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Direct epoxidation of propylene with molecular oxygen over $Ag–MoO_3/ZrO_2$ catalyst

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Abstract

Direct gas-phase epoxidation of propylene to propylene oxide (PO) by molecular oxygen was studied over the MoO_3-modified supported-silver catalyst. The effect of promoter and support on the performance of the $Ag–MoO_3$ catalyst and their role were investigated by XPS, XRD, SEM, BET surface area, NH_3-TPD, CO_2-TPD techniques and so on. As the promoter, MoO_3 plays a great role of electron- and structure-type bi-functional promoter. Of all the supports studied, ZrO_2 is the most suitable one for the $Ag–MoO_3$ catalyst. The presence of support can regulate the size of the $Ag–MoO_3$ particles and the pore radii of catalyst, and decrease the loading of MoO_3 from ~50 wt.% in the unsupported $Ag–MoO_3$ catalyst to ~4 wt.% in the $Ag–MoO_3/ZrO_2$ catalyst. The properly weak Lewis acidic sites, the larger size of the $Ag–MoO_3$ particles and pore channel on the $Ag–MoO_3/ZrO_2$ catalyst are beneficial to improve epoxidation performance of the catalyst. The effect of the reaction temperature and space velocity on the catalytic epoxidation of propylene was also investigated. The low temperature or high space velocity can decrease the deep oxidation of propylene oxide to improve the selectivity to PO. Over the $20\%Ag–4\%MoO_3/ZrO_2$ catalyst at 400 °C, 0.1 MPa and space velocity of $7500\ h^{-1}$, the selectivity to PO of 60.3% was achieved with the O_2 conversion of 4.8%; under the space velocity of $12\,000\ h^{-1}$, the selectivity to PO was 71.5% with 2.5% O_2 conversion.

Keywords: Epoxidation of propylene; Oxygen; Catalyst; Silver; Molybdenum oxide; Zirconium oxide

1. Introduction

Propylene oxide (PO) is a very important raw material for the organic chemical industry, and commercially produced via the well-known process of chlorohydrin or Halcon [1]. The former suffers from the bad corrosion of the equipments and environment pollution from waste water produced in process; the latter disadvantageously produces equimolar amounts of the co-products, whose value lies on a demand in the market. Many methods of producing PO by oxidizing propylene directly with molecular oxygen or other oxidant have been developed. Of all the methods, the direct gas-phase epoxidation of propylene to PO by molecular oxygen over a solid catalyst is most attractive in view of the economy, green chemistry and safety.

For the direct gas-phase epoxidation of propylene with molecular oxygen, silver and copper modified by promoter are the effective catalysts, and the support affects obviously the performance of catalyst. Using silver catalyst supported on $CaCO_3$ and NO, EtCl and CO_2 as additives in the feedstock gas, the PO selectivity of 64.0% was attained with the propylene conversion of 1.5% [2]. Over the unsupported-silver catalyst containing NaCl as the promoter, 54.0% C_3H_6 conversion and 26.3% selectivity to PO were obtained, in which air was used as an oxygen source [3]. The PO selectivity of 43.4% was achieved with a propylene conversion of 0.19% over the NaCl-modified VCe_xCu_{1-x} oxide in the presence of O_2 [4]. Some of the heterogeneous molybdenum catalysts can catalyze epoxidation of alkene by molecular oxygen [5]. It was lately reported an epoxidation of propylene to PO with molecular oxygen over the catalyst prepared by impregnating titanium sulfate on zirconia, and found that the performance of catalyst was related to its surface acidity [6]. We have reported the modified silver and Ag–Mo catalysts for the gas-phase epoxidation of propylene with oxygen [3,7,8], and over the modified Ag–Mo catalyst, the PO selectivity of 53.1% and 6.8% O_2 conversion were achieved under no any additive added in feedstock. Now, the key problem in face of us is still to increase the selectivity to PO under keeping the higher conversion of propylene or oxygen.

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For the mechanism of silver catalyzing epoxidation of propylene to PO, Nakatsuji and co-workers [9,10] suggest that the route leading to PO also exists on the silver surface, but the combustion path is more favorable than that of an epoxidation. The formation of epoxide is initiated by the reaction of olefinic carbon with adsorbed oxygen, while the combustion is initiated by the abstraction of allylic hydrogen by adsorbed oxygen. Roberts et al. [11] consider that in a course of combustion of propylene on silver, the initial step is an acid–base reaction between allylic H (acid) and adsorbed oxygen (O_{ad} (base)). This step leads to the formation of surface hydroxyl groups (OH_{ad}) and chemisorbed allyl species that are further reacted to CO_2 and H_2O.

In this work, MoO_3 is used as a promoter of the Ag catalyst supported on ZrO_2, and the effects of MoO_3 and support ZrO_2 on its performance for an epoxidation are studied. By studying the electron properties, physical texture and surface acid–base properties of the catalysts, the roles of MoO_3 and ZrO_2 on increasing the selectivity to PO are discussed.

2. Experimental

2.1. Catalyst preparation

Method 1. A silver–ammonium complex solution was firstly synthesized by adding Ag_2O (3.39 g) to a mixed aqueous solution of $C_2H_8N_2$ (ethylenediamine, 2.63 g) and $C_2H_2O_4$ (oxalic acid, 5.52 g), Ag_2O:$C_2H_8N_2$:$C_2H_2O_4$:H_2O = 1:3:3:20 (mole), and then $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (ammonium molybdate, 0.78 g) was slowly added into this solution under stirring at room temperature; after that the support material (12.00 g) was added to this mixed solution to form a slurry. The slurry was vigorously stirred with ultrasonic and slowly heated to 60 °C. After the water in slurry was vaporized, it was dried at 110 °C for 4 h, and calcined at 400 °C for 4 h to obtain the precursor of catalyst. This precursor was washed with ethanol to remove the residual organic compounds, and then dried at 80 °C for 2 h, to get the supported 20%Ag–4%MoO_3 catalyst. Changing the amount of Ag_2O and $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ in the process above, the supported catalysts with different composition of Ag and MoO_3 may be prepared. If the support material was not used, the unsupported Ag–MoO_3 catalyst was obtained. If it is not specially noted in the text, the catalyst was prepared by method 1.

