Propylene epoxidation over silver supported on titanium silicalite zeolite

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Epoxidation of propylene to propylene oxide over Ag/TS-1 in the presence of oxygen and hydrogen was carried out in a fixed-bed, quartz flow reactor. The effects of Ag loading, Si/Ti ratio of TS-1 and calcination temperature and calcination method of Ag/TS-1 on the propylene epoxidation were investigated. The results show that Ag loading, the calcination temperature and calcination method of Ag/TS-1 as well as the Si/Ti ratio of TS-1 have a great effect on the catalytic properties. The optimum Ag loading, calcination temperature and calcination method of Ag/TS-1 and Si/Ti ratio of TS-1 are 2 wt%, 450 °C in air and 64 respectively. Over 2.0 wt% Ag/TS-1($n_{Si}/n_{Ti} = 64$) catalyst, at a space velocity of 3000 h^{-1}, 0.92% propylene conversion with 91.21% selectivity to propylene oxide is obtained at 150 °C. The deactivation of Ag/TS-1 catalyst is not due to the changes of active species, but because of the coke of the catalyst, which can be easily regenerated by calcination at 450 °C in air.

KEY WORDS: propylene; epoxidation; molecular oxygen; Ag/TS-1.

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 coproduction (Halcon) routes [1]. The chlorohydrin route generates chlorinated by-products, mainly dichloropropane and $CaCl_2$. The coproduction 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.* opened a new route for the synthesis of propylene oxide [3,4]. 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. However, the cost of H_2O_2 is very high.

Recently much attention has been paid to the direct synthesis of propylene oxide by oxygen or air in the gas phase, which is mainly focused on Au and Ag catalysts at ambient pressure. Au nanoparticles deposited on TiO_2 [5], micro- and mesoporous titanosilicalites, such as TS-1, TS-2, Ti-β and Ti-MCM-41/48 [6–8] have been studied by Haruta *et al.* When Au was supported on TS-1, the propylene conversion and the PO selectivity were 0.71 and 93% respectively. Over Au/Ti-MCM-48, about 5% propylene conversion with more than 90% selectivity was obtained. The gas-phase epoxidation of ethylene to ethylene oxide (EO) using molecular oxygen, which is one of the greatest discoveries in heterogeneous catalysis, has been commercialized. However, if the catalyst is used directly for the epoxidation of propylene, very poor results are obtained. However, over the silver catalyst modified by K, Cl, Mo, W, Re and $CaCO_3$, 3.2% propylene conversion with 59% selectivity to propylene oxide are obtained [9–13]. Recently, Lu and Zuo [14] found that the propylene conversion and selectivity to PO are 54 and 26.3% respectively, over silver pellet with 3.8% NaCl as the promoter. Li *et al.* [15] used 10 wt% NaCl-modified silver catalyst with air as the oxidant and got 12.4% propylene conversion and 31.6% selectivity to PO at 350 °C, and over a $VCe_{0.2}Cu_{0.8}$-NaCl(20) catalyst, the PO selectivity was about 70%, but the propylene conversion was lower than 1% [16]. Up until now, there is no report on the propylene epoxidation over Ag/TS-1. In this paper, the epoxidation of propylene with hydrogen and oxygen over Ag/TS-1 catalyst was investigated in detail.

2. Experimental

2.1. Catalyst preparation

TS-1 was prepared according to the literature [17]. Ag/TS-1 catalysts were prepared by the deposition–precipitation (DP) method [18]. In a typical preparation method for Ag/TS-1, 1.5 g TS-1 was suspended in 200 mL 0.05 M Na_2CO_3 solution, and 100 mL $AgNO_3$ solution varied corresponding to the silver loading was added to the suspension under vigorous stirring. It was separated from the liquid after 1 h of stirring, and then washed with distilled water, dried at 90 °C overnight and finally calcined by heating at a rate of 1 °C/ min and

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maintaining the final temperature, ranging from 300–500 °C, for 5 h in air.

