Epoxidation of propylene by molecular oxygen over modified Ag–MoO_3 catalyst

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Epoxidation of propylene to propylene oxide by molecular oxygen was studied over a modified Ag–MoO_3 catalyst. The results show that MoO_3 plays an important role in improving the efficiency of the catalyst, and a suitable content of MoO_3 is 40–50 wt%. XPS reveals that some of the silver and molybdenum in the catalyst exist as Ag^+ and $Mo^{(6-\delta)^+}$, respectively. The promotion effect of NaCl, $Ce(NO_3)_3$, $BaCl_2$ and $CsNO_3$ on the Ag–MoO_3 catalyst was studied. As a modifier of the Ag–MoO_3 catalyst, NaCl or $Ce(NO_3)_3$ are more suitable than $BaCl_2$ or $CsNO_3$ and the optimal loading of NaCl or $Ce(NO_3)$ is about 2 wt%. Using a feedstock gas of 15.6% C_3H_6, 12.2% O_2 and balance N_2 without any addition of NO, EtCl or CO_2 at a space velocity of 4500 h^{-1}, 6.8% O_2 conversion and 53.1% selectivity to propylene oxide were achieved over the Ag–MoO_3–2.0% NaCl catalyst at 400 °C. At 450 °C the O_2 conversion and selectivity to propylene oxide were 11.4 and 43.6%, respectively.

KEY WORDS: propylene; epoxidation; silver–molybdenum oxide; catalyst; promoter.

1. Introduction

Propylene oxide (PO) is used to alkoxylate alcohols to form polypropylene polyether polyols, and very important intermediates in the manufacture of propylene glycol, dipropylene glycol, isopropanolamine, etc. PO is produced commercially via the well-known chlorohydrin and Halcon processes, which rely on the oxygen transfer from an organic hydroperoxide or peroxycarboxylic acid to an olefin [1]. The former suffers from the production of a low-concentration salt stream and the corrosion of equipment and pollution by waste water produced in the process; the latter disadvantageously produces equimolar amounts of a co-product, whose value must be captured in the market place. Many different methods for the preparation of PO by oxidizing propylene directly with oxygen or other oxidizing agents have been developed, in which the direct gas-phase epoxidation of propylene to PO by oxygen on a solid catalyst, like the process of ethylene to ethylene oxide, is most attractive in view of the operating costs and process facility. Unfortunately, so far, the most effective silver catalyst for ethylene epoxidation has not proved very useful in the epoxidation of higher olefins like propylene.

The epoxidation of ethylene by molecular oxygen over a silver catalyst is the main commercial method of producing ethylene oxide. Many years of continuing research and development have led to an increase of the selectivity to ethylene oxide from <70% in the late 1960s to close to 90% at present in the laboratory; plants are already operating with selectivity >80% [2,3]. Hu *et al.* [4] studied the mechanisms of epoxidation and complete oxidation of propylene on a silver surface by the dipped adcluster model (DAM). Their results indicate that the route leading to propylene oxide also occurs on a silver surface, but the combustion path is more favorable than the epoxidation mechanism. Epoxide formation is initiated by the reaction of the olefinic carbon and adsorbed oxygen, while combustion is initiated by the abstraction of the allylic hydrogen by adsorbed oxygen. Roberts *et al.* [5] considered that in the course of combustion of propylene on silver, the initial step is an acid–base reaction between the allylic H (acid) and $O_{(a)}$ (base). This step leads to the formation of a surface hydroxyl group ($OH_{(a)}$) and chemisorbed allyl species that are further reacted to CO_2 and H_2O. Lu *et al.* prepared unsupported silver catalysts containing NaCl as promoter, over which 54.0% C_3H_6 conversion and 26.3% selectivity to PO were obtained in the epoxidation of propylene with air as the oxygen source [6]. ARCO chemists reported that using a feedstream containing NO, EtCl and CO_2, 60–64% selectivity to PO was attained over their catalyst, but the conversion of propylene was only 1.5–2.5% [7].