Method 2. $AgNO_3$ (4.97 g) was added to distilled water (5 ml) to form $AgNO_3$ aqueous solution, and then ZrO_2(12.00 g) was slowly added into it to form a slurry under vigorously stirring with ultrasonic at room temperature. After the slurry was heated at 80 °C to nearly waterless, it was dried at 110 °C for 4 h and calcined at 450 °C for 4 h to form the precursor of catalyst. This precursor was impregnated by aqueous solution (5 ml) of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (0.78 g), dried at 110 °C for 4 h and calcined at 300 °C for 4 h, to gain the 20%Ag–4%MoO_3/ZrO_2 (wt.%) catalyst.

Method 3. $AgNO_3$ (9.56 g) and $C_6H_{12}O_6\cdot H_2O$ (dextrose, 1.37 g) were added into distilled water (100 ml) to form a mixed solution, and then KOH aqueous solution (10 ml, 10.0 M) was slowly added into this mixed solution at room temperature under stirring to produce the silver precipitation. After aged at 60 °C for 1 h, the precipitate was filtered, washed with the distilled water and dried at 110 °C for 4 h to get active silver sample. The mixture of the active silver (3.16 g) and ZrO_2 (12.00 g) was milled time after time in the agate mortar and then compressed and broken to 20–40 meshes. The granular samples were impregnated with the equal-volume aqueous solution of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (0.78 g) and dried at 110 °C for 4 h, calcined at 300 °C for 4 h, to gain the 20%Ag–4%MoO_3/ZrO_2 (wt.%) catalyst.

TiO_2–ZrO_2 (atomic ratio 1:1) was prepared by co-precipitation. A mixed aqueous solution (300 ml) of $TiCl_4$ (10 ml) and $ZrOCl_2\cdot 8H_2O$ (29.33 g) was slowly added to aqueous ammonia (60 ml, 10 M) under vigorous stirring to form a precipitation. After aged at the room temperature overnight, the precipitate was washed with distilled water to remove Cl^- (verified by $AgNO_3$), and then dried at 110 °C for 24 h, calcined at 550 °C for 4 h.

TiO_2–SiO_2 (atomic ratio 1:1) was prepared by the sol–gel method. $(C_2H_5O)_4Si$ (37.86 g) and HNO_3 (0.5 ml, 5 M) were added into ethanol (300 ml) under stirring at 80 °C for 2 h, in which a hydrolysis of $(C_2H_5O)_4Si$ occurred. Then it was cooled to room temperature and $TiCl_4$ aqueous solution (40 ml, 4.55 M) was added into it under vigorous stirring to form gel. After aged at room temperature for 48 h, the gel washed with the distilled water to Cl^--free (verified by $AgNO_3$), dried at 110 °C for 24 h and calcined at 550 °C for 4 h.

2.2. Characterization of catalyst

XPS spectra were measured in a Perkin-Elmer PHI 550 ESCA/SAM spectrometer, Mg Kα radiation (1253.6 eV) and at 1×10^{-9} to 2×10^{-10} Torr, and the binding energy (284.6 eV) of adventitious C 1s was used as a reference. XRD patterns were recorded with a Rigaku D/max-2550/PC powder diffractometer, Cu Kα. SEM micrographs were obtained on a JEOL JSM-6360LV scanning electron microscopy. BET surface areas were measured in the ST-03A Instrument of Surface Area and Pore Size Distribution (Beijing Analytic Instrument Plant). The experiments of NH_3-TPD and CO_2-TPD were conducted on a conventional flow apparatus, a quartz U-tube reactor and thermal conductivity detector were used, the flow rate of He was 30 ml/min and the heating rate was 8 °C/min.

2.3. Activity testing of catalyst

The catalytic epoxidation of propylene was performed in a micro-reactor–GC system. The size of the stainless steel

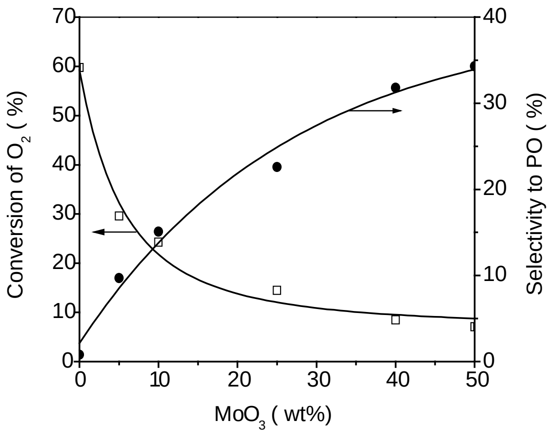

Fig. 1. Effect of MoO_3 loading on the performance of the Ag–MoO_3 catalyst. (Reaction conditions: 400 °C, 0.14 MPa and space velocity (SV) of 4500 h^{-1}. Composition of the feedstock: 15.6%C_3H_6; 12.2%O_2 and balance N_2 without any additive.)

fixed-bed reactor is Ø5 mm × 300 mm, in which 0.5 ml catalyst was filled. The feedstock gas consisted of 22.7%C_3H_6, 9.0%O_2 and balance N_2, without any modifier such as nitrogen oxide, alkyl halide or carbon dioxide. The composition of feedstock and effluent gas was analyzed by two on-line gas chromatographs with three packed columns (407 porous polymer, silica gel and 5A zeolite) and TCD.

The method of carbon balance was used to verify the consumption of propylene in the reaction. Carbon balance was described as $(n_f - n_e)/n_f$ (n_f, total mole of carbon in the feedstock gas; n_e, total mole of carbon in the effluent gas). In this study the carbon balance was $<\pm 4.0\%$.

Because O_2 was insufficient in comparison with C_3H_6 in feedstock, the activity of the catalyst was expressed with the conversion of O_2 rather than that of C_3H_6 in the text.

3. Results and discussion

3.1. Study of the unsupported Ag–MoO_3 catalyst

Fig. 1 presents the performance of the unsupported Ag–MoO_3 catalyst (calcined at 450 °C for 2 h) as a function of the MoO_3 loading. Over the MoO_3-free Ag catalyst, the O_2 conversion of 59.8% was obtained with the PO selectivity of 0.8%. With an increase of the MoO_3 content in the Ag catalyst, the selectivity to PO increased and the O_2 conversion decreased. When the content of MoO_3 reached 40–50 wt.%, the activity and selectivity to PO of catalyst changed little with the increase of the MoO_3 content. At 400 °C, 0.14 MPa and SV of 4500 h^{-1}, over the 50%Ag–50%MoO_3 catalyst, the conversion of O_2 and selectivity to PO were 7.1 and 34.3%, respectively. These results show that the presence of MoO_3 can obviously improve the performance of the Ag catalyst for the epoxidation of propylene.

