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Modification of $Ag–MoO_3/ZrO_2$ catalyst with metallic chloride for propylene epoxidation by molecular oxygen

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The modification of the $Ag–MoO_3/ZrO_2$ catalyst with metallic chloride was studied for a gas-phase epoxidation of propylene by molecular oxygen. As a modifier, the presence of NaCl, CsCl or $CaCl_2$ can effectively regulate an electronic property of the $Ag–MoO_3/ZrO_2$ catalyst and improve obviously its catalytic epoxidation performance. When NaCl (1000 ppm), CsCl (1500 ppm) or $CaCl_2$ (1000 ppm) was used to modify the 20%Ag–4%MoO_3/ZrO_2 catalyst, the selectivity to propylene oxide (PO) increased to 63.5%, 66.7% and 62.9%, from 47.9%, respectively, and the corresponding O_2 conversion was 7.3%, 7.7% and 8.1%, respectively. The studies of XPS indicates that the electron-interaction between the active component of catalyst and metallic chloride has occurred obviously, and the presence of chloride can enhance the electron-deficient property of Ag to improve the electrophilic property of adsorbed oxygen and inhibit an isomerization and deep oxidation of PO to improve the selectivity to PO.

KEY WORDS: epoxidation of propylene; oxygen; catalyst; silver–molybdenum oxide; metallic chloride; modifier.

1. Introduction

Propylene oxide (PO) is an important chemical intermediate producing resins such as polyurethane, and is commercially produced by Chlorohydrin and Halcon methods, but those two processes have the disadvantages of the bad environment pollution and high production cost. The epoxidation of propylene with H_2O_2 over the TS-1 zeolite catalyst has a high conversion and selectivity to PO under the mild conditions; however, the high costs of H_2O_2 and TS-1 make this process be not commercialized so far [1]. For the epoxidation of propylene with O_2 and H_2 over Au/TiO_2 [2] or Pd–Pt/TS-1 [3], the selectivity to PO is higher than 90% and propylene conversion is 1–2%, but this process need to consume large quantities of H_2 and a careful handling is strictly required for the explosive mixture of $H_2–O_2$. Therefore, in view of an economy and green chemistry, the direct epoxidation of propylene by molecular oxygen over a solid catalyst is the most ideal process of manufacturing PO. ARCO chemists reported that the propylene conversion of 1.5% and selectivity to PO of 64% were achieved over the modified $Ag/CaCO_3$ catalyst by oxygen with EtCl, NO and CO_2 additives [4]. Lu *et al.* [5,6] reported that NaCl-modified Ag catalyst had a good epoxidation performance for propylene by air, the propylene conversion of 54.0% and selectivity to PO of 26.3% were achieved [5].

During the adsorption of oxygen on silver surface, the transfer of electrons from silver to the adsorbed oxygen makes the adsorbed oxygen possess the electronegative property [7,8]. The mechanism of propylene oxidation on the silver surface has been studied by Nakatsuji and co-workers [9,10], they think that the formation of PO is initiated by the reaction of an olefinic carbon (—C=C—) and adsorbed oxygen, and the combustion reaction is initiated by the abstraction of an allylic hydrogen (α-H) by adsorbed oxygen. Roberts and co-workers [11] consider that in the course of propylene combustion on silver, the initial step is an acid–base reaction between an allylic hydrogen (acid) and adsorbed oxygen (O_{ad}(base)). This step leads to a formation of the surface hydroxyl group (OH_{ad}) and chemisorbed allyl species, that are further reacted to CO_2 and H_2O. Therefore, lowering an electron density (electronegative property or basicity) of the O_{ad} on the silver sites to reduce the reaction chances between the O_{ad} and allylic hydrogen is an important way to improve the selectivity to PO. Based on the idea above, we have developed the $Ag–MoO_3$ and $Ag–MoO_3/ZrO_2$ catalysts for an epoxidation of propylene [12–15]. The Mo species in catalyst can acquire the electrons from silver lattice, to increase the binding energy of Ag $3d_{5/2}$ and the electron-deficient property of Ag, and to decrease the electron density of the O_{ad} on the Ag sites, which promotes the reaction of an olefinic carbon and O_{ad} to form PO, and inhibits the reaction of an allylic hydrogen and O_{ad}, to improve the selectivity to PO.