In this paper, Ag–MoO_3 catalysts modified with alkali, alkaline earth or rare earth chloride or nitrate salts were studied. Firstly, MoO_3 was added into the silver catalyst to modify the properties of the active sites in order to inhibit the adsorption of allylic hydrogen of propylene on adsorbed $O_{(a)}$ and to make the olefinic carbon of propylene adsorb easily. Meanwhile, adding a promoter to the catalyst can decrease the negative charge property of the surface of the catalyst, to block the acid–base reaction between allylic hydrogen and $O_{(a)}$ adsorbed on the surface of the catalyst.

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2. Experimental

The catalyst was prepared as follows. A silver–ammonium complex solution was synthesized by adding Ag_2O to a mixed aqueous solution of ethylenediamine and oxalic acid, then stoichiometric ammonium molybdate was slowly added to this solution to form a slurry. The slurry was vigorously stirred and slowly heated to 60 °C so that the silver–ammonium complex and ammonium molybdate could be mixed efficiently. The slurry was evaporated to nearly no water, dried at 110 °C for 2 h and then was calcined at 400 or 450 °C for 2 h to obtain the precursor of the Ag–MoO_3 catalyst. This precursor was washed with ethanol to remove the residual organic compounds, and then was dried at 80 °C. It was then compressed into discs and broken to 20–40 mesh. This granular Ag–MoO_3 catalyst was impregnated with equal-volume aqueous solutions of stoichiometric NaCl, $Ce(NO_3)_3$, $BaCl_2$ or $CsNO_3$ and dried at 110 °C for 2 h to obtain the Ag–MoO_3 catalyst modified with NaCl, $Ce(NO_3)_3$, $BaCl_2$ or $CsNO_3$.

The catalytic epoxidation of propylene was performed in a micro-reactor GC system. The size of the stainless steel fixed-bed reactor was 5×300 mm, in which 0.5 ml catalyst was placed. The activity testing was carried out at a space velocity of $4500\,h^{-1}$ and 0.14 MPa absolute pressure. The feedstock gas consisted of 15.6% C_3H_6, 12.2% O_2 and balance N_2, without any additives such as nitrogen oxide, alkyl halide or carbon dioxide. The composition of the feedstock and effluent gas was analyzed by two on-line gas chromatographs with three packed columns (407 porous polymer, silica gel and 5A zeolite), in which a TCD was used.

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 moles of carbon in the feedstock gas; n_e, total moles of carbon in the effluent gas). In this study the carbon balance was less than ±4.0%.

X-ray photoelectron spectroscopy (XPS) was carried out using a Perkin-Elmer PHI550 ESCA/SAM spectrometer at 10 kV, 40 mA. The X-ray source was Mg$K\alpha$ (1253.6 eV) and the base pressure of the test chamber was 2×10^{-10}–10^{-9} torr. The values of binding energy were calibrated using the contaminant carbon (C $1s = 284.6$ eV).

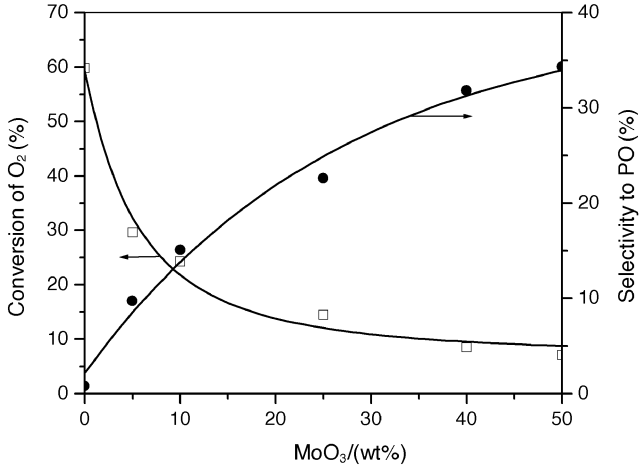

Figure 1. Effect of MoO_3 loading on the performance of Ag–MoO_3 catalyst at 400 °C.

3. Results and discussion

3.1. Effect of MoO_3 loading on the performance of Ag–MoO_3 catalyst

Figure 1 shows the O_2 conversion and PO selectivity as a function of MoO_3 loading in the Ag–MoO_3 catalyst. Over the MoO_3-free Ag catalyst, an O_2 conversion of 59.8% was obtained with a PO selectivity of 0.8%. With an increase of MoO_3 content in the Ag–MoO_3 catalyst, the selectivity to PO increased, but O_2 conversion decreased. When the MoO_3 content reached 40–50 wt% the effect of the MoO_3 content on the O_2 conversion and selectivity to PO was less. Over the 50% Ag–50% MoO_3 catalyst at 400 °C, the conversion of O_2 and selectivity to PO was 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 to PO.

