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Epoxidation of Propylene by Molecular Oxygen Over the Ag–Y_2O_3–K_2O/α-Al_2O_3 Catalyst

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Abstract The Ag/α-Al_2O_3 catalyst modified with rare earth metal oxide (Y_2O_3) and alkali metal oxide (K_2O) for the epoxidation of propylene by molecular oxygen were prepared and characterized by TG-DTA, XRD and XPS. The results show that a small quantity of Y_2O_3 added plays a role of electron and structure-type promoters, and can change the binding energies of Ag3d and restrain the sintering of Ag crystallites during catalyst preparation. The effects of promoters loading, Ag loading, reaction temperature, and calcination atmosphere on the performance of Ag catalyst were investigated. The results show that the loadings of K_2O, Y_2O_3 and Ag, and reaction temperature affect obviously the catalytic performance of Ag–Y_2O_3–K_2O/α-Al_2O_3 for the epoxidation of propylene to propylene oxide. Under the reaction conditions of 0.1 MPa, 245 °C, GHSV of 2000 h^{-1} and the feed gas of 20%C_3H_6/8%O_2/N_2, the conversion of propylene of 4% and the selectivity to propylene oxide of 46.8% were achieved over the 20%Ag–0.1%Y_2O_3–0.1%K_2O/α-Al_2O_3 catalyst.

Keywords Epoxidation of propylene · Molecular oxygen · Propylene oxide · Silver catalyst · Y_2O_3 promoter

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1 Introduction

Propylene oxide (PO) is an important chemical intermediate used for the manufacture of polyurethane, unsaturated resins, surfactants and other chemicals. Epoxidation of propylene by molecular oxygen over the heterogeneous catalysts is an important but difficult task in the catalysis field. Many researchers have been exploring new routes for the production of PO in the industry. However until now, propylene oxide is still produced by the chlorohydrin process and the Halcon process [1]. The major drawback of the chlorohydrin process is that it requires a large deal of chlorine that is expensive, toxic and can also erode equipments. Moreover, some chlorinated by-products also give rise to serious environmental problems. In the Halcon process, PO is produced together with the equimolar amount of co-product whose value depends on its demand in the market.

The direct epoxidation of ethylene has been widely used in the industrial production of ethylene oxide for many years. Many researchers attempted to attain the epoxidation of propylene over the similar catalysts. However, the selectivity to PO was less than 15% with the conversion of propylene less than 15% [2]. Previous studies suggested that the low selectivity to PO was due to the more easily connecting of allylic hydrogen with the adsorbed oxygen species to form the resonance-stabilized allyl radical or anion that can be easily further oxidized to CO_2 and H_2O [3–7]. However, Kitson and Lambert [8] and Grant and Lambert [9] presumed that the valence charge state of the adsorbed atomic oxygen (O_{ad}) determined the reaction selectivity. A lower valence charge density on O_{ad} was a better electrophile for the epoxidation reaction. A higher valence charge density on O_{ad} was thought to result in an allylic hydrogen (α-H) abstraction from the methyl group and hence combustion. If the modified silver catalyst could produce the mild electrophilic oxygen species to attack the C=C bond of the alkenes, the catalyst would be highly effective for the epoxidation of propylene. By the kinetics studies of adsorption and desorption of O_2 over the modified Ag/α-Al_2O_3 catalyst, Atkins et al. [10, 11] found that Cl or Cs could weaken the strength of Ag–O bond and block the adsorption of oxygen onto the stepped Ag surface, resulting in the increase of the selectivity to ethylene oxide from 75% to 85%. Some patents claimed that the conversion of propylene of 1.5–12.6% and the selectivity to PO of 32–60% were achieved over the K, W, Re and Cl modified Ag/$CaCO_3$, CaF_2, $CaHPO_4$, $CaMoO_4$ and $BaTiO_3$ catalysts [12–17]. Jin et al. [18, 19] have investigated the modified silver catalysts with Mo for the gas-phase epoxidation of propylene with molecular oxygen, and a conversion of oxygen of 6.8% and a selectivity to PO of 53.1% were achieved. Using unsupported Ag catalysts promoted with NaCl or $BaCl_2$ for the gas-phase epoxidation of propylene with air, the conversion of propylene of 18.6% and the selectivity to PO of 33.4% were obtained at 350 °C and GHSV of 17,500 h^{-1} [20]. Lu et al. [21] claimed that the selectivity to PO was 43.4% when the conversion of propylene was 0.19% over the NaCl-modified $VCe_{1-x}Cu_x$ catalyst with molecular oxygen as an oxidant. Luo et al. [22] claimed that the conversion of propylene of 1.64% and the selectivity to PO of 30.6% were achieved over the Ag/CuCl catalyst at 350 °C.

