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Article

Gas-phase epoxidation of propylene by molecular oxygen over Ag-Cu-Cl/BaCO₃ catalyst: Effects of Cu and Cl loadings

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ABSTRACT

Ag-Cu-Cl/BaCO₃ catalysts with different Cl and Cu loadings, prepared by the reduction deposition impregnation method, were investigated for gas-phase epoxidation of propylene by molecular oxygen and characterized by X-ray diffraction, X-ray photoelectron spectroscopy and O₂ temperature programmed desorption. Ag-Cu-Cl/BaCO₃ catalyst with 0.036 wt% Cu and 0.060 wt% Cl exhibited the highest catalytic performance for gas-phase epoxidation of propylene by molecular oxygen. A propylene oxide selectivity of 83.7% and propylene conversion of 1.2% were achieved under the reaction conditions of 20% C₃H₆-10% O₂-70% N₂, 200 °C, 0.1 MPa and 3000 h⁻¹. Increasing the Cl loading allowed Ag to ensemble easier, whereas changing the Cu loading showed little effect on Ag crystallite size. The appropriate Cl loading of Ag-Cu-Cl/BaCO₃ catalyst can reduce the dissociation adsorption of oxygen to atomic oxygen species leading to the combustion of propylene to CO₂, which benefits epoxidation of propylene by molecular oxygen. Excessive Cl loading of Ag-Cu-Cl/BaCO₃ catalyst decreases propylene conversion and propylene oxide selectivity remarkably because of Cl poisoning. The appropriate Cu loading of Ag-Cu-Cl/BaCO₃ catalyst is efficient for the epoxidation of propylene by molecular oxygen, and an excess Cu loading decreases propylene oxide selectivity because the aggregation of Cu species increases the exposed surfaces of Ag nanoparticles, which was shown by slight increases in atomic oxygen species adsorbed. The appropriate loadings of Cu and Cl of Ag-Cu-Cl/BaCO₃ catalyst are important to strike the balance between molecular oxygen and atomic oxygen species to create a favorable epoxidation of propylene by molecular oxygen.

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1. Introduction

Propylene oxide (PO), with a worldwide market capacity exceeding 7 Mt per year [1], is an important chemical intermediate widely used to produce polyurethane, propylene glycols, polyether polyols, surfactants and other commercial products. PO is produced mainly by the chlorohydrin process, the Halcon process and the hydroperoxide process. However, the chloro-

hydrin process is environmentally harmful, the Halcon process generates equimolar coproducts, which values depend on their demands in the market [2], and the commercialization of the hydroperoxide process is hindered by the expense and the transport of H₂O₂ [3–5]. The gas-phase epoxidation of propylene by molecular oxygen is the most ideal reaction process with a high atomic economy; however, it remains a great challenge for researchers to achieve high PO selectivity. Various

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Ag-based catalysts [6–12] and Cu-based catalysts [13–20] have been investigated extensively and exhibit much better catalytic performance for the epoxidation of propylene by molecular oxygen than unpromoted Ag or Cu catalysts.

The epoxidation of ethylene by molecular oxygen over Ag-based catalysts has been widely used in the industrial production of ethylene oxide, achieving a selectivity of 83%–95% for several decades [21–23]. Therefore, many researchers have attempted to apply Ag-based catalysts to the epoxidation of propylene by molecular oxygen; however, their results showed inefficient PO formation with PO selectivities below 10% [24–26]. The low PO selectivity may be because of the high reactivity of the allylic hydrogens in propylene, causing the complete combustion of propylene to CO₂. Various promoters have been used to modify Ag-based catalysts to improve PO selectivity, and the loadings of promoters were optimized to improve the catalytic performance for epoxidation of propylene by molecular oxygen. Ag-CuCl catalysts with the ratios of Ag to CuCl of 1/0.3–1/0.6 showed a high catalytic activity because of the formation of AgCl and CuO, which may be effective for the epoxidation of propylene [27]. Over Ag-Cu bimetallic catalyst, a small quantity of Cu can withdraw electrons from nearby Ag, which made oxygen species adsorbed more electrophilic and increased PO selectivity [9].

