Regeneration of lamina TS-1 catalyst in the epoxidation of propylene with hydrogen peroxide

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The deactivation and regeneration of the lamina titanium silicalite (TS-1) catalyst for the epoxidation of propylene with dilute H_2O_2 was investigated in a fixed-bed reactor. In the scale-up experiment, the dosage of the lamina TS-1 catalyst is 2.5 kg, after 1000 h reaction the catalyst still exhibits good performance and further increases the reaction time, the conversion of H_2O_2 begins to decrease. TG and BET analyses of the deactivated catalysts show that the main species occluded within the zeolite pore are propylene oxide oligomers, and these species occupying the active Ti site and blocking the pores of the lamina TS-1 are the main reason for the deactivation of catalyst. The deactivated catalyst can be regenerated by different regeneration methods. The activity of deactivated catalysts regenerated by dilute H_2O_2 or heat treatment by using air or nitrogen as a calcination media can be fully recovered, but a decline in propylene oxide (PO) selectivity of the regenerated catalyst has been observed during the first hours of reaction. However, water vapor treatment of the deactivated catalyst can improve the PO selectivity with the same activity as that of the fresh lamina TS-1 catalyst.

KEY WORDS: propylene, propylene oxide, epoxidation, lamina TS-1, deactivation, regeneration.

1. Introduction

Propylene oxide (PO) is one of the most important chemical feedstocks for producing polyether polyol polymers, such as polyurethane. Commercially, PO is manufactured by either the chlorohydrin or co-production (Halcon) routes [1]. The chlorohydrin route generates chlorinated by-products, mainly dichloropropane and $CaCl_2$. The co-production route [2] is capital intensive and its economics is linked to the economic fortunes of the by-products namely styrene or *tert*-butyl alcohol. Since 1983, the invention of titanium silicate-1 (TS-1) by Taramasso *et al.* [3] opened a new route for the selective oxidation, such as phenol hydroxylation [4], olefins epoxidation [5], cyclohexanone ammoximation [6], alkane oxidation [7], oxidation of ammonia to hydroxylamine [8], secondary amines to dialkylhydroxyl-amines [9]. It is noteworthy that in the epoxidation of propylene with H_2O_2, high H_2O_2 conversion and high selectivity to PO can be obtained over TS-1 under mild conditions. Moreover, it is an environment friendly method, whose by-product is H_2O. Therefore, the epoxidation of propylene catalyzed by TS-1 has been investigated in more detail recently [5,10].

Although TS-1 exhibits excellent catalytic performance in the propylene epoxidation, the deactivation of the catalysts occurs with time on stream [11]. Therefore, regeneration of the deactivated catalyst would be greatly preferred. At present, the regeneration methods of deactivated TS-1 are mainly focused on: (1) heat treatment at higher temperature in the presence of different media, such as air, vapor and inert gas; the regeneration temperature is from 300 to 700 °C [12–16]; (2) oxidation by dilute H_2O_2, and the regeneration temperature is lower than 100 °C [17–19]; (3) extraction by different solvents, and methanol is preferred; the regeneration temperature is from 140 to 240 °C [20–22].

Our previous study shows that the lamina TS-1 catalyst exhibits good catalytic performance [10]. In this paper, stability of lamina TS-1 in the propylene epoxidation has been investigated, and the deactivated catalysts is characterized by TGA, BET and FT-IR. At the same time, the deactivated lamina TS-1 catalysts were regenerated with different methods.

2. Experimental

2.1. Catalyst preparation

Titanium silicalite (TS-1) was prepared according to the literature [23]. The lamina TS-1 catalyst was made by spraying the mixture of powdery TS-1 and bond on the small inert ceramic balls whose diameter is in the range of 1 to 3 mm [24]. The obtained lamina TS-1 catalyst was dried at 120 °C for 3 h and calcined at 540 °C for 5 h.

2.2. Catalyst characterization

The thickness of the TS-1 lamina in the catalyst was determined on a Japan JEM-1200EX scanning electron microscope (SEM) after some catalyst particles were smashed into pieces. FT-IR spectra were recorded on a

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Nicolet FT-5DX spectrophotometer using KBr wafer technique. TGAwas performed in a thermogravimetric analyzer (Mettler-Toledo TGA/SDTA851^e) with a nitrogen flow rate of 40 mL/min. The sample was heated from ambient temperature to 600 °C with a heating rate of 20 °C/min. Pore distribution was obtained on an USA Quantachrome AUTOSORB-1 autosorber using BET method.