2.2. Catalyst characterization

X-ray diffraction patterns were obtained on a D/max-2400 diffractometer using Cu K_α radiation. TEM photographs were obtained on JEX-2000EX, accelerated voltage 150 kV. ESR spectra were measured on JES-FE1XG, and the *g* value was calculated with $MnSO_4$ as a reference. TG-DTG analysis was performed in a thermogravimetric analyzer (Mettler-Toledo TGA/SDTA851^e). Approximately 20 mg sample was placed in an Al_2O_3 ceramic pan. The sample was heated from an ambient temperature to 600 °C at a constant heating rate (10 °C/ min). The nitrogen flow rate was 20 mL/min.

2.3. Catalytic test

The catalytic reaction was carried out in a fixed-bed, quartz glass reactor with an inner diameter of 8 mm at atmospheric pressure. About 0.6 g catalyst was placed in the middle of the tube reactor between quartz beads. The typical reaction conditions were as follows: 150 °C, $V_{O_2}:V_{C_3H_6}:V_{H_2}:V_{N_2} = 1:2:3:8$, space velocity: 3000 h^{-1}.

Analysis of the products was carried out by GC-MS (HP 6890 GC/5973 MSD) and GC (GC7890F equipped with an FID with 50 m × 0.25 mm × 0.4 μm PEG20M capillary column and SRI 8610C equipped with a TCD with 2.5 m × 3 mm GDX-101 packed column). The activity of the catalyst was calculated on the basis of the carbon balances [19]. $X_{C_3H_6}$ is the propylene conversion and S_{PO} is the selectivity to PO.

3. Results and discussion

3.1. Effect of Ag loading

The effects of different Ag loadings on the propylene epoxidation at 150 °C, as shown in figure 1, show that the amount of Ag loading has a great effect on the catalytic properties. When pure TS-1($n_{Si}/n_{Ti} = 33$) is used as the catalyst, the propylene conversion and the selectivity to PO are 0.09% and 13.26% respectively. The main product is acetone, whose selectivity is 70.97%. Over Ag/TS-1 catalyst, the products are aldehyde, propanal, acetone, acrolein and CO_2. When 0.5 wt% Ag is loaded on TS-1, the propylene conversion and the selectivity to PO increase to 0.34% and 86.98% respectively. With the increase in the amount of Ag loading, the propylene conversion increases and then levels off, and the selectivity to PO increases to the maximum, then decreases. This shows that the excess of Ag loading does not favor the formation of PO. When the amount of Ag loading is 2.0 wt%, the propylene conversion and the selectivity to PO are 0.58 and 86.87% respectively.

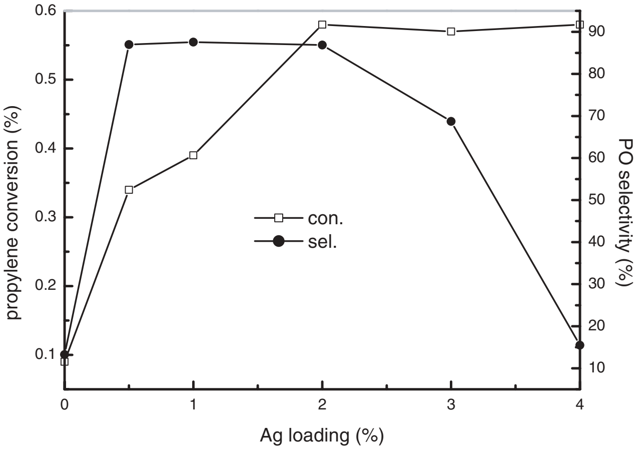

Figure 1. Effect of Ag loading on the epoxidation of propylene in the gas phase. Reaction conditions: The amount of the catalyst is 0.6 g. The reaction temperature is 150 °C atmospheric pressure. The space velocity is 3000 h^{-1}. $V_{O_2}:V_{C_3H_6}:V_{H_2}:V_{N_2} = 1:2:3:8$. The catalyst is calcined at 400 °C in air. n_{Si}/n_{Ti} is 33. Reaction time is 20 min.

Figure 2 exhibits the XRD spectra of Ag/TS-1 with different Ag loading. It can be seen that when Ag loading is 2%, the silver crystalline peak at 38° begins to appear, and with the Ag loading increasing, the intensity of the peak increases. TEM shows that with Ag loading increasing, the number of 10 ~12-nm-sized Ag particles increases.

