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Gas-phase epoxidation of propylene over Ag/Ti-containing catalysts

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Abstract

The effects of calcination atmosphere of the Ag/TS-1 catalyst and other Ti-containing supports on propylene epoxidation using oxygen as the oxidant in a fixed-bed quartz reactor were investigated. The samples were characterized by XRD, UV–vis, ESR, TEM and FT-IR. The results show that 2 wt.% Ag/TS-1 calcined in air is optimum; the Ag/Ti-containing (prepared by chemical vapor deposition (CVD) or impregnation (IMP) method) catalysts have catalytic activities in the reaction. The framework titanium species plays an important role, while the extra framework titanium species (280–290 nm) also has weak epoxidation activity in the gas-phase epoxidation of propylene; excessive extra framework titanium species (280–290 nm) can decrease PO selectivity. The oxidized silver ions are the main active sites for the gas-phase epoxidation of propylene.

Keywords: Propylene oxide; Propylene; Ag/TS-1; Oxygen; CVD; IMP

1. Introduction

Propylene oxide (PO) is one of the most important chemical feedstocks, which can be used to produce polyether polyol polymers, such as polyurethane. Major conventional manufacturing methods include the chlorohydrin route and the co-production (Halcon) route. The chlorohydrin route generates chlorinated by-products, mainly dichloropropane and $CaCl_2$, which results in serious equipment corrosion and environment problems. The co-production route is capital intensive and its economics depends on the economic fortunes of the by-products namely styrene or *tert*-butyl alcohol. The invention of titanium silicate-1 (TS-1) by Taramasso et al. opened a new route for the synthesis of propylene oxide [1,2]. 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 quite high, the process has not been commercialized as yet. In order to solve this problem, in situ generated hydrogen peroxide has been investigated widely. Xi et al. [3] reported the exciting result of 91% propylene conversion based on 2-ethylanthrahydroquinone (EAHQ) with 94% selectivity to PO based on propylene in the 2-ethylanthraquinone (EAQ)/EAHQ system, with $[\pi\text{-}C_5H_5NC_{16}H_{33}]_3$ $[PO_4(WO_3)_4]$ as a catalyst at 65 °C for 5 h. Moreover, epoxidation of propylene has been studied over Pt–Pd/TS-1 [4,5] and Au supported on TiO_2 [6], TS-1, TS-2, Ti-β and Ti-MCM-41/48 [7–9] catalysts with in situ generated H_2O_2 system. It was found that the improved yield of PO could be ascribed to the maintenance of palladium in its +2 oxidation state over Pt–Pd/TS-1 and only Au particles with diameters smaller than 4 nm are effective for the reaction over Au/TiO_2 [6], and the poor PO selectivity for Au/TS-1, Au/TS-2 is due to the low loadings of Au [8], as well as the strong protonic acidity of Au/Ti-β [10]. Recently Haruta and coworkers reported that over Au/Ti-MCM-48 catalyst [9], about 5% propylene conversion with 90% PO selectivity could be obtained.

In analogy to ethylene epoxidation, much attention has been paid to the direct oxidation of propylene using air or oxygen as the oxidant directly. However, if the catalyst for ethylene epoxidation is used directly for the epoxidation of propylene, very poor results are obtained. When the catalyst is well modified, better results can be obtained. Over the silver catalyst modified by K, Cl, Mo, W, Re and $CaCO_3$, 3.2% propylene conversion with 59% selectivity to PO is obtained [11–15]. Lu and Zuo [16] 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 and coworkers [17] using 10 wt.% NaCl-modified

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silver catalyst with air as the oxidant can get 12.4% propylene conversion and 31.6% selectivity to PO at 350 °C. But the PO selectivity using oxygen or air as the oxidant is quite low.

Up to now, there is no report concerned with the epoxidation of propylene over Ag/TS-1 in the hydrogen and oxygen system. In this paper, the effects of calcination atmosphere of Ag/TS-1 catalyst and other Ti-containing supports on the propylene epoxidation in the presence of hydrogen and oxygen were investigated in detail.

