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Epoxidation of propylene over Ag–CuCl catalysts using air as the oxidant

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Ag–CuCl catalysts were found to be active and selective for the epoxidation of propylene using air as the oxidant. Ag catalyst gives a propylene conversion of 31.6%, with a propylene oxide (PO) selectivity of 0.42% at a reaction temperature of 350 °C after 220 min of reaction. Addition of CuCl significantly improves the selectivity to PO, and suppresses the conversion of propylene. The Ag–CuCl (1/0.6) catalyst gives propylene conversion of about 3% and a PO selectivity of about 30% at a reaction temperature of 350 °C after 500 min of reaction. The activity of the Ag–CuCl catalyst increases with the reaction time and the selectivity to PO is very stable for this catalyst. It is found that AgCl and CuO phases formed during the catalyst preparation are beneficial to the epoxidation of propylene.

KEY WORDS: epoxidation of propylene; silver; CuCl; air.

1. Introduction

Propylene oxide (PO) is one of the most important chemical compounds and is used for the production of many useful chemicals [1]. Commercially, PO is manufactured by either the chlorohydrin or Halcon routes [2]. The former route generates chlorinated by-products. The latter route is capital intensive and linked to the economic fortunes of the co-product. TS-1 catalyst can catalyze the epoxidation of propylene with dilute hydrogen peroxide as the oxidant and usually gives high conversion and selectivity in the liquid phase [3]. However, because of the relatively high cost of hydrogen peroxide and TS-1 catalyst, the process has not been commercialized to date.

Haruta *et al.* [4] have reported that Au/TiO_2 catalysts show a selectivity of greater than 90% for the production of PO using O_2 and H_2 at relatively low temperatures. Oliveira *et al.* [5] have found that titania-supported silver catalysts give quite high selectivity to PO. However, the catalyst is deactivated very rapidly.

The gas-phase epoxidation of ethylene to ethylene oxide uses molecular oxygen, which is one of the greatest discoveries in heterogeneous catalysis. With the requirements of green chemistry, a reaction with high atom efficiency and no pollution is desired. The direct synthesis of PO, by using oxygen or air as oxidant, has long been desired and is one of the most challenging reactions of catalysis [6]. Since epoxidation of ethylene on silver catalysts was successfully commercialized, many researches have attempted the production of PO with silver catalysts, but the activity and selectivity to PO are usually very low [7–12]. For most cases, the selectivity to PO over a silver catalyst is never greater than 15% at a conversion of less than 15% [2]. Some patents claimed that high selectivity to PO over supported metal catalysts could be possible; however, there are very few papers published. Duma and Hönicke reported a selectivity to PO of 40–60% at propylene conversions in the range 6–12% over silica-supported iron oxide catalysts, when nitrous oxide was used as the oxidant [13]. Therefore, the development of a process for the direct gas epoxidation of propylene is of great importance and is still a challenge. The main reason for the low selectivity is that the easy attack of the allylic hydrogen by the nucleophilic oxygen species absorbed on the Ag surface leads to the formation of other oxygen-containing organic compounds or CO_2 [9]. It is anticipated that if a silver catalyst is properly modified and the nature of adsorbed oxygen species might be changed, it might be possible that the silver catalyst may be also effective for the epoxidation of propylene.

In this paper, we report recent results for the epoxidation of propylene on Ag–CuCl catalysts using air as the oxidant. We found that the catalytic performance of the Ag catalysts for epoxidation of propylene can be significantly improved when CuCl is added as the promoter. These catalysts were characterized by XRD and TPR techniques, and the influence of CuCl on the catalytic behavior is also discussed.

2. Experimental

2.1. Preparation of Ag–CuCl catalysts

The silver catalyst was prepared as follows. $AgNO_3$ and the same molar amount of dextrose were dissolved in distilled water at 30 °C, and an aqueous solution

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containing the same concentration of KOH as $AgNO_3$ was added to the mixed solution under stirring. The suspension was aged for 1 h at 75 °C with continuous stirring. The precipitate was then filtered and washed with distilled water several times in order to remove the potassium ions. The powder was heated at 120 °C for 10 h to obtain the Ag catalyst.