2.3. Catalyst test

The epoxidation of propylene was carried out in a fixed-bed reactor [25]. The reaction conditions of the scale-up experiment are as follows: the amount of catalyst, 2.5 kg; solvent, methanol; reaction temperature, 45–65 °C; the mixed feeding amount of methanol and hydrogen peroxide, 2.5 kg/h; the molar ratio of MeOH to H_2O_2 is 22; the feeding amount of propylene, 0.4 kg/h; the molar ratio of C_3H_6 to H_2O_2 is 3; pressure, 3.0 MPa; the total weight hour space velocity (WHSV) is 1.16 h^{-1} and WHSV(C_3H_6) is 0.16 h^{-1}.

The typical reaction conditions in lab are as follows: the amount of catalyst, 8 g; solvent, methanol; reaction temperature, 60 °C; the molar ratio of MeOH to H_2O_2 is 23.6; the molar ratio of C_3H_6 to H_2O_2 is 4.17; pressure, 3.0 MPa; WHSV(C_3H_6), 0.2 h^{-1}.

The residual H_2O_2 was measured by iodometric titration. The products of reaction were analyzed on a SHIMADZU GC-8A gas chromatography using a flame ionization detector and a polyethylene glycol 20 M column (40 m × 0.25 mm). Propylene oxide is the main product. Propylene glycol (PG) and its mono-methyl ethers (MMEs) are the by-products.

Results of the reaction were given by these criteria:

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

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

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

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

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

3. Results and discussion

3.1. The catalytic performance of propylene epoxidation over lamina TS-1 in the scale-up experiment

Figure 1 shows the SEM photograph of lamina TS-1. It can be seen that the core of lamina TS-1 is an inert ball used as the support, and its shell is active TS-1 of 0.1–0.2 mm, which has been used to catalyze the propylene epoxidation.

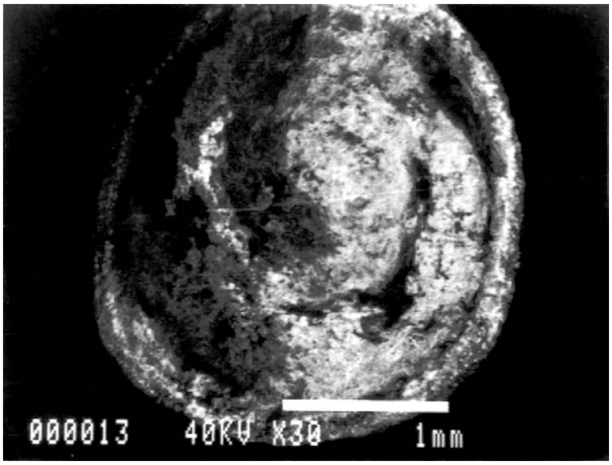

Figure 1. SEM photograph of lamina TS-1.

Figure 2 exhibits the epoxidation of propylene with H_2O_2 over the lamina TS-1 in the scale-up experiment. It can be seen from figure 2 that lamina TS-1 exhibits good catalytic performance and stability within about 1000 h. The H_2O_2 conversion ($X_{H_2O_2}$) is 96 $\sim$ 98%; propylene conversion is around 31.6%; the utilization of H_2O_2 ($U_{H_2O_2}$) is 98%, and the selectivity to PO (S_{PO}) is 90–95 %. The support in lamina TS-1 catalyst is a good heat radiator that can transmit the reaction heat quickly to maintain a stable reaction temperature. This is one of the reasons for the higher PO selectivity over lamina TS-1 catalyst. On the other hand, the shorter the diffusion path it is, the less chances there are for PO to contact with the acid sites of TS-1, which inhibits the side reaction of PO with methanol or water to form monomethyl ethers or glycol.