As we know, in the liquid-phase oxidation of propylene with H_2O_2, both high propylene conversion and high selectivity to PO can be achieved over the TS-1 catalyst. When Ag is loaded on TS-1, both the utilization of H_2O_2 and its yield to PO decrease owing

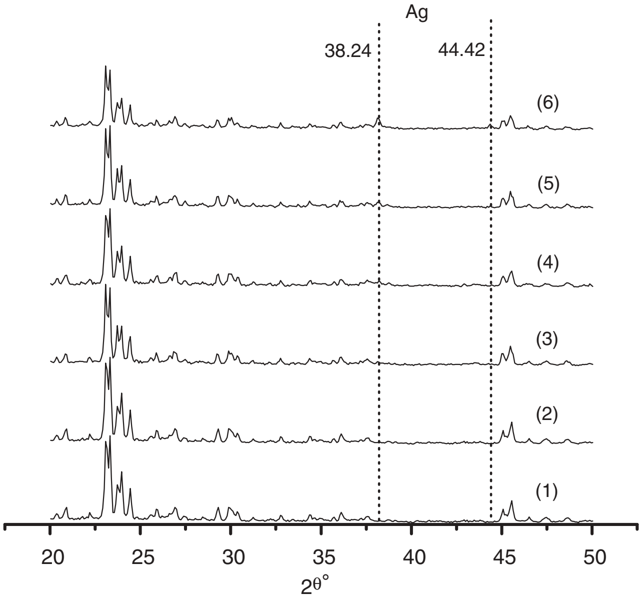

Figure 2. XRD patterns of Ag/TS-1 with different Ag loading. (1) 0.5%, (2) 1.0%, (3) 2.0%, (4) 3.0%, (5) 4.0% and (6) 5.0%.

Table 1
Propylene epoxidation with hydrogen peroxide as an oxidant over Ag/TS-1 with different loading

w(Ag) (%)	$X_{H_2O_2}$ (%)	S_{PO} (%)	$U_{H_2O_2}$ (%)	S_{MME} (%)	Y (%)
0	96.21	90.22	96.18	9.78	92.53
0.3	62.89	96.87	97.78	3.03	61.62
0.5	71.88	97.02	60.91	2.98	43.78
1.0	90.43	96.53	46.16	3.47	41.74
2.0	93.22	93.40	19.52	6.60	19.52
3.0	97.66	97.76	10.89	2.24	10.64
4.0	99.03	75.61	5.31	24.39	5.26

Note: Reaction conditions: m(Ag/TS-1) = 0.4 g, $T = 60\,^{\circ}C$, $p = 0.4$ MPa, $t = 1.5$ h, methanol as solvent.
w: Ag loading; $X_{H_2O_2}$: conversion of H_2O_2; S_{PO}: selectivity to PO; $U_{H_2O_2}$: utilization of H_2O_2; S_{MME}: Selectivity to propylene glycol monomethyl ether; Y: yield of H_2O_2.

to the coverage of Ti active sites by Ag, which can be seen in table 1. However, in the gas-phase oxidation of propylene with oxygen in the presence of hydrogen, the loading of Ag on TS-1 favors the formation of PO. This shows that the reaction mechanism in the gas phase is different from that in the liquid phase.

3.2. *Effect of different support*

The above results show that Ag/TS-1 exhibits good performance in the gas-phase epoxidation of propylene with oxygen in the presence of hydrogen. In order to exploit the effect of TS-1, different support loaded with 2.0 wt% Ag was prepared. Their catalytic activities for the epoxidation of propylene are investigated and shown in table 2.

It can be seen from table 2 that when using anatase type TiO_2 (Degussa P_{25}) as the support, there is no product to be detected. The result is not in agreement with that reported by Oliveira [20]. Using SiO_2 as the support, the propylene conversion is very low, and the selectivity to PO is about 50%. When using HZSM-5 or silicalite-1 as the support, the propylene conversion is 16.02 and 7.68% respectively. However, the selectivity to PO is poor, and a large amount of carbon dioxide is formed. While using TS-1($n_{Si}/n_{Ti} = 64$) as the support, the propylene conversion is 0.92%, and the selectivity to PO is about 92%. This shows that the support has a great influence on the catalytic properties of the silver supported catalyst. The result is similar to that of Oliveira [20]. Combined with the above results, it can be concluded that TS-1 is the best support, and there is a synergy between Ag and TS-1 in the gas-phase epoxidation of propylene.

