Promotional effect of Y_2O_3 on the performance of Ag/α-Al$_2$O$_3$ catalyst for epoxidation of propylene with molecular oxygen

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Abstract

The Ag/α-Al$_2$O$_3$ catalysts modified with rare earth, alkali and alkaline earth metal oxides for the epoxidation of propylene by molecular oxygen were prepared and characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), CO_2-temperature programmed desorption (CO_2-TPD), BET surface area and pore diameter distribution. The results show that the appropriate pore diameter and high surface area of α-Al$_2$O$_3$ support, and the suitable basic sites on the surface of catalyst are necessary to the highly effective Ag catalyst for the epoxidation of propylene. The presence of a small quantity of Y_2O_3 can restrain the sintering of Ag particles on the surface of α-Al$_2$O$_3$ and adjust the surface basicity of catalyst. The loadings of promoters and reaction temperature obviously affect the performance of Ag catalysts. Under the reaction condition of 0.1 MPa, 245 °C, space velocity 2000 h^{-1} and the feed of 20% C$_3$H$_6$/8% O$_2$/N$_2$, 4% conversion of propylene and 46.8% selectivity to propylene oxide were obtained over the 20 wt% Ag–0.1% Y_2O_3–0.1% K$_2$O/α-Al$_2$O$_3$ catalyst.
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Keywords: Silver/alumina catalyst; Y_2O_3 promoter; Epoxidation of propylene; Molecular oxygen

1. Introduction

Propylene oxide (PO) is an extremely important organic intermediate to manufacture polyurethane, unsaturated resins, surfactants and other products. At present PO is mainly produced commercially by the chlorohydrin process and the organic-hydroperoxide (Halcon) process [1]. The chlorohydrin process requires a great deal of chlorine that is expensive, toxic and erosive. In addition, the chlorinated by-products and the disposal of CaCl$_2$ also give rise to serious environmental problems. The disadvantage of the Halcon process is to produce equimolar amounts of co-products whose value lies on a demand in the market. Recently, the new processes and catalysts under development for the production of PO were discussed [2]. For example, the invention of titanium silicate-1 (TS-1) by Taramasso et al. opened a novel route to the epoxidation of propylene with hydrogen peroxide (H$_2$O$_2$) as an oxidant under mild reaction conditions, in which >95% PO selectivity based on propylene or 70%–99% based on H$_2$O$_2$ was obtained. However, the relatively

high cost of H$_2$O$_2$ and TS-1 catalyst hinder the commercialization of this process so far [3–5]. In order to reduce the cost of H$_2$O$_2$, Sato and Miyake [6] and Meiers et al. [4] used Pd or Pd–Pt impregnated TS-1 catalyst to produce H$_2$O$_2$ *in situ* with a mixture of molecular oxygen and hydrogen, in which 46% PO selectivity was obtained over the TS-1 catalyst loaded with 1 wt% Pd and 0.02 wt% Pt. Although gold has historically been regarded as being poorly active for most chemical reactions, the highly dispersed nano-Au supported on 3D mesoporous silylated titanosilicate or titanosilicate is a highly effective catalyst for the epoxidation of propylene by the mixture of O$_2$ and H$_2$ at relatively low temperature, in which the PO selectivity of >90% and the propylene conversion of about 8% can be obtained [7,8]. Xi and co-workers [9–12] have prepared H$_2$O$_2$ *in situ* by the redox reaction of 2-ethylanthraquinone/2-ethylanthrahydroquinone, which could be used for the homogeneous catalytic epoxidation of olefins over a tungsten-containing catalyst. After the epoxidation reaction is finished, the catalyst can precipitate, be filtered and reused again. This process combines the advantages of both homogenous and heterogeneous catalysts in one system through reaction-controlled phase transfer of the catalyst. If this technique of producing PO would be used commercially, the key lies in how to improve the concentration of PO in the

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reaction medium and overcome the recycling problem of the catalyst.

