

Effect of preparation condition on performance of Ag–MoO₃/ZrO₂ catalyst for direct epoxidation of propylene by molecular oxygen

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Abstract

The Ag–MoO₃/ZrO₂ catalyst for an epoxidation of propylene by molecular oxygen was prepared by the precipitation/impregnation method, and characterized by N₂ adsorption at low temperature, XRD, NH₃-TPD and CO₂-TPD. The effects of preparation condition of ZrO₂ support on its physicochemical properties and catalytic performance were studied. The results show that suitably low surface area, big pore size, and modest and weak surface acidity–basicity for the Ag–MoO₃/ZrO₂ catalyst are in favor of the selective formation of propylene oxide. High surface area, abundant micro-pore structure and strong acidity–basicity or acidity-free are liable to the deep oxidation of propylene to CO₂ and H₂O. As the support of the Ag–MoO₃ catalyst for an epoxidation of propylene, the monoclinic phase of ZrO₂ is preferable to tetragonal one. Suitably larger particles of Ag and highly dispersed MoO₃ on the Ag–MoO₃/ZrO₂ catalyst are beneficial to improve the selectivity to propylene oxide.

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1. Introduction

Propylene oxide (PO) is an important intermediate for the organic chemistry industry and there is an increasing demand for it in marketplace. Currently, PO is commercially produced by two conventional processes of chlorohydrin and hydroperoxide. Chlorohydrin method has the disadvantages of producing stoichiometric amount of waste salts and some chlorinated byproducts; the disadvantage of hydroperoxide method is that the co-product (styrene or *tert*-butylalcohol) is produced in a fixed amount. The direct synthesis of PO from propylene and oxygen has long been desired and considered as one of the most important and challenging chemical reactions to remain unsolved by catalysis [1]. The molten-salt method can directly epoxidize propylene by oxygen [2],

but high energy consumption makes it not be commercialized up to date. For the catalytic epoxidation of propylene by O₂/H₂ over Au/TiO₂ or Pd–Pt/TS-1, the selectivity to PO is higher than 90%, but the conversion of propylene is 1–2% only [3–5], in which large quantities of H₂ is consumed to react with O₂ to H₂O and a careful handling is strictly required for the explosive mixture of H₂–O₂. Therefore, in view of economic and green chemistry, the direct epoxidation of propylene by molecular oxygen over a solid catalyst is a most ideal technique of producing PO.

Attempts to directly epoxidize propylene, similar to what is done in the epoxidation of ethylene over the silver catalyst, have been tried and some good results have been obtained. Using silver supported on CaCO₃, the PO selectivity of 64.0% was attained with the propylene conversion of 1.5% when NO, EtCl and CO₂ additives were added in the feedstock [6]. Lu and Zuo prepared the unsupported silver catalyst containing NaCl as the promoter, over which 54.0% C₃H₆ conversion and 26.3% selectivity to PO were achieved

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for the epoxidation of propylene by air [7]. The epoxidation of propylene with air over the similar NaCl-modified silver catalyst was also recently reported [8]. The mechanism for an oxidation of propylene by molecular oxygen over the silver catalyst has been studied in detail over the past years; it is thought that the routes leading to PO and CO₂ coexist on the surface of silver catalyst [9–11]. It was reported that alkenes was oxidized to epoxide by molecular oxygen over the heterogeneous molybdenum catalyst [12]. Recently, NaCl-modified VCe_xCu_{1-x} mixed oxide [13], Ti-modified high silica zeolite [14] and Ti-modified sulfated zirconia [15] were reported to be effective for direct epoxidation of propylene with molecular oxygen.

We have reported the supported Ag–Mo catalyst for direct epoxidation of propylene by molecular oxygen [16–18], and found that the promoter and support have a very important influence on the performance of catalyst, MoO₃ in catalyst plays the roles of electric- and structure-type bifunctional promoter, and ZrO₂ is an excellent support. In this paper, by changing preparation condition of ZrO₂ support, the Ag–MoO₃/ZrO₂ catalysts with different physicochemical properties were prepared. Based on correlating the epoxidation performance with the physicochemical properties of catalyst, the effect of preparation condition or physicochemical properties of ZrO₂ on the epoxidation performance of the Ag–MoO₃/ZrO₂ catalyst is discussed.