In our previous work [28], Ag-CuCl₂/BaCO₃ catalyst with 0.036 wt% Cu and 0.040 wt% Cl was effective for the epoxidation of propylene by molecular oxygen, in which a propylene conversion of 1.3% and PO selectivity of 71.2% were achieved under the reaction conditions of 20% C₃H₆–10% O₂–70% N₂, 200 °C, 0.1 MPa and 3000 h⁻¹. The appropriate CuCl₂ doping of Ag-CuCl₂/BaCO₃ catalyst can make molecular oxygen species more active to produce PO easily, and depress the dissociation adsorption of oxygen to atomic oxygen species leading to the combustion of propylene, which benefits the epoxidation of propylene by molecular oxygen. However, the disadvantage of using CuCl₂ as the promoter is the fixed ratio of Cu to Cl. In this work, Cu(NO₃)₂ and NH₄Cl in place of CuCl₂ were used as the precursors of Cu and Cl elements, respectively. The loadings of Cu and Cl of Ag-Cu-Cl/BaCO₃ catalyst were optimized to achieve a higher PO selectivity, and the roles of Cu and Cl were investigated by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and O₂ temperature programmed desorption (TPD).

2. Experimental

2.1. Preparation of catalysts

Ag/BaCO₃ catalyst was prepared by the reduction deposition method as follows [29]: 8 g of BaCO₃ support was first immersed into ethylene diamine aqueous solution for 12 h and dried under vacuum at 60 °C for 4.5 h. After, 2 g of formaldehyde was dissolved in 40 mL of deionized water as the reductant, into which the dried amine-pretreated BaCO₃ support was added to form a slurry in an ice-water bath at 10 °C. After stirring for 20 min, 0.6 g of AgNO₃ dissolved in 40 mL of deionized water was added dropwise into the above slurry, then the solid

was washed with deionized water and ethanol several times and dried overnight at room temperature. Ag-Cu-Cl/BaCO₃ catalysts were prepared by the incipient wetness impregnation of the dried Ag/BaCO₃ catalyst without calcination with the mixture of Cu(NO₃)₂ and NH₄Cl aqueous solution for 12 h, dried at 60 °C and then calcined in an N₂ atmosphere at 250 °C for 4 h.

2.2. Epoxidation of propylene

The epoxidation of propylene was performed in a fixed-bed quartz reactor under the reaction conditions of 0.6 g catalyst, 200 °C, 0.1 MPa and a gas hourly space velocity of 3000 h⁻¹. The feed gas consisted of 20% of propylene, 10% of O₂ and N₂ balance. Reaction products were analyzed by two on-line gas chromatographs equipped with a two packed columns (G.D.X-401 and Porapak Q) with flame ionization and thermal conductivity detectors. All lines between the reactor exit and the gas chromatographs were heated to 120 °C to prevent condensation of products. PO selectivity and propylene conversion were calculated on a carbon balance basis.

2.3. Characterization of catalysts

Elemental analysis was performed by inductively coupled plasma atomic emission spectroscopy (ICP-AES) using a TJA IRIS ADVANTAG 1000 instrument.

XRD patterns were performed on a Bruker AXS D8 Focus diffractometer operated at 40 kV, 40 mA (Cu K_α radiation, λ = 0.15406 nm).

XPS spectra were recorded on a Thermo ESCALAB 250 spectrometer with a monochromatized Al K_α X-ray source (1486.6 eV) and a passing energy of 20 eV. C1s (binding energy of 284.6 eV) of adventitious carbon was used as the reference.

O₂-TPD was measured using a Micromeritics AutoChem 2920 II chemisorption analyzer with a Hiden HPR 20 mass spectrometer. 500 mg samples of 40–60 mesh were loaded in a quartz reactor and pretreated in a He flow of 30 mL/min at 250 °C for 30 min. After cooling to room temperature, a gas flow of O₂-He (3 vol% O₂) was introduced into the reactor, the reactor temperature was raised to 200 °C at a rate of 10 °C/min and held at 200 °C for 30 min, then cooled down to room temperature. A He flow of 20 mL/min was applied. When the baseline was stable, the reactor temperature was raised to 600 °C at a heating rate of 10 °C/min. The signals of O₂ (*M_r/z* = 32) were recorded by the mass spectrometer.