The direct gas-phase epoxidation of propylene with oxygen or air as an oxidant has long been the most desirable as well as challenging goal in the catalysis field. ARCO chemists [13–18] claimed that the propylene conversion of 1.5%–12.6% and selectivity to PO of 32%–60% were achieved over the K, W, Re and Cl modified Ag catalyst supported on $CaCO_3$, CaF_2, $CaHPO_4$, $CaMoO_4$ or $BaTiO_3$. The composition of gas phase feed was typically 10% C_3H_6, 5% O_2, optionally 5%–25% CO_2, and balance N_2, as well as 50–500 ppm ethyl chloride, or 20–500 ppm NO. The reaction temperature was 220–280 °C and GHSV was 800–3000 h^{-1}. Lu and Zuo [19] have reported the unsupported Ag catalyst promoted with NaCl or $BaCl_2$. At the condition of GHSV of 17,500 h^{-1}, 350 °C, 10% C_3H_6 and balance air, the C_3H_6 conversion of 18.6% and the selectivity to PO of 33.4% were obtained. Recently, Jin et al. have investigated the Mo-modified silver catalysts for the gas-phase epoxidation of propylene with oxygen. When the oxygen conversion was 6.8%, the selectivity to PO reached 53.1% at 350–450 °C [20,21]. Li et al. [22] claimed that the selectivity to PO was 43.4% when propylene conversion was 0.19% over the NaCl-modified $VCe_{1-x}Cu_x$ catalyst with molecular oxygen as an oxidant.

For the mechanism of silver-catalyzed epoxidation of propylene to PO, Nakatsuji and co-workers [23,24] suggested that the low selectivity to PO was due to a decreased rate of epoxidation of propylene and an increased rate of propylene combustion on the silver surface by different reaction pathways. The epoxidation of olefins was attributed to the reaction of the adsorbed oxygen species with the olefinic carbon atoms to form a α bond between oxygen and olefinic carbon with a breaking of the C−C π bond, and the propylene combustion was initiated by the formation of the resonance-stabilized allyl radical or anion through the abstraction of allylic hydrogen by adsorbed oxygen [25–28]. Roberts et al. [29] have proposed a mechanism for the complete oxidation of propylene, that is, an acid–base reaction between atomically adsorbed oxygen and an allylic C−H bond, which leads to the formation of surface hydroxyl groups and chemisorbed allyl species that are further oxidized to CO_2 and H_2O.

In this paper, the effects of different promoters on the catalytic performance of Ag/α-Al_2O_3 were studied. The rare earth, alkali and alkaline earth metal oxides were used as the promoters. We have found that the selectivity to PO could be obviously improved when rare earth element Y was added into the catalyst as promoter. In addition, the influences of the physicochemical properties of the modified α-Al_2O_3 supports and catalysts on the catalytic performance were also investigated.

2. Experimental

2.1. Catalyst preparation

The catalyst was prepared as follows: $Y(NO_3)_3$, KNO_3, $Ba(NO_3)_2$ or $Ca(NO_3)_2$ was dissolved in distilled water, and

then α-Al_2O_3 (BET surface area of 10.3 m^2/g, 20–40 mesh) was impregnated with this solution for 1 h at 60 °C. The particles impregnated were dried at 120 °C for 5 h, and calcined at 450–800 °C for 2 h. Subsequently, a silver–ammonium complex solution was synthesized by adding silver oxalate to an aqueous ethylenediamine solution. After modified α-Al_2O_3 was dunked into the silver–ammonium complex solution for 0.5 h at 60 °C, the particles were dried at 120 °C for 4 h and calcined at 280 °C for 10 min.

Four kinds of α-Al_2O_3 (A–D) with different surface areas and pore diameter distributions were used to study the effects of support on the performance of Ag catalysts. If it is without the special label, α-Al_2O_3 (D, 10.3 m^2/g) was used as the support of Ag catalysts.

2.2. Catalytic epoxidation of propylene

The catalytic epoxidation of propylene was carried out in a micro-reactor system. The size of the stainless steel fixed-bed reactor was Ø5 mm × 360 mm, in which 0.25 ml catalyst was placed. The catalytic epoxidation conditions were at 200–300 °C, 0.1 MPa and space velocity of 2000 h^{-1}. The feedstock gas consisted of 20% C_3H_6, 8% O_2 and balance N_2, and their flow rate was controlled by three mass flow meters.