2. Experimental

2.1. Preparation of catalyst

2.1.1. Method A

Zr(NO₃)₄ aqueous solution was slowly added in 10 M NaOH aqueous solution under stirring and at room temperature, and its pH value was about 12. After aged at room temperature for 12 h (or at 100 °C for 160 h), the precipitate was filtered and washed repeatedly with distilled water until the pH value of filtrate was about 7, and then dried at 110 °C for 24 h and calcined at 500 °C for 4 h to obtain ZrO₂. ZrO₂ was impregnated by a stoichiometric aqueous solution of AgNO₃ (Ag:ZrO₂ = 20:76%, w/w) under ultrasonic stirring and at room temperature, and then dried at 110 °C for 4 h, calcined at 450 °C for 4 h. After that it was impregnated with an equal-volume aqueous solution of (NH₄)₆Mo₇O₂₄ (Ag:ZrO₂:MoO₃ = 20:76:4%, w/w/w), dried at 110 °C for 4 h and calcined at 300 °C for 4 h to obtain the 20% Ag–4% MoO₃/ZrO₂ catalyst named as AM/Z(500) (or AM/Z*(500)). Z and Z* represents ZrO₂, the former is aged at room temperature for 12 h and the latter marked star is aged at 100 °C for 160 h, and 500 within bracket is the calcination temperature (°C) of ZrO₂.

2.1.2. Method B

A mixed aqueous solution of AgNO₃ and Zr(NO₃)₄ (Ag:ZrO₂ = 20:76%, w/w) was slowly added in 10 M NaOH aqueous solution under stirring and at room temperature, and

its pH value was about 12. The precipitate was aged at room temperature for 12 h, filtered and washed repeatedly with distilled water until the pH value of filtrate was about 7, and then dried at 110 °C for 24 h and calcined at 500 °C for 4 h to obtain the Ag–ZrO₂ precursor. This precursor was crushed and impregnated by an equal-volume aqueous solution of (NH₄)₆Mo₇O₂₄ (Ag:ZrO₂:MoO₃ = 20:76:4%, w/w/w), and then it was dried at 110 °C for 4 h and calcined at 300 °C for 4 h to obtain the 4% MoO₃/20% Ag–ZrO₂ catalyst named as M/AZ(500). AZ represents Ag–ZrO₂ and 500 within bracket is the calcination temperature (°C) of Ag–ZrO₂.

2.2. Characterization of catalyst

The BET surface area and pore size distribution of catalyst were measured with ST-03A Instrument of Surface Area and Pore Size Distribution (Beijing Analytic Instrument Plant) at liquid-N₂ temperature. The crystalline structure of catalyst was identified by XRD with Rigaku D/max/2550/PC, Cu K α radiation. The NH₃-TPD and CO₂-TPD experiments were conducted in the conventional flow apparatus equipped with a thermal conductivity detector (TCD). The sample (300 mg) was pretreated under helium stream (30 ml/min) at 500 °C for 2 h, and then with the mixture of NH₃-He (or CO₂-He) at 50 °C for 1 h and with helium stream at 50 °C for 1 h to remove physisorbed NH₃ (or CO₂). TPD of adsorbed NH₃ (or CO₂) was measured from 50 to 450 °C at the heating rate of 8 °C/min.

2.3. Activity testing of catalyst

The catalytic epoxidation of propylene by molecular oxygen was performed in the micro-reactor-GC system. The stainless steel reactor in the fixed-bed is Ø5 mm × 300 mm and 0.5 ml catalyst (20–40 mesh) was filled. The reaction condition is 0.1 MPa and 7500 h⁻¹ of space velocity at 350 °C. The feedstock gas consisted of 22.7% C₃H₆, 9.0% O₂ and balance N₂, without any additive such as nitrogen oxide, alkyl halide, carbon dioxide or hydrogen. 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 5 Å zeolite), in which TCD was used. The method of carbon balance was used to verify the consumption of propylene during the reaction. As O₂ was insufficient in comparison with C₃H₆ in feedstock, the activity of catalyst was expressed by the conversion of O₂ rather than that of C₃H₆ hereinafter.

3. Results and discussion

3.1. Characterization of catalyst

3.1.1. BET surface area

The BET surface areas of the catalysts prepared are listed in Table 1. The results show that the preparation condition

Table 1
Performances of the catalysts for epoxidation of propylene^a

Catalyst ^b	S (m ² /g) ^c	Conversion (%)		Selectivity (%)				
		O ₂	C ₃ H ₆	PO	AC	ACR	HC	CO ₂
AM/Z*(500 ^d)	128	100	9.3	1.8	0	0	3.2	95.0
AM/Z*(600)	117	97.9	9.1	2.1	0	0	3.4	94.5
AM/Z*(700)	105	43.6	4.5	7.8	0	0	7.1	85.1
AM/Z*(850)	21.7	7.3	1.0	40.3	0	0	2.2	57.5
AM/Z*(950)	3.6	15.7	1.9	20.8	0	0	7.9	71.3
AM/Z(500)	44.0	15.3	1.8	20.6	0	0	5.5	73.9
AM/Z(600)	26.4	6.8	1.0	39.3	0	0	4.5	56.2
AM/Z(700)	24.1	6.4	0.9	41.5	0	0	3.4	55.1
AM/Z(850)	17.1	3.5	0.6	57.9	0	0	0	42.1
M/AZ(500)	59.9	67.2	6.3	2.8	0	0	3.8	93.4
M/AZ(600)	39.7	54.0	5.3	5.4	0	0	5.6	89.0
M/AZ(700)	24.9	14.3	1.7	25.9	0	0	4.3	69.8
M/AZ(850)	18.2	2.9	0.5	53.8	0	0	2.6	43.6

PO: propylene oxide, AC: acetone, ACR: acrolein, HC: hydrocarbons of C₁ + C₂ + C₃ + C₄ + C₅ + C₆.