Ag–CuCl, Ag–$CuCl_2$, Ag–$FeCl_2$, Ag–$MnCl_2$, and Ag–$AuCl_3$ catalysts with molar ratio (Ag/chloride salt) in the range of 1/0.1–1/1 were prepared by calcining a mixture of chloride salt and the Ag catalyst in air at 350 °C for 3 h.

2.2. *Catalytic performance measurements*

Epoxidation of propylene over 0.2 mL catalyst was carried out in a fixed-bed quartz reactor (10 mm i.d.) at atmospheric pressure. Air was used as the oxidant. The catalytic reaction was operated at a C_3H_6/O_2 (in air) ratio of 1/2 and, except where noted otherwise, at a space velocity of 18 000 h^{-1}.

Reaction products were analyzed using online GC analysis. A GC920 with a FID detector and PEG-20M capillary column (0.32 mm × 30 m) and a GC7890II with a TCD detector were used. The method of carbon balance was used to calculate the conversion of propylene and selectivity to PO. Conversion of propylene = moles of all products containing carbon/moles of propylene fed; selectivity to PO = moles of each product containing carbon/moles of all products containing carbon.

2.3. *X-ray powder diffraction (XRD)*

XRD patterns were collected using a Rigaku Rotaflex (RU-200B) powder diffractometer equipped with a Cu target and a Ni grating monochromator system. The working voltage of the instrument was 40 kV and the current was 50 mA.

2.4. *Temperature-programmed reduction (TPR)*

TPR of the Ag–CuCl catalysts was carried out using 10% H_2 in Ar flow as reducing agent. The amount of H_2 consumed during the reduction was estimated based on the analysis with a thermal conductivity detector. The gas flow rate was 30 ml/min. The weight of sample was 10 mg, and the heating rate of TPR was 20 °C/min. Water produced during TPR was trapped in a molecular sieve (5 Å).

3. Results and discussion

3.1. *Effects of promoters on the silver catalyst*

Table 1 lists the results for the epoxidation of propylene using air as the oxidant with various promoters. From table 1 it can be seen that the addition of chloride salts depresses catalytic activity, while remarkably increases selectivity to PO. The catalytic performance depends on the nature of the chloride salts. The Ag–CuCl (1/0.3) catalyst showed the highest selectivity for PO formation. Considering that the Ag–CuCl catalyst gives the highest selectivity of epoxide, the following experiments are carried out on the Ag–CuCl catalysts.

3.2. *Epoxidation of propylene on Ag–CuCl catalysts*

Table 2 lists the results for the epoxidation of propylene over Ag–CuCl catalysts with different CuCl contents. The Ag catalyst exhibits substantial conversion of propylene, but the selectivity to PO is very low, and becomes even lower with reaction time. Addition of a small amount of CuCl significantly improves the selectivity to PO, while the conversion is dramatically suppressed. This result indicates that the presence of CuCl can suppress deep oxidation of propylene and improve the PO formation. When the Ag/CuCl ratio is in the range 1/0.3–1/0.6, the conversion of propylene is about 2% and the selectivity to PO can be as high as 30% after about 300 min of reaction. However, when the CuCl/Ag ratio is beyond 0.7/1, both the conversion and selectivity are decreased. Meanwhile, aldehyde, acetone and acrolein are also produced besides PO. AgCl and CuCl exhibit a low conversion for the propylene oxidation, but no epoxide product is detected. CuO

Table 1
The results for the epoxidation of propylene on Ag catalyst with various promoters at 350 °C[a]

Catalyst	Conversion (%)	Selectivity (%)			
		PO	Aldehyde	Acetone	Acrolein
Ag	31.6	0.42	–	–	–
Ag–CuCl (1/0.3)	1.64	30.6	–	–	–
Ag–$CuCl_2$ (1/0.25)	1.28	12.8	–	–	4.62
Ag–$FeCl_2$ (1/0.25)	13.1	1.06	0.35	–	–
Ag–$MnCl_2$(1/0.25)	15.9	2.89	0.54	0.66	–
Ag–$AuCl_3$ (1%)[b]	0.71	–	–	–	62.7

[a] Reaction time: 60 min.