The reaction products were identified qualitatively by the quadrupole mass spectrometer (IPC 400, INFICON Ltd.). The concentrations of feedstock and reaction 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 of PO. The conversion of propylene was equal to $(n_f - n_e)/n_f$ (n_f is the total mole of carbon in propylene fed and n_e is the total mole of carbon in effluent propylene), and the selectivity to PO was equal to $n_p/(n_f - n_e)$ (n_p is the total mole of carbon in PO produced).

2.3. Characterization of catalyst

The BET surface area and pore size distribution of samples were measured on a Micromeritics ASAP 2020M Sorptometer. Before being analyzed, the samples were evacuated at 90 °C for 0.5 h and at 350 °C for 5 h under vacuum. The SEM micrographs were obtained on a JEOL JSM-6360LV scanning electron microscopy. The X-ray powder diffraction (XRD) patterns were collected on a Rigaku D/max-2550/PC powder diffractometer equipped with the Cu Kα radiation.

Temperature programmed desorption (CO_2-TPD) of adsorbed CO_2 was carried out in the conventional flow system equipment with the thermal conductivity detector (TCD). The sample (600 mg) was pretreated at 500 °C for 1 h at N_2 of 30 ml/min, and then it was quenched to room temperature and allowed to adsorb CO_2 to saturation at 20 °C for 1.5 h. Physically adsorbed CO_2 was removed by flushing the sample with N_2 gas for 1 h at adsorption temperature. The heating rate was 20 °C/min.

Table 1
Performance of the modified Ag/α-Al$_2$O$_3$ catalyst for the epoxidation of propylene at 245 °C

Catalyst[a]	Conversion of C$_3$H$_6$ (%)	Selectivity (%)			
		PO	PRO	AC	ACR
Ag/α-Al$_2$O$_3$	4.6	0	0	0	0
Ag–K$_2$O/α-Al$_2$O$_3$	8.0	4.3	0	0	0
Ag–BaO/α-Al$_2$O$_3$	3.1	2.5	0	0	0
Ag–CaO/α-Al$_2$O$_3$	1.6	1.7	0	0	0
Ag–Y$_2$O$_3$/α-Al$_2$O$_3$	2.5	0	0.23	0.33	0
Ag–Y$_2$O$_3$-BaO/α-Al$_2$O$_3$	2.0	3.8	0	0	0
Ag–Y$_2$O$_3$-CaO/α-Al$_2$O$_3$	1.5	2.4	0	0	0
Ag–Y$_2$O$_3$–K$_2$O/α-Al$_2$O$_3$	4.0	46.8	0.64	0.70	0

PO, propylene oxide; PRO, propanal; AC, acetone; ACR, acrolein.

[a] The loadings (wt%) were 20% Ag, 0.1% Y$_2$O$_3$, 0.1% K$_2$O, 1% BaO, and 0.5% CaO.

3. Results and discussion

3.1. Effect of promoter on the performance of Ag/α-Al$_2$O$_3$ catalyst

The influences of different promoters on the performance of silver catalyst for the epoxidation of propylene are listed in Table 1. The results show that PO or other oxygen-containing by-products cannot be gained except for CO$_2$ and H$_2$O over the unmodified Ag/α-Al$_2$O$_3$ catalyst. The modification with rare earth metal oxide, alkali and alkaline earth metal oxides has an obvious influence on the efficiency of Ag/α-Al$_2$O$_3$ catalysts. After the catalyst is modified with K$_2$O, BaO, or CaO, PO can be gained; over the catalyst modified with Y$_2$O$_3$, propanal and acetone can be gained. Adding 0.1 wt% Y$_2$O$_3$ into Ag/K$_2$O/α-Al$_2$O$_3$ catalyst increases the selectivity to PO from 4.3% to 46.8%. For the Ag/BaO/α-Al$_2$O$_3$ or Ag/CaO/α-Al$_2$O$_3$ catalyst, the presence of 0.1 wt% Y$_2$O$_3$ affects hardly their catalytic performance.