3. Results and discussion

3.1. Effect of Cl loading

3.1.1. Catalytic performance of Ag-Cu-Cl/BaCO₃ with different Cl loadings

Table 1 shows the effect of Cl loading on the catalytic performance of Ag-Cu-Cl/BaCO₃ for the epoxidation of propylene by molecular oxygen with 0.036 wt% Cu loading. Ag loadings of all Ag-Cu-Cl/BaCO₃ catalysts were similar at 4.3 wt% as meas-

Table 1

Effect of Cl loading on the catalytic performance of Ag-Cu-Cl/BaCO₃ catalysts.

Cu loading (wt%)	Cl loading (wt%)	Propylene conversion (%)	Selectivity (%)			Ag crystallite size (nm) ^a
			PA	CO ₂	PO	
0.036	0.040	1.6	0.2	27.9	71.9	21
0.036	0.050	1.3	0.4	19.5	80.1	26
0.036	0.060	1.2	0.5	15.8	83.7	31
0.036	0.070	0.2	1.1	41.6	57.3	44

Reaction conditions: 0.6 g catalyst, 20% C₃H₆-10% O₂-70% N₂, 200 °C, 0.1 MPa, 3000 h⁻¹.

^a Determined from XRD patterns by Scherrer's equation.

ured by ICP-AES. The loadings of 0.036 wt% Cu and 0.040 wt% Cl achieved a propylene conversion of 1.6% and a PO selectivity of 71.9%, which was similar to that (propylene conversion of 1.3% and PO selectivity of 71.2%) over Ag-CuCl₂/BaCO₃ catalyst with CuCl₂ as the promoter at 0.036 wt% Cu and 0.040 wt% Cl [28]. This result indicates that the performance using a co-modification of Cu(NO₃)₂ and NH₄Cl as the promoters is almost the same as using CuCl₂. NO₃⁻ nor NH₄⁺ ions showed a negative effect. As shown in Table 1, with an increase in Cl loading from 0.040 wt% to 0.070 wt% in the Ag-Cu-Cl/BaCO₃ catalyst, propylene conversion decreased gradually from 1.6% to 0.2%. A propylene conversion of only 0.2% was obtained at 0.070 wt% Cl loading because Cl poisons the active sites of Ag at excessive levels [30]. With an increase in Cl loading from 0.040 wt% to 0.070 wt%, PO selectivity increased first and then decreased. Ag-Cu-Cl/BaCO₃ catalyst with 0.036 wt% Cu and 0.060 wt% Cl achieved the highest PO selectivity of 83.7% at a propylene conversion of 1.2%. By further increasing Cl loading, PO selectivity decreased significantly to 57.3%. Besides the main by-product of CO₂, there was another by-product of acrolein (PA) with a low selectivity that can be ignored.

3.1.2. XRD results

Fig. 1 shows XRD patterns of Ag-Cu-Cl/BaCO₃ catalysts with different Cl loadings. As shown in Fig. 1, no characteristic diffraction peaks of Cu(NO₃)₂ and NH₄Cl were detected because of their low loadings. XRD patterns of Ag-Cu-Cl/BaCO₃ catalysts with different Cl loadings were similar to those of Ag/BaCO₃ and Ag-CuCl₂/BaCO₃ catalysts, in which the characteristic diffraction peak of Ag (111) at $2\theta = 38.1^\circ$ and the diffraction peaks of BaCO₃ support were observed [9]. The diffraction peak of Ag (111) became sharper and sharper with increasing Cl loading. Ag crystallite size was determined from XRD patterns by Scherrer's equation with the full peak width at half maximum height of the diffraction peak of Ag (111), which is shown in Table 1. The Ag crystallite size was 21 nm in the Ag-Cu-Cl/BaCO₃ catalyst with 0.036 wt% Cu and 0.040 wt% Cl and increased to 44 nm for 0.070 wt% Cl. The Ag crystallite size of Ag-Cu-Cl/BaCO₃ catalyst with 0.036 wt% Cu and 0.060 wt% Cl, which exhibit the highest catalytic performance, was 31 nm. The presence of Cl benefits the formation of Ag ensembles, and the Ag crystallite size grows with increasing Cl loading [25]. The formation of Ag ensembles and the occupation of active sites by the modification of Cl inhibit the adsorption of oxygen,