3.2. Deactivation of lamina TS-1

3.2.1. The catalytic performance of spent lamina TS-1 reacted in lab

Although lamina TS-1 exhibits good catalytic performance in the scale-up experiment, the catalytic activity of catalyst decreases gradually with time on stream. The H_2O_2 conversion decreased to 86% when run time is about 1200 h. Figure 3 shows the catalytic performance of spent lamina TS-1 obtained from the above scale-up experiment reacted continuously in fixed-bed reactor in lab. It can be seen from Figure 3 that with an increase in reaction time, the catalytic activity of lamina decreases gradually. The $X_{H_2O_2}$ is only 65% for less than 30 h. It indicates that the deactivation of spent lamina TS-1 catalyst occurs, and hereafter the spent catalysts are labeled as deactivated lamina TS-1.

3.2.2. Characterization of the deactivated lamina TS-1

Figure 4 shows the TGA of the deactivated lamina TS-1 catalyst. The differential curves of the TGA

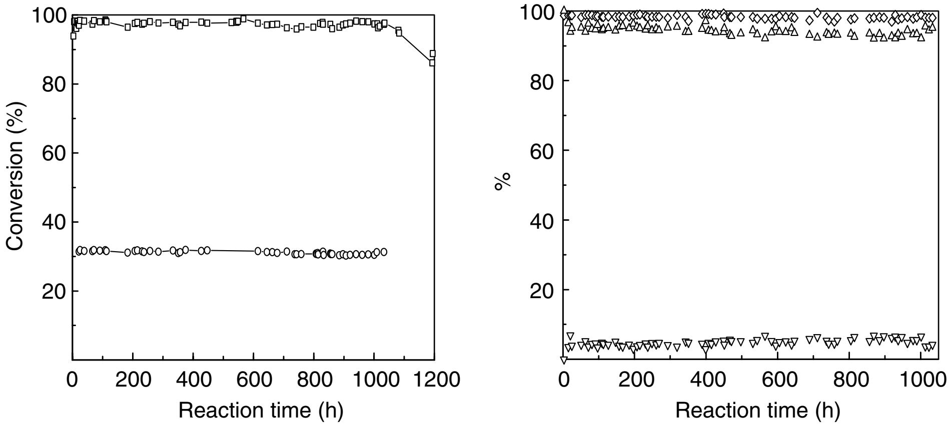

Figure 2. The catalytic performance of lamina TS-1 catalyst in single-tube experiment (□) $X_{H_2O_2}$; (O) $X_{C_3H_6}$ (propylene conversion); (◇) $U_{H_2O_2}$; (△) S_{PO}; (▽) S_{MME}. Reaction conditions: temperature 45–65 °C; pressure, 3.0 MPa; C_3H_6/H_2O_2 (molar ratios) 3; solvent, methanol; CH_3OH/H_2O_2 (molar ratio) 22; total WHSV of C_3H_6, 1.16 h^{-1}; size of ceramic sphere, 0.9–1.25 mm; the content of TS-1 in the catalyst is 31 wt%.

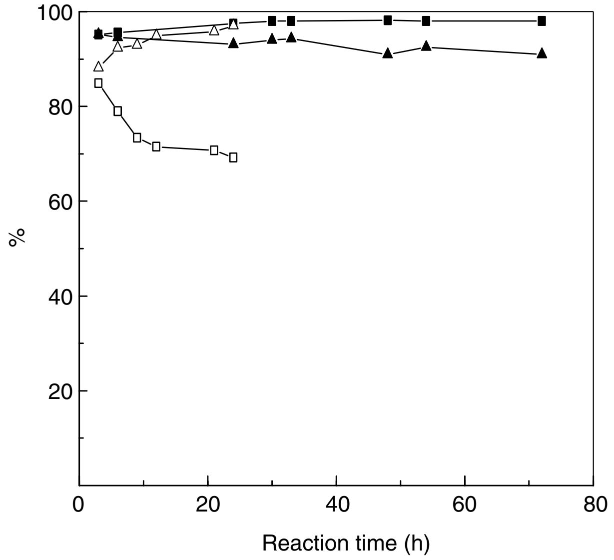

Figure 3. The catalytic performance of spent lamina TS-1 in a fixed bed reactor in lab. Fresh lamina TS-1:(■) $X_{H_2O_2}$; (▲) S_{PO}. Spent lamina TS-1:(□) $X_{H_2O_2}$; (△) S_{PO}. Reaction conditions: temperature, 60 °C; pressure, 3.0 MPa; C_3H_6/H_2O_2 (molar ratio) 4.17; solvent, methanol; CH_3OH/H_2O_2 (molar ratio) 23.6; WHSV of C_3H_6, 0.20 h^{-1}; NH_4OH concentration, 4 mmol/L.

indicate that the main weight loss is formed at 73, 205, 308, 433 and 496 °C. The peak centered at 73 °C in DTG is probably due to the physisorption of solvent (such as methanol, water) and the main product PO. The next weight loss formed around 205 °C is mainly due to oligomers of the products [26]. The other peaks should be attributed to higher polymers of the products. The main weight loss of the deactivated catalyst observed in TG curves is not high.