The influences of Y$_2$O$_3$, K$_2$O, BaO and CaO loading on the catalytic performance of Ag/α-Al$_2$O$_3$ are shown in Fig. 1. There is a maximum of the selectivity to PO with an increase in the promoter loading. When 0.1 wt% K$_2$O is added into the Ag/α-Al$_2$O$_3$ catalyst, the maximum selectivity to PO is 8.0% with 4.3% conversion of propylene; as the loading of BaO is 1%, the highest selectivity to PO is 2.5% with 3.1% conversion of propylene; as the loading of CaO is 0.5 wt%, the highest selectivity to PO is 1.7% with 1.6% conversion of propylene. As a single additive, the promoting efficiency is K$_2$O > BaO > CaO, and Y$_2$O$_3$ is almost ineffective.

When a small quantity of Y$_2$O$_3$ is added into the Ag–(0.1%)K$_2$O/α-Al$_2$O$_3$ catalyst, the conversion of propylene decreases to half and the PO selectivity increases noticeably. These results indicate that Y$_2$O$_3$ and K$_2$O may play a role as cooperative electron-type promoters, and affect the electronic density of the adjacent silver atoms that produce the proper adsorbed oxygen species to inhibit the total oxidation of propylene, resulting in obvious enhancement of the PO selectivity.

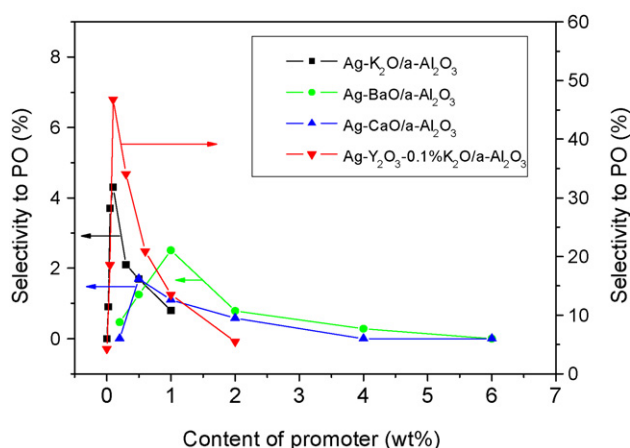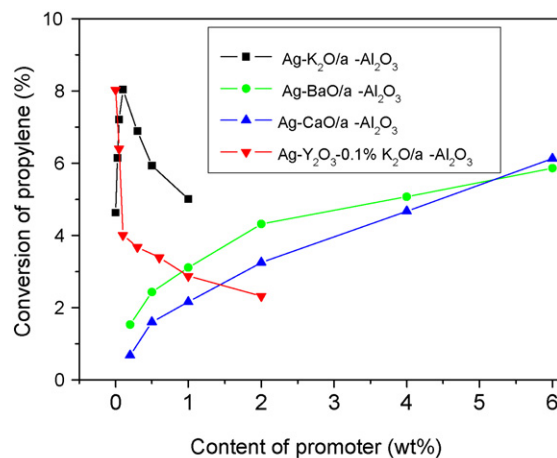The effects of the reaction temperature on the propylene conversion and selectivity of PO over the Ag–Y$_2$O$_3$–K$_2$O/α-

Fig. 1. Effect of the promoter loading on the catalytic performance of 20% Ag/α-Al$_2$O$_3$(wt%) for the propylene epoxidation at 245 °C.

Al$_2$O$_3$ catalyst are listed in Table 2. With the ascent of reaction temperature, the propylene conversion increases, and the PO selectivity reaches to the maximum 46.8% at 245 °C and then sharply decreases. At >300 °C, PO is totally oxidized to CO$_2$ and H$_2$O.

3.2. Effect of α-Al$_2$O$_3$ support

It is well known that the surface area and pore diameter distribution of α-Al$_2$O$_3$ support affect obviously the performance

Table 2
Effect of the reaction temperature on the performance of 20% Ag–0.1% Y$_2$O$_3$–0.1% K$_2$O/α-Al$_2$O$_3$(wt%) for the epoxidation of propylene

Reaction temperature (°C)	Conversion of C$_3$H$_6$ (%)	Selectivity (%)			
		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

PO, propylene oxide; PRO, propanal; AC, acetone; ACR, acrolein.