2. Experimental

2.1. Catalyst preparation

TS-1 ($n_{Si}/n_{Ti} = 33$) was prepared according to the literature [18]. Ti-containing supports were prepared by CVD method and IMP method. For the CVD method preparation, the Si-1 was purged at 450 °C by N_2 for 2 h; cooled to 300 °C, and then substituted by $TiCl_4$ in a sealed bottle at the atmospheric pressure, in the presence of N_2 at a flow rate of 30 ml/min for 1, 5, 10 and 20 h, respectively. Continuously, purged at 300 °C for 2 h, and then cooled down to the room temperature in the presence of N_2. For the IMP method, tetrabutylorthotitanate (TBOT) was dissolved in *i*-propanol solution; Si-1 was added to the mixture (the volume ratio of TBOT:Si-1 = 1:20) for 10 h at room temperature, the weight ratio of TiO_2:Si-1 is 5%, and then dried at 90 °C for 20 h, calcined at 90, 200, 300, 450, 600 °C for 3 h, respectively. The supports were then used directly for preparing the Ag/Ti-containing catalysts.

Ag/Ti-containing catalysts were prepared by deposition–precipitation (DP) method, as described in reference [19]. In a typical preparation method for Ag/TS-1, 1.5 g TS-1 was suspended in the 200 ml 0.05 M Na_2CO_3 solution, and 100 ml 2.8 mmol/L $AgNO_3$ water solution was added to the suspension under vigorous stirring. When ended, the pH value of the solution is 11–12. 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 first by heating at a rate of 1 °C/min and then maintaining the final temperature for 5 h in air.

2.2. Catalyst characterization

X-ray diffraction patterns were collected on a D/max-2400 diffractometer using Cu Kα radiation. TEM photographs were obtained on JEX-2000EX, accelerated voltage 100 kV. IR measurements were recorded on a Nicolet 20DXB FT-IR spectrometer. The sample was ground with KBr and pressed into thin wafers. UV–vis characterization was conducted on a Jasco V-550. ESR spectra were measured on JES-FE1XG, and g value was calculated with $MnSO_4$ as a reference. ICP analysis was performed on ICP 1014.

2.3. Catalytic test

The catalytic reaction was carried out in a vertical fixed-bed, quartz reactor with an inner diameter of 8 mm at atmospheric pressure. About 0.6 g catalyst was placed in the middle of the reactor with quartz beads support at each end. The typical reaction conditions were as follows: 150 °C, $V_{C_3H_6}:V_{O_2}:V_{H_2}:V_{N_2} = 1:2:3:12$, space velocity: $4000\,h^{-1}$. Since the concentration of the reactants was within the explosion limits, safety should be noticed.

Analysis of the products was carried out by GC–MS (HP 6890 GC/5973 MSD) and GC (GC7890F equipped with a FID detector with 50 m × 0.25 mm × 0.4 μm PEG20M capillary column and SRI 8610C equipped with a TCD detector with 2.5 m × 3 mm GDX-101 packed column). The activity of the catalyst was calculated by the carbon balances [17]. $X_{C_3H_6}$ is the propylene conversion, and PO formation rate (F_{PO}) is calculated on the grams of PO produced per kg catalyst per hour and S_{PO} is the selectivity to PO calculated on the products.

3. Results and discussion

3.1. Characterization of TS-1

The XRD pattern of the synthesized TS-1 ($n_{Si}/n_{Ti} = 33$) shows the characteristic of MFI type structure. The FT-IR spectrum of the sample exhibits a distinct band at $960\,cm^{-1}$, which is attributed to the incorporation of titanium into the framework. The UV–vis spectrum shows that there are three absorbance peaks at 213, 280 and 330 nm, which belong to tetrahedral titanium, hexahedral titanium and anatase TiO_2, respectively [20]. The ICP analysis shows that the actual Ti content of TS-1 is 2.19%.

3.2. Characterization of other Ti-containing supports

XRD patterns of Ti-containing supports prepared by CVD and IMP methods do not show any changes compared with that of Si-1. The content of Ti in Ti-containing supports prepared by CVD substituted for 1, 5 and 20 h is 0.35%, 0.55% and 0.78%, respectively.

Fig. 1(a) and (b) is the subtracted UV–vis spectra of Ti-containing supports prepared by CVD and IMP methods from Si-1 spectra, respectively. From Fig. 1 it can be seen that there is no framework titanium species at 213 nm. With the substitution time increasing, absorbance of the peak centered at about 280 nm increases in Fig. 1(a); the peak centered at about 290 nm does not show any difference in Fig. 1(b). Moreover, the FT-IR spectra of Ti-containing supports prepared by CVD and IMP methods (Figs. 2 and 3) do not show any absorbance at $960\,cm^{-1}$.