Figure 5 shows the pore distribution of fresh and deactivated lamina TS-1 catalysts. It can be seen that pore size of the lamina catalysts is 0.5–0.6 nm, however the pore volume and specific surface area of deactivated

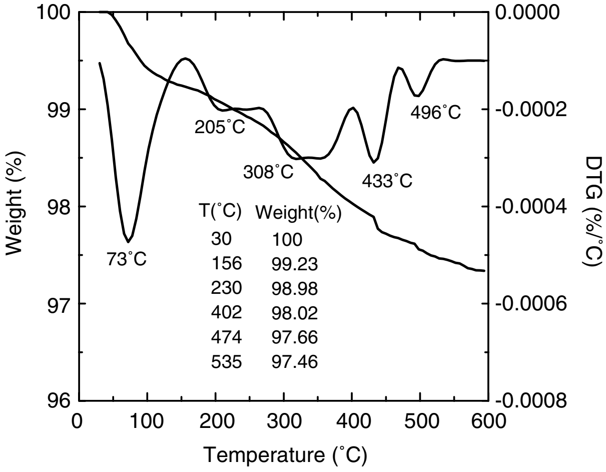

Figure 4. The TG–DTG curves of deactivated lamina TS-1.

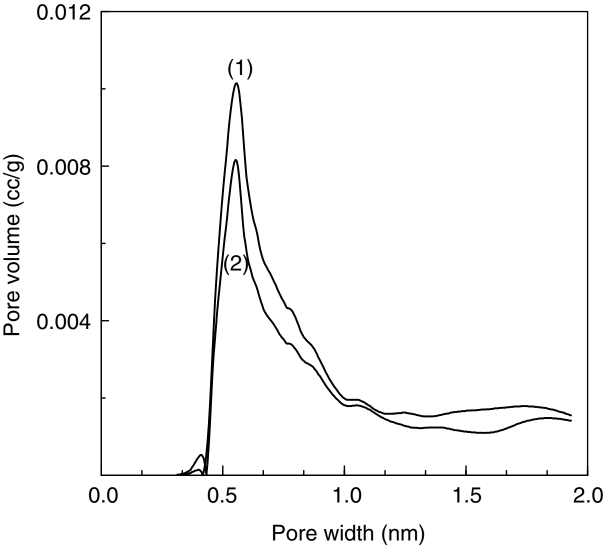

Figure 5. Pore size of lamina TS-1 catalyst. (1) fresh lamina TS-1; (2) deactivated lamina TS-1.

Table 1
The catalytic properties of deactivated lamina TS-1 regenerated at different temperature in air

Catalyst	$X_{H_2O_2}$ (%)	S_{PO} (%)	S_{MME} (%)
Fresh lamina TS-1	95.7	90.8	9.1
Deactivated lamina TS-1*	84.0	98.4	1.6
The deactivated TS-1 regenerated at (°C)			
200	92.0	92.7	7.3
300	93.3	90.9	9.0
400	96.0	88.6	11.2
540	96.3	87.5	12.3

Regeneration conditions: regeneration time 24 h, in air. Reaction conditions: temperature, 60 °C; pressure, 3.0 MPa; C_3H_6/H_2O_2 (molar ratios) 4.17; methanol is solvent; CH_3OH/H_2O_2 (molar ratio) 23.6; WHSV of C_3H_6, 0.20 h^{-1}; NH_4OH concentration 4 mmol/L; data are the average results run for 72 h, but the reaction time of deactivated catalyst is 3 h.

lamina TS-1 is smaller than that of the fresh one. It indicates that partly pores have been blocked by large deposit species during the reaction, which restrains the reaching of reactant to the active sites of catalyst and decreases the catalytic activity. In addition, that the reactants or products occupied the catalytic active sites is also considered as the reason that causes the deactivation of the lamina TS-1 catalyst.