We report herein that modifying the $Ag–MoO_3/ZrO_2$ catalyst with metallic chloride is a very effective method to improve its catalytic performance for propylene epoxidation by molecular oxygen without any additive

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in the feedstock. Through investigation of the electronic interaction between a modifier and the components of catalyst, the relationship between epoxidation performance and electronic property of catalyst and modifier is discussed.

2. Experimental

2.1. Preparation of catalyst

20%Ag–4%MoO_3/ZrO_2 was used as a model catalyst and is prepared by impregnation method. $AgNO_3$ (12.5g) was solved in distilled water (12.5 mL) to form $AgNO_3$ aqueous solution. ZrO_2 (30.0 g) was slowly added into this $AgNO_3$ aqueous solution to form slurry under stirring vigorously with ultrasonic at room temperature, and the slurry was heated at 80 °C to nearly waterless, and then dried at 110 °C for 4 h and calcined at 450 °C for 4 h in air to form the precursor. This precursor was impregnated with aqueous solution (12.5 mL) of $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ (1.95 g), dried at 110 °C for 4 h and calcined at 300 °C for 4 h in air to get the 20%Ag–4% MoO_3/ZrO_2 catalyst. After its treatment with an equal-volume of the metallic chloride (AR) aqueous solution, and dried at 110 °C 4 h, the modified catalysts were obtained.

2.2. Activity testing of catalyst

The catalytic epoxidation of propylene was performed in a micro-reactor-GC system. The size of the stainless steel fixed-bed reactor is φ 5 × 300 mm, in which 0.5 mL catalyst (20–40 meshes) was filled. The reaction condition was 400 °C, 0.1 MPa and space velocity of 7500 h^{-1}. The feedstock gas consisted of 22.7% C_3H_6, 9.0%O_2 and balance N_2, without any additive such as NO_x, EtCl or CO_2. The composition of feedstock and effluent gas was analyzed by two on-line gas chromatographs with three packed columns (G.D.X-401, 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 is 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 is i$\pm$4.0%. Because O_2 was insufficient in comparison with C_3H_6 in feedstock, the activity of catalyst is expressed with the conversion of O_2 rather than that of C_3H_6 in the text.

2.3. Characterization of catalyst

The XPS spectra of catalysts were obtained in a Perkin–Elmer PHI 550 ESCA/SAM spectrometer at 1×10^{-9}–2×10^{-10} Torr, MgKα radiation (1253.6 eV), and the binding energy (284.6 eV) of adventitious C_1 was used as a reference.

3. Results and discussion

3.1. Effect of adding NaCl, CsCl and $CaCl_2$ on performance of catalyst

The effect of adding NaCl, CsCl and $CaCl_2$ on the epoxidation performance of the 20%Ag–4%MoO_3/ZrO_2 catalyst is shown in Figure 1. With an increase of NaCl or CsCl content, the conversion of O_2 decreases to a minimum, and then increases and reaches a maximum. Unlike NaCl and CsCl, with increasing $CaCl_2$ content the conversion of O_2 increases to a maximum, and then decreases. For the selectivity to PO, three kinds of metallic chlorides have a similar effect of promoter. When 600 ppm NaCl was added in the catalyst, the O_2 conversion decreases from 10.9% to 5.8%, the selectivity to PO increases from 47.9% to 55.0%; as NaCl content was increased to 1000 ppm, the selectivity to PO reaches the maximum (63.5%) with 7.3% conversion of O_2. When 1500 ppm CsCl was added in the catalyst, the selectivity to PO reaches the maximum (66.7%) with 7.7% conversion of O_2; as CsCl content was increased to 2000 ppm, the O_2 conversion

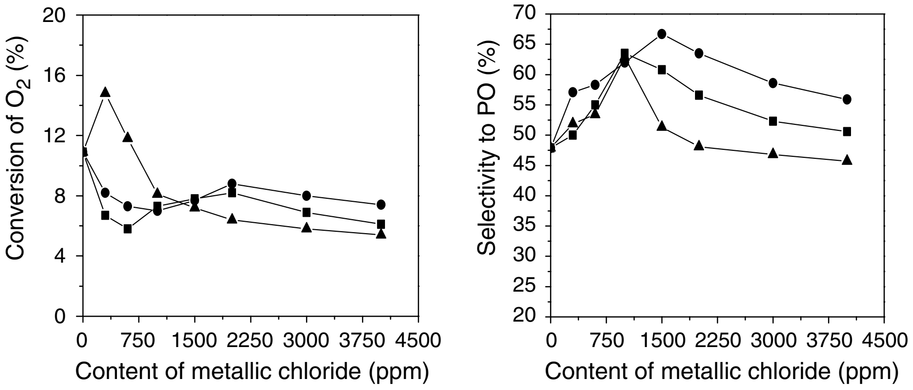

Figure 1. Effect of the metallic chloride content on the epoxidation performance of 20%Ag–4%MoO_3/ZrO_2 modified with NaCl (■), CsC (●) and $CaCl_2$ (▲) at 400 °C, 0.1 MPa and SV of 7500 h^{-1}.