Fig. 1. XRD patterns of Ag-Cu-Cl/BaCO₃ catalysts with different Cl loadings.

which explains the decline of propylene conversion with an increase in Cl loading. As for low loadings of Cu(NO₃)₂ and NH₄Cl, no characteristic diffraction peaks of AgCl were observed, which is beneficial for PO formation over Ag-based catalysts modified with chlorides [27,31].

3.1.3. XPS results

To study the valence states of Ag, Cu and Cl, XPS of Ag-Cu-Cl/BaCO₃ catalysts with different Cl loadings was performed. As shown in Fig. 2(a), the satellite peak at 942 eV was not detected in the Ag-Cu-Cl/BaCO₃ catalysts, which implied the absence of Cu²⁺ species. The binding energies of Cu 2p_{3/2} and Cu 2p_{1/2} of all the catalysts were 934.0 and 954.0 eV, respectively, which indicated that the valence state of Cu was between +1 and +2, and there is a strong interaction between Cu species and Ag. Fig. 2(b) shows Cl 2p XPS spectra of Ag-Cu-Cl/BaCO₃ catalysts, in which the binding energy was 198 eV, which is assignable to Cl⁻ species [32]. The peak intensity of Cl 2p was weak and barely detected. As shown in Fig. 2(c), the binding energies of Ag 3d_{3/2} and Ag 3d_{5/2} were 374.1 and 368.1 eV, respectively, corresponding to Ag⁰ [11,33]. An increase in Cl loading did not change the binding energies of Cu, Cl or Ag probably because of the small difference in Cl loading, which indicated that the interactions among Cu, Cl and Ag were not affected by the increase in Cl loading.

Table 2 shows the surface composition of Ag-Cu-Cl/BaCO₃ catalysts with different Cl loadings determined by XPS. With an increase in Cl loading from 0.040 wt% to 0.070 wt%, the surface concentration of Ag decreased from 11.9 at% to 4.5 at%, and the surface concentration of Cu decreased gradually from 2.9 at% to 1.5 at%. The ratio of Ag to Cu decreased from 4.1 at 0.040 wt% Cl loading to the minimum of 2.7 at 0.060 wt% Cl loading, and then increased to 3.0 with a further increase in Cl loading to 0.070 wt%. The Ag-Cu-Cl/BaCO₃ catalyst with the surface ratio of Ag to Cu of 2.7 exhibited the highest catalytic performance. XPS results indicated that the surface of Ag-Cu-Cl/BaCO₃ catalyst was covered by Cl with an increase in Cl loading until the occurrence of Cl poisoning.

Fig. 2. Cu 2p XPS (a), Cl 2p XPS (b) and Ag 3d XPS (c) spectra of Ag-Cu-Cl/BaCO₃ catalysts with different Cl loadings.

3.1.4. O₂-TPD results

The reaction process of the epoxidation of propylene by molecular oxygen over Ag-CuCl₂/BaCO₃ catalyst is propylene in the gas phase reacts with molecular oxygen species adsorbed to produce PO and with atomic oxygen species adsorbed to produce CO₂. The distribution of oxygen species adsorbed on the surface of Ag-CuCl₂/BaCO₃ catalyst determines its catalytic performance [28]. Therefore, O₂-TPD profiles of Ag-Cu-Cl/BaCO₃ catalysts with different Cl loadings were performed to investigate the change in the distribution of oxygen species adsorbed on the surface of Ag-Cu-Cl/BaCO₃ catalysts,

Table 2

Surface composition of Ag-Cu-Cl/BaCO₃ catalysts with different Cl loadings.