In this paper, the effects of promoter (Y_2O_3 and K_2O) loading, Ag loading, the calcination atmosphere of catalyst and reaction temperature on the catalytic performance of Ag/α-Al_2O_3 catalyst for the epoxidation of propylene by molecular oxygen were investigated.

2 Experimental

2.1 Preparation of Catalyst

The catalyst was prepared as follows: α-Al_2O_3 support (20–40 mesh, $S_{BET} = 10.3\ m^2/g$, the average pore size = 146 nm) was impregnated with $Y(NO_3)_3$ and KNO_3 aqueous solution at 60 °C for 1 h, and dried at 120 °C for 5 h, and then calcined at 550 °C for 2 h. The modified α-Al_2O_3 support was dunked into the silver–ammonium complex solution (synthesized by adding silver oxalate to ethylenediamine aqueous solution) for 0.5 h at 60 °C, and dried at 80 °C for 2.5 h, and then calcined at 280 °C for 10 min. The silver loading of the catalyst was varied by changing the amount of silver oxalate in the ethylenediamine aqueous solution. The weight composition of catalysts was (5–30%)Ag–(0–2%)Y_2O_3–(0–1%)K_2O/α-Al_2O_3(wt%).

2.2 Catalytic Epoxidation Reaction

The epoxidation of propylene was carried out in the micro-reactor system at 245 °C, 0.1 MPa and GHSV of 2000 h^{-1}. About 0.5 mL catalyst was packed in the stainless-steel fixed-bed reactor (Ø5 × 360 mm). The composition of feed gas (20%C_3H_6, 8%O_2 and balance N_2) was controlled by three mass flow meters. The products were qualitatively identified by INFICON IPC400 quadrupole spectrometer. The compositions of feed gas and products were analyzed quantitatively by two on-line gas chromatographs with three packed columns (G.D.X−401, silica gel and 5A zeolite) and TCD detectors. Carbon balance was used to calculate the conversion of propylene and selectivity to PO in the epoxidation reaction.

2.3 Characterization of Catalyst

TG-DTA was carried out on a PerkinElmer Pyris Diamond TG-DTA analyzers, the temperature was heated programmedly from 50 to 500 °C at 10 °C/min in nitrogen or air (50 mL/min). XRD patterns were recorded on a Rigaku D/max-2550VB/PC diffractometer operated at 40 kV, 100 mA (CuKα radiation, $\lambda = 0.15406$ nm). XPS spectra were recorded on a Thermo ESCALAB 250 spectrometer with a monochromatized AlKα X-ray source (1486.6 eV), and a passing energy of 20 eV. C1s (binding energy of 284.6 eV) of adventitious carbon was used as the reference.

3 Results and Discussion

3.1 Effect of the Promoters

Table 1 shows the effect of the promoters of Y_2O_3 and K_2O on the epoxidation of propylene over Ag/α-Al_2O_3 catalysts. As shown from Table 1, the promoters of rare earth metal (Y) and alkali metal (K) oxide have obvious influence on the catalytic performance of Ag/α-Al_2O_3 catalyst. PO or any other by-products containing oxygen could not be gained except CO_2 and H_2O over the unmodified Ag/α-Al_2O_3 catalyst. The presence of K_2O could inhibit the complete oxidation of propylene, resulting in significant enhancement of PO selectivity. When 0.1%K_2O was added into Ag/α-Al_2O_3 catalyst, the conversion of propylene and the selectivity to PO were 8% and 4.3%, respectively. After the catalyst was modified with Y_2O_3, propanal and acetone could be gained. Adding 0.1% Y_2O_3 into Ag–K_2O/α-Al_2O_3 catalyst made the selectivity to PO increase from 4.3% to 46.8%, while the propylene conversion was 4% and the selectivity to propanal and acetone was 0.64% and 0.70%, respectively.