reaches a maximum (8.8%) with 63.5% selectivity to PO. Using 300 ppm $CaCl_2$ as the modifier, the conversion of O_2 reaches a maximum (14.8%) with 51.9% PO selectivity; after the catalyst was modified with 1000 ppm $CaCl_2$, the selectivity to PO reaches the maximum (62.9%) with 8.1% O_2 conversion.

The results in figure 1 show that different metallic chlorides have obviously different effect on the epoxidation performance of the catalyst, and there is a most suitable content for each metallic chloride added. When the content of NaCl (CsCl or $CaCl_2$) in the catalyst is about 1000 ppm (1500 or 1000 ppm), the selectivity to PO reaches the maximum (Table 1). Over the unmodified catalyst, the by-products are mainly HC (18.7%) and CO_2 (29.2%). Using the catalyst modified with NaCl, CsCl or $CaCl_2$, the selectivity to HC and CO_2 decreases obviously, but HC and CO_2 selectivity reaches still 8.3–10.9% and 22.8–25.1%. So that in order to increase the PO selectivity, the formation of HC and CO_2 must be inhibited.

3.2. XPS characterization of catalyst

The XPS spectra of the unmodified catalyst and catalysts modified by NaCl (1000 ppm), CsCl (1500 ppm) or $CaCl_2$ (1000 ppm) are presented in Figures 2–7.

For the 20%Ag–4%MoO_3/ZrO_2 catalyst, the binding energy (BE) of Ag $3d_{5/2}$, Mo $3d_{5/2}$ and Zr $3d_{5/2}$ is 368.6, 231.8 and 182.5 eV, respectively. Compared with the BE of Ag $3d_{5/2}$ of metallic Ag (367.9 eV), Mo $3d_{5/2}$ of MoO_3 (232.65 eV) and Zr $3d_{5/2}$ of ZrO_2(182.4 eV), Ag is electron-deficient (the BE increase of Ag $3d_{5/2}$), Mo^{6+} probably obtains the electrons from Ag to form the Mo oxyanion (the BE decrease of Mo $3d_{5/2}$) and the BE of Zr^{4+} is the same as that of ZrO_2.

After the 20%Ag–4%MoO_3/ZrO_2 catalyst was modified by 1000 ppm NaCl, the BE of Ag $3d_{5/2}$ and Mo $3d_{5/2}$ further increases to 368.9 eV and 232.1 eV respectively, and the BE of Zr $3d_{5/2}$ is unchanged; the BE of Na 1s is 1070.8 eV (figure 5) that is obviously lower than one of Na 1s (1071.5 eV) in pure NaCl crystal, and the BE of Cl 2p is 197.6 eV (figure 5) that is lower than Cl 2p BE in pure NaCl crystal (198.0 eV). This indicates that NaCl has interacted electronically with the active components of catalyst. Na^+ probably acquires the electrons from Ag and Mo^{6+} to lead to an increase of the BEs of Ag $3d_{5/2}$ and Mo$3d_{5/2}$, that is, Ag and Mo have a stronger positive-charge property. As the BE of Cl 2p (197.6 eV) in the catalyst is similar to the BE of Cl 2p (197.5 eV) in pure AgCl crystal, it is suggested there exists the AgCl in the catalyst modified by NaCl [6].

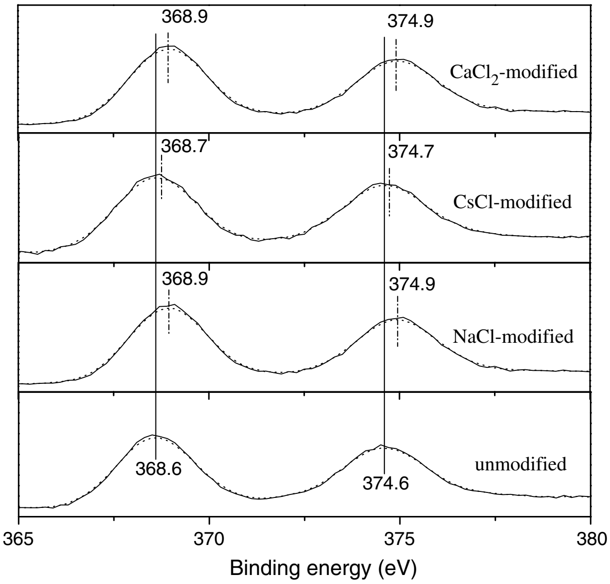

Figure 2. Ag 3d XPS spectra of 20%Ag–4%MoO_3/ZrO_2 modified by metallic chloride.