^a Reaction condition: 350 °C, 0.1 MPa and 7500 h⁻¹ of space velocity.

^b AM/Z* and AM/Z 20% Ag–4% MoO₃/ZrO₂; M/AZ: 4% MoO₃/20% Ag–ZrO₂.

^c S: BET surface areas.

^d Calcination temperature (°C).

of ZrO₂ has an obvious influence on the surface area of the catalyst. With an increase of the calcination temperature of Z, Z* or AZ, the surface areas of the AM/Z, AM/Z* and M/AZ catalysts decrease continuously. For the AM/Z* catalysts, when the calcination temperature of Z* increased from 500 to 700 °C, the surface area of AM/Z* decreased slowly from 128 to 105 m²/g; after Z* was calcined at 850 °C (or 950 °C), the surface area of AM/Z* decreased sharply to 21.7 (or 3.6 m²/g). As the calcination temperature of Z and AZ increased from 500 to 850 °C, the surface area of AM/Z decreased from 44.0 to 17.1 m²/g, and that of M/AZ decreased from 59.9 to 18.2 m²/g.

The difference between Z* and Z is that their precursor's (Zr(OH)₄ precipitate) aging condition is different. The precursor of Z* was aged for longer time (160 h) at higher temperature (100 °C), made AM/Z* have higher surface area; that of Z was aged for shorter time (12 h) at lower temperature (25 °C), made AM/Z have smaller surface area. Such as, the surface area of AM/Z*(500) is 128 m²/g and that of AM/Z(500) is 44 m²/g. The surface area of M/AZ(500) is 60 m²/g. With a rise of the calcination temperature of Z*, Z and AZ, the difference of surface area between AM/Z*(850), AM/Z(850) and M/AZ(850) is reduced gradually. When Z*, Z and AZ was calcined at 850 °C, AM/Z*(850), AM/Z(850) and M/AZ(850) have the near surface areas, 21.7, 17.1 and 18.2 m²/g, respectively.

3.1.2. Pore diameter distribution

The pore diameter distributions of AM/Z*(500) and AM/Z*(850) are shown in Figs. 1 and 2, respectively. As can be seen, the pore diameter of AM/Z*(500) is 2–10 nm and its most probable pore diameter is 5.23 nm, and that of AM/Z*(850) is 2–50 and 14.9 nm, respectively. With increasing calcination temperature of Z*, the pore diameter of AM/Z* increases and its surface area decreases. The results

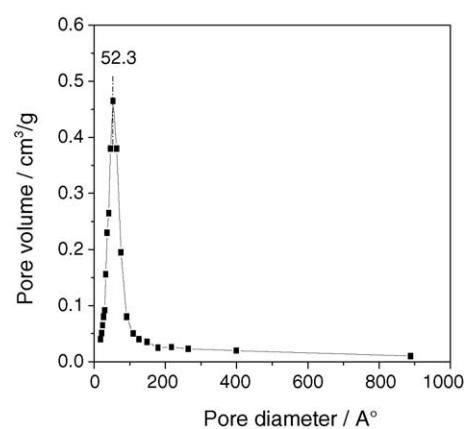


Fig. 1. Pore diameter distribution of AM/Z*(500).

above show that the sample with abundant micropores (such as AM/Z*(500)) possesses a large surface area, and the sample with larger pores (such as the AM/Z*(850)) possesses a smaller surface area. For the AM/Z and M/AZ samples,

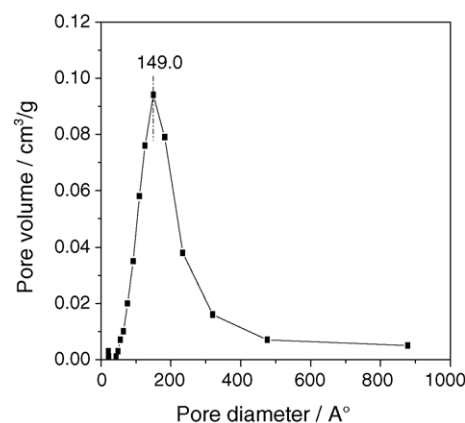


Fig. 2. Pore diameter distribution of AM/Z*(850).