3.2. Study of the supported Ag–MoO_3 catalyst

3.2.1. Support

The catalytic performance of 20%Ag–4%MoO_3 supported on different materials for the epoxidation of propylene is shown in Table 1. The results show that the presence of support obviously affects the epoxidation performance of the catalyst. Using $CaCO_3$ as the support, the O_2 conversion was nearly 100%, but no PO was detected at 350 °C. When TiO_2–ZrO_2 and TiO_2–SiO_2 were used as the support, the catalysts had very high O_2 conversion and low selectivity to PO at 300 °C. Using CaF_2 as the support, 77.2% O_2 conversion and 6.3% selectivity to PO were obtained at 380 °C. In comparison with $CaCO_3$, TiO_2–ZrO_2, TiO_2–SiO_2 and CaF_2, SiO_2, TiO_2 and ZrO_2 are available supports for the 20%Ag–4%MoO_3 catalyst. At 400 °C, 0.1 MPa and SV of 7500 h^{-1}, over the 20%Ag–4%MoO_3/SiO_2 catalyst, 22.5% conversion of O_2 and 10.7% selectivity to PO were obtained; over the 20%Ag–4%MoO_3/TiO_2 catalyst, the O_2 conversion and selectivity to PO were 32.4 and 14.1%, respectively; over the 20%Ag–4%MoO_3/ZrO_2 catalyst, the maximum selectivity to PO of 60.3% was achieved at O_2 conversion of 4.8%.

When SiO_2 or TiO_2 was used as a support, at the same pressure (0.1 MPa) and space velocity (7500 h^{-1}), and 320 or 300 °C, they had the near O_2 conversion (4.9 or 4.7%, respectively), and their selectivity to PO was 16.6 and 22.1%, respectively. At the similar O_2 conversion (4.8%), the

Table 1
Effect of support on the performance of the 20%Ag–4%MoO_3 catalyst for the epoxidation of propylene[a]

Support	BET surface area (m^2/g)	Reaction temperature (°C)	O_2 conversion (%)	Selectivity (%)[b]				
				PO	ACR	AC	HC	CO_2
$CaCO_3$	1.2	350	98.9	0	0	0	4.4	95.6
CaF_2	4.5	380	77.2	6.3	0	0	10.2	83.5
SiO_2	5.1	400	22.5	10.7	0	0	9.7	79.6
TiO_2	8.5	400	32.4	14.1	0	0	16.5	69.4
ZrO_2	6.7	400	4.8	60.3	0	0	2.4	37.3
TiO_2–ZrO_2	99.2	300	95.2	1.8	0	0	6.5	91.7
TiO_2–SiO_2	209.1	300	99.4	2.0	0	1.7	3.6	92.7

[a] Reaction conditions: 0.1 MPa and SV of 7500 h^{-1}.

[b] PO—propylene oxide, ACR—acrolein, AC—acetone, HC—hydrocarbons of $C_1 + C_2 + C_3 + C_4 + C_5 + C_6$.

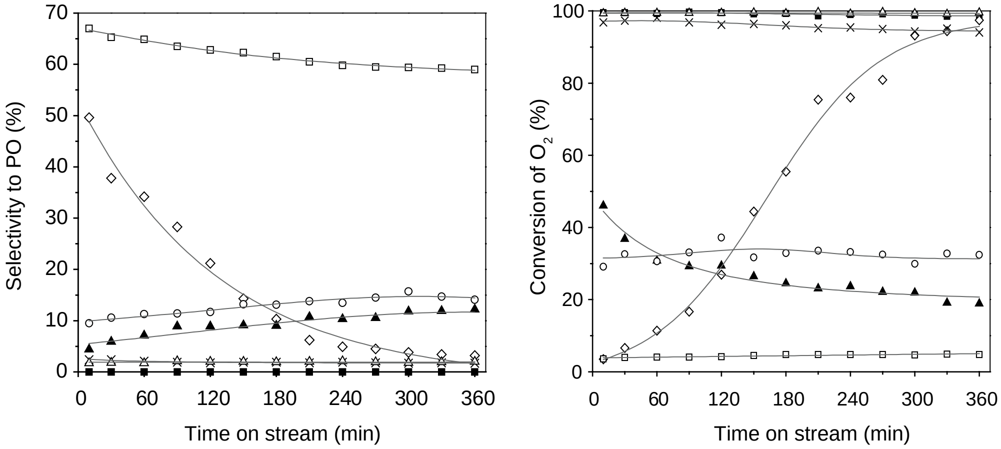

Fig. 2. Catalytic performance of the 20%Ag–4%MoO_3 catalysts supported on $CaCO_3$ (■, 350 °C), CaF_2(◇, 380 °C), SiO_2(▲, 400 °C), TiO_2 (○, 400 °C), TiO_2–ZrO_2 (×, 400 °C), TiO_2–SiO_2 (△, 300 °C) and ZrO_2 (□, 300 °C) for the epoxidation of propylene at 0.1 MPa and SV of 7500 h^{-1}.

catalyst supported on ZrO_2 presented the highest selectivity to PO (60.3%). It indicates that ZrO_2 is more suitable support than SiO_2 or TiO_2 for the 20%Ag–4%MoO_3 catalyst for an epoxidation of propylene.

The change in an epoxidation performance of the supported catalysts with the time on stream is shown in Fig. 2. With the time on stream, over the 20%Ag–4%MoO_3/ZrO_2 catalyst, the selectivity to PO slowly decreased, the O_2 conversion hardly changed; for the 20%Ag–4%MoO_3/CaF_2 catalyst, the selectivity to PO sharply decreased and the O_2 conversion drastically increased, which indicates a very poor stability of this catalyst. For the catalysts using SiO_2 or TiO_2 as the support, with the time on stream, there was a similar change trend for the selectivity to PO, but O_2 conversion was different: on SiO_2, the O_2 conversion slowly decreased, and on TiO_2, it hardly changed. Over the catalysts supported on TiO_2–ZrO_2 or TiO_2–SiO_2, both the selectivity to PO and O_2 conversion did not obviously change with the time on stream, the former kept on a very low level and the latter, a very high level. Over the 20%Ag–4%MoO_3/$CaCO_3$, no PO was detected and all oxygen nearly reacted with propylene to CO_2 and H_2O in the whole course of reaction.