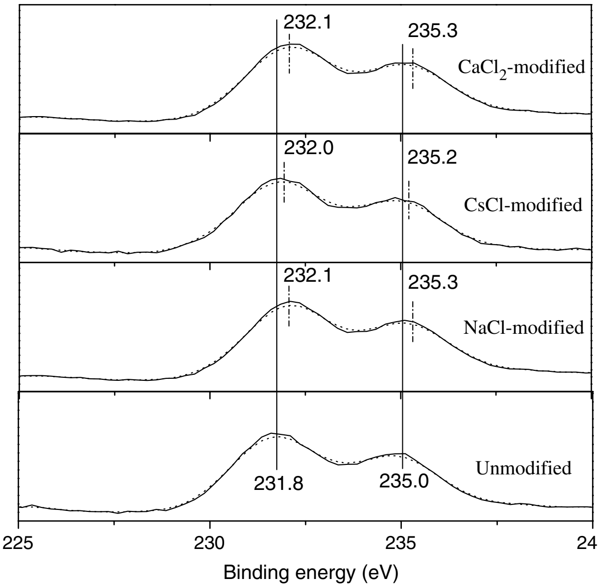

Figure 3. Mo 3d XPS spectra of 20%Ag–4%MoO_3/ZrO_2 modified by metallic chloride.

Table 1
Performance of the chloride-modified 20%Ag–4%MoO_3/ZrO_2 catalysts for the propylene epoxidation by oxygen[a]

Promoter	Conversion (%)		Selectivity (%)[b]				
	O_2	Propylene	PO	AC	ACR	HC	CO_2
No	10.9	2.7	47.9	2.3	1.9	18.7	29.2
1000 ppm NaCl	7.3	2.0	63.5	1.7	1.0	8.7	25.1
1500 ppm CsCl	7.7	2.2	66.7	1.3	0.9	8.3	22.8
1000 ppm $CaCl_2$	8.1	2.3	62.9	2.5	0.6	10.9	23.1

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

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

Compared with 20%Ag–4%MoO_3/ZrO_2, the presence of CsCl (1500 ppm) makes the BE of Ag $3d_{5/2}$ increase to 368.7 eV, the BE of Mo $3d_{5/2}$ increase to

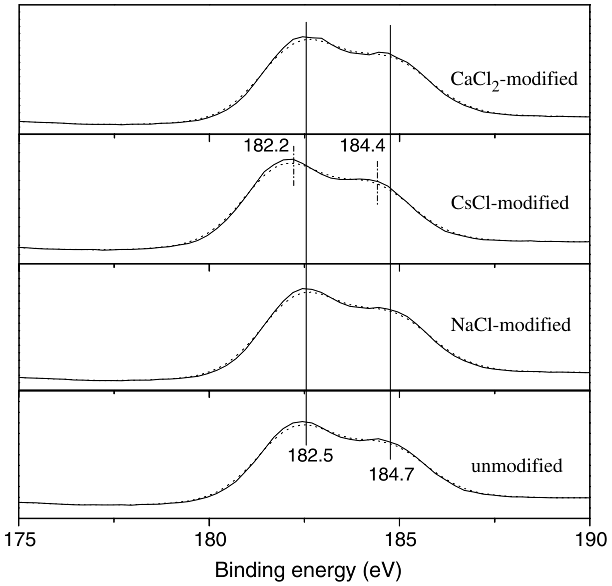

Figure 4. Zr 3d XPS spectra of 20%Ag–4%MoO$_3$/ZrO$_2$ modified by metallic chloride.