Table 1 Effect of Y_2O_3 and K_2O promoters on the epoxidation of propylene over Ag/α-Al_2O_3 catalysts

Catalyst	Conversion of propylene (%)	Selectivity (%)[a]			
		PO	PRO	AC	ACR
20%Ag/α-Al_2O_3	4.6	0	0	0	0
20%Ag/0.1%K_2O/α-Al_2O_3	8.0	4.3	0	0	0
20%Ag/0.1%Y_2O_3/α-Al_2O_3	2.5	0	0.23	0.33	0
20%Ag/0.1%Y_2O_3–0.1%K_2O/α-Al_2O_3	4.0	46.8	0.64	0.70	0

[a] PO, propylene oxide; PRO, propanal; AC, acetone; ACR, acrolein

Figures 1 and 2 show effects of K_2O and Y_2O_3 loading on the epoxidation performance of 20%Ag/α-Al_2O_3 catalysts. As seen from Figure 1, there were maximums of PO selectivity and propylene conversion with the increase of K_2O loading. When 0.1% K_2O was added into Ag/α-Al_2O_3 catalyst, the maximum of propylene conversion and selectivity to PO was 8% and 4.3%, respectively. As seen from Figure 2, with the increase of Y_2O_3 loading, the conversion of propylene declined sharply, and the selectivity to PO reached a maximum and then decreased significantly. When adding 0.1% Y_2O_3 into 20%Ag–0.1%K_2O/α-Al_2O_3 catalyst, the selectivity to PO increased from 4.3% to 46.8%, and the conversion of propylene decreased from 8% to 4%. The results above indicate that the presence of Y_2O_3 in 20%Ag–0.1%K_2O/α-Al_2O_3 catalyst can restrain the complete oxidation of propylene and increase noticeably the selectivity to PO.

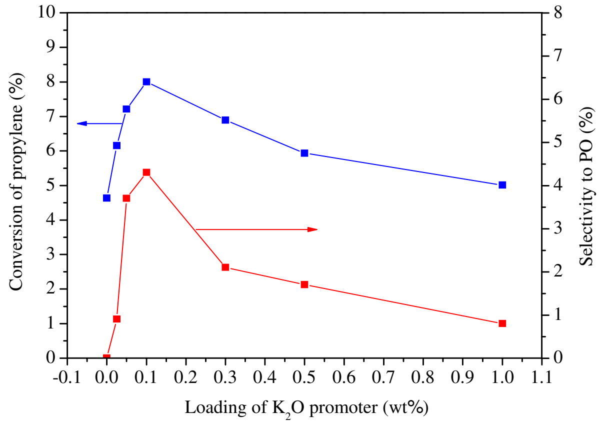

Fig. 1 Effect of K_2O loading on the epoxidation performance of 20%Ag/α-Al_2O_3 catalyst

3.2 Effect of Ag Loading

Figure 3 shows the effect of Ag loading on the epoxidation performance of Ag–0.1%Y_2O_3–0.1%K_2O/α-Al_2O_3 catalyst. With the increase of Ag loading from 5 to 30 wt%, the conversion of propylene increased obviously, and the selectivity to PO increased sharply to a maximum and then declined significantly. When Ag loading was 20 wt%, the selectivity to PO reached the maximum of 46.8% with the conversion of propylene of 4.0%. When Ag loading increased further, the conversion of propylene increased from 3.43% to 7.89% and the selectivity to PO decreased from 46.8% to 19.4% with the main by-products of CO_2 and H_2O. These results show that Ag loading was a highly sensitive parameter and the suitable Ag loading was 20 wt%.