Catalyst	Surface composition		
	Ag (at%)	Cu (at%)	Ag/Cu
Ag-0.036%Cu-0.040%Cl/BaCO ₃	11.9	2.9	4.1
Ag-0.036%Cu-0.050%Cl/BaCO ₃	8.7	2.6	3.3
Ag-0.036%Cu-0.060%Cl/BaCO ₃	6.7	2.5	2.7
Ag-0.036%Cu-0.070%Cl/BaCO ₃	4.5	1.5	3.0

which are shown in Fig. 3. The desorption temperatures of molecular oxygen species and atomic oxygen species were 118 and 215 °C, respectively, which were the active oxygen species responsible for the epoxidation of propylene by molecular oxygen at the reaction temperature of 200 °C [28]. As shown in Fig. 3, the O₂ uptakes decreased gradually with an increase in Cl loading, which explained the decrease in propylene conversion with an increase in Cl loading shown in Table 1. The intensities of the desorption peak of molecular oxygen species at 118 °C were similar, and the intensities of the desorption peak of atomic oxygen species at 215 °C declined gradually, which lowers the complete combustion of propylene and enhances PO selectivity. This result is consistent with the catalytic performance shown in Table 1. When the Cl loading was 0.070 wt%, Cl poisoning occurred and oxygen was difficult to adsorb on the surface of Ag-Cu-Cl/BaCO₃ catalyst, leading to a propylene conversion of 0.2% and PO selectivity of 57.3%. From the XPS results, excess Cl can mainly locate on the surface of Ag nanoparticles and suppress the dissociation adsorption of oxygen to atomic oxygen species, leading to the combustion of propylene to CO₂ [34]. The appropriate Cl doping strikes the balance between molecular oxygen and atomic oxygen species to enhance PO selectivity [35].

3.2. Effect of Cu loading

3.2.1. Catalytic performance of Ag-Cu-Cl/BaCO₃ catalysts with different Cu loadings

The Ag-Cu-Cl/BaCO₃ catalyst with 0.036 wt% Cu and 0.060

Fig. 3. O₂-TPD profiles of Ag-Cu-Cl/BaCO₃ catalysts with different Cl loadings.

Table 3

Effect of Cu loading on the catalytic performance of Ag-Cu-Cl/BaCO₃ catalysts.

Cu loading (wt%)	Cl loading (wt%)	Propylene conversion (%)	Selectivity (%)			Ag crystallite size (nm) ^a
			PA	CO ₂	PO	
0.036	0.060	1.2	0.5	15.8	83.7	31
0.046	0.060	1.2	0.5	18.4	81.1	32
0.056	0.060	1.3	0.5	18.5	81.0	31
0.066	0.060	1.4	0.6	20.3	79.1	31

Reaction conditions: 0.6 g catalyst, 20% C₃H₆-10% O₂-70% N₂, 200 °C, 0.1 MPa, 3000 h⁻¹.

^a Determined from XRD patterns by Scherrer's equation.

wt% Cl showed the highest catalytic performance for the epoxidation of propylene by molecular oxygen. The Cu loading was optimized with 0.060 wt% Cl to achieve the high PO selectivity. The results are shown in Table 3. With an increase in Cu loading from 0.036 wt% to 0.066 wt%, propylene conversion increased slightly from 1.2% to 1.4% and PO selectivity decreased gradually from 83.7% to 79.1%, but the differences between the loadings were small. When 0.066 wt% Cu and 0.060 wt% Cl were loaded, a PO selectivity of nearly 80% and propylene conversion of 1.4% were achieved. Besides the main by-product of CO₂, there was another PA with a selectivity of below 0.6%, which is negligible. Therefore, after the optimization of Cu and Cl loadings, Ag-Cu-Cl/BaCO₃ catalyst with 0.036 wt% Cu and 0.060 wt% Cl exhibited the highest catalytic performance with a propylene conversion of 1.2% and PO selectivity of 83.7% at the reaction conditions of 200 °C, 0.1 MPa and 3000 h⁻¹.

3.2.2. XRD results

Fig. 4 shows XRD patterns of Ag-Cu-Cl/BaCO₃ catalysts with different Cu loadings, and they were similar to Fig. 1. As shown in Table 3, Ag crystallite sizes of Ag-Cu-Cl/BaCO₃ catalyst with different Cu loadings were similar at 31 nm, which indicated that an increase in Cu loading has little effect on Ag crystallite size, which is different to increasing the Cl loading.