232.0 eV, and the BE of Zr 3d$_{5/2}$ decrease to 182.2 eV. As the amount of CsCl added is very low, its effects on the BE of Ag, Mo and Zr is weaker. The XPS spectra of CsCl in figure 6 show that, the BE (724.1 eV) of Cs 3d$_{5/2}$ is higher than the BE (723.5 eV) of Cs 3d$_{5/2}$ in the pure CsCl crystal, the BE (197.2 eV) of Cl 2p is lower than its BE (197.7 eV) in the pure CsCl crystal. An increase of the BE of Cs 3d$_{5/2}$ in the CsCl-catalyst means that Cs provides the electrons to the components of catalyst. Based on the fact above, an increase of the BE of Ag 3d$_{5/2}$ and a decrease of the BE of Zr 3d$_{5/2}$, it is inferred that the electrons donated by Cs are probably accepted by both Ag and ZrO$_2$ of P-type semiconductor. Although Cs provides electrons to catalyst, the positive-charge property of Ag and Mo is still enhanced by Cl acquiring electrons from catalyst. Like the NaCl-catalyst, the decrease of the BE of Cl 2p in the CsCl-catalyst means that AgCl has formed.

Like the NaCl-catalyst, the presence of CaCl$_2$ (1000 ppm) causes an increase of the BE of Ag 3d$_{5/2}$ (368.9 eV) and Mo 3d$_{5/2}$ (232.1 eV), and the BE of Zr 3d$_{5/2}$ change little. As can be seen in figure 7, the BE of Ca 2p$_{3/2}$ (347.5 eV) is lower than that of Ca 2p$_{3/2}$ (348.1 eV) in the pure CaCl$_2$ crystal, the BE of Cl 2p is 197.3 eV. Therefore, it is inferred there existed the obvious electron-interaction between CaCl$_2$, Ag and Mo. Like Na^{+} in the NaCl-catalyst, Ca^{2+} has obtained the electrons from Ag and Mo to increase the BEs of Ag 3d$_{5/2}$ and Mo 3d$_{5/2}$ further, which increases the positive-charge property of Ag and Mo in the catalyst.

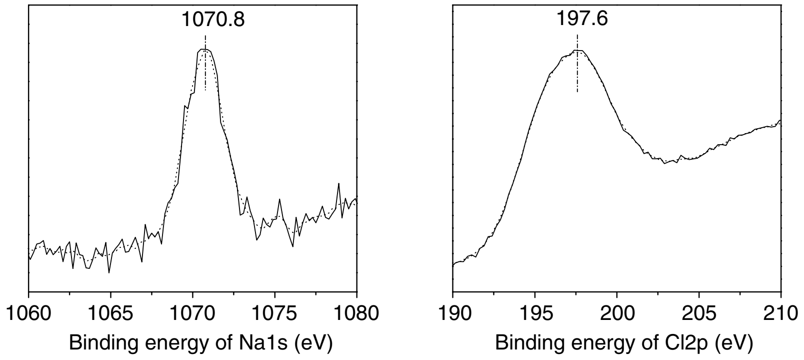

Figure 5. XPS spectra of 20%Ag–4%MoO$_3$/ZrO$_2$ modified by NaCl.

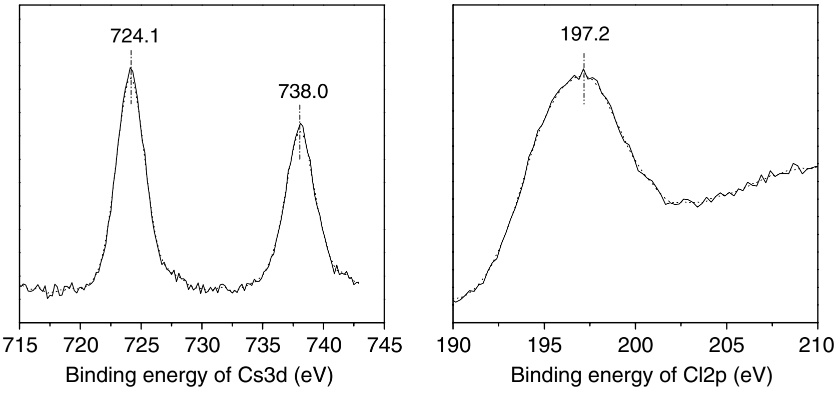

Figure 6. XPS spectra of 20%Ag–4%MoO$_3$/ZrO$_2$ modified by CsCl.