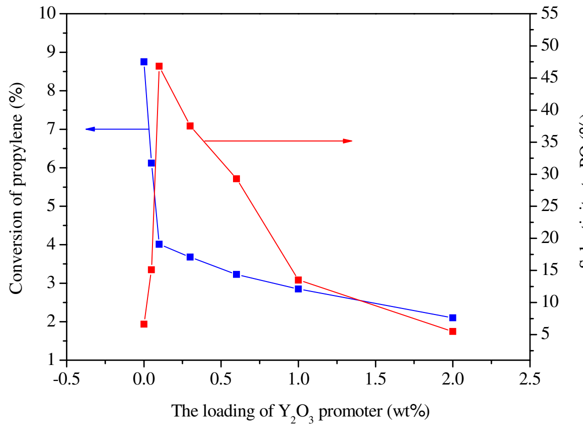

Fig. 2 Effect of Y_2O_3 loading on the epoxidation performance of 20%Ag–0.1%K_2O/α-Al_2O_3 catalyst

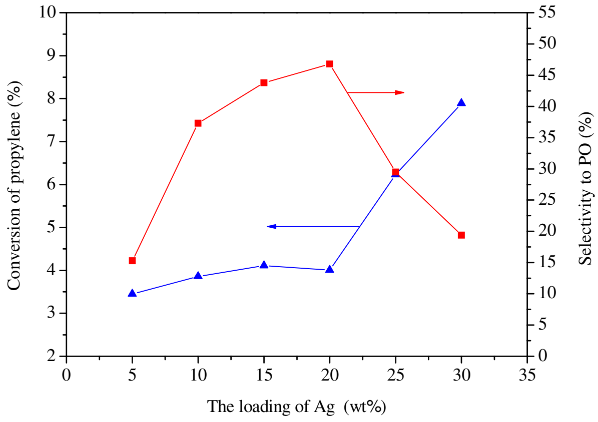

Fig. 3 Effect of Ag loading on the epoxidation performance of Ag–0.1%Y_2O_3–0.1%K_2O/α-Al_2O_3 catalyst

3.3 Effect of Reaction Temperature

Table 2 shows the effect of reaction temperature on the epoxidation performance of 20%Ag–0.1%Y_2O_3–0.1%K_2O/α-Al_2O_3 catalyst. With the increase of the reaction temperature, the conversion of propylene increased, and the selectivity to PO increased to a maximum and then decreased quickly. At 245 °C, the selectivity to PO reached the maximum of 46.8% with the conversion of propylene of 4%. At 300 °C, propylene was nearly oxidized to CO_2 and H_2O.

3.4 TG-DTA

Figures 4 and 5 show the TG-DTA profiles of 20%Ag–0.1%Y_2O_3–0.1%K_2O/α-Al_2O_3 catalyst before calcination. As seen from Figure 4, the first step of weight loss of 8.87% was located at 90–150 °C in air, accompanied by an endothermic peak at 120 °C, which was attributed to the thermal decomposition of silver–ammonium complex and then the formation of Ag crystallites. The second step of weight loss of 0.91% was located at 255–330 °C, accompanied by an exothermic peak at 282 °C, which was due to the combustion of some organic species. As seen from Figure 5, there were two similar steps of weight loss in N_2 as those in air (Figure 4), i.e., the first step of weight loss of 9.15% at 105–160 °C, and the second step of weight loss of 0.75% at 285–370 °C. Compared with those in air (Figure 4), there were temperature difference of 5 °C between both endothermic peaks and 43 °C between both exothermic peaks, which indicates that the thermal decomposition of silver–ammonium complex was similar in different calcination atmospheres, but the combustion of organic species was more difficult in nitrogen.

Table 2 Effect of the reaction temperature on the epoxidation performance of 20%Ag–0.1%Y_2O_3–0.1%K_2O/α-Al_2O_3 catalyst

Reaction temperature (°C)	Conversion of C_3H_6 (%)	Selectivity (%)[a]			
		PO	PRO	AC	ACR
205	1.8	3.5	0	0	0
225	2.4	13.1	0	0	0
245	4.0	46.8	0.64	0.7	0
265	7.7	20.8	0.56	1.5	0
285	8.6	6.7	0.78	1.3	0
300	8.9	0	0.21	0.6	0

[a] PO, propylene oxide; PRO, propanal; AC, acetone; ACR, acrolein

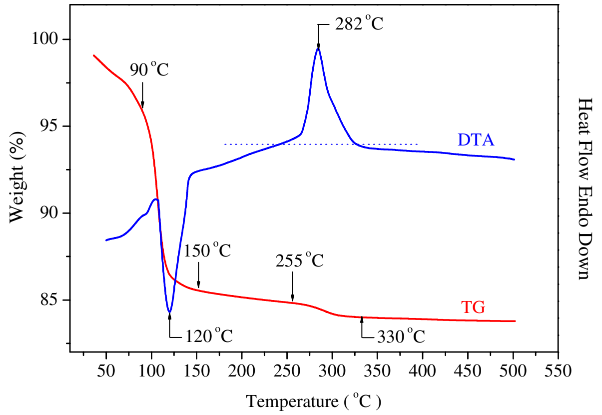

Fig. 4 TG-DTA profiles of as-prepared Ag–0.1%Y_2O_3–0.1%K_2O/α-Al_2O_3 catalyst in air