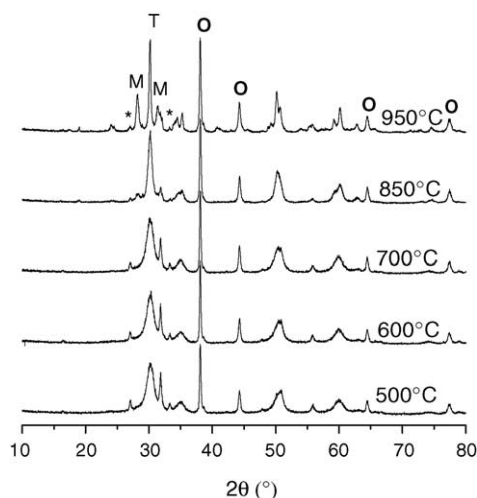


Fig. 3. XRD patterns of the AM/Z* catalysts (500–950 °C is the calcination temperature of Z*; M, monoclinic ZrO₂; T, tetragonal ZrO₂; *, MoO₃; O, Ag).

their smaller surface areas are corresponding to their larger pores.

3.1.3. X-ray diffraction (XRD)

The XRD patterns of AM/Z*, AM/Z and M/AZ are shown in Figs. 3–5, respectively. There are four diffraction peaks for all the catalysts at $2\theta = 38.1^\circ$, 44.3° , 64.4° and 77.4° , that are corresponding to the crystal faces of Ag (1 1 1), (2 0 0), (2 2 0) and (3 1 1), respectively. The very poor diffraction peaks at $2\theta = 27.0^\circ$ and 33.3° are attributed to the MoO₃ crystal. The diffraction peaks at $2\theta = 28.2^\circ$ and 31.4° are assigned to monoclinic ZrO₂, and the diffraction peak of tetragonal ZrO₂ is at $2\theta = 30.2^\circ$.

The XRD patterns of AM/Z* in Fig. 3 show that, with the calcination temperature of ZrO₂ increasing from 500 to 700 °C, the crystalline structure of Z* in AM/Z* that they

hold does not obviously change and consists of main tetragonal phase and minor monoclinic phase. After ZrO₂ is calcined at 850–950 °C, its diffraction peaks obviously narrow, that is to say, the particle (or of crystal) dimension of ZrO₂ has increased. But the diffraction peaks of Ag and MoO₃ are hardly affected by the calcination temperature of ZrO₂. Comparing with the very poor diffraction peaks of MoO₃, the diffraction peaks of Ag are strong and narrow, which suggests that Ag distributes on the surface of ZrO₂ with larger particles, and MoO₃ is highly dispersed on ZrO₂.

The results in Fig. 4 show that, ZrO₂ in the AM/Z catalyst consists of the monoclinic and metastable tetragonal phases. With increasing calcination temperature of ZrO₂ from 500 to 850 °C, the metastable tetragonal phase reduces and the monoclinic phase gradually increases. After calcined at 850 °C, the tetragonal ZrO₂ has transformed to the monoclinic phase for the most part. The diffraction peaks of Ag and MoO₃ change hardly with the calcination temperature of ZrO₂, and Ag has strong diffraction peaks and that of MoO₃ is hardly observed, which is similar to the situation of the AM/Z* catalysts.

For the M/AZ catalysts, ZrO₂ in M/AZ(500) exists mainly in the metastable tetragonal phase and very weak monoclinic phase (Fig. 5). The diffraction peaks of monoclinic ZrO₂ strengthen and that of tetragonal ZrO₂ weaken with an increase of the calcination temperature, but there is still appreciable proportion of tetragonal ZrO₂ in the M/AZ(850) catalyst, unlike the AM/Z(850) catalyst in that the tetragonal phase of ZrO₂ has nearly entirely transformed to the monoclinic phase. With an increase of the calcination temperature of Ag–ZrO₂, the diffraction peaks of Ag strengthen and the very poor peaks of MoO₃ hardly change.

It was reported that the initial temperature of phase transformation from the metastable tetragonal phase to the monoclinic phase for pure ZrO₂ is about 600 °C, and this transformation can end at 650–700 °C. Moreover, this

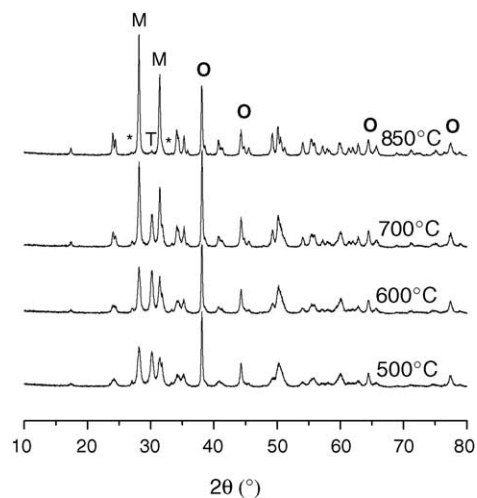


Fig. 4. XRD patterns of the AM/Z catalysts (500–850 °C is the calcination temperature of Z; M, monoclinic ZrO₂; T, tetragonal ZrO₂; *, MoO₃; O, Ag).