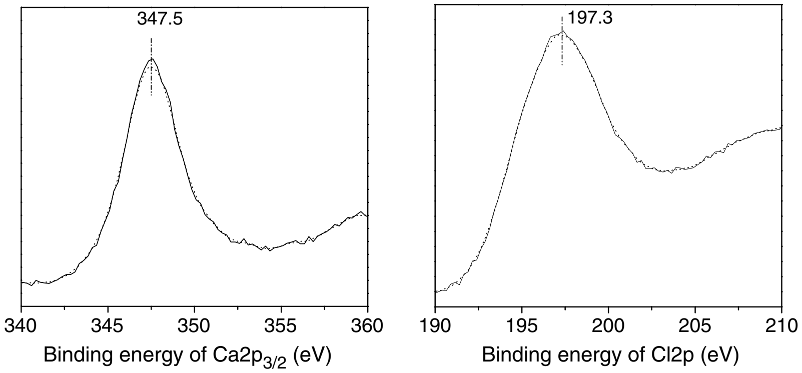

Figure 7. XPS spectra of 20%Ag–4%MoO_3/ZrO_2 modified by $CaCl_2$.

3.3. Discussion for the role of metallic chloride in catalyst

The studies above show that the metallic chloride plays a great role in improving the epoxidation performance. As a modifier of catalyst, metallic chloride may change the electronic property of the active sites by interacting with the active components, to regulate the electrophilic property of the adsorbed species (O_{ad}) on the surface of catalyst; on the other hand, the modifier may react with the active components to form new compounds (such as AgCl) and adjust the chemical property of the active sites.

Correlating the epoxidation performance with the XPS analytic results of catalyst, it is found there is a direct relationship between the epoxidation performance of catalyst and the electronic property of the Ag active sites. For the catalyst modified by NaCl or $CaCl_2$, like Mo species playing the role of electron-type promoter, Na^+ or Ca^{2+} acquires the electrons from the Ag lattices to increase the electrophilic property of O_{ad} on the Ag sites, which is advantageous of the olefinic carbons (–C=C–) of propylene attacking O_{ad} to produce PO and blocks up an abstraction of allylic H (H^+ property) by O_{ad} to form CO_2 and H_2O. The presence of NaCl or $CaCl_2$ makes the BE of Mo $3d_{5/2}$ increase, to enhance a potential of Mo acquiring the electrons from the Ag lattices. On the other hand, the formation of AgCl is beneficial to the selective synthesis of PO [6]. After modified with NaCl, the activity of the 20%Ag–4%MoO_3/ZrO_2 catalyst decreases and its selectivity to PO increases. Unlike NaCl, when 300 ppm $CaCl_2$ was added in catalyst, both the conversion of O_2 and the selectivity to PO increase (figure 1). The reason is possibly that adding a small amount of $CaCl_2$ (e.g. 300 ppm) in catalyst may promote oxygen adsorption and the presence of Ca^{2+} may inhibit an isomerization and oxidation of PO. If a large amount of $CaCl_2$ was added in catalyst, both a rate of oxygen adsorption and total oxygen uptake would decrease, which is similar to the situation of the NaCl-catalyst.

For the CsCl-catalyst, although Cs donates the electrons to the active components of catalyst, the electron-deficient property of the Ag sites are still enhanced by Cl and ZrO_2 of P-type semiconductor accepting electrons; meanwhile, the presence of Cs can inhibit the further oxidation and isomerization of PO. So the selectivity to PO can be improved. Otherwise, like NaCl and $CaCl_2$, CsCl can improve the positive-charge property of Mo species, which enhances its potential of acquiring the electrons from the Ag lattices.

But the suitable amount of adding metallic chloride should be controlled. If more amount of chloride were added in catalyst, a high concentration of Cl would decrease the activity of catalyst and improve an isomerization rate of PO, which makes the epoxidation performance of catalyst decrease.

4. Conclusions

As a modifier of the Ag–MoO_3/ZrO_2 catalyst for the epoxidation of propylene, adding NaCl, CsCl and $CaCl_2$ can improve obviously the selectivity to PO, and decrease the activity of the catalyst. The suitable content of NaCl, CsCl and $CaCl_2$ in the catalyst is 1000, 1500 and 1000 ppm, respectively. The studies show that adding metallic chloride improves the epoxidation performance of catalyst via three aspects:(1) enhance the electrophilic properties of O_{ad} on the Ag sites by acquiring the electrons from Ag lattice and forming AgCl; (2) improve the positive-charge property of Mo species to enhance its potential of acquiring the electrons from the Ag lattice; (3) inhibit an isomerization and deep oxidation of the product PO.

Acknowledgments

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