[b] Loading of Au.

Table 2
The results for the epoxidation of propylene on Ag–CuCl catalysts with different CuCl contents[a]

Catalyst	Run time (min)	Conversion (%)	Selectivity (%)			
			PO	Aldehyde	Acetone	Acrolein
Ag	57	33.2	0.86	–	–	–
	220	31.6	0.42	–	–	–
Ag–CuCl (1/0.1)	100	1.85	15.7	–	–	–
	302	2.51	13.8	–	–	–
Ag–CuCl (1/0.3)	109	1.64	30.6	–	–	–
	329	2.40	29.7	–	–	–
Ag–CuCl (1/0.4)	90	1.63	30.5	–	–	–
	150	2.33	33.6	–	–	–
Ag–CuCl (1/0.5)	110	1.84	29.9	–	–	–
	185	1.90	30.5	–	–	–
Ag–CuCl (1/0.6)	121	1.60	29.6	–	–	–
	304	2.31	30.0	–	–	–
Ag–CuCl (1/0.7)	90	1.49	27.7	6.84	6.52	6.02
Ag–CuCl (1/0.8)	91	1.52	26.7	15.14	7.41	9.00
	285	2.04	27.9	–	–	–
Ag–CuCl (1/1)	68	1.43	14.4	1.92	3.86	8.49
	169	1.47	13.3	1.62	4.93	5.20
CuCl	60	1.82	–	32.7	42.3	–
AgCl	60	0.25	–	–	–	–
CuO	60	33.6	–	–	–	0.98

[a] Reaction temperature: 350 °C.

shows high activity for the propylene oxidation, giving mostly combustion products.

The conversion of propylene and the selectivity to PO for Ag, Ag–CuCl (1/0.1), Ag–CuCl (1/0.3), Ag–CuCl (1/0.6) and Ag–CuCl (1/1) with reaction time are shown in figures 1 and 2, respectively. Except for Ag catalyst, the conversion of propylene increases with reaction time for all CuCl-containing catalysts. For example, the conversion increases from 1.4% at 26 min to 3.0% at 504 min for Ag–CuCl (1/0.6) catalyst. As shown in figure 2, the selectivity decreases with reaction time for Ag catalyst. Very interestingly, for CuCl-containing catalysts the selectivity does not decline but gradually increases with the reaction time for most cases. For instance, for Ag–CuCl (1/0.3), Ag–CuCl (1/0.6) and Ag–CuCl (1/1) catalysts the selectivity increases for the first 100 min, then remains steady. This implies that there is an induction period for the reaction.

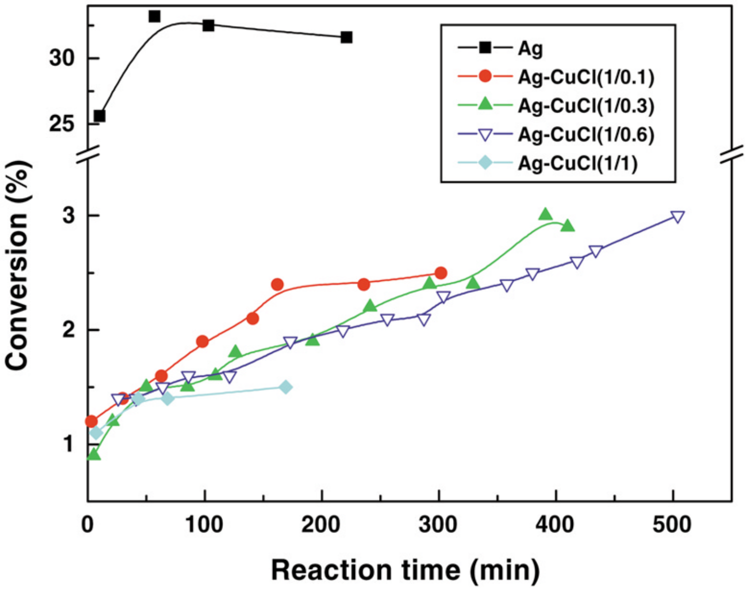

Figure 1. Conversion of propylene with reaction time over Ag, Ag–CuCl (1/0.1), Ag–CuCl (1/0.3), Ag–CuCl (1/0.6) and Ag–CuCl (1/1) catalysts. Reaction temperature: 350 °C.