Table 1 is the crystal cell parameters of Si-1 and Ti-containing supports prepared by CVD and IMP methods (denoted as Ti-CVD and Ti-IMP). The length of Ti–O bond

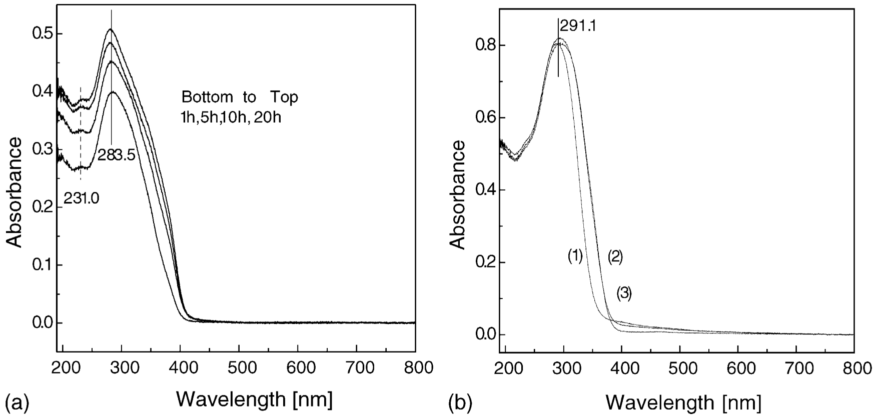


Fig. 1. UV–vis spectra of Ti-containing supports prepared by CVD and IMP methods. (a) CVD method substituted with 1, 5, 10, 20 h; (b) IMP method calcined at (1) 90 °C, (2) 450 °C, and (3) 600 °C.

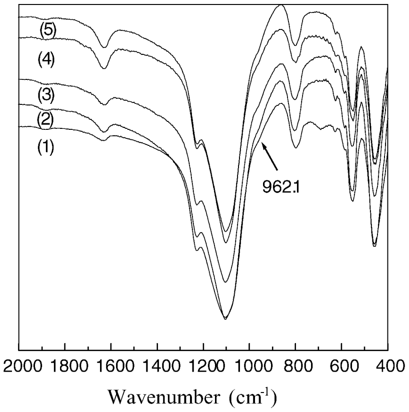


Fig. 2. FT-IR spectra of Ti-containing supports prepared by CVD method. (1) 0 h, (2) 1 h, (3) 5 h, (4) 10 h, and (5) 20 h.

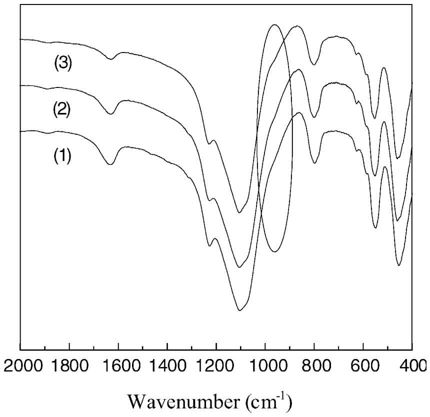


Fig. 3. FT-IR spectra of Ti-containing supports prepared by IMP method. (1) 90 °C, (2) 450 °C, and (3) 600 °C.

Table 1
Crystal cell parameters of the three samples

Sample	*a* (Å)	*b* (Å)	*c* (Å)
Silicalit-1	20.123	20.002	13.437
Ti-CVD	20.140	19.916	13.483
Ti-IMP	20.148	19.904	13.459

is 1.7 Å, which is longer than Si–O bond (1.6 Å), but the crystal cell volume of the prepared supports are not augmented, which means that the titanium species did not get into the framework of Si-1. Therefore, it can be concluded that the Ti-containing supports prepared by CVD and IMP methods do not have framework titanium.

3.3. Effect of calcination atmosphere

The effect of calcination atmosphere of Ag/TS-1 on the propylene epoxidation was investigated, and the results are listed in Table 2. It can be seen that calcination atmosphere has an important effect on the catalytic properties. When the catalyst was calcined in air, it exhibits the optimum catalytic activity, 0.43% propylene conversion with 92.75% PO selectivity. However, when the catalyst was calcined in nitrogen or hydrogen, its activity decreases obviously. At the same time, the catalytic activity decreases gradually with time on stream. The results related to the catalyst deactivation and regeneration have been reported in literature [19].