The above results show that the selection of a support was very important to the Ag–MoO_3 catalyst for an epoxidation of propylene, and ZrO_2 is the most suitable support among seven support materials studied.

3.2.2. MoO_3 loading

Fig. 3 shows the O_2 conversion and PO selectivity as a function of the MoO_3 loading over the 20%Ag–MoO_3/ZrO_2 catalyst at 400 °C, 0.1 MPa and SV of 7500 h^{-1}. Over the 20%Ag/ZrO_2 catalyst (MoO_3-free), the O_2 conversion of 84.4% was obtained, but the selectivity to PO was only 0.6%. When 1.0 wt.% MoO_3 was added to 20%Ag/ZrO_2, the selectivity to PO sharply reached 43.5% and the O_2 conversion decreased to 8.6%. With an increase of MoO_3 loading, the selectivity to PO increased to the maximum, and then decreased; the conversion of O_2 decreased very slowly as the loading of MoO_3 was more than 1%. When ∼4% MoO_3 was loaded on the catalyst, the selectivity to PO reached the maximum 60.3% with O_2 conversion of 4.8%. This demonstrates that MoO_3 is also an excellent promoter of the Ag/ZrO_2 catalyst and played a very important role in the selective formation of PO, like in the unsupported Ag–MoO_3 catalyst.

3.2.3. Ag loading

The effect of silver loading on the performance of the Ag–4%MoO_3/ZrO_2 catalyst is shown in Fig. 4, at 400 °C, 0.1 MPa and SV of 7500 h^{-1}. With an increase of silver loading, the selectivity to PO decreased obviously, but the O_2 conversion firstly increased and then decreased. When the silver loading was ∼40.0 wt.%, the O_2 conversion reached the maximum (∼7.0%). The increase of silver loading means to decrease the concentration of the promoter MoO_3 in the catalyst, which leads to the reduction of the selectivity to PO. So it is necessary to keep a suitable ratio of Ag to MoO_3 loading.

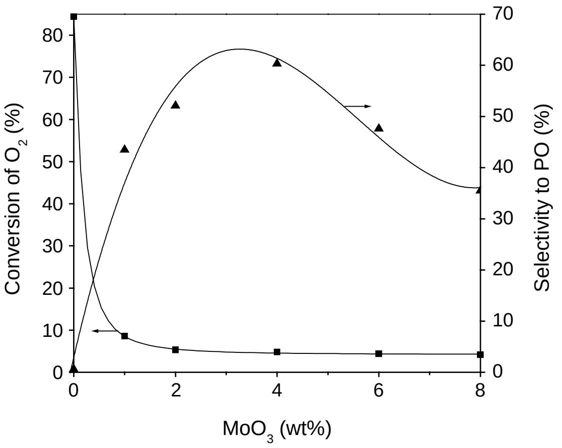

Fig. 3. Effect of MoO_3 loading on the epoxidation performance of the 20%Ag–MoO_3/ZrO_2 catalyst at 400 °C, 0.1 MPa and SV of 7500 h^{-1}.

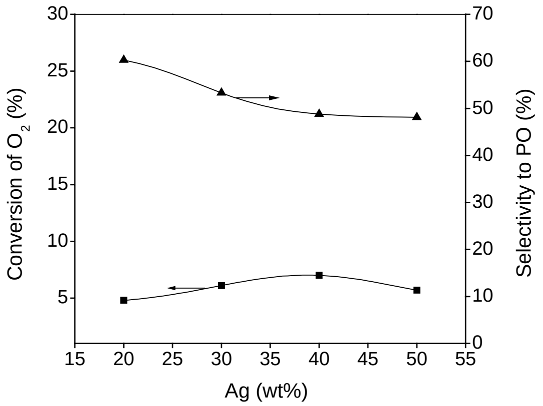

Fig. 4. Effect of Ag loading on the epoxidation performance of the Ag–4%MoO_3/ZrO_2 catalyst at 400 °C, 0.1 MPa and SV of 7500 h^{-1}.

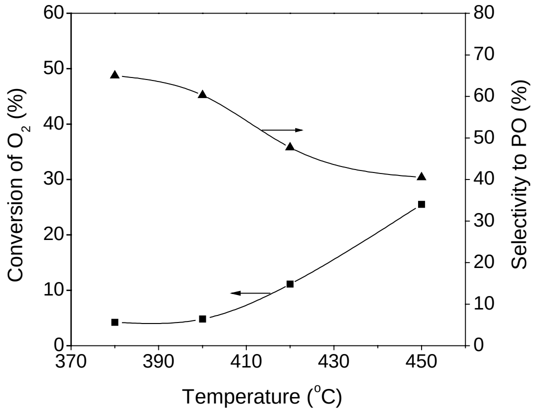

Fig. 5. Effect of reaction temperature on the epoxidation performance of the 20%Ag–4%MoO_3/ZrO_2 catalyst at 0.1 MPa and SV of 7500 h^{-1}.

Table 2
Effect of preparation method on the performance of the 20%Ag–4%MoO_3/ZrO_2 catalyst for the epoxidation of propylene[a]

Method of preparation	O_2 conversion (%)	Selectivity (%)[b]				
		PO	ACR	AC	HC	CO_2
1	4.8	60.3	0	0	2.4	37.3
2	14.8	41.3	0	0	23.9	34.8
3	9.8	39.6	0	0	25.0	35.4

[a] Reaction conditions: 400 °C, 0.1 MPa and SV of 7500 h^{-1}.

[b] PO—propylene oxide, ACR—acrolein, AC—acetone, HC—hydrocarbons of $C_1 + C_2 + C_3 + C_4 + C_5 + C_6$.

3.2.4. Preparation method

The influence of preparation method on the epoxidation performance of catalyst is given in Tables 2 and 3. As seen in Table 2, under the same reaction conditions, for the 20%Ag–4%MoO_3/ZrO_2 catalysts, one prepared by method 1 had higher selectivity to PO and lower conversion of O_2 than ones prepared by methods 2 and 3. Over the latter two catalysts, besides CO_2, large numbers of mixed hydrocarbons of C_1 to C_6 were produced. Through changing the reaction temperature, the similar conversions of O_2 were obtained for three catalysts. At 400, 320 and 350 °C, respectively, three catalysts had the near O_2 conversion (4.6–4.9%), but their selectivity to PO were obvious different (Table 3), the catalyst prepared by method 1 had the highest selectivity of PO (60.3%). These results show that an influence of preparation method on the epoxidation performance of the Ag–MoO_3/ZrO_2 catalyst is obvious, and the catalyst prepared by method 1 behaves the best epoxidation performance.