The XPS data for the 50% Ag–50% MoO_3 catalyst are shown in table 1. For the fresh catalyst, the binding energies of Ag $3d_{5/2}$ and Ag $3d_{3/2}$ are 368.7 and 374.3 eV, respectively, which are higher than that of silver metal (Ag $3d_{5/2}$ 367.9 eV and Ag $3d_{3/2}$ 373.9 eV). This indicates that some of the silver species in the catalyst exist as Ag^+. The binding energies of Mo $3d_{5/22}$ and Mo $3d_{3/2}$ are 231.8 and 235.2 eV, respectively, which are lower than that of Mo^{6+} (Mo $3d_{5/2}$ 232.65 eV and Mo $3d_{3/2}$ 235.85 eV). This indicates that some of the molybdenum species in the catalyst exist as $Mo^{(6-\delta)^+}$. Therefore, it can be inferred that the electron transfer from Ag to MoO_3 leads to Mo having a chemical valance of $6 - \delta$ and existing as a Mo oxyanion, and to Ag being electron deficient. According to the DAM theory [4], in the course of the adsorption of oxygen on the silver surface, electron transfer from silver to adsorbed oxygen makes oxygen

Table 1
XPS data for the 50% Ag–50% MoO_3 catalyst

	Binding energy (eV)			
	Ag $3d_{5/2}$	Ag $3d_{3/2}$	Mo $3d_{5/2}$	Mo $3d_{3/2}$
Fresh	368.7	374.3	231.8	235.2
Used [a]	368.5	374.2	231.7	235.2

[a] After it has been used in the reaction.

take on negative ion properties. The presence of MoO_3 in the catalyst may compete with the adsorbed oxygen for silver lattice electrons, and lead to the reduction of the effective charge and the increase of the electrophilic property of the adsorbed oxygen. As a result, the allylic H (positive charge state) of propylene attacks the adsorbed oxygen, which leads to complete oxidation of propylene to CO_2 and H_2O. On the contrary, the olefinic carbons of propylene have more chance to combine with adsorbed oxygen to form PO. Hence, adding Mo into the Ag catalyst can increase the selectivity to PO. In addition, the presence of MoO_3 may improve the acidic environment of the silver active sites, to block the acid–base reaction between the allylic H of propylene and the adsorbed oxygen.

Compared to the fresh catalyst, the binding energies of Ag $3d_{5/2}$, Ag $3d_{3/2}$ and Mo $3d_{5/2}$ of the used catalyst are not much reduced (table 1). This shows that there is hardly any change of the catalyst after having been used in the reaction, but there is probably one trend of some Ag^+ and Mo^{6+} being reduced very slowly in the process of reaction.

3.2. *Effect of the promoter on the performance of the catalyst*

The effects of NaCl, $Ce(NO_3)_3$, $BaCl_2$ and $CsNO_3$ as promoters on the performance of the catalyst are shown in table 2. The results show that the catalyst modified by NaCl or $Ce(NO_3)_3$ has higher activity and higher selectivity to PO than that modified by $BaCl_2$ or $CsNO_3$. At 400 °C a PO selectivity of 53.1% was achieved with an O_2 conversion of 6.8% over the Ag–MoO_3–2% NaCl catalyst; over the Ag–MoO_3–2% $Ce(NO_3)_3$ catalyst the O_2 conversion and selectivity to PO were 7.3 and 46.7%, respectively. When $BaCl_2$ was used as a promoter 42.1% selectivity to PO and 3.0% conversion of oxygen were obtained. Like $BaCl_2$, $CsNO_3$ is also a useful promoter, and over the Ag–MoO_3–$CsNO_3$ catalyst the O_2 conversion and selectivity to PO were 5.1 and 42.5%, respectively. These results show that the presence of the cation from chloride or nitrate salt obviously affects the performance of the catalyst. It is possible that Na^+, Ce^{3+}, Ba^{2+} or Cs^+ further reduce the negative charge of $O_{(a)}$ on the silver surface and weaken the acid–base reaction between allylic hydrogen (acid) of propylene and $O_{(a)}$ (base) on the silver surface, and promote the adsorption of the olefinic carbon with a nucleophilic property on the $O_{(a)}$, to inhibit the complete oxidation of propylene and increase the selectivity to PO. On the other hand, Cl^- or NO_3^- can poison partially the strong active center to avoid PO being further oxidized to CO_2 and H_2O. Compared with $BaCl_2$ and $CsNO_3$, NaCl and $Ce(NO_3)_3$ are better promoters. As Na^+ (0.97 Å) and Ce^{3+} (1.034 Å) have smaller ion radii than Cs^+ (1.67 Å) and Ba^{2+} (1.34 Å), Na^+ and Ce^{3+} can be dispersed better in the catalyst and modify the properties of active sites on the catalyst more efficiently than Cs^+ and Ba^{2+}.