3.3. *Effect of Si/Ti ratio of TS-1*

Haruta *et al.* [21,22] have found that the Si/Ti ratio of Ti-containing mesoporous materials has an important effect on their catalytic properties in the gas-phase epoxidation of propylene. For the different titanium-containing support, the catalyst has a different optimum Si/Ti ratio. In our experiment, TS-1 with a different Si/Ti ratio loaded with 2 wt% Ag was prepared, and the catalytic activity is shown in table 3.

From table 3, it can be seen that the Si/Ti ratio of TS-1 has a great effect on the propylene epoxidation. With an increase in the Si/Ti ratio of TS-1, both the propylene conversion and the selectivity to PO increase. However, when the Si/Ti ratio is 128, the propylene conversion decreases to 0.06% and no PO is detected in the product. This shows that neither low Si/Ti ratio nor high Si/Ti ratio favors the formation of PO, and the result is similar to that of Haruta *et al.* [21,22]. When the Si/Ti

Table 2
Effect of support on the propylene epoxidation in the gas phase

Catalyst	Conversion of C_3H_6 (%)	Selectivity for products (%)			
		Aldehyde	Propylene oxide	Propanal	CO_2
Ag/TiO_2	0	0	0	0	0
Ag/SiO_2	0.04	51.71	48.29	0	0
Ag/silicalite-1[a]	7.68	0.26	0	0.20	98.53
Ag/HZSM-5	16.02	0.90	3.33	0	95.78
Ag/TS-1($n_{Si}/n_{Ti} = 64$)	0.92	2.32	91.21	5.54	0

Note: Reaction conditions: The loading of Ag is 2 wt%. The amount of the catalyst is 0.6 g. The reaction temperature is 150 °C. The space velocity is $3000\,h^{-1}$. $V_{O_2} : V_{C_3H_6} : V_{H_2} : V_{N_2} = 1 : 2 : 3 : 8$. The catalyst is calcined at 400 °C in air. Reaction time is 70 min.
[a]The space velocity is $4000\,h^{-1}$. $V_{C_3H_6} : V_{O_2} : V_{H_2} : V_{N_2} = 1:2:3:12$. The catalyst is calcined at 450 °C in air.

Table 3
Effect of Si/Ti ratio on the propylene epoxidation in the gas phase

Si/Ti	Conversion of C_3H_6 (%)	Selectivity for products (%)			
		Aldehyde	Propylene oxide	Propanal	Acetone
16	0.07	0	41.54	50.54	7.91
33	0.32	1.83	91.77	6.40	0
64	0.92	2.32	91.21	5.54	0.93
128	0.06	0	0	87.74	12.26

Note: Reaction conditions: The loading of Ag is 2 wt%. The amount of the catalyst is 0.6 g. The reaction temperature is 150 °C. The space velocity is 3000 h^{-1}. $V_{O_2}:V_{C_3H_6}:V_{H_2}:V_{N_2} = 1:2:3:8$. The catalyst is calcined at 400 °C in air. Reaction time is 70 min.

ratio is lower, it contains more Ti species, which is not suitable to the propylene epoxidation; thus the catalyst exhibits poor performance, 0.07% propylene conversion and 41.54% selectivity to PO. When the Si/Ti ratio is higher, it contains less Ti species for the propylene epoxidation. When the Si/Ti ratio is 64, the catalyst exhibits optimum performance, 0.92% propylene conversion and 91.21% PO selectivity. Over TS-1, there are two kinds of titanium species, framework titanium and extra-framework titanium, and extra framework is divided into two kinds [23]. Up until now, we still cannot make sure which titanium species is synergetic with Ag and favors the formation of PO.

3.4. *Effect of calcination temperature of Ag/TS-1*

The effect of calcination temperature of 2 wt% Ag/TS-1($n_{Si}/n_{Ti} = 33$) catalyst on the propylene epoxidation were investigated, and the results are shown in figure 3. It can be seen that with an increase in the calcination temperature, both the propylene conversion and the selectivity to PO increase. When the catalyst is calcined at 450 °C, it exhibits optimum performance, 0.43% propylene conversion and 92.57% selectivity to PO. When the catalyst is calcined at higher temperature, the propylene conversion increases continuously, however, the selectivity to PO decreases. Figures 4 and 5 show that the Ag particles calcined at 500 °C are 2 ~ 4 nm larger than that of the ones calcined at 450 °C. Maybe a slight increase in particle size of Ag results in the decrease of the selectivity to PO.