3.3. Study of the reaction condition

3.3.1. Reaction temperature

The effect of reaction temperature on the performance of the 20%Ag–4%MoO_3/ZrO_2 catalyst is shown in Fig. 5. With increasing the reaction temperature, the selectivity to PO decreased and the O_2 conversion increased. At 380 °C, the selectivity to PO of 65.0% was achieved with the O_2 conversion of 4.2%. At 450 °C, the selectivity to PO decreased to 40.5%, and the O_2 conversion sharply increased to 25.0%. It is obvious that the efficiency of the 20%Ag–4%MoO_3/ZrO_2 catalyst is quite sensitive to the reaction temperature.

3.3.2. Space velocity

In the above studies the SV was controlled at 7500 h^{-1}. The results in Fig. 6 show that the SV affect the catalytic performance of 20%Ag–4%MoO_3/ZrO_2. With an increase of SV, the selectivity to PO went up and the O_2 conversion dropped. At the SV of 4500 h^{-1}, the selectivity to PO of 49.4% was achieved with the O_2 conversion of 10.6%; when the SV was 12 000 h^{-1}, the selectivity to PO increased to 71.5% and the O_2 conversion decreased to 2.5%. Its reason is mainly that a higher SV shortened the stay time of PO inside the bed of catalyst to lessen the deep oxidation of PO to CO_2 and H_2O.

Table 3
Effect of preparation method on the performance of the 20%Ag–4%MoO_3/ZrO_2 catalyst for the epoxidation of propylene (at a similar O_2 conversion)[a]

Method of preparation	Reaction temperature (°C)	O_2 conversion (%)	Selectivity (%)[b]				
			PO	ACR	AC	HC	CO_2
1	400	4.8	60.3	0	0	2.4	37.3
2	320	4.6	53.9	0	0	16.8	29.3
3	350	4.9	47.7	0	0	20.7	31.6

[a] Reaction conditions: 0.1 MPa and SV of 7500 h^{-1}.

[b] PO—propylene oxide, ACR—acrolein, AC—acetone, HC—hydrocarbons of $C_1 + C_2 + C_3 + C_4 + C_5 + C_6$.

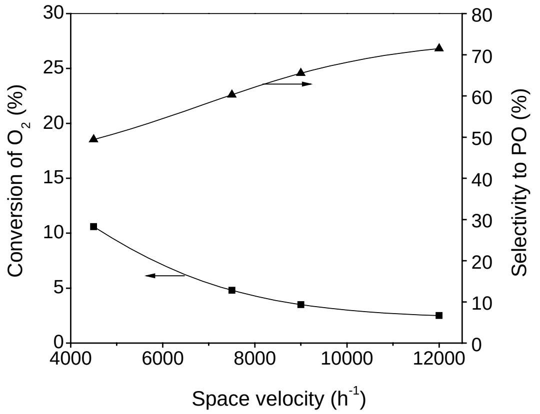

Fig. 6. Effect of space velocity on the epoxidation performance of the 20%Ag–4%MoO_3/ZrO_2 catalyst at 400 °C and 0.1 MPa.

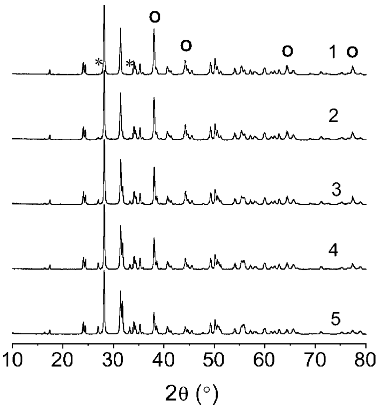

Fig. 8. XRD patterns of the 20%Ag–MoO_3/ZrO_2 catalysts. MoO_3 loading (wt.%): (1) 0, (2) 2.0, (3) 4.0, (4) 6.0, (5) 8.0 (○: Ag, *: MoO_3).

3.4. Characterization of the catalyst

3.4.1. XPS

The binding energy (BE) of Ag $3d_{5/2}$ and Mo $3d_{5/2}$ of the 50%Ag–50%MoO_3 catalyst was obtained by XPS. The BE of Ag $3d_{5/2}$ is 368.7 eV, which is higher than that of metallic silver (Ag $3d_{5/2}$, 367.9 eV). The BE of Mo $3d_{5/2}$ is 231.8 eV that is lower than that of Mo^{6+} in MoO_3 (Mo $3d_{5/2}$, 232.65 eV).

The XPS spectra of 20%Ag–4%MoO_3/ZrO_2 is shown in Fig. 7. The BE of Ag $3d_{5/2}$ is higher than one of the metallic Ag. The BE of Mo $3d_{5/2}$ is lower than one of Mo^{6+} in MoO_3. The BE of Zr $3d_{5/2}$ equals one of Zr $3d_{5/2}$ (182.4 eV) of ZrO_2, which means that the compounds of ZrO_2 and Ag (or Mo) are not formed or detected by XPS.

The facts that the BE of Ag $3d_{5/2}$ and Mo $3d_{5/2}$ in the unsupported Ag–MoO_3 and Ag–MoO_3/ZrO_2 catalysts is different to that of the metallic Ag and Mo^{6+} in MoO_3, means that the valence of Mo and Ag may be $6-\delta$ and δ^{+}, respectively. This suggests that the electron transfers from silver to MoO_3 to make the Mo oxyanion. This indicates that Mo has a valance of $6-\delta$ and silver is electron-deficient, and MoO_3 plays a role of electron-type promoter. Yang et al. investigated Re-modified Ag catalyst for the epoxidation of ethylene, and found that adding Re into the Ag catalyst led to Ag electron-deficient and Re^{7+} transforming to $Re^{7-\delta}$ [12]. Lu et al. reported that a part of Ag atoms in the NaCl-modified Ag catalyst existed as cation, and the high oxidative state Ag was helpful to produce electrophilic oxygen species and played some role in the propylene epoxidation [13]. Their results are in agreement with the situation observed here.