Table 2
Performance of the modified Ag–MoO_3 catalyst for epoxidation of propylene at 400 °C

Catalyst[a]	CT[b] (°C)	Conversion (O_2 %)	Selectivity[c] (PO %)
Ag–MoO_3	400	14.0	24.8
	450	7.1	34.3
Ag–MoO_3–2.0% NaCl	400	9.7	48.7
	450	6.8	53.1
Ag–MoO_3–2.0% $Ce(NO_3)_3$	400	12.2	40.3
	450	7.3	46.7
Ag–MoO_3–$BaCl_2$	400	7.9	28.5
	450	3.0	42.1
Ag–MoO_3–$CsNO_3$	400	8.8	31.0
	450	5.1	42.5

[a] 50 wt% Ag–50 wt% MoO_3, the loading of Cl^- or NO_3^- is unchanged.
[b] CT: calcination temperature of Ag–MoO_3.
[c] In addition to PO and CO_2, no other products were detected.

The modified Ag–MoO_3 catalyst was prepared by impregnating Ag–MoO_3 with aqueous solutions of NaCl, $Ce(NO_3)_3$, $BaCl_2$ or $CsNO_3$. The results in table 2 show that the calcination temperature of Ag–MoO_3 affects the performance of the modified Ag–MoO_3 catalyst: increasing the calcination temperature of Ag–MoO_3 reduces the activity of the catalyst and increases the selectivity to PO. For instance, using the Ag–MoO_3 (calcined at 450 °C) catalyst modified with 2.0 wt% NaCl, the conversion of oxygen and the selectivity to PO at 400 °C were 6.8 and 53.1%, respectively. When the calcination temperature of Ag–MoO_3 was 400 °C, the conversion of oxygen and the selectivity to PO at 400 °C were 9.7 and 48.7%, respectively. The higher calcination temperature favors the growth of silver particles (or clusters) on the catalyst surface, and results in the catalytic properties of the active sites of silver changing.

3.3. *Effect of the loading of NaCl or $Ce(NO_3)_3$ on the performance of the catalyst*

The effect of the loading of NaCl and $Ce(NO_3)_3$ on the performance of the 50% Ag–50% MoO_3 catalyst at 400 °C is shown in figures 2 and 3. The results of figure 2 show that the O_2 conversion and selectivity to PO over the Ag–MoO_3–NaCl catalyst changed with an increase of the NaCl loading. As 0.5 wt% NaCl was added in the catalyst, the highest O_2 conversion (9.8%) was obtained. The selectivity to PO first increased and then decreased. When the loading of NaCl was about 2.0 wt%, the highest selectivity of 53.1% was obtained.

At 1.0 wt% $Ce(NO_3)_3$ loading (figure 3), the highest conversion of O_2 (about 9.0%) was obtained. When

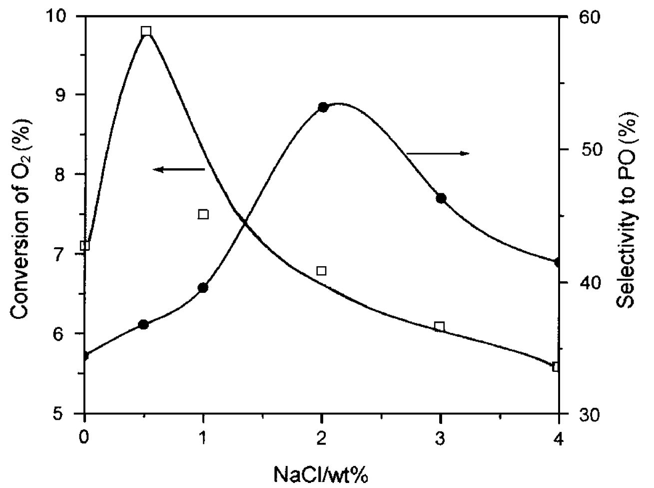

Figure 2. Effect of NaCl loading on the performance of the 50% Ag–50% MoO_3 catalyst at 400 °C.