Table 3
Effect of surface area of α-Al$_2$O$_3$ on the performance of 20% Ag–0.1% Y$_2$O$_3$–0.1% K$_2$O/α-Al$_2$O$_3$ (wt%) catalyst for the epoxidation of propylene at 245 °C

α-Al$_2$O$_3$	BET surface area (m^2/g)	Conversion of C$_3$H$_6$ (%)	Selectivity (%)			
			PO	PRO	AC	ACR
A	0.6	2.1	19.1	0	0	0
B	3.2	3.2	45.5	0.49	0.59	0
C	7.5	3.7	44.8	0.28	0.37	0
D	10.3	4.0	46.8	0.64	0.70	0

PO, propylene oxide; PRO, propanal; AC, acetone; ACR, acrolein.

of supported silver catalyst for the epoxidation of ethylene. Four kinds of α-Al$_2$O$_3$ with different surface areas and pore diameter distributions were used as the supports of Ag catalyst. Their surface areas and pore diameter distribution curves are shown in Table 3 and Fig. 2, respectively. The results in Table 3 show that, with the increase in the surface area of support, the conversion of C$_3$H$_6$ and selectivity to PO increase. When the surface area of support is larger than 3.2 m^2/g, the selectivity to PO is hardly changed (45.5%–46.8%) and a small amount of by-products containing oxygen is formed.

As shown in Fig. 2, the pore diameter of support (A) is about 1.3 μm, and the pore diameters of support (B–D) are only 0.1–0.15 μm, and the pore sizes of supports reduce with an increase in their surface areas. Conventionally, α-Al$_2$O$_3$ support with large pore ($\sim$1 μm) had higher selectivity to ethylene oxide for the epoxidation of ethylene. However, the pore diameters of the support (B), (C) and (D) distribute in 0.08–0.4 μm and their most probable pore diameters are 0.1–0.15 μm. Correlation of the surface areas and pore diameters of α-Al$_2$O$_3$ supports with the epoxidation performances of the catalysts indicates that the surface area of α-Al$_2$O$_3$ support is a key factor in improving the conversion of propylene and the PO selectivity.
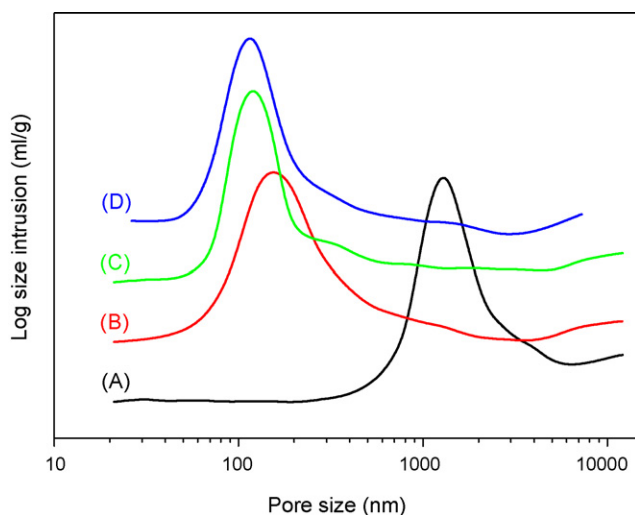

Fig. 2. Pore size distribution curves of α-Al$_2$O$_3$ supports with BET surface area of 0.6 m^2/g (A), 3.2 m^2/g (B), 7.5 m^2/g (C) and 10.3 m^2/g (D).
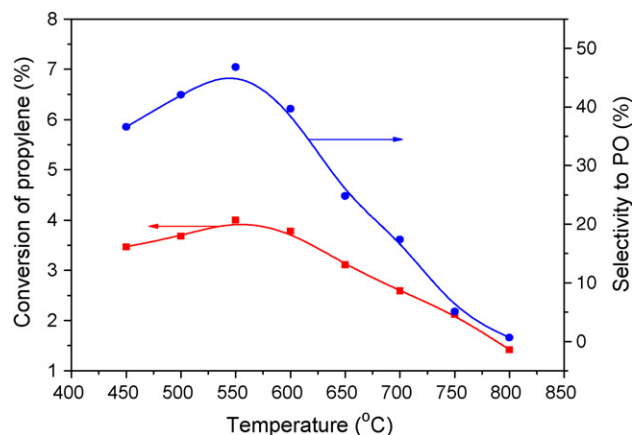

Fig. 3. Effect of the calcination temperature of modified α-Al$_2$O$_3$ on the epoxidation performance of 20% Ag/0.1% Y$_2$O$_3$–0.1% K$_2$O/α-Al$_2$O$_3$ (wt%) at 245 °C.