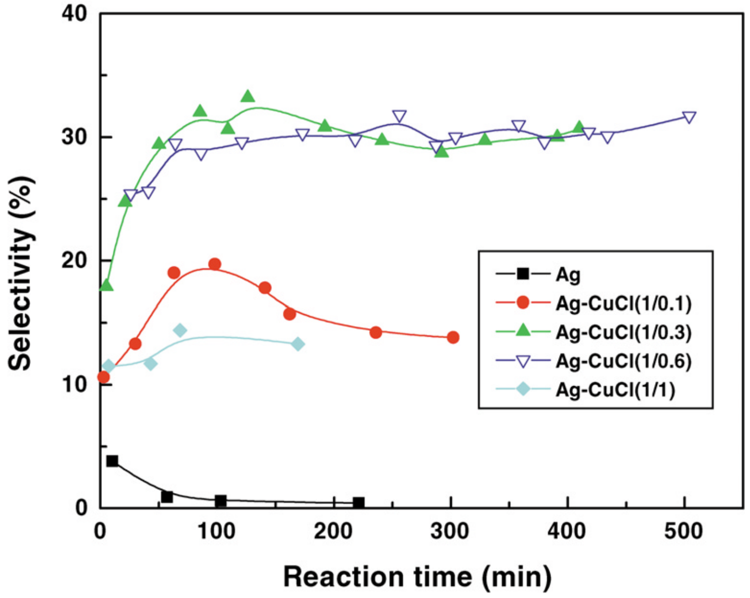

Figure 2. Selectivity to PO with reaction time over Ag, Ag–CuCl (1/0.1), Ag–CuCl (1/0.3), Ag–CuCl (1/0.6) and Ag–CuCl (1/1) catalysts. Reaction temperature: 350 °C.

Table 3 lists the conversion and selectivity of propylene epoxidation on Ag–CuCl (1/0.5) catalyst at different temperatures. With the reaction temperature increasing, the conversion of propylene increases and the selectivity to PO is highest at 350 °C. Table 4 lists the conversion and selectivity of propylene epoxidation on Ag–CuCl (1/0.5) catalyst after different calcination treatments. Both conversion and selectivity decrease as the catalyst is calcined at higher temperatures. The selectivity is similar when the catalyst calcined at 300 and 400 °C, but declines when the catalyst is calcined at greater than 400 °C. Therefore, the optimum reaction and calcination temperatures seem to be around 350 °C.

Table 5 lists the conversion and selectivity of propylene epoxidation on Ag–CuCl (1/0.5) catalyst at different $C_3H_6:O_2$ ratios. When the ratio of propylene to oxygen

Table 3
The conversion and selectivity of propylene epoxidation on Ag–CuCl (1/0.5) catalyst at different reaction temperatures[a]

Reaction temperature (°C)	Conversion (%)	Selectivity (%)			
		PO	Aldehyde	Acetone	Acrolein
330	2.56	25.6	–	–	–
350	3.05	31.7	–	–	–
380	5.08	22.9	–	2.03	2.60

[a] Run time: 500 min.

Table 4
The conversion and selectivity of propylene epoxidation on Ag–CuCl (1/0.5) catalyst calcined at different temperatures[a]

Calcination temperature (°C)	Run time (min)	Conversion (%)	Selectivity (%)			
			PO	Aldehyde	Acetone	Acrolein
350	110	1.84	29.9	–	–	–
	185	1.90	30.5	–	–	–
400	130	1.40	29.1	–	–	–
	180	1.50	29.3	–	–	–
500	110	1.40	12.9	–	–	–
	195	1.53	13.7	–	–	–
650	100	0.51	16.1	–	–	13.8

[a] Reaction temperature: 350 °C.