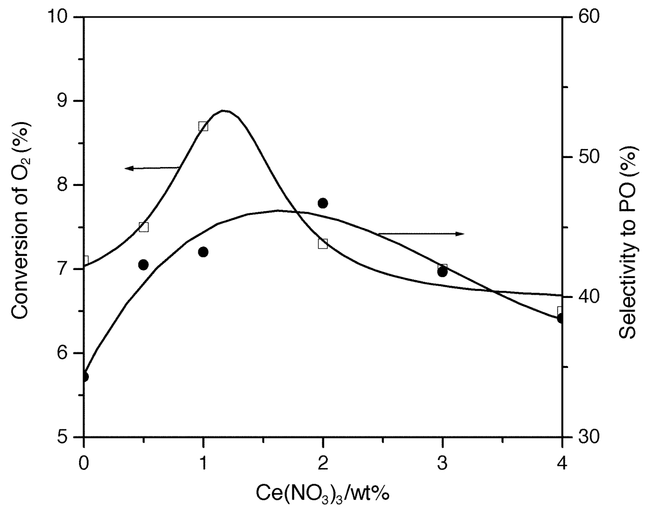

Figure 3. Effect of $Ce(NO_3)_3$ loading on the performance of the 50% Ag–50% MoO_3 catalyst at 400 °C.

Table 3
Effect of reaction temperature on the performance of the catalyst

Catalyst[a]	T (°C)	Conversion (O_2 %)	Selectivity[b] (PO %)
Ag–MoO_3	400	7.1	34.3
	450	27.4	30.5
Ag–MoO_3–2% NaCl	400	6.8	53.1
	450	11.4	43.6
Ag–MoO_3–2.0% $Ce(NO_3)_3$	400	7.3	46.7
	450	10.6	40.5
Ag–MoO_3–$BaCl_2$	400	3.0	42.1
	450	8.2	36.7
Ag–MoO_3–$CsNO_3$	400	5.1	42.5
	450	8.3	39.4

[a] Ag–MoO_3 was calcined at 450 °C; the lowest decomposing temperature of $Ce(NO_3)_3$ and $CsNO_3$ is 450 and 600 °C, respectively.

[b] In addition to PO and CO_2, no other products were detected.

the loading of $Ce(NO_3)_3$ was about 2 wt%, the highest selectivity to PO of 46.7% was obtained, but the conversion of oxygen was only 7.3%.

3.4. Effect of the reaction temperature on the performance of the catalyst

The evaluation of catalysts was carried out at 400 and 450 °C and the results are shown in table 3. With an increase of the reaction temperature the catalytic activities increased, but the selectivities to PO decreased. In order to increase the selectivity to PO, the lower reaction temperature should be adopted.

4. Conclusions

Ag–MoO_3 is an effective catalyst for the epoxidation of propylene to PO by molecular oxygen. The MoO_3 content, promoter, calcination temperature of Ag–MoO_3 and reaction temperature can affect obviously the epoxidation performance of the catalysts. In order to improve the efficiency of the Ag–MoO_3 catalyst for the epoxidation of propylene to PO, the MoO_3 content should be controlled in the range 40–50 wt%. NaCl, $Ce(NO_3)_3$, $BaCl_2$ or $CsNO_3$ can be used as promoters, but NaCl and $Ce(NO_3)_3$ are more suitable than $BaCl_2$ and $CsNO_3$. The optimal loading of NaCl and $Ce(NO_3)_3$ is about 2.0 wt%. A higher calcination temperature of Ag–MoO_3 can improve the selectivity to PO, but reduces the activity of the catalyst. A higher reaction temperature can improve the activity of the catalyst, but reduces the selectivity to PO.

Acknowledgments

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