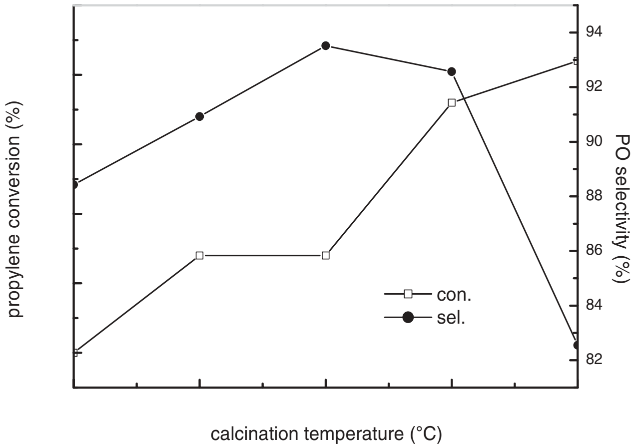

Figure 3. Effect of calcination temperature on the epoxidation of propylene. Reaction conditions: The loading of Ag is 2 wt%. The amount of the catalyst is 0.6 g. The reaction temperature is 150 °C The space velocity is 3000 h^{-1}. $V_{O_2}:V_{C_3H_6}:V_{H_2}:V_{N_2} = 1:2:3:8$. n_{Si}/n_{Ti} is 33. Reaction time is 40 min.

3.5. *Effect of calcination method*

The effect of calcination method of Ag/TS-1 catalysts was investigated, and the results are listed in table 4. From table 4, it can be seen that the calcination method has an important effect on the reaction. When the catalyst is calcined in air at 450 °C, it exhibits the optimum activity. However, when the catalyst is calcined in hydrogen at 450 °C, its activity decreases drastically. When the catalyst is calcined in nitrogen at 450 °C, its activity also decreases.

Figure 6 shows the ESR spectra of Ag/TS-1 calcined at different atmospheres. It can be seen that when Ag/TS-1 is calcined in H_2, there is a signal at 2.0061, which belongs to Ag^0. While treated in air or N_2, there is no

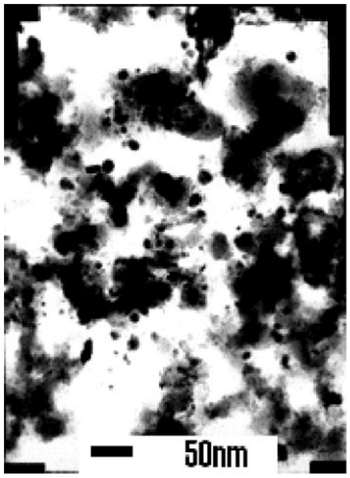

Figure 4. TEM of 2% Ag/TS-1($n_{Si}/n_{Ti} = 33$) calcined at 450 °C.

Figure 5. TEM of 2% Ag/TS-1($n_{Si}/n_{Ti} = 33$) calcined at 500 °C.

signal in the spectra. TEM shows that when Ag/TS-1 is calcined in N_2 and H_2, a large part of the Ag particles become very small, only about 2–4 nm, and a few larger particles are about 30 nm. Combined with the reaction results, it can be concluded that neither big nor small metal silver particles is beneficial to the formation of PO, but the Ag^+ existing in some form favors the propylene epoxidation in the gas phase.

3.6. Catalyst deactivation

Figure 7 shows the relationship of the propylene conversion and the selectivity to PO with reaction time over 2 wt% Ag/TS-1($n_{Si}/n_{Ti} = 64$). It can be seen that the propylene conversion decreases gradually, and the selectivity to PO increases a little before 150 min. From figure 7, it is also noted that, when the catalyst is exposed in air for a long time, the propylene conversion decreases drastically, from 1.02 to 0.43%, but it hardly has any influence on the selectivity to PO.

Figure 8 shows the regeneration activity of the spent catalyst calcined at 450 °C in air. From figure 8, it can be seen that the catalytic activity can be recovered. This indicates that the deactivation is not due to the change of the active species, but because of the coke of the catalyst.