3.3. *Regeneration of the deactivated lamina TS-1*

3.3.1. *Regeneration by heat treatment method under different media*

The propylene epoxidation of deactivated lamina TS-1 regenerated by heat treatment in air at different temperature is listed in table 1. It can be seen from table 1 that the catalytic performance can be improved obviously after heat treatment in air. With an increase in the calcination temperature, the catalytic activity of the deactivated catalyst increases gradually at an expense of PO selectivity. When the heat treatment temperature reaches to 400 °C, the catalytic activity of deactivated lamina TS-1 can be recovered, which is in accordance with the result reported in the literature [5]. It is noteworthy that with an increase in the heat treatment temperature, the S_{MME} increases gradually. It means that with the recovering of the catalytic activity of catalyst, it also quickens the side reaction of PO with methanol.

Figure 6 shows the FT-IR spectra of the deactivated lamina TS-1 regenerated by heat treatment in air at different temperature. Fresh lamina TS-1 presents a band at 960 cm^{-1}, which is commonly assigned in the literature to the stretching vibration of $[SiO_4]$ units linked to Ti atoms, confirming that the Ti atoms are linked to the zeolite framework [27,28]. It can be seen from Figure 6 that among the lamina catalysts there is some difference both in the position and in the intensity of the band near 960 cm^{-1}. Compared with the fresh one, the band at 960 cm^{-1} of the deactivated lamina TS-1 is shifted to a higher wavenumber and its intensity decreases, but there is little difference between the regenerated and deactivated catalyst. It confirms that changes in the framework Ti of zeolite take place during the reaction and regeneration process, which may resulted in the difference of PO selectivity of regenerated catalysts, compared with that of the fresh one.

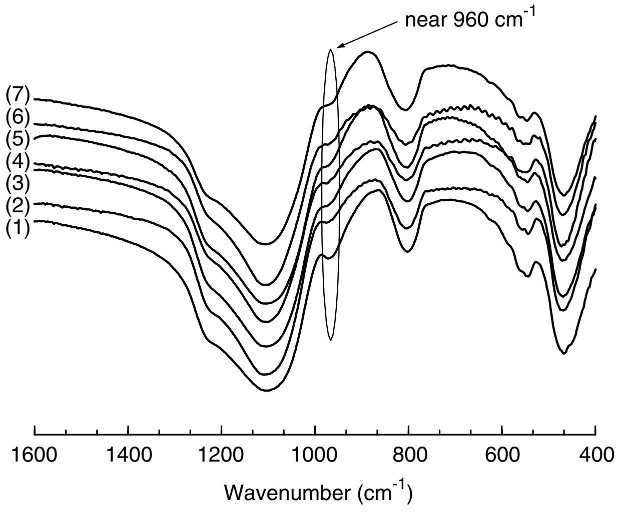

Figure 6. FT-IR spectra of lamina TS-1 regenerated at different temperature in air:(1) fresh lamina TS-1; (2) deactivated lamina TS-1; (3) 200 °C; (4) 300 °C; (5) 400 °C; (6) 500 °C; (7) 540 °C.

Using N_2 as a media, the propylene epoxidation of deactivated lamina TS-1 regenerated by heat treatment at different temperature is shown in table 2. It can be seen that the results are similar to that obtained when using air as a media. When the heat treatment temperature reaches to 300 °C, the activity of catalyst was fully

Table 2
The catalytic properties of deactivated lamina TS-1 regenerated at different temperature in N_2

Catalyst	$X_{H_2O_2}$ (%)	S_{PO} (%)	S_{MME} (%)
Fresh lamina TS-1	95.7	90.8	9.1
Deactivated lamina TS-1	84.0	98.4	1.6
The deactivated TS-1 regenerated at (°C)			
200	89.2	91.2	8.4
300	96.2	83.4	15.7
400	95.5	88.8	10.9
500	96.2	86.4	12.8

Regeneration conditions: N_2 flow rate 20 ml/min, regeneration time 24 h. Reaction conditions: temperature, 60 °C; pressure, 3.0 MPa; C_3H_6/H_2O_2(molar ratios) 4.17; methanol is solvent; CH_3OH/H_2O_2 (molar ratio) 23.6; WHSV of C_3H_6, 0.20 h^{-1}; NH_4OH concentration 4 mmol/L; data are the average results run for 72 h, but the reaction time of deactivated catalyst is 3 h.