ESR spectra of Ag/TS-1 calcined in different atmospheres show that when Ag/TS-1 was calcined in H_2, there is a signal at 2.0061, which belongs to Ag^0 [21]. While treated in air or N_2, there is no signal in the spectra. However, XRD patterns of Ag/TS-1 ($2\theta = 36–42^\circ$ was in Fig. 4) calcined

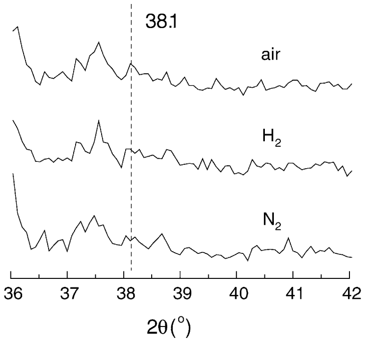


Fig. 4. XRD patterns of Ag/TS-1 calcined in different atmospheres.

Table 2
Effect of calcination method on the gas-phase epoxidation of propylene

Calcination method	$X_{C_3H_6}$ (%)	F_{PO} ($g\,kg^{-1}\,h^{-1}$)	Selectivity for products (%)			
			Aldehyde	PO	Propanal	Acrolein
Air	0.43	5348.96	3.17	92.75	4.08	0
N_2	0.16	1989.45	0	92.71	7.29	0
H_2	0.06	685.77	0	85.22	7.20	7.57

Note: 2 wt.% Ag/TS-1 calcined at 450 °C, 0.4 g; 150 °C; atmospheric pressure; $V_{O_2}:V_{C_3H_6}:V_{H_2}:V_{N_2} = 1:2:3:8$; space velocity, 4000 h^{-1}; n_{Si}/n_{Ti} is 33; reaction time, 40 min.

in different atmospheres show that when the catalyst was calcined in air, there is a weak metal silver diffraction peak at 38.1°; while calcined in N_2 and H_2, no silver peak appears. During the preparation of Ag/TS-1 catalyst, the silver species was deposited on the titanium sites, and then covered it. The FT-IR spectra of 2% Ag/TS-1 calcined in different atmospheres is shown in Fig. 5. It can be seen that the peak centered at 960 cm^{-1} decreases in the order of air, H_2 and N_2, which indicates that the covered Ti species increases accordingly. As a result, the silver particles should be decreased in turn (the more silver particles it has, the weaker titanium absorbance it is).

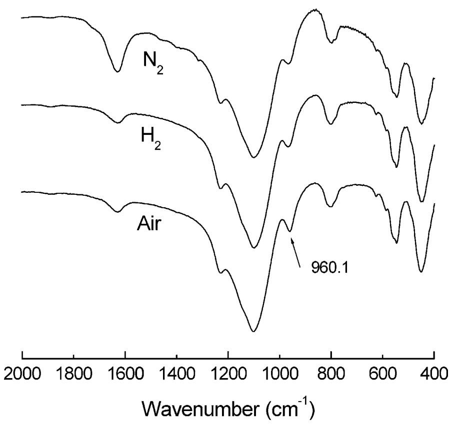
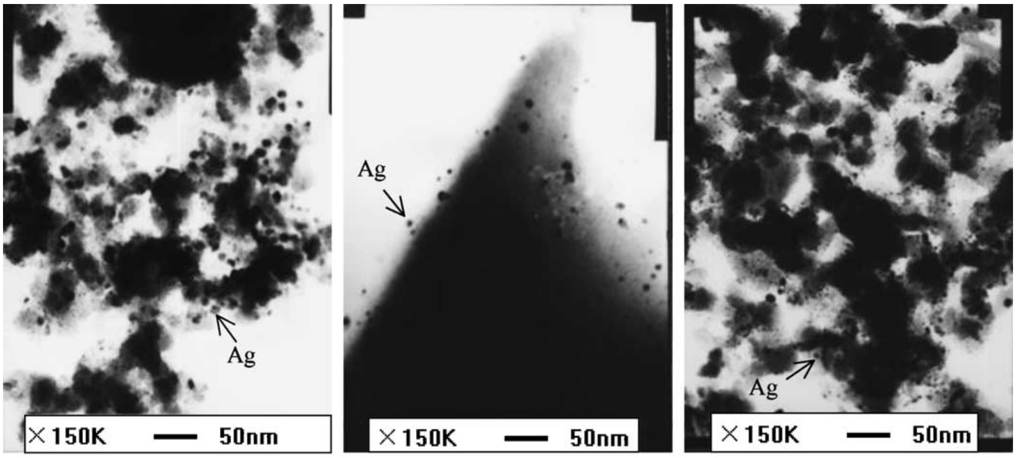


Fig. 5. FT-IR spectra of Ag/TS-1 calcined in different atmospheres.