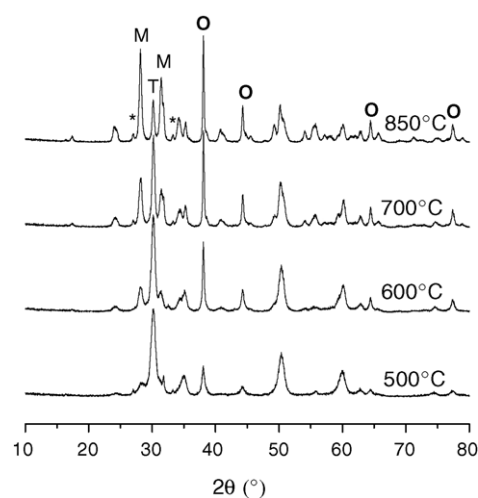


Fig. 5. XRD patterns of the M/AZ catalysts (500–850 °C is the calcination temperature of AZ; M, monoclinic ZrO₂; T, tetragonal ZrO₂; *, MoO₃; O, Ag).

transformation is affected sensitively by the impurities or additives, which can stabilize usually the metastable tetragonal form to higher temperature [19,20].

In the AM/Z* catalyst, the crystalline structure and phase transformation of ZrO₂ are thoroughly different from the results reported [19,20], this is probably because of preparing ZrO₂ with different procedure. ZrO₂ in AM/Z* is a stable tetragonal phase, unlike ZrO₂ in AM/Z (or M/AZ) that is a metastable tetragonal phase, its crystalline phase transformation with the calcination temperature is similar to that reported [19,20] and does not finish until about 850 °C. The fact that there are still some metastable tetragonal ZrO₂ in the M/AZ(850) catalyst suggests that the presence of the active Ag particles can retard the transformation of crystalline phase of ZrO₂ from the metastable tetragonal phase to the stable monoclinic phase.

3.1.4. NH₃-TPD and CO₂-TPD

The acid–base properties of catalyst were investigated by NH₃-TPD and CO₂-TPD. The NH₃-TPD and CO₂-TPD profiles of AM/Z*, AM/Z and M/AZ are shown in Figs. 6–11. The results show that the acidic and basic sites co-exist on the surface of all the catalysts except for AM/Z*(950).

For AM/Z* (Figs. 6 and 7), with increasing the calcination temperature of Z* (ZrO₂), the strength of acidity and basicity (top temperature of NH₃ and CO₂ desorption peak) on the surface of catalyst decreases, and the concentration (peak area) of acidic and basic sites decreases quite slowly for the AM/Z*(500–700) samples and the peak area sharply decreases for AM/Z*(850). It suggests that there are abundant and stronger acidic and basic sites on the surface of AM/Z*(500–700), and some acidic and basic sites on the surface of AM/Z*(850). There are few acidic and basic sites on AM/Z*(950).

There are two peaks of NH₃-desorption at 50–180 °C in the NH₃-TPD curves of AM/Z (Fig. 8), which corresponds to two kinds of acidic sites. Their peak areas of NH₃ desorption

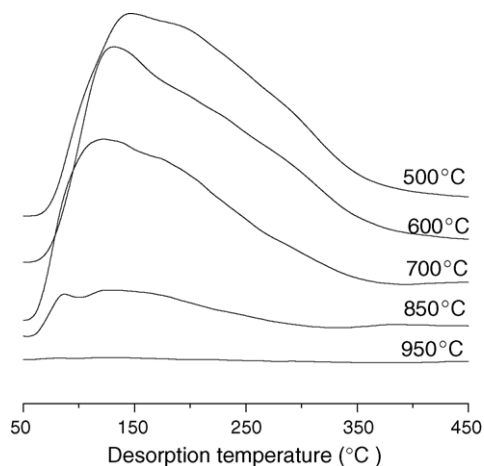


Fig. 6. NH₃-TPD profiles of the AM/Z* catalysts (500–950 °C is the calcination temperature of Z*).