Table 5
The conversion and selectivity of propylene epoxidation on Ag–CuCl (1/0.5) catalyst at different $C_3H_6:O_2$ ratios [a]

$C_3H_6:O_2$ ratio (mol)	Reaction time (min)	Conversion (%)	Selectivity to PO (%)
4 : 1	145	1.30	28.7
1 : 1	165	1.91	28.0
1 : 2	185	1.90	30.5
1 : 4	150	4.03	17.0

[a] Reaction temperature: 350 °C.

is 1 : 4, the conversion of propylene and the selectivity to PO are 4.0 and 17.0%, respectively. The low selectivity is due to the total oxidation of propylene by excess oxygen. With an increase of propylene content in the feedstock (a larger $C_3H_6:O_2$ ratio), the selectivity increases, while the conversion decreases. When the ratio of propylene to oxygen is 1 : 2, the conversion is 1.90% and the selectivity reaches 30.5% after 185 min of reaction. These results imply that the optimum propylene/oxygen ratio is 1 : 2 for the epoxidation reaction, which is in agreement with the results reported previously [14,15].

3.3. *XRD characterization of Ag–CuCl catalysts*

Table 6
Phase composition of Ag–CuCl catalysts calcined at 350 °C

Catalyst	Phase composition
Ag	Ag
Ag–CuCl (1/0.1)	Ag, AgCl, CuO
Ag–CuCl (1/0.3)	AgCl, Ag, CuO
Ag–CuCl (1/0.4)	AgCl, CuO, Ag
Ag–CuCl (1/0.5)	AgCl, CuO, Ag
Ag–CuCl (1/0.6)	AgCl, CuO, Ag
Ag–CuCl (1/0.7)	AgCl, CuCl, Cu_2O, CuO, Ag
Ag–CuCl (1/0.8)	AgCl, CuCl, Cu_2O, CuO, Ag
Ag–CuCl (1/1)	AgCl, CuCl, Cu_2O, CuO, Ag

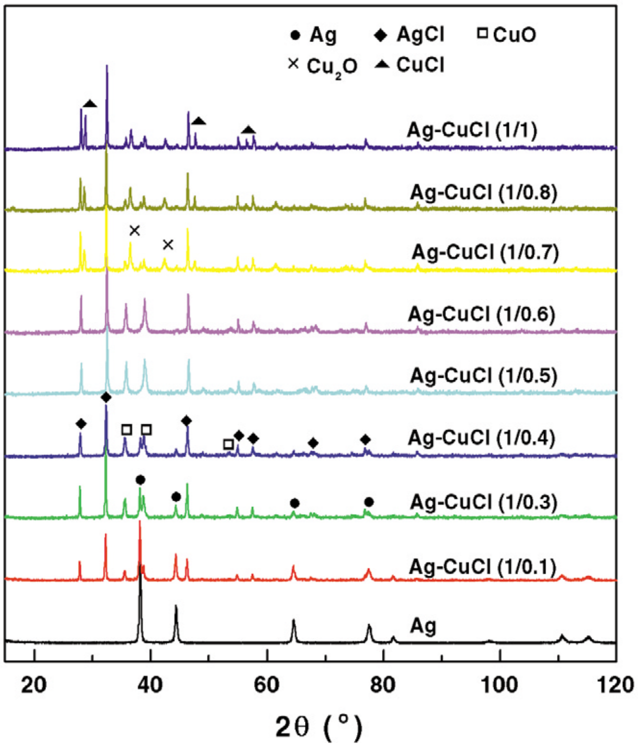

Figure 3. XRD patterns of Ag–CuCl catalysts calcined at 350 °C.