TEM (Fig. 6) indicates that when Ag/TS-1 was calcined in N_2, most part of the silver particles becomes quite small, only about 2–4 nm. The silver particles calcined in H_2 are 1–3 nm smaller than those calcined in air, which is in agreement with XRD and FT-IR. That is to say, when the catalyst was calcined in air, the silver species is mainly existed in oxidized state. Combined with the reaction results, it can be concluded that the oxidized silver ions are the main active sites for the propylene epoxidation in the gas phase; the catalytic activity of metal silver is quite poor.

3.4. Propylene epoxidation over Ag/Ti-containing catalysts

Our previous results showed that TS-1 is a good support, and there is a synergy between Ag and TS-1 [19]. Over TS-1, there are two kinds of titanium species: framework titanium and extra framework titanium, and extra-framework is divided into two kinds [22]. Moreover, the previous studies showed that both anatase TiO_2 and rutile TiO_2 are not effective for the reaction. In order to further understand which kind of titanium species is synergetic with Ag to favor the formation of PO, different Ti-containing supports were prepared and the catalytic properties of 2% Ag/Ti-containing catalysts are shown in Tables 3 and 4.



(1) Air (2) H_2 (3) N_2

Fig. 6. TEM photographs of Ag/TS-1 calcined in different atmospheres.

Table 3
Effect of substitution time on propylene epoxidation over Ag/Ti-containing (CVD) catalysts

Substitution time (h)	$X_{C_3H_6}$ (%)	F_{PO} (g kg^{-1} h^{-1})	Selectivity for products (%)			
			Aldehyde	PO	Propanal	Acetone
0	7.68	0	0.26	0	0.20	0.48
1	0.29	163.73	7.63	10.83	42.66	10.28
5	0.35	1026.93	5.19	56.28	28.15	10.39
10	0.66	343.83	15.26	10.08	31.33	14.95
20	13.11	8495.57	5.59	12.43	13.39	8.63
20[a]	0.52	1821.22	4.47	67.18	0	0

Notes are the same as in Table 2 except that: catalyst, 0.6 g; $V_{C_3H_6}:V_{O_2}:V_{H_2}:V_{N_2} = 1:2:3:12$; reaction time, 70 min.

[a] Reaction temperature, 100 °C.

Table 4
The catalytic properties of Ag/Ti-containing (IMP) catalysts calcined at different temperature

Calcination temperature (°C)	$X_{C_3H_6}$ (%)	F_{PO} (g kg^{-1} h^{-1})	Selectivity for products (%)			
			Aldehyde	PO	Propanal	CO_2
90	0.81	484.36	12.84	11.47	0	75.69
200	0.17	558.62	19.92	63.03	17.05	0
300	0.14	379.39	31.90	51.98	16.12	0
450	0.29	495.44	40.16	32.77	3.79	0
600	0.20	376.93	36.31	36.15	0	0

Notes are the same as in Table 3.

It can be seen from Table 3 that with the substitution time increasing, the propylene conversion increases; the selectivity to PO increases to the maximum, then decreases. When the pure Si-1 was used as the support, the propylene conversion is 7.68%, but there is no PO detected; the main product is CO_2, which selectivity is 98.53%. When Si-1 was substituted by $TiCl_4$ for 5 h, the PO selectivity is highest, 56.28%. While substituted for 20 h, the propylene conversion reaches to 13.11%, but the PO selectivity decreases to 12.43%; however, the PO selectivity increases to 67.18%, when it reacted at 100 °C.

From Table 4 it can be seen that all the Ag/Ti-containing (IMP) catalysts have catalytic properties of propylene epoxidation, but the selectivity to PO is quite poor. At the same conditions, 0.78% propylene conversion with 94.85% PO selectivity was obtained over 2% Ag/TS-1 catalyst. That is to say, the extra framework titanium species also has weak catalytic properties of propylene epoxidation. It can be concluded that titanium species is essential for the reaction; the framework titanium species plays an important role in the gas-phase epoxidation of propylene, but large amount of extra framework titanium species in the support can decrease the PO selectivity, when reacted at higher temperature.

4. Conclusions

The gas-phase epoxidation of propylene was carried out in a fixed bed, quartz reactor in the presence of hydrogen and oxygen. The effects of calcination atmosphere as well as other Ti-containing supports on the catalytic properties were investigated in detail. The framework titanium species plays an important role in the reaction, but the extra framework titanium species (centered at about 280–290 nm) also has weak epoxidation activity. It can be concluded that excessive extra framework titanium species (hexahedral) can decrease the PO selectivity; the oxidized silver ions favor the formation of PO in the gas phase.

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