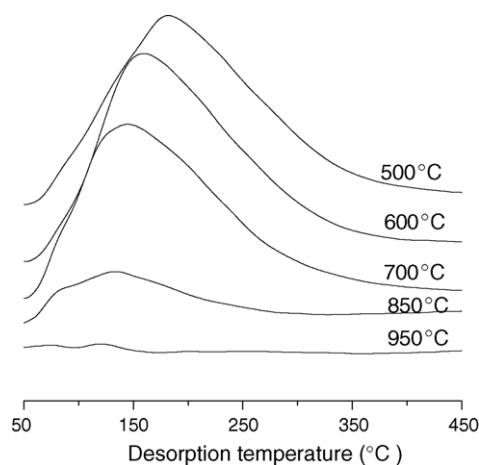


Fig. 7. CO₂-TPD profiles of the AM/Z* catalysts (500–950 °C is the calcination temperature of Z*).

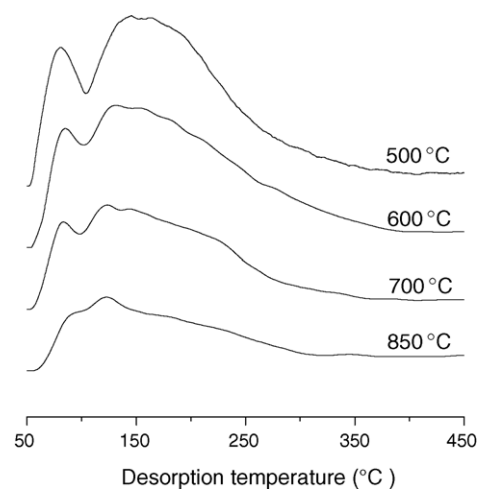


Fig. 8. NH₃-TPD profiles of the AM/Z catalysts (500–850 °C is the calcination temperature of Z).

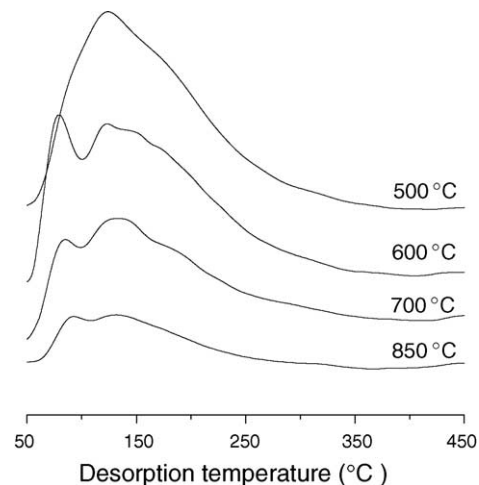


Fig. 9. CO₂-TPD profiles of the AM/Z catalysts (500–850 °C is the calcination temperature of Z).

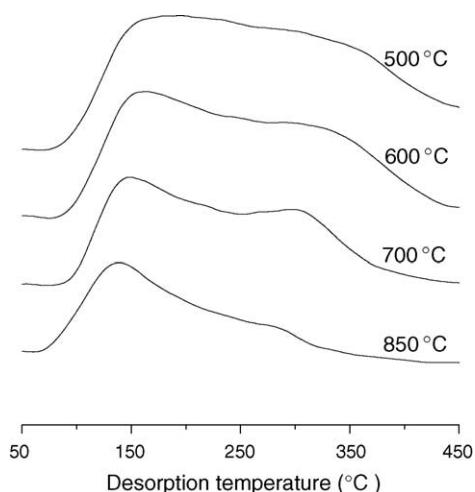


Fig. 10. NH_3 -TPD profiles of the M/AZ catalysts (500–850 °C is the calcination temperature of AZ).

decrease with a rise of the calcination temperature of Z. In the CO_2 -TPD curve (Fig. 9) of AM/Z(500), there is one peak of CO_2 desorption (one kind of basic site). With increasing calcination temperature of Z, this peak (one kind of basic site) divides into two peaks (two kinds of basic sites) and their peak areas of CO_2 desorption decrease.

The NH_3 -TPD and CO_2 -TPD profiles of M/AZ shown in Figs. 10 and 11 do not resemble those of AM/Z* and AM/Z, in which the concentration of basic sites is far smaller than that of acidic sites. In the NH_3 -TPD profiles of M/AZ (Fig. 10), there are two peaks at ~ 150 °C (α peak) and 290–340 °C (β peak), and α peak shifts to low temperature and β peak disappears gradually with an increase of the calcination temperature of AZ (Ag– ZrO_2). In the CO_2 -TPD profiles of M/AZ(500) (Fig. 11), two peaks (two kinds of basic sites) are observed, and both peaks incorporate to one peak and then disappear with increasing the calcination temperature of AZ from 500 to 850 °C.