3.3. Effect of the calcination temperature of modified α-Al$_2$O$_3$ support

The effects of the calcination temperature of modified α-Al$_2$O$_3$ on the performance of 20% Ag/0.1% Y$_2$O$_3$–0.1% K$_2$O/α-Al$_2$O$_3$ (wt%) catalyst for the epoxidation of propylene are shown in Fig. 3. With an increase in the calcination temperature of modified α-Al$_2$O$_3$ from 450 to 800 °C, the conversion of propylene and the selectivity to PO increase to the maximum, and decrease. When the support is calcined at 550 °C, the catalyst shows the best epoxidation performance, in which the propylene conversion is 4.0% and the selectivity to PO is 46.8%.

The SEM micrographs of α-Al$_2$O$_3$, 0.1% K$_2$O/α-Al$_2$O$_3$ and 0.1% Y$_2$O$_3$–0.1% K$_2$O/α-Al$_2$O$_3$ calcined at different temperatures for 2 h are shown in Fig. 4. Fig. 4a shows that bare α-Al$_2$O$_3$ has a rather structureless surface with some floccule-crystals. When K$_2$O-modified α-Al$_2$O$_3$ is calcined at 550 °C, large (0.3–0.6 μm) and small (0.05–0.1 μm) particles exist simultaneously (Fig. 4b). On the surface (Fig. 4c) of Y$_2$O$_3$–K$_2$O/α-Al$_2$O$_3$ calcined at 550 °C, there are some small nearly spherical particles (0.1–0.2 μm). When Y$_2$O$_3$–K$_2$O/α-Al$_2$O$_3$ is calcined at 800 °C, its surface morphology (Fig. 4d) is changed compared with Fig. 4c; the spherical particles of 0.1–0.2 μm accumulates to result in an increase (0.2–0.6 μm) in the particle sizes and pores, and a reduction of surface area, which leads to a decline of catalytic performance (Fig. 3). The above results indicate that Y$_2$O$_3$ is structure-type promoter and can effectively restrain the surface sintering of modified α-Al$_2$O$_3$.