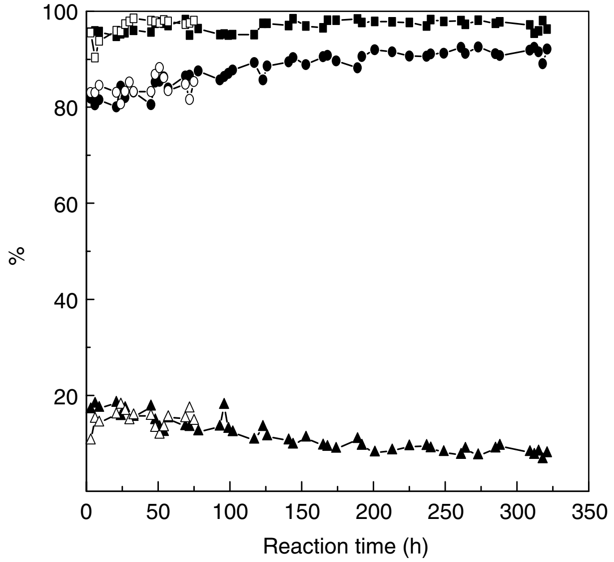

Figure 7. The catalytic performance of deactivated lamina TS-1 regenerated by heat treatment in the presence of N_2. N_2, 300 °C, 24 h:(■) $X_{H_2O_2}$; (●) S_{PO}; ▲ S_{MME}. N_2, 300 °C, 24 h; air, 540 °C, 24 h: (□) $X_{H_2O_2}$; (○) S_{PO}; (△) S_{MME}. Reaction conditions: temperature, 60 °C; pressure, 3.0 MPa; C_3H_6/H_2O_2 (molar ratios) 4.17; solvent, methanol; CH_3OH/H_2O_2 (molar ratio) 23.6; WHSV of C_3H_6, 0.20 h^{-1}; NH_4OH concentration, 4 mmol/L; catalyst, 8 g.

recovered. It indicates that heat treatment temperature play an important role in recovering the catalytic activity of the deactivated catalyst.

To ensure that the deactivated catalyst has been regenerated at 300 °C completely in the presence of nitrogen. The catalyst after regeneration was recalcined at 540 °C for 24 h in the air, and the catalytic properties of propylene epoxidation of the regenerated catalyst are shown in Figure 7. It can be seen that the catalytic performance of deactivated lamina TS-1 regenerated by heat treatment in N_2 has been recovered. The regenerated catalyst exhibits good stability for about 300 h. From Figure 4 it can be seen that there is still some species existing when the temperature is more than 300 °C in the presence of N_2. When the regenerated catalyst was recalcined at 540 °C in air, the remained species has been burned off. Combined with the reaction results, it can be seen that the catalytic activity of the catalysts hardly has any change, which further identifies that the remained species has little effect on the catalytic activity. It is noteworthy that the PO selectivity is still a little lower in the initial time, and reaches to the same value as that of the fresh TS-1 with an increase in the reaction time.

3.3.2. *Regeneration by dilute hydrogen peroxide*

The catalytic properties of propylene epoxidation over the deactivated lamina TS-1 regenerated by dilute hydrogen peroxide are shown in Figure 8. It can be seen that the activity of the deactivated lamina TS-1 has been recovered completely, but the PO selectivity is lower than that of the fresh one in the initial time. With an increase in the reaction time, the PO selectivity increases. The PO selectivity is almost similar to that of the fresh one after 27 h. The stability of regenerated catalyst can be maintained for more than 120 h. This regeneration is due to the oxidative breakdown of the pore blocking compounds by hydrogen peroxide [6].