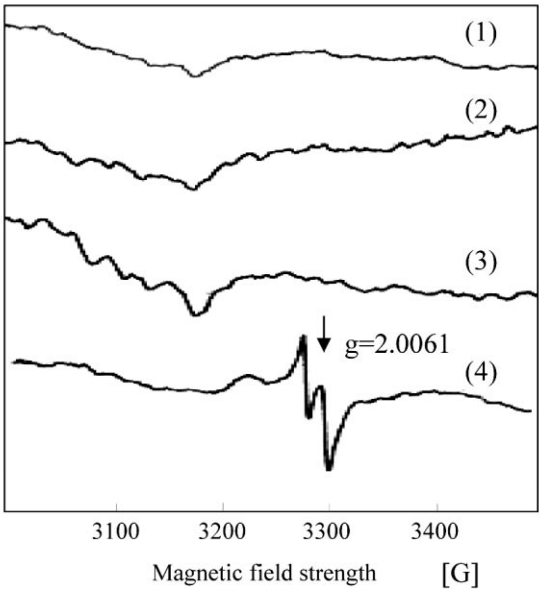

Figure 6. ESR spectra of TS-1 ($n_{Si}/n_{Ti} = 33$) and Ag/TS-1 with a different calcination method. (1) TS-1; (2) Ag/TS-1 calcined in air; (3) Ag/TS-1 calcined in N_2 and (4) Ag/TS-1 calcined in H_2.

The TEM photograph shows that the silver particle size of the spent catalyst has a little increase compared with that of the fresh one. An explanation for the deactivation of Ag/TS-1 catalysts could be the deposition of a reaction product on the catalyst, either blocking the active silver sites or the titanium sites. The thermogravimetrical analysis (seen in figure 9) of the spent Ag/TS-1 catalyst shows two combustion peaks at 58 and 363 °C respectively. The catalyst-poisoning compound will probably be the product and a polymer of propylene oxide.

Apart from the organic products or its polymers being the cause of the deactivation of the catalysts, the presence of water may be one of the species resulting in the deactivation of the Ag/TS-1 catalysts (seen in figure 7), which is not in agreement with that reported by Makkee *et al.* [24]. Haruta *et al.* [25] have reported that the activity of the deactivated catalysts cannot be recovered by thermal treatment at ≥250 °C in the oxygen stream. However, in our experiment the activity of the spent catalysts can be easily recovered to the original value, when the catalyst is calcined at 450 °C in air.

Table 4
Effect of calcination method on the propylene epoxidation in the gas phase

Calcination method	Conversion of C_3H_6 (%)	Selectivity for products (%)			
		Aldehyde	Propylene oxide	Propanal	Acrolein
Air	0.43	3.17	92.75	4.08	0
Nitrogen	0.16	0	92.71	7.29	0
Hydrogen	0.06	0	85.22	7.20	7.57

Note: Reaction conditions: The loading of Ag is 2 wt%. The amount of the catalyst is 0.4 g. The reaction temperature is 150 °C. atmospheric pressure. The space velocity is 4000 h^{-1}. $V_{O_2} : V_{C_3H_6} : V_{H_2} : V_{N_2} = 1:2:3:8$. The catalyst is calcined at 450 °C. n_{Si}/n_{Ti} is 33. Reaction time is 40 min.

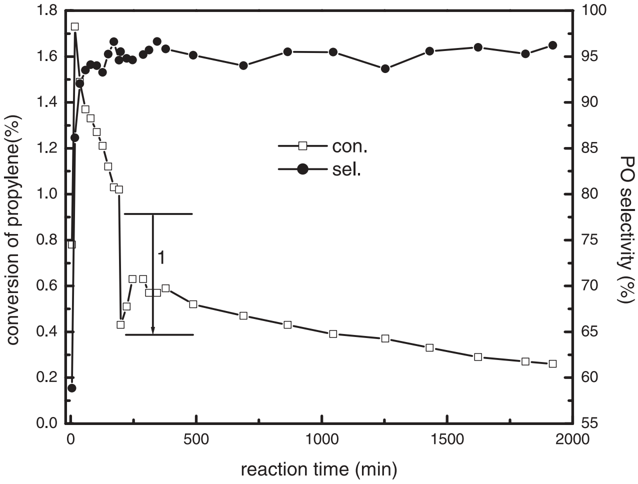

Figure 7. Relation of the catalytic activity with reaction time over the Ag/TS-1 catalyst. Reaction conditions: The loading of Ag is 2 wt%. The amount of the catalyst is 0.6 g. The reaction temperature is 150 °C. The space velocity is $4000\,h^{-1}$. $V_{C_3H_6}:V_{O_2}:V_{H_2}:V_{N_2} = 1:2:3:12$. The catalyst is calcined at 450 °C in air. n_{Si}/n_{Ti} is 64. 1: the catalyst was exposed in air for a long time and reused without any pretreatment.