Fig. 4. XRD patterns of Ag-Cu-Cl/BaCO₃ catalysts with different Cu loadings.

3.2.3. XPS results

Fig. 5 shows XPS spectra of Ag-Cu-Cl/BaCO₃ catalysts with different Cu loadings. Similar to Ag-Cu-Cl/BaCO₃ catalysts with different Cl loadings, the valence state of Cu of Ag-Cu-Cl/BaCO₃ catalysts with different Cu loadings was between +1 and +2. The valence states of Cl and Ag were -1 and 0, respectively. An increase in Cu loading did not change the binding energies of Cu, Cl or Ag probably because of the small difference in Cu loading, which indicated that small differences in Cu loading have little effect on the interactions among Cu, Cl and Ag.

Table 4 shows the surface composition of Ag-Cu-Cl/BaCO₃

Fig. 5. Cu 2p XPS (a), Cl 2p XPS (b) and Ag 3d XPS (c) spectra of Ag-Cu-Cl/BaCO₃ catalysts with different Cu loadings.

Table 4

Surface composition of Ag-Cu-Cl/BaCO₃ catalysts with different Cu loadings.

Catalyst	Surface composition		
	Ag (at%)	Cu (at%)	Ag/Cu
Ag-0.036%Cu-0.060%Cl/BaCO ₃	6.7	2.5	2.7
Ag-0.046%Cu-0.060%Cl/BaCO ₃	7.0	2.5	2.8
Ag-0.056%Cu-0.060%Cl/BaCO ₃	7.0	2.3	3.0
Ag-0.066%Cu-0.060%Cl/BaCO ₃	7.1	1.8	3.9

catalysts with different Cu loadings determined by XPS. With an increase in Cu loading from 0.036 wt% to 0.066 wt%, the surface concentration of Ag increased slightly from 6.7 at% to 7.1 at%, which indicated that a slight increase in exposed Ag nanoparticles on the surface. The surface concentrations of Cu were similar at 2.5 at% for 0.036 wt%, 0.046 wt% and 0.056 wt% Cu loadings, and then decreased to 1.8 at% for 0.066 wt% Cu. An increase in Cu loading surprisingly decreased the surface concentration of Cu, probably because of the aggregation of Cu species [36]. The aggregation was prominent for the Ag-Cu-Cl/BaCO₃ catalyst with a 0.066 wt% Cu loading. The ratio of Ag to Cu increased from 2.7 to 3.9 with an increase in Cu loading from 0.036 wt% to 0.066 wt%. XPS results indicate that a high Cu loading is not beneficial for PO formation because of the aggregation of Cu species.

3.2.4. O₂-TPD results

Fig. 6 shows O₂-TPD profiles of Ag-Cu-Cl/BaCO₃ catalysts with different Cu loadings. Similar to the O₂-TPD profiles of Ag-Cu-Cl/BaCO₃ catalysts with different Cl loadings shown in Fig. 3, the desorption temperatures of molecular oxygen species and atomic oxygen species were 118 and 215 °C, respectively [28]. As shown in Fig. 6, the O₂ uptakes increased gradually with an increase in Cu loading, which explained the increase in propylene conversion shown in Table 3. With an increase in Cu loading over Ag-Cu-Cl/BaCO₃ catalysts, the intensities of the desorption peak of molecular oxygen species at 118 °C were similar and those of atomic oxygen species at 215 °C increased gradually, which shows increased complete combustion

Fig. 6. O₂-TPD profiles of Ag-Cu-Cl/BaCO₃ catalysts with different Cu loadings.

Fig. 7. Stability of Ag-Cu-Cl/BaCO₃ catalyst with 0.036 wt% Cu and 0.060 wt% Cl.

tion of propylene and reduced PO selectivity. This result is consistent with the catalytic performance shown in Table 3. From the XRD and XPS results, an increase in Cu loading does not change the crystallite size of Ag, but aggregates Cu species and exposes Ag nanoparticles with a slight increase in atomic oxygen species adsorbed, which results in a slight decrease in PO selectivity.