Figure 3 shows the XRD patterns of Ag–CuCl catalysts. The crystalline phases were identified by comparing with ICDD files (Ag: 04-783; AgCl: 31-1238; CuO: 45-0937; Cu_2O: 34-1354; and CuCl: 01-0793). Table 6 lists the phase composition of Ag–CuCl catalysts on the basis of the XRD results. When the Ag/CuCl ratio is from 1/0.1 to 1/0.6, the mixture phases AgCl, CuO and Ag are observed. When the Ag/CuCl ratio is 1/0.7, 1/0.8 and 1/1, the mixture phases AgCl, CuO, Ag, Cu_2O and CuCl are observed. When the Ag/CuCl ratio is from 1/0.3 to 1/1, the intensity of the diffraction peak of AgCl remains stable. The intensity of the diffraction peaks of CuO increases with increasing CuCl content, and reaches a maximum at an Ag/CuCl ratio of 1/0.5, while the intensity of the diffraction peak of Ag decreases and reaches a minimum at an Ag/CuCl ratio of 1/0.5. Comparing the reaction results (table 1) and phase composition of the catalysts (table 6), it is found that when the three phases CuO, Ag and CuCl coexist, the catalyst gives higher selectivity of epoxide. And only PO is detected as a reaction product besides CO_2. When the five phases (Ag, CuCl, Cu_2O, CuO and AgCl) coexist, the selectivity to PO decreases and aldehyde, acetone and acrolein are also detected. This indicates that the existence of Cu_2O and CuCl phases are unfavorable for the production of PO, which makes selectivity to PO decrease. Therefore, the simultaneous presence of Ag and AgCl and CuO phases is responsible for the epoxidation of propylene.

In the case of epoxidation of ethylene, the addition of chlorine in the feedstock is helpful for increasing the epoxidation selectivity. This is explained in terms of modification of the electronic nature of adsorbed oxygen species on the Ag surface [16], and even AgCl was found [17,18]. The existence of AgCl may affect the electronic density of the silver atoms nearby, thus making the adsorbed oxygen species with proper electron density, which is favorable for the epoxidation. For our catalyst, Ag–CuCl, it seems that the existence of CuCl may modify the electronic properties of the silver surface, thus altering the activity and selectivity of the catalyst. However, excess CuCl may cover the active sites. This may be a reason why the Ag–CuCl catalysts (1/0.7–1/1) show lower activity and selectivity.

3.4. *Reduction properties of Ag–CuCl catalysts*

Figure 4 shows the TPR profiles of the Ag–CuCl catalysts. There are two reduction peaks (α and β) for

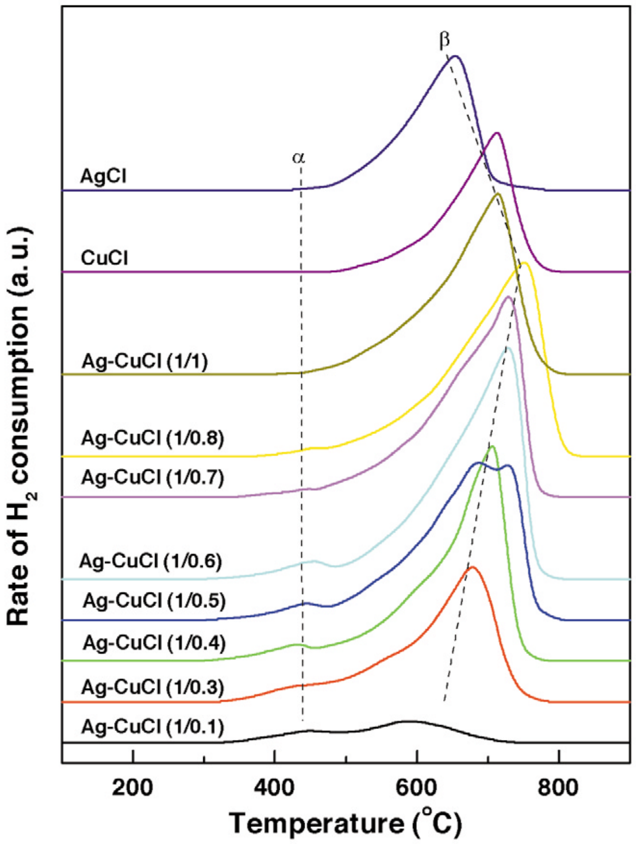

Figure 4. TPR profiles of Ag–CuCl catalysts calcined at 350 °C.