4. Conclusions

The Ag/TS-1 catalyst prepared by the DP method exhibits good performance in the epoxidation of propylene to PO in the presence of C_3H_6, O_2, H_2 and N_2. The catalyst calcination temperature, calcination methods, Si/Ti ratio of TS-1 and the silver loading have an obvious influence on the catalytic performance. The optimum Ag loading, calcination temperature and method of Ag/TS-1 and Si/Ti ratio of TS-1 are 2 wt%, 450 °C in air and 64 respectively. Over the 2% Ag/TS-1($n_{Si}/n_{Ti} = 64$) catalyst, the propylene conversion is 0.92% and the selectivity to propylene oxide is 91.21%. Combining the results with the characterization, it can be concluded that there is a synergy between silver and Ti species. Neither big nor small silver particles favor the epoxidation of propylene. Moreover, the catalyst deactivation can be easily recovered by calcination at 450 °C in air.

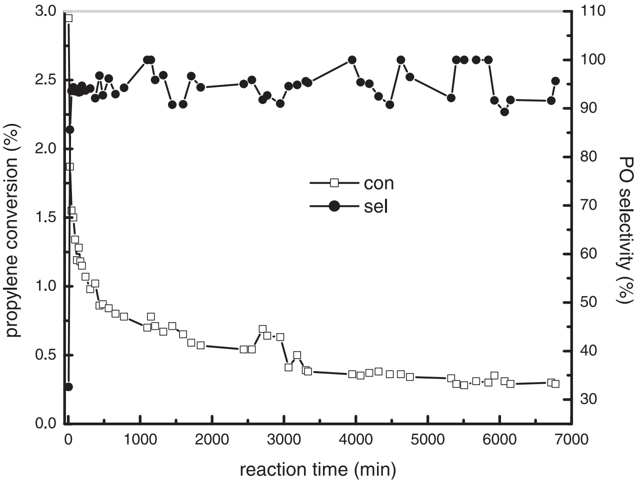

Figure 8. Relation of the catalytic activity with reaction time over the regenerated Ag/TS-1 catalyst. Reaction conditions: The loading of Ag is 2 wt%. The amount of the catalyst is 0.6 g. The reaction temperature is 150 °C. The space velocity is $4000\,h^{-1}$. $V_{C_3H_6}:V_{O_2}:V_{H_2}:V_{N_2} = 1:2:3:12$. The catalyst is calcined at 450 °C in air. n_{Si}/n_{Ti} is 64.

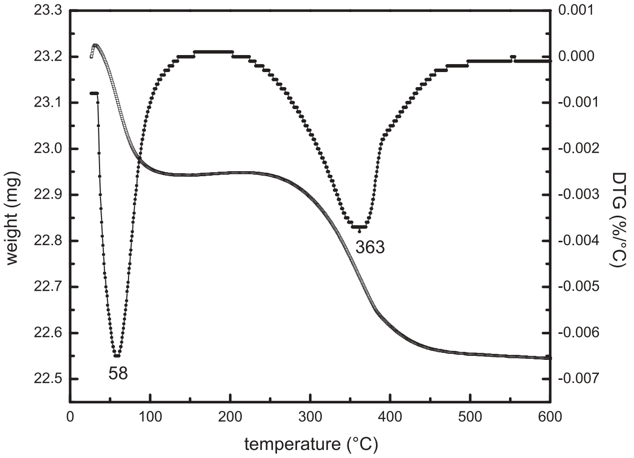

Figure 9. TG and DTG curves of the spent 2 wt% Ag/TS-1 ($n_{Si}/n_{Ti} = 64$) catalyst.

Acknowledgments

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