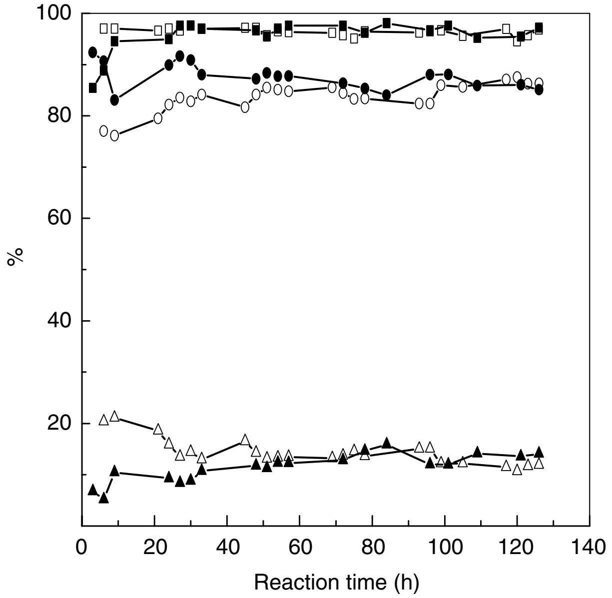

Figure 8. The catalytic performance of the deactivated TS-1 regenerated by dilute H_2O_2. Fresh lamina TS-1:(■) $X_{H_2O_2}$; (●) S_{PO}; ▲ S_{MME}. Regenerated lamina:TS-1 (□) $X_{H_2O_2}$; (○) S_{PO}; (△) S_{MME}. Reaction conditions: temperature, 60 °C; pressure, 3.0 MPa; C_3H_6/H_2O_2 (molar ratios) 4.17; solvent, methanol; CH_3OH/H_2O_2 (molar ratio) 23.6; WHSV of C_3H_6, 0.2 h^{-1}; NH_4OH concentration, 4 mmol/L; catalyst, 8 g. Regeneration method: temperature, 80 °C; washed by CH_3OH, 6 h;1.5%H_2O_2, 12 h; washed by reaction liquid (containing NH_4OH), 3 h.

3.3.3. *Regeneration by water vapor treatment*

The average results of propylene epoxidation over regenerated catalysts for 72 h by water vapor treat-

Table 3
The effect of calcination method on regeneration performance of deactivated lamina TS-1

Calcination media	Regeneration condition	$X_{H_2O_2}$ (%)	S_{PO} (%)	S_{MME} (%)
Fresh lamina TS-1	–	95.7	90.8	9.1
Deactivated lamina TS-1	–	84.0	98.4	1.6
Air	500 °C, 24 h	96.2	86.4	12.8
H_2O	300 °C, 24 h	96.3	90.1	9.8
Air + H_2O	500 °C, 24 h; 300 °C, 6 h	97.5	90.4	6.6

Reaction conditions: temperature, 60 °C; pressure, 3.0 MPa; C_3H_6/H_2O_2 (molar ratios) 4.17; methanol is solvent; CH_3OH/H_2O_2 (molar ratio) 23.6; WHSV of C_3H_6, 0.20 h^{-1}; NH_4OH concentration 4 mmol/L; data are the average results run for 72 h, but the reaction time of deactivated catalyst is 3 h.

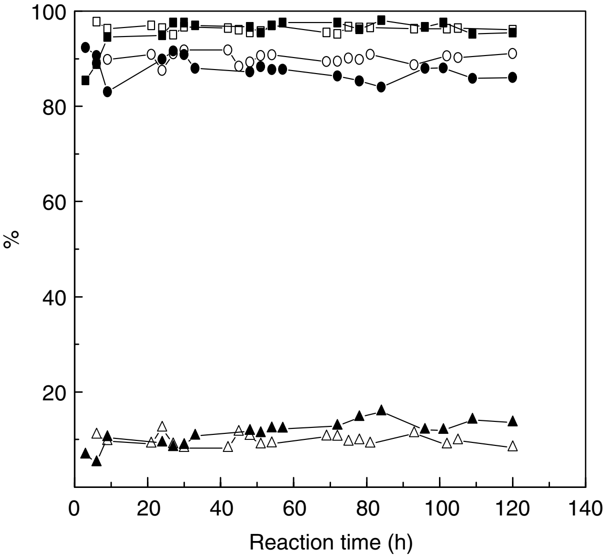

Figure 9. The regeneration performance of the deactivated lamina TS-1 by water vapor treatment. Fresh lamina TS-1: (■) $X_{H_2O_2}$; (●) S_{PO}; ▲ S_{MME}. Regenerated lamina TS-1: (□) $X_{H_2O_2}$; (○) S_{PO}; (△) S_{MME}. Regeneration conditions: WHSV (H_2O) 3 h^{-1}, temperature, 300 °C. Reaction conditions: temperature, 60 °; pressure, 3.0 MPa; C_3H_6/H_2O_2 (molar ratios) 4.17; solvent, methanol; CH_3OH/H_2O_2 (molar ratio) 23.6; WHSV of C_3H_6, 0.2 h^{-1}; NH_4OH concentration, 4 mmol/L; catalyst 8 g.