3.3. Stability of Ag-Cu-Cl/BaCO₃ catalyst

Fig. 7 shows the stability of Ag-Cu-Cl/BaCO₃ catalyst with 0.036 wt% Cu and 0.060 wt% Cl, which showed the highest initial catalytic performance with a propylene conversion of 1.2% and PO selectivity of 83.7%. The PO selectivity decreased dramatically from 83.7% to 15.2% after a time on stream of 150 min, and then declined gradually to 11.3% after reaction for 500 min; however, propylene conversion remained constant, which indicated that this catalyst deactivated rapidly with increasing time on stream.

Table 5 shows a comparison of XPS and XRD characterizations between fresh and deactivated Ag-Cu-Cl/BaCO₃ catalysts with 0.036 wt% Cu and 0.060 wt% Cl after reaction for 500 min. Ag nanoparticles did not increase in size during catalysis and remained at 31 nm. The surface content of Cu of the deactivated catalyst was 1.0 at%, which was much lower than that of the fresh catalyst (2.5 at%). The surface content of Ag decreased slightly from 6.7 at% to 6.4 at%. The ratio of Ag to Cu increased significantly from 2.7 to 6.4. These results indicate that the catalyst surface is partly covered and coke is deposited after reaction for 500 min, which results in a catalyst deactivation similar to using Ag-CuCl₂/BaCO₃ catalyst [28].

Fig. 8 shows O₂-TPD profiles of fresh and deactivated

Table 5

Comparison between fresh and deactivated Ag-Cu-Cl/BaCO₃ catalysts with 0.036 wt% Cu and 0.060 wt% Cl after reaction for 500 min.

Catalyst	Surface composition ^a			Ag crystallite size (nm) ^b
	Ag (at%)	Cu (at%)	Ag/Cu	
Fresh	6.7	2.5	2.7	31
Deactivated	6.4	1.0	6.4	31

^a Determined from XPS.

^b Determined from XRD patterns by Scherrer's equation.

Fig. 8. O₂-TPD profiles of fresh (1) and deactivated (2) Ag-Cu-Cl/BaCO₃ catalysts with 0.036 wt% Cu and 0.060 wt% Cl after reaction for 500 min.

Ag-Cu-Cl/BaCO₃ catalysts with 0.036 wt% Cu and 0.060 wt% Cl after reaction for 500 min. The desorption peak of atomic oxygen species over the deactivated catalyst shifted to a lower temperature from 215 to 198 °C with a significantly increased intensity, which indicated that more atomic oxygen species became more active in favor of the complete combustion of propylene, causing a lower PO selectivity.

4. Conclusions

Effects of loadings of Cu and Cl on the catalytic performance of Ag-Cu-Cl/BaCO₃ catalysts for the epoxidation of propylene by molecular oxygen were investigated. Ag-Cu-Cl/BaCO₃ catalyst with 0.036 wt% Cu and 0.060 wt% Cl exhibited the highest catalytic performance, in which a PO selectivity of 83.7% and propylene conversion of 1.2% were achieved under the reaction conditions of 20% C₃H₆-10% O₂-70% N₂, 200 °C, 0.1 MPa and 3000 h⁻¹. The appropriate Cl loading is important because Cl occupies the active sites of Ag nanoparticles where atomic oxygen species are adsorbed, which leads to a decrease in propylene conversion, but an increase in PO selectivity. Excessively high Cl loading decreases both propylene conversion and PO

selectivity severely because of Cl poisoning. An increase in Cu loading increases propylene conversion and decreases PO selectivity slightly. The modification of Cu does not affect the crystallite size of Ag, but the aggregation of Cu species with high Cu loadings exposes more surfaces of Ag nanoparticles with a slight increase in atomic oxygen species adsorbed, which lowers PO selectivity.

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Graphical Abstract

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Gas-phase epoxidation of propylene by molecular oxygen over Ag-Cu-Cl/BaCO₃ catalyst: Effects of Cu and Cl loadings

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The appropriate loadings of Cu and Cl of Ag-Cu-Cl/BaCO₃ catalyst are important to the balance between molecular and atomic oxygen species, which benefits the epoxidation of propylene by molecular oxygen.