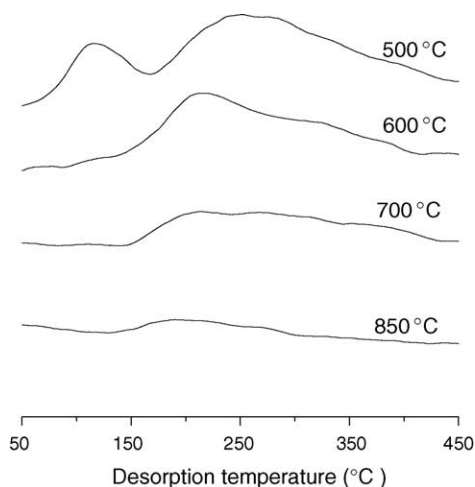


Fig. 11. CO_2 -TPD profiles of the M/AZ catalysts (500–850 °C is the calcination temperature of AZ).

3.2. Epoxidation of propylene

The evaluation results of the catalysts for propylene epoxidation at 350 °C, 0.1 MPa and the space velocity of 7500 h^{-1} , are presented in Table 1. The byproducts are mainly hydrocarbons (C_1 – C_6) and CO_2 . Over the AM/Z*(500–700) catalysts, with increasing calcination temperature of Z*(ZrO_2), the selectivity to PO increases from 1.8 to 7.8% and the O_2 conversion decreases from 100 to 43.6%. Over the AM/Z*(850) catalyst, the selectivity to PO sharply increases to 40.3% and the O_2 conversion decreases to 7.3%. Using Z* calcined at 950 °C as the support of AM/Z*(950), the selectivity to PO decreases to 20.8%.

Using the AM/Z catalysts, with the calcination temperature of ZrO_2 increasing from 500 to 850 °C, the selectivity to PO increases from 20.6 to 57.9% and the O_2 conversion decreases from 15.3 to 3.5%.

Using the M/AZ catalysts, with the calcination temperature of AZ (Ag– ZrO_2) increasing from 500 to 850 °C, the selectivity to PO increases from 2.8 to 53.8% and the conversion of O_2 decreases from 67.2 to 2.9%.

The above results show that the preparation condition of ZrO_2 support has a great influence on the physicochemical characteristics of the Ag– $\text{MoO}_3/\text{ZrO}_2$ catalyst and its surface, consequently, their epoxidation performance is affected markedly by different preparation condition of ZrO_2 .

3.3. Discussion

3.3.1. Relationship between the surface area, pore size, crystalline form and acidity–basicity

The above results show that, increasing calcination temperature of ZrO_2 or Ag– ZrO_2 makes the pore size of catalyst increase, the surface area and acidity–basicity of catalyst decrease, and the crystalline form of ZrO_2 support transform. At higher temperature, the phase transformation and grain growth of ZrO_2 is a main reason of leading the surface area of catalyst to decrease [19,20]. For the AM/Z* catalyst, the decrease of its surface area mainly results from the grain growth of ZrO_2 ; for the AM/Z and M/AZ catalysts, the decrease of their surface area mainly results from the crystalline phase transformation.

Correlating the pore size, surface area and acidity–basicity of the Ag– MoO_3 – ZrO_2 catalysts, it can be found that the catalyst having abundant micro-pores and high surface area possesses abundant acidic and basic sites on its surface and vice versa.

The studies of the acid–base properties of ZrO_2 by the adsorption of CO_2 and NH_3 /pyridine showed that there are Lewis acid sites and no Brønsted acid sites on the surface of ZrO_2 [21,22]. On the Ag– MoO_3 – ZrO_2 catalyst, the acidic and basic sites co-exist independently, and this situation is similar to that of ZrO_2 reported in Ref. [19]. But the preparation condition of catalyst has a great influence on the acidic and basic properties on the surface of the Ag– MoO_3 – ZrO_2 catalyst.

3.3.2. Relationship between the epoxidation performance and physicochemical properties of catalyst

Correlating the epoxidation performance with the surface area of catalyst, we can see that the selectivity to PO increases and the O₂ conversion decreases with the decrease of the surface area of the Ag–MoO₃–ZrO₂ catalysts, except for AM/Z*(950) having no any acidic and basic properties on its surface. For the M/AZ catalyst, with its surface area decreasing slowly (from 59.9 to 18.2 m²/g), the selectivity to PO increases sharply (from 2.8 to 53.8%); for the AM/Z* catalyst, when its surface area decreases from 127.8 to 21.7 m²/g, the selectivity to PO increases and the O₂ conversion decreases; when its surface area decrease further to 3.6 m²/g, on the contrary, the selectivity to PO obviously decreases and the O₂ conversion increases. So there is no parallel relationship between the epoxidation performance and the surface area of catalyst. But the suitably low surface area and large pores is in favor of a diffusion of PO out of the catalyst, to avoid PO to be deeply oxidized to CO₂ and H₂O and to improve the selectivity to PO.