ment are listed in table 3. It can be seen that the catalytic performance of the deactivated catalyst regenerated by water vapor treatment is the same as that of fresh one. It indicates that the regeneration method of water vapor treatment can solve the problem of PO selectivity existed in the above regeneration methods. The effect of regeneration time on the catalytic performance of the deactivated catalyst is shown in Figure 9. It can be seen that the catalytic performance of the deactivated lamina TS-1 regenerated by water vapor treatment has been fully recovered. The catalytic properties of the deactivated catalyst regenerated by heat treatment in air, and then continued to be regenerated by vapor treatment for 6 h at 300 °C, especially the PO selectivity, has been recovered completely. Figure 10 is the catalytic performance of the deactivated catalyst regenerated by dilute H_2O_2 and water vapor treatment. The PO selectivity can also be recovered completely. It shows that water vapor treatment can improve the PO selectivity of the regeneration catalyst. Therefore, it can be concluded that the water vapor treatment regeneration method or the method containing the vapor process can be used for the regeneration of deactivated lamina TS-1 catalyst.

4. Conclusion

Lamina TS-1 exhibits good catalytic performance and stability in the propylene epoxidation with hydrogen peroxide. The deactivation of catalysts is due to the pore blocking, products and its oligomers occupying the active site of catalyst. The catalytic activity of deactivated catalysts can be fully recovered by suitable regeneration method. However the PO selectivity of regenerated catalysts is a little lower than that of fresh one in the initial time after regeneration by dilute H_2O_2 or air (nitrogen) heat treatment. The regeneration method by (or containing) water vapor treatment process can get over the bad effect on the PO selectivity, which is strongly recommended to use.

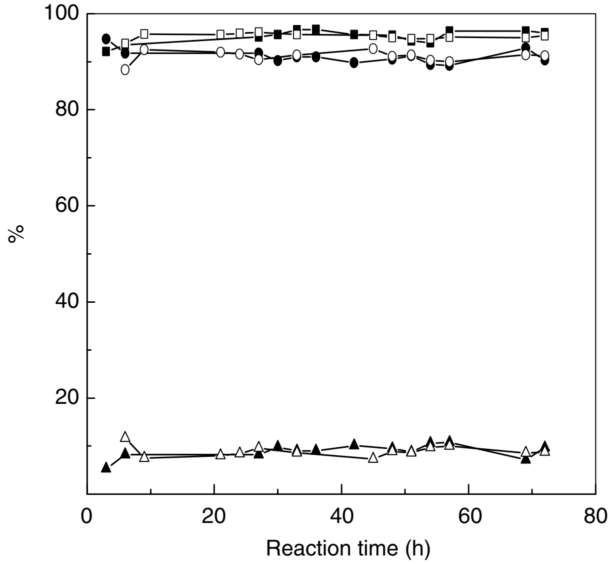

Figure 10. The catalytic performance of the deactivated lamina TS-1 regenerated by dilute H_2O_2 and water vapor treatment. Fresh lamina TS-1: (■) $X_{H_2O_2}$; (●) S_{PO}; ▲ S_{MME}. Regenerated lamina TS-1:(□) $X_{H_2O_2}$; (○) S_{PO}; (△) S_{MME}. Regeneration method: 80 °C, CH_3OH 6 h, 1.5 wt% H_2O_2 12 h; vapor 200 °C, 6 h. Reaction conditions: temperature, 60 °C; pressure, 3.0 MPa; C_3H_6/H_2O_2 (molar ratios) 4.17; solvent, methanol; CH_3OH/H_2O_2 (molar ratio) 23.6; WHSV of C_3H_6, 0.2 h^{-1}; NH_4OH concentration, 4 mmol/L; catalyst, 8 g.

Acknowledgements

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