3.4.2. XRD

XRD patterns of the 20%Ag–(0–8%)MoO_3/ZrO_2 catalysts are shown in Fig. 8. There are four diffraction peaks at $2\theta = 38.12°$, 44.30°, 64.44° and 77.38° for all the catalysts, which are corresponding to the crystal faces of Ag (1 1 1), (2 0 0), (2 2 0) and (3 1 1), respectively. With an increase of MoO_3 loading from 0 to 8.0 wt.%, the diffraction peaks of Ag weakened, and the diffraction peaks of MoO_3 at $2\theta = 27.08°$ and 33.32° enhanced. It indicates that MoO_3 also played a role of structure-type promoter besides electron-type promoter, that is, it can regulate the size of Ag particles to some extent and effectually retard the sinter of the active Ag sites during calcination and reaction by increasing the dispersion of Ag phase.

Fig. 9 shows the XRD patterns of the 20%Ag–4%MoO_3 catalysts supported on the different materials. According to

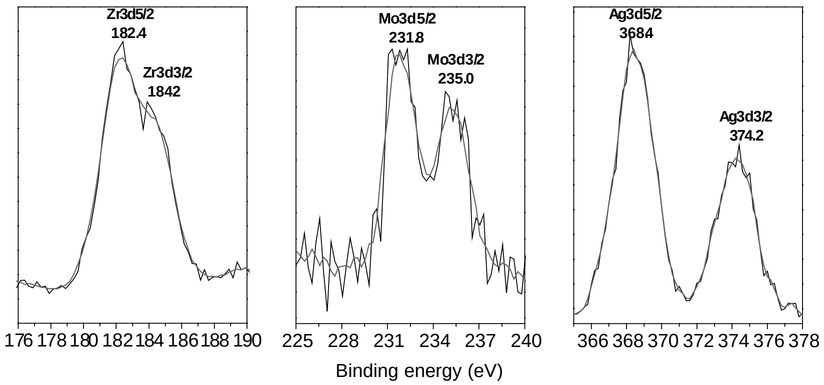

Fig. 7. XPS spectra of the 20%Ag–4%MoO_3/ZrO_2 catalyst.

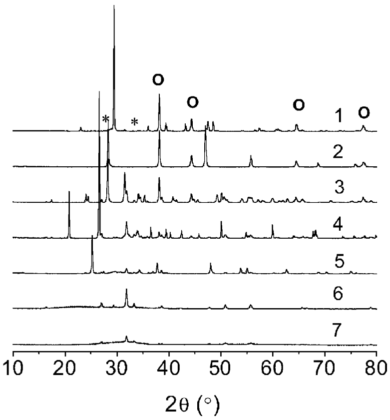

Fig. 9. XRD patterns of the 20%Ag–4%MoO_3 catalysts supported on $CaCO_3$ (1), CaF_2 (2), ZrO_2 (3), SiO_2 (4), TiO_2 (5), TiO_2–SiO_2 (6) and TiO_2–ZrO_2 (7) (○: Ag, *: MoO_3).

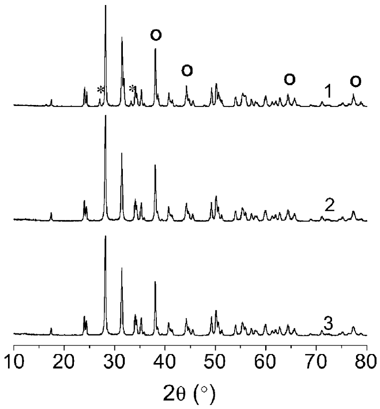

Fig. 10. XRD patterns of the 20%Ag–4%MoO_3/ZrO_2 catalysts prepared by method 1 (1), method 2 (2) and method 3 (3) (○: Ag, *: MoO_3).

the scanning tunneling microscopy (STM) measurements of Chen et al. [14], Ag clusters deposited on TiO_2 at room temperature are remarkably stable upon annealing to 900 K, that is, Ag can still sufficiently disperse on TiO_2 at higher calcination temperature. As the active metal is supported on TiO_2, there exists a strong interaction between metal and TiO_2, called strong-metal support interaction (SMSI), at least in part, which is due to an encapsulation of the metal particles by the reduced TiO_x overlayers [15]. Recently, this phenomenon was revisited using surface science techniques [16–19]. Therefore, no diffraction peaks of Ag was found in the spectra of 20%Ag–4%MoO_3/TiO_2–ZrO_2, 20%Ag–4%MoO_3/TiO_2–SiO_2 and 20%Ag–4%MoO_3/TiO_2, indicates that Ag sufficiently dispersed on TiO_2–ZrO_2, TiO_2–SiO_2 and TiO_2, and may be partly encapsulated by the reduced TiO_x overlayers. Compared with TiO_2–ZrO_2 and TiO_2–SiO_2 having large surface area, TiO_2 of low surface area was used as a support of catalyst, the encapsulation effect was probably more enhanced.

In the XRD spectra of the 20%Ag–4%MoO_3/$CaCO_3$ and 20%Ag–4%MoO_3/CaF_2 catalysts, there are the strong diffraction peaks of Ag, which shows that Ag distributes on the support as the big particles. In the XRD spectrum of 20%Ag–4%MoO_3/SiO_2 the diffraction peaks of Ag is poor. The strength of diffraction peaks of Ag in the XRD pattern of 20%Ag–4%MoO_3/ZrO_2 is a mean between 20%Ag–4%MoO_3/SiO_2 and 20%Ag–4%MoO_3/CaF_2. The interesting phenomenon is that no diffraction peak of MoO_3 can be seen in the XRD spectra of 20%Ag–4%MoO_3/$CaCO_3$ and 20%Ag–4%MoO_3/CaF_2. This is possible that MoO_3 is highly dispersed on the catalyst or involved inside the silver particles, because of the low loading of MoO_3. Associating with the BET surface area and the catalytic performance in Table 1, we can see, there seems to be no direct relationship between an epoxidation performance and specific surface area of catalyst, and the dispersion or particle dimension of Ag and MoO_3 on the catalyst is not definitely relative to the epoxidation performance of the catalyst supported on the different support. Therefore, the physicochemical properties of the support material itself probably played a more important role in improving PO selectivity of the catalyst.

The XRD patterns of the 20%Ag–4%MoO_3/ZrO_2 catalysts prepared by different methods are shown in Fig. 10. The results show that the strength order of diffraction peaks of Ag on three catalysts is (1) > (2) ≈ (3). No diffraction peaks of MoO_3 are found in the XRD patterns of the catalysts prepared by methods 2 and 3; this shows that MoO_3 is more highly dispersed on the latter two catalysts compared to the former.

