO_2 catalyst.

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