3.4. Effect of Y$_2$O$_3$ on Ag crystallite size

Fig. 5 shows the XRD patterns of 20% Ag/0.1% Y$_2$O$_3$–0.1% K$_2$O/α-Al$_2$O$_3$ and 20% Ag/0.1% K$_2$O/α-Al$_2$O$_3$. The diffraction peaks of Y$_2$O$_3$ or K$_2$O cannot be observed due to their low loadings. The diffraction peaks of α-Al$_2$O$_3$ support are located at 2θ (°) = 25.6, 35.2, 43.4, 52.6, 57.5, 66.5 and 68.2. There are four diffraction peaks of Ag at 2θ (°) = 38.1, 44.3, 64.4 and 77.4, corresponding to the crystal faces of Ag(1 1 1), (2 0 0), (2 2 0)
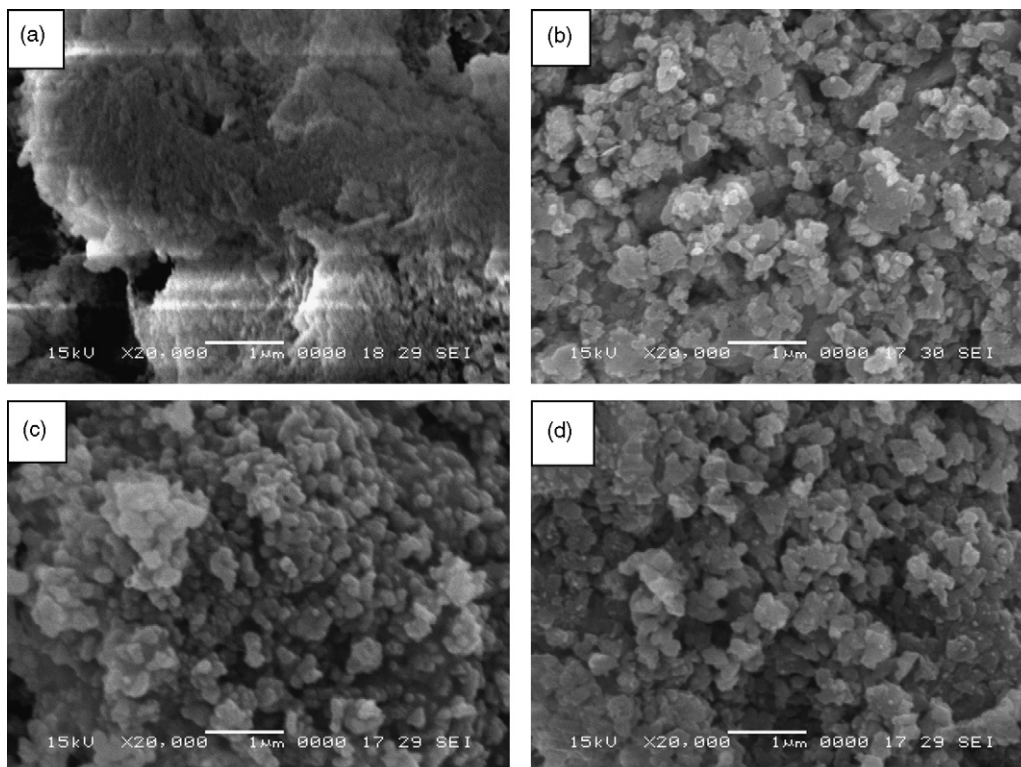
Fig. 4. SEM micrographs of α-Al$_2$O$_3$ (a), K$_2$O/α-Al$_2$O$_3$ calcined at 550 °C for 2 h (b), Y$_2$O$_3$–K$_2$O/α-Al$_2$O$_3$ calcined at 550 °C for 2 h (c) and at 800 °C for 2 h (d).

and (3 1 1), respectively for two samples. The intensities of Ag diffraction peaks of the catalyst (A) are slightly higher compared with (B). The crystallite size of Ag was estimated by Scherrer's equation and the full width at half maximum of the diffraction peak of Ag(1 1 1). Ag crystallites of catalyst (A) are larger than those of catalyst (B), and the presence of 0.1% Y$_2$O$_3$ makes the Ag crystallite size decrease from 17.4 to 15.7 nm. It shows that a small quantity of Y$_2$O$_3$ can effectively regulate the size of Ag crystallite to restrain agglomeration. Zemichael and co-workers [30] suggested that there was a correlation between K$_2$O loading and Ag particle size for the Ag/CaCO$_3$ catalyst, and found

that higher K$_2$O loadings caused extensive agglomeration of the individual Ag crystallites and that the catalysts containing Ag crystallites size of 20–40 nm gave maximum PO yields. However, Lu et al. [31] claimed that the addition of NaCl increased the size of silver particles for the Ag/CaCO$_3$ catalyst, and found that Ag particles of 400–700 nm gave the highest selectivity to PO. The above results indicate that K$_2$O and NaCl can accelerate the agglomeration of Ag crystallites. The effect of different Ag crystallites sizes on its catalytic performance might be ascribed to the different promoters and preparation methods.