3.4.3. SEM

The SEM micrographs in Fig. 11 show, there are 300–500 nm Ag–MoO_3 particles irregularly distributing on the surface of the 20%Ag–4%MoO_3/ZrO_2 catalyst papered by method 1. For the catalyst prepared by method 2, the Ag–MoO_3 particles uniformly distributing on the surface are about 100 nm. The size of the particles on the catalyst prepared by method 3 is 100–200 nm. These results are in agreement with the XRD patterns in Fig. 10. Comparing with the catalysts prepared by methods 2 and 3, some large pores may be found in the catalyst prepared by method 1. Relating with the epoxidation performance of three catalysts, we can see, the larger size of the Ag–MoO_3 particles on the catalyst prepared by method 1 is beneficial to formation of PO, and the pores with big dimension are helpful to the diffusion of PO to avoid to be further oxidized to CO_2 and H_2O. The similar results were reported in the epoxidation of ethylene [20,21]. Hayashi et al. researched selective vapor-phase epoxidation of propylene over the Au/TiO_2 catalyst in the presence of O_2 and H_2, and found that reaction pathway could be tuned by carefully controlling the size of the Au particles (switch effect of Au particles). When the Au particles were 2–4 nm, PO was produced, and when they were smaller than 2 nm, propane was produced [22]. The higher selectivity to HC and lower selectivity to PO over the catalysts prepared by methods 2 and 3 is probably caused by the smaller size of the Ag–MoO_3 particles.

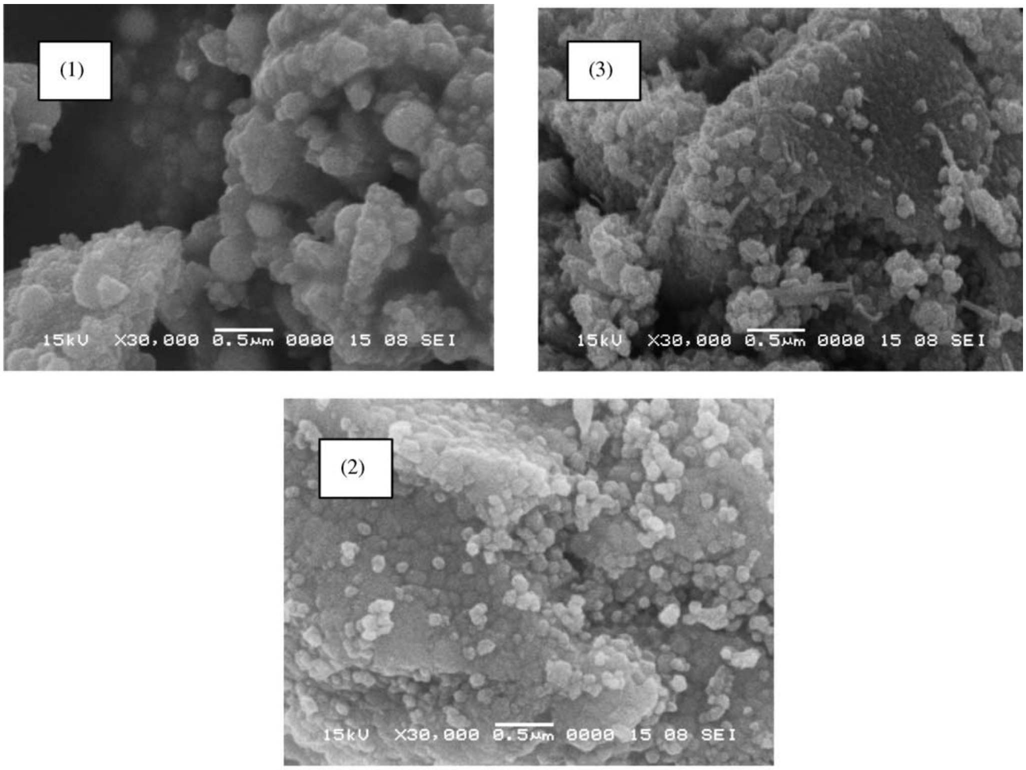

Fig. 11. SEM micrographs of the 20%Ag–4%MoO_3/ZrO_2 catalysts prepared by method 1 (1), method 2 (2) and method 3 (3).

Based on the XRD spectra of the 20%Ag–4%MoO_3/ZrO_2 catalyst shown in Figs. 8 and 10, that the data of the Ag diffraction peaks was not affected by adding MoO_3, and the lower loading of MoO_3, the Ag–MoO_3 particles observed in the SEM graphs in Fig. 11 should consist mainly of the metallic Ag.

3.4.4. NH_3-TPD and CO_2-TPD

The NH_3-TPD profiles of the supported 20%Ag–4%MoO_3 catalysts are shown in Fig. 12. There are obvious desorption peaks of NH_3 on 20%Ag–4%$MoO_3/TiO_2–SiO_2$, 20%Ag–4%$MoO_3/TiO_2–ZrO_2$ and 20%Ag–4%MoO_3/ZrO_2, and the top temperature of peak is 140–180 °C. The peak areas of 20%Ag–4%$MoO_3/TiO_2–SiO_2$ are larger than that of 20%Ag–4%$MoO_3/TiO_2–ZrO_2$, and the peak areas of 20%Ag–4%MoO_3/ZrO_2 are very small. It may be correlative with the surface area of catalyst, the formers have larger surface areas and the latter has low surface areas. On the 20%Ag–4%MoO_3 catalysts supported on TiO_2, SiO_2, CaF_2 or $CaCO_3$, the desorbed NH_3 was hardly detected. The results above indicate that, the two catalysts supported on $TiO_2–SiO_2$ and $TiO_2–ZrO_2$ have many weak acid sites on the surface, and there are a few weak acid sites on the 20%Ag–4%MoO_3/ZrO_2 catalyst. No acidic sites are found on the 20%Ag–4%MoO_3 catalysts supported on TiO_2, SiO_2, CaF_2 or $CaCO_3$.

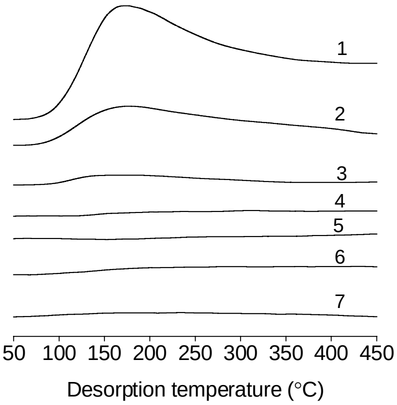

Fig. 12. NH_3-TPD profiles of the 20%Ag–4%MoO_3 catalysts supported on $TiO_2–SiO_2$ (1), $TiO_2–ZrO_2$ (2), ZrO_2 (3), TiO_2 (4), SiO_2 (5), CaF_2 (6) and $CaCO_3$ (7).