For the AM/Z and M/AZ catalysts, the weak acidity and basicity on its surface makes the selectivity to PO increase. Using the AM/Z*(500–700) catalyst with the abundant acidic and basic sites, the PO selectivity is quite low; using the AM/Z*(850) catalyst containing a small quantity of weaker acidic sites and basic sites, the high selectivity to PO can be obtained; for the AM/Z*(950) catalyst without the acidic and basic sites, its epoxidation performance is very poor. The above phenomena show that, the acidity and basicity on the surface of catalyst has an obvious influence on its epoxidation performance, the modest and weaker acidity and basicity is beneficial to form PO selectively. If there are stronger acidity and basicity or acidity-free on the surface of catalyst, the deep oxidation of propylene or PO to CO₂ and H₂O will occur advantageously.

When there are modest Lewis acidic sites on the Ag–MoO₃/ZrO₂ catalyst, those acidic sites can acquire electrons from the oxygen adsorbed (O_{ad}) on the Ag sites to make O_{ad} possess stronger electrophilic character, which is beneficial to the olefinic carbons of propylene react with O_{ad} to produce PO, and inhibits the acid–base reaction between allylic H (H⁺ properties) and O_{ad} to a certain extent [11]. If the acidity on the catalyst is excessively strong, the action between propylene and O_{ad} is too strong to crack propylene to form CO₂ and H₂O. If there are many strong basic sites on the catalyst, the acid–base reaction (or dehydrogenation) between allylic H and basic sites can occur, thus propylene is also completely oxidized to CO₂ and H₂O, as a result, the conversion of O₂ increases and the selectivity to PO decreases.

For the AM/Z*(850), AM/Z(850) and M/AZ(850) catalysts calcined at 850 °C, they have the near surface areas (21.7, 17.1 and 18.2 m²/g, respectively) and similar surface acidity and basicity (such as AM/Z*(850) and AM/Z(850)), but their crystalline structure of ZrO₂ and epoxidation performance are obviously different. Relating the crystalline struc-

ture of ZrO₂ with the epoxidation performance of catalyst shows that the Ag–MoO₃ catalyst supported on monoclinic ZrO₂ has higher selectivity to PO than the catalyst supported tetragonal ZrO₂. It is possible that the monoclinic ZrO₂ can make Ag keep the metallic properties to reduce its electron loss, which leads the O_{ad} on Ag to have the stronger electrophilic properties. This situation is similar to the Pt catalyst supported on ZrO₂ promoted by tungstate, i.e., the crystalline structure of ZrO₂ has an obvious effect on the metallic properties of the Pt catalyst [23,24].

The XRD results show that the particle size of Ag on AM/Z* and AM/Z does not vary obviously with the calcination temperature of ZrO₂ support. But with an increase of calcination temperature of Ag–ZrO₂, the Ag particles on M/AZ increase sharply and its surface area and surface acidity–basicity decrease slowly, meanwhile the epoxidation performance of catalyst is improved sharply. Based on the above facts, it can be inferred that the particle size of Ag on catalyst is also a more important factor of affecting the selectivity to PO, and the catalyst having the Ag particles with properly larger size behaves a higher performance for the epoxidation of propylene. In the epoxidation of ethylene, it has been found that the large Ag particles are more effective than small Ag crystallites [25,26]. This size effects result from a change of the surface Ag structure, the small Ag particles have higher surface energy and more surface defects, on which the adsorbed oxygen behaves stronger activity to result in the deep oxidation of propylene to CO₂ and H₂O.

On the basis of above discussion, it can be found that the epoxidation performance of the catalyst is affected by many factors that should include the particle size of the active silver, the crystalline form of ZrO₂ support, and the surface acidity–basicity, the surface area and pore size of catalyst, which can be put into practice by optimizing the preparation conditions of the ZrO₂ support and catalyst.

4. Conclusions

The physicochemical properties of the Ag–MoO₃/ZrO₂ catalyst are significantly affected by the preparation conditions of the ZrO₂ support. When ZrO₂ is prepared by the precipitation method, a long aging time at higher temperature is liable to form the tetragonal phase, and a shorter aging time at room temperature is liable to form the monoclinic phase. With the increase of the calcination temperature of ZrO₂ or Ag–ZrO₂, the pore sizes of the catalyst enlarge, the surface area and acidity and basicity of the catalyst decrease, and the crystalline phase of ZrO₂ will transform. The suitably low surface area and big pore diameter, modest and weaker acidity and basicity on the surface of catalyst are beneficial to form PO selectively; the high surface area and abundant micropore structure, strong acidity and basicity or acidity-free are liable to the deep oxidation of propylene to CO₂ and H₂O. The monoclinic ZrO₂ is an excellent support of the Ag–MoO₃ catalyst for an epoxidation of propylene. The properly larger

particle size of Ag should be kept for improving the epoxidation performance of the catalyst. The suitable preparation conditions of ZrO₂ are that the Zr(OH)₄ precipitate is aged at room temperature for 12 h, dried at 110 °C for 24 h and calcined at 850 °C.

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