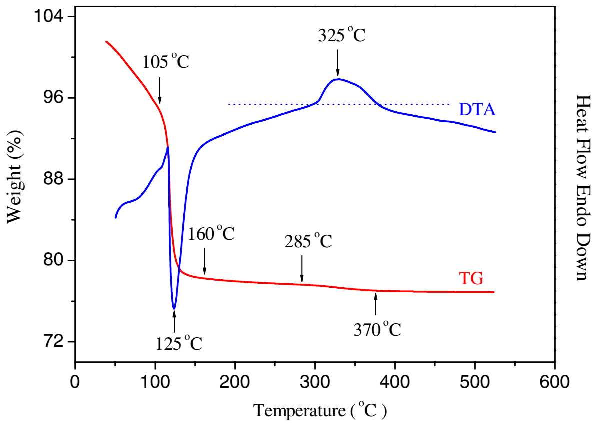

Fig. 5 TG-DTA profiles of as-prepared Ag–0.1%Y_2O_3–0.1%K_2O/α-Al_2O_3 catalyst in N_2

Table 3 shows the effect of the calcination atmosphere of the catalyst on the epoxidation performance of 20%Ag–0.1%Y_2O_3–0.1%K_2O/α-Al_2O_3 catalyst. The results show that there was no obvious difference in the epoxidation performance of the catalyst calcined in different atmospheres, which was consistent with a little temperature difference of the endothermic peak in the thermal decomposition of silver–ammonium complex to form Ag crystallites in air or N_2.

Table 3 Effect of the calcination atmosphere on the epoxidation performance of 20%Ag–0.1%Y_2O_3–0.1%K_2O/α-Al_2O_3 catalyst

Calcination atmosphere	Conversion of C_3H_6 (%)	Selectivity (%)[a]			
		PO	PRO	AC	ACR
Air	4.0	46.8	0.64	0.70	0
N_2	4.2	45.1	0.71	0.58	0

[a] PO, propylene oxide; PRO, propanal; AC, acetone; ACR, acrolein

3.5 XRD

Figure 6 shows the XRD patterns of 20%Ag–0.1%Y_2O_3–0.1%K_2O/α-Al_2O_3 catalysts calcined in different calcination atmospheres. Figure 7 shows the XRD patterns of 20%Ag–0.1%K_2O/α-Al_2O_3 and 20%Ag–0.1%Y_2O_3–0.1%K_2O/α-Al_2O_3 catalysts. The results show that, the diffraction peaks of Ag and α-Al_2O_3 were observed, but the diffraction peaks of Y_2O_3 and K_2O did not appear. The diffraction peaks of α-Al_2O_3 support located at $2\theta = 25.6$, 35.2, 43.4, 52.6, 57.5, 66.5 and 68.2°. There were four diffraction peaks of Ag at $2\theta = 38.1$, 44.3, 64.4 and 77.4°, corresponding to the crystal faces of Ag(111), (200), (220) and (311), respectively. The diffraction peaks of silver oxides were not observed.

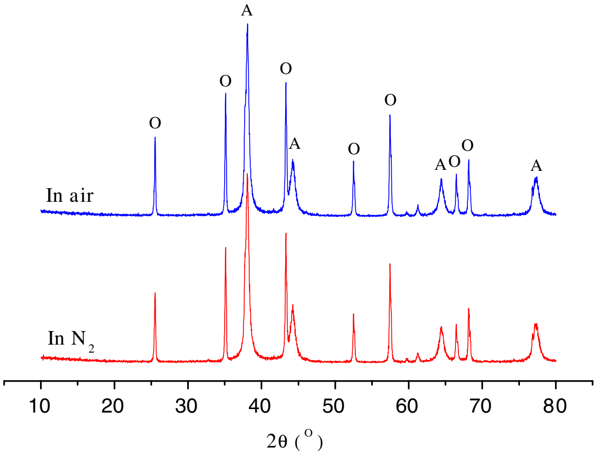

Fig. 6 XRD patterns of 20%Ag–0.1%Y_2O_3–0.1%K_2O/α-Al_2O_3 catalysts calcined at 280 °C for 10 min in different atmospheres (O, α-Al_2O_3; A, Ag)