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分子氧气相环氧化丙烯反应的 Ag-Cu-Cl/BaCO₃ 催化剂: Cu 和 Cl 负载量的影响

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摘要: 环氧丙烷 (PO) 是一种重要的有机化工中间体, 可以用来生产聚氨酯、丙二醇和表面活性剂等化工产品, 具有很高的工业应用价值。然而, 目前 PO 的生产工艺仍然存在着环境污染、副产物、原料经济性等不足之处。考虑到环保、技术、资金等关键性问题, 丙烯气相环氧化工艺是 PO 生产工艺未来的发展方向, 利用分子氧作为氧化剂的丙烯气相环氧化反应是最理想、原子经济性最高的反应, 也是当今催化界最具挑战性的课题之一。研究报道 Ag 基催化剂和 Cu 基催化剂催化丙烯气相环氧化反应可得到较好的催化性能。尽管 Ag 催化剂催化乙烯氧化制环氧乙烷反应已成功实现工业化, 但是 Ag 催化剂催化丙烯环氧化反应得到的 PO 选择性低于 10%, 这是由于丙烯比乙烯多出的甲基中的 α -H 受双键影响变得非常活泼, C-H 键易断裂, 导致丙烯容易发生完全氧化反应生成 CO₂。因此, 研究报道采用不同助剂对 Ag 催化剂进行改性以提高 Ag 基催化剂的催化性能。

我们在前期研究中制备了 Ag-CuCl₂/BaCO₃ 催化剂, 当 CuCl₂ 的负载量为 0.036 wt% Cu 和 0.040 wt% Cl 时, 催化剂具有最优的催化性能, 可以得到 1.3% 的丙烯转化率和 71.2% 的 PO 选择性。适量 CuCl₂ 的改性使得催化剂表面吸附分子氧物种, 同时抑制原子氧物种的形成, 从而提高 PO 选择性。但是 CuCl₂ 作为前驱体有一个不足之处, 就是引入的 Cu 和 Cl 的比例是恒定的, 不可调节。因此, 我们以 Cu(NO₃)₂ 和 NH₄Cl 作为 Cu 和 Cl 的前驱体, 采用还原-沉积-等体积浸渍法制备 Ag-Cu-Cl/BaCO₃ 催化剂, 分别通过调节 Cu 和 Cl 的负载量来进一步提高 Ag-Cu-Cl/BaCO₃ 催化剂的催化性能, 采用粉末 X 射线衍射 (XRD)、X 射线光电子能谱 (XPS) 和氧气程序升温脱附 (O₂-TPD) 等表征手段来研究催化剂中 Cu 和 Cl 的作用。研究发现, Cl 负载量的提高更容易导致大尺寸 Ag 颗粒的形成, 而 Cu 负载量的提高对 Ag 颗粒尺寸影响不大。适当的 Cl 负载量可抑制氧气在催化剂表面解离吸附形成原子氧物种, 从而抑制了丙烯的完全氧化, 提高 PO 选择性。过高的 Cl 负载量会导致催化剂发生 Cl 中毒, 从而降低了催化性能。适当的 Cu 负载量有利于丙烯气相环氧化反应生成 PO, 但当 Cu 负载量过高时容易导致 Cu 物种发生聚集, 更多原子氧物种吸附于 Ag 颗粒表面, 有利于丙烯完全氧化反应生成 CO₂, 降低了 PO 选择性。适当的 Cu 和 Cl 负载量使得催化剂表面吸附的分子氧物种和原子氧物种达到平衡, 有利于丙烯气相环氧化反应。当 Cu 和 Cl 负载量分别为 0.036 wt% 和 0.060 wt% 时, Ag-Cu-Cl/BaCO₃ 催化剂具有最优的催化性能, 在 200 °C, 0.1 MPa, 3000 h⁻¹ 反应条件下可得到 1.2% 的丙烯转化率和 83.7% 的 PO 选择性。

关键词: 丙烯环氧化; 环氧丙烷; 分子氧; Ag 基催化剂; 铜; 氯

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