3.5. CO$_2$-TPD

The CO$_2$-TPD curves of the modified supports and catalysts are shown in Fig. 6. In the CO$_2$-TPD curves of the samples A–C, there is a desorption peak at near 820 °C, that is, the samples A–C have some strong basic sites on their surface. For 20% Ag/α-Al$_2$O$_3$ (D) and α-Al$_2$O$_3$ (E) samples, there is no desorption peak of CO$_2$, that is, no surface basic sites. This shows that modified α-Al$_2$O$_3$ with alkali metal oxide possesses some strong surface basic sites. When 0.1 wt% Y$_2$O$_3$ is added into 0.1% K$_2$O/α-Al$_2$O$_3$ (B), a small shoulder peak is observed at about 720 °C and the desorption peak at 820 °C reduces obviously, that is, the strong basic sites decrease. The Ag/Y$_2$O$_3$–K$_2$O/α-Al$_2$O$_3$ catalyst (C) has two desorption peaks at 790 and 820 °C, and the peak at 720 °C has been included in the broad peak of 630–790 °C. The peak at 790 °C can be ascribed to the interaction between Ag particles and basic sites. It is concluded that the suitable basic sites are necessary to a highly effective Ag catalyst for the epoxidation of propylene.
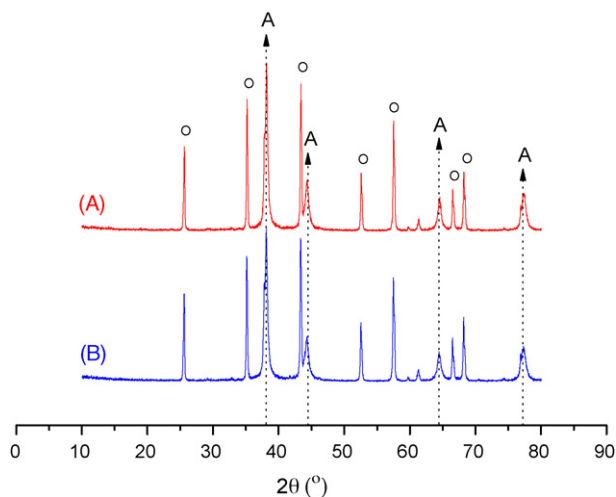

Fig. 5. XRD patterns of Ag–K$_2$O/α-Al$_2$O$_3$ (A) and Ag–Y$_2$O$_3$–K$_2$O/α-Al$_2$O$_3$ (B) (20 wt% Ag; 0.1% K$_2$O; 0.1% Y$_2$O$_3$; ($\bigcirc$) α-Al$_2$O$_3$; A–Ag).
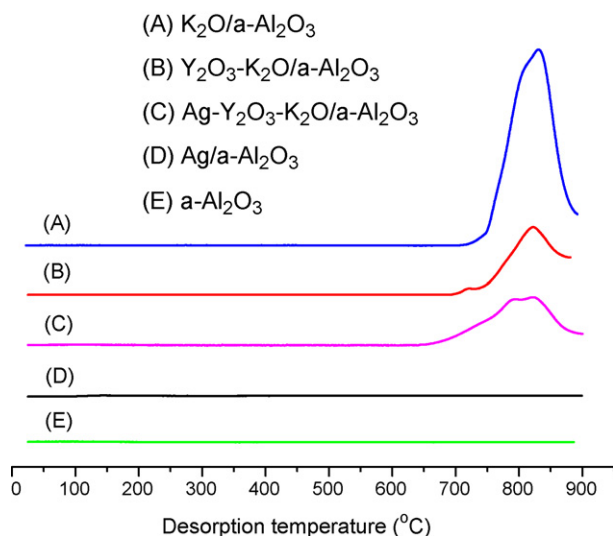
Fig. 6. CO$_2$-TPD profiles of the supports and catalysts (20 wt% Ag; 0.1% K$_2$O; 0.1% Y$_2$O$_3$).

4. Conclusion

Modified Ag/α-Al$_2$O$_3$ with Y$_2$O$_3$ and K$_2$O is a highly effective catalyst for the epoxidation of propylene to PO. The physicochemical properties of α-Al$_2$O$_3$ support affect the performance of the Ag/Y$_2$O$_3$–K$_2$O/α-Al$_2$O$_3$ catalyst. For the α-Al$_2$O$_3$ support, the most probable pore diameters distribution at 0.1–0.15 μm and higher surface area are appropriate to the supported Ag catalyst. The suitable basic sites are necessary to a highly effective Ag catalyst for the epoxidation of propylene. The presence of a small quantity of Y$_2$O$_3$ in the Ag catalyst can adjust its surface basic sites and evidently improve its performance. As a structure-type promoter, Y$_2$O$_3$ can restrain the sintering of Ag particles on the surface of α-Al$_2$O$_3$.

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