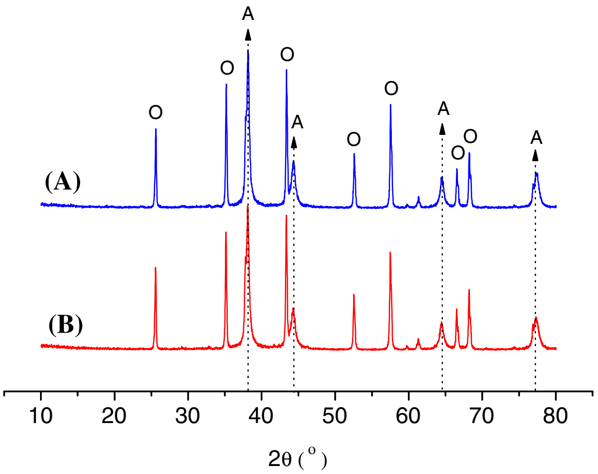

Fig. 7 XRD patterns of 20%Ag–0.1%K_2O/α-Al_2O_3 (A) and 20%Ag–0.1%Y_2O_3–0.1%K_2O/α-Al_2O_3 (B) calcined at 280 °C for 10 min in air (O, α-Al_2O_3; A, Ag)

The size of Ag crystallites was determined by Scherrer's equation with the full width at half maximum height of the diffraction peak of Ag(111). Based on the diffraction peak of Ag(111) shown in Figure 6, the size of Ag crystallites calcined at 280 °C for 10 min in air or N_2 was determined to be 15.7 nm and 16.0 nm, respectively, which indicates that there was a little difference in the size of Ag crystallites calcined in air or N_2. It is interesting that the presence of a small quantity of Y_2O_3 made the size of Ag crystallites decrease from 17.4 nm to 15.7 nm determined by the data in Figure 7, which indicates that a small quantity of Y_2O_3 could regulate the size of Ag crystallites to restrain agglomeration, and Y_2O_3 played a role of structure-type promoter.

3.6 XPS

Figures 8 and 9 show the Ag3d and Y3d XPS spectra of 20%Ag–0.1%Y_2O_3–0.1%K_2O/α-Al_2O_3 catalyst, respectively. The binding energies of Ag3d$_{5/2}$ and Ag3d$_{3/2}$ were 368.8 and 374.7 eV, respectively. Compared with the binding energies of metallic Ag3d$_{5/2}$ (367.9 eV) and Ag3d$_{3/2}$ (373.9 eV), the presence of Y_2O_3 made these two binding energies increase obviously. This was due to the electron interaction between Y and Ag, and the electron of Ag was transferred to Y, which made Y negatively charged and Ag3d peaks shift to higher binding energy. Zatko reported that Ag^+ as well as Ag^{3+} might occur under practical catalytic reaction conditions [23]. The similar results were reported by other researchers. The results of XPS [24] over Ag–MoO_3 catalyst showed that the valence of Mo and Ag were $6-\delta$ and δ^+, respectively, which indicated that the electron transferred from silver to MoO_3 to make the Mo oxyanion. It was also reported that the presence of Cs and Cl would cause the appearance of