Fig. 13 shows the CO_2-TPD profiles of the supported 20%Ag–4%MoO_3 catalysts. There is one desorption peak of CO_2 at 170–180 °C in the CO_2-TPD curve of 20%Ag–4%$MoO_3/TiO_2–ZrO_2$. For 20%Ag–4%$MoO_3/TiO_2–SiO_2$, one broad peak at 180–380 °C exists. For the catalysts supported on ZrO_2 or other materials, no CO_2 desorption could be detected. This shows that there are some basic sites on the surface of 20%Ag–4%MoO_3 supported on $TiO_2–SiO_2$ or $TiO_2–ZrO_2$, and no basic sites on the surface of 20%Ag–4%MoO_3 supported on ZrO_2, TiO_2, SiO_2, CaF_2 or $CaCO_3$.

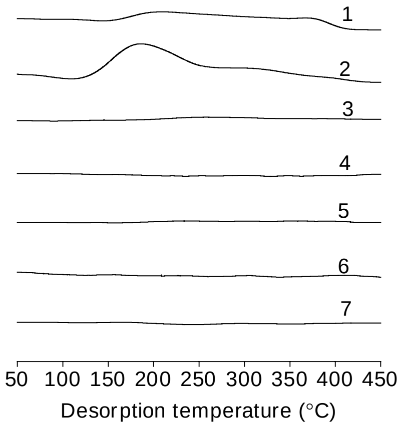

Fig. 13. CO_2-TPD profiles of the 20%Ag–4%MoO_3 catalysts supported on TiO_2–SiO_2 (1), TiO_2–ZrO_2 (2), ZrO_2 (3), TiO_2 (4), SiO_2 (5), CaF_2 (6) and $CaCO_3$ (7).

3.5. *Discussion for the effects of promoter MoO_3 and support ZrO_2*

The above results show that the presence of MoO_3 promoter and ZrO_2 support in the Ag–MoO_3/ZrO_2 catalyst can promote obviously its catalytic performance for the epoxidation of propylene. The roles of MoO_3 and ZrO_2 might be described as follows.

(1) The presence of Mo^{6+} in the catalyst can acquire electrons from the silver elements to lead to silver having positive charges and weakening the effective charge of the adsorbed oxygen (O_{ad}) on the silver sites, which makes the O_{ad} have a stronger electrophilic property. As a result, the allylic H (positive charge state) of propylene attacking on the O_{ad}, that makes the complete oxidation of propylene to CO_2 and H_2O, can be inhibited to some extent. On the contrary, the olefinic carbons of propylene have more chances to combine with the O_{ad} on the silver to form PO.

(2) The support acts as a promoter of catalyst. ZrO_2 is a p-type semiconductor oxide having the removable positive charges [23], and can accept the electrons from Ag to result in Ag electron-deficient further to reduce the negative charge of the O_{ad} on the Ag sites, which makes the O_{ad} have stronger electrophilic property to be attacked by olefinic carbons of propylene to form PO. This effect is similar to add Na^+, Ce^+, Ba^{2+} or Cs^+ cations in the Ag–MoO_3 catalyst [8]. On the other hand, the presence of the ZrO_2 support decreases the content of MoO_3 as the electron-type promoter from ∼50 wt.% in the unsupported Ag–MoO_3 catalyst [8] to ∼4 wt.% in the Ag–MoO_3/ZrO_2 catalyst.

(3) Lewis acidic sites on the catalyst can accept electrons from the O_{ad}. Based on the mechanism of propylene epoxidation over the Ag suggested by Nakatsuji and co-workers [9,10] and Roberts et al. [11], the reaction between propylene and the O_{ad} on the Ag sites leads to the formation of the surface hydroxyl group (OH_{ad}) and chemisorbed allyl species that are further reacted to CO_2 and H_2O. The properly weak Lewis acidic sites on the Ag–MoO_3/ZrO_2 catalyst could accept electrons from the O_{ad} to lead to the O_{ad} possessing more strong electrophilic property, to increase the chances of the olefinic carbons of propylene attacking the O_{ad} to form PO and block up the combination of the allylic H (H^+ property) and the O_{ad} to form CO_2 and H_2O. If there are abundant or/and strong acidic sites on the catalyst, the catalytic cracking and polymerization of propylene will occur. On the other hand, if there are basic sites on the catalyst, the allylic H (H^+ property) of propylene will react with the basic sites (acid–base reaction) to finally produce CO_2 and H_2O to decrease epoxidation performance of the catalyst.

(4) The presence of support is available to control the size of the Ag–MoO_3 particles and pore channels of catalyst. Using the support and fitting method of preparing catalyst, the size of the Ag–MoO_3 particles and pores of catalyst may be controlled. The above studies shows that the larger particle size of Ag–MoO_3 (300–500 nm) on the catalyst prepared by method 1 is available to the formation of PO and its pore channels with big dimension are helpful to the diffusion of PO to avoid to be further oxidized to CO_2 and H_2O.

4. Conclusions

In the Ag–MoO_3 catalyst for the epoxidation of propylene, MoO_3 as the electron and structure-type promoter improved obviously the epoxidation performance of the catalyst by accepting electron from the Ag elements and regulating the particle size of Ag. The presence of support can regulate the size of Ag–MoO_3 particles and the pore radii of catalyst by the interaction between an Ag metal and support, and decrease the loading of MoO_3 from ∼50 to ∼4 wt.%. After the Ag–MoO_3 catalyst is supported on ZrO_2, its catalytic performance is obviously promoted. The preparation method affected the epoxidation performance of the Ag–MoO_3/ZrO_2 catalyst. The bigger Ag–MoO_3 particles (e.g. 300–500 nm) and pore channels are helpful to improve the selectivity to PO. The low reaction temperature or high space velocity helps to inhibit the deep oxidation of PO to increase the PO selectivity. Over the 20%Ag–4%MoO_3/ZrO_2 catalyst at 400 °C, 0.1 MPa and SV of 7500 h^{-1} (or 12 000 h^{-1}), the selectivity to PO of 60.3% (or 71.5%) is achieved with the O_2 conversion of 4.8% (or 2.5%), in which no any additive such as NO_x, CH_2CHCl or CO_2 was added into the feedstock.

Acknowledgements

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