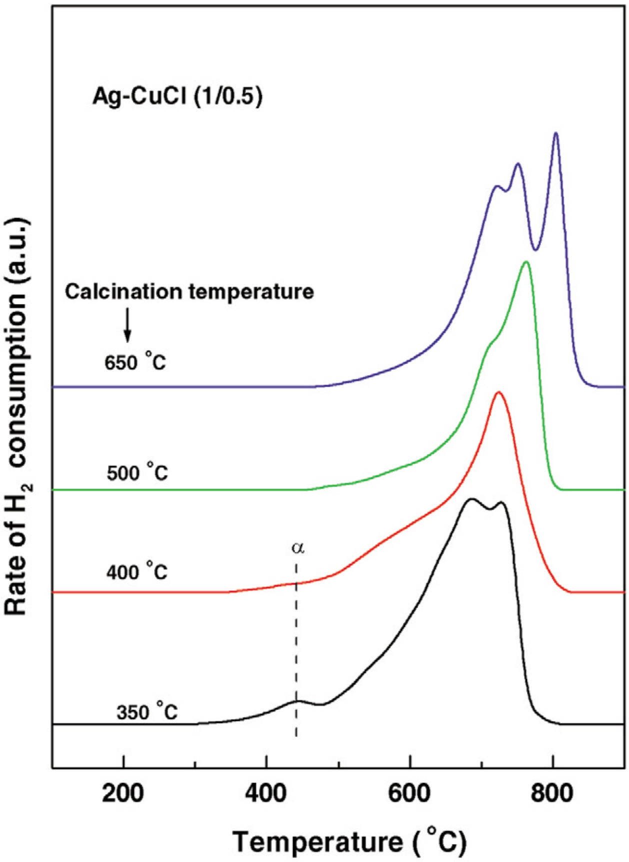

Figure 5. TPR profiles of Ag–CuCl (1/0.5) catalyst calcined at different temperatures.

Ag–CuCl (1/0.1–1/0.8) samples, while there is only one peak (β) for AgCl, CuCl and Ag–CuCl (1/1) samples. Ag does not show an evident reduction peak in the temperature range 100–900 °C. It is found that the β peak consists of two peaks which overlap each other. The position of the high-temperature peak (β peak) shifts to higher temperatures with increasing CuCl content except for the Ag–CuCl (1/1) samples, while that of the low-temperature peak remains stable. The intensity of the α peak increases with increasing CuCl content and reaches a maximum at an Ag/CuCl ratio of 1/0.5, then decreases with further increase of CuCl content. For Ag–CuCl (1/1) samples, the α peak disappears. Figure 5 shows the TPR profiles of Ag–CuCl (1/0.5) catalyst calcined at different temperatures. As the calcination temperature increases, the TPR peaks shift to high temperature, and become complex. When the catalyst is calcined at 500 and 650 °C, the low-temperature (~450 °C) TPR peak disappears. The XRD result shows that the phase composition of all catalysts calcined at different temperatures is Ag, CuO and AgCl. From the above results, we believe that the α peak (~450 °C) may correspond to adsorbed oxygen species of the catalyst surface. The β peak corresponds to reduction of CuO, CuCl, AgCl and Cu_2O. Comparing with the result of reaction (table 2), it is found that the selectivity to PO is consistent with the intensity of adsorbed oxygen species of the catalyst surface (figure 4). So we suggest that adsorbed oxygen species of the catalyst surface may be the active site for the epoxidation of propylene.

4. Conclusions

A series of Ag–CuCl catalysts (Ag/CuCl = 1/0.1–1/1) were prepared by calcining a mixture of Ag and CuCl. It was found that Ag–CuCl (1/0.3–1/0.6) catalysts show quite high catalytic activity and selectivity for epoxidation of propylene using air as the oxidant. Under the reaction conditions of 350 °C, space velocity $1.8 \times 10^4\ h^{-1}$ and $C_3H_6 : O_2 = 0.5$, selectivities to PO of about 30% at propylene conversion of about 3% were obtained. It was found that AgCl and CuO formed during the catalyst preparation may be effective in the epoxidation of propylene. There were two reduction peaks (α and β) for Ag–CuCl (1/0.1–1/0.8) samples. It was found that the selectivity to PO is consistent with the intensity of adsorbed oxygen species of the catalyst surface. So we suggest that adsorbed oxygen species of the catalyst surface may be the active site for the epoxidation of propylene.

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