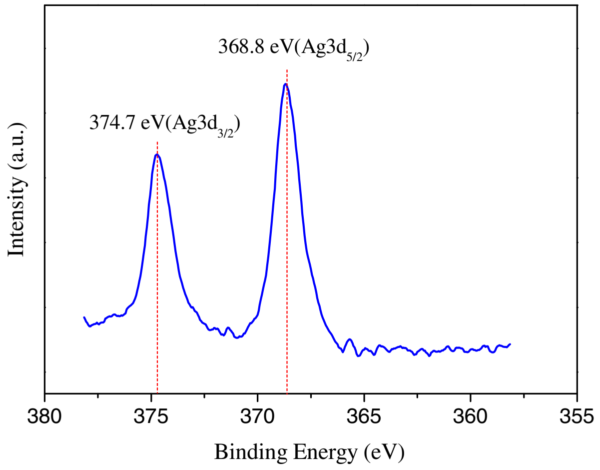

Fig. 8 Ag3d XPS spectra of 20%Ag–0.1%Y_2O_3–0.1%K_2O/α-Al_2O_3 catalyst

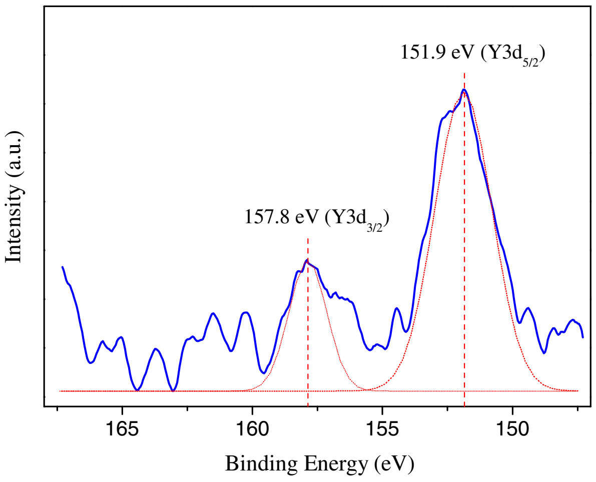

Fig. 9 Y3d XPS spectra of 20%Ag–0.1%Y_2O_3–0.1%K_2O/α-Al_2O_3 catalyst

cationic species of silver on the surface of Ag/α-Al_2O_3 catalysts, and thus the selectivity to ethylene oxide was increased greatly [25–27]. Two peaks in Figure 8 could be assigned to higher oxidation states of Ag, and indicated the presence of the subsurface layer of electropositive Ag atoms, which was a prerequisite to produce active sites where electrophilic oxygen atoms could be absorbed and played an important role in the epoxidation of propylene.

The results in Figure 9 show that, the binding energies of Y3$d_{5/2}$ and Y3$d_{3/2}$ in the catalyst were 151.9 and 157.8 eV, and lower than those (Y3$d_{5/2}$ 156.4 eV, Y3$d_{3/2}$ 158.2 eV) of pure Y_2O_3 powder. It shows that the oxidative state of Y in the catalyst was lower than Y^{3+}, that is to say, Y has obtained the electrons from Ag and the valence of Y and Ag should be $3-\delta$ and δ^+, respectively. Yang et al. [28] reported the similar results by investigating the modified Ag catalyst with Re for the epoxidation of ethylene, and found that adding Re into Ag catalyst led to Ag electron-deficient and Re^{7+} transforming to $Re^{7-\delta}$. Lu et al. [29] reported that a part of Ag atoms in the NaCl-modified Ag catalyst existed as cation, and the high oxidative state of Ag was favorable to produce electrophilic oxygen species. Therefore, Y_2O_3 played a role of electron-type promoter that could strongly polarize nearby electron cloud of Ag, which made the absorbed oxygen hold proper electrophilic character and was beneficial to the olefinic carbon of propylene converting to PO.

4 Conclusion

Y_2O_3 and K_2O are the effective promoters for Ag/α-Al_2O_3 catalyst used in the epoxidation of propylene by molecular oxygen. Y_2O_3 plays a role of cooperative electron and structure-type bi-functional promoter by obtaining electron charge from Ag and restraining the aggregation of Ag crystallites to the suitable size, which improves the epoxidation performance of Ag–K_2O/α-Al_2O_3 catalyst. The K_2O loading, Y_2O_3 loading, Ag loading, and reaction temperature affect obviously the catalytic performance of Ag–Y_2O_3-K_2O/α-Al_2O_3 catalyst for the epoxidation of propylene to PO. Under the reaction condition of 0.1 MPa, 245 °C, GHSV of 2,000 h^{-1} and the feed gas of 20%C_3H_6/8%O_2/N_2, the conversion of propylene of 4% and the selectivity to PO of 46.8% were achieved over 20%Ag–0.1%Y_2O_3–0.1%K_2O/α-Al_2O_3 catalyst.

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