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Journal of Catalysis 241 (2006) 225–228

JOURNAL OF CATALYSIS

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Research Note

Copper-catalyzed propylene epoxidation by molecular oxygen: Superior catalytic performances of halogen-free K^+-modified CuO_x/SBA-15

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Received 23 December 2005; revised 28 March 2006; accepted 6 April 2006

Abstract

A halogen-free K^+-modified CuO_x/SBA-15 exhibits significantly better catalytic performance than other Cu-based catalysts reported so far for the epoxidation of propylene by molecular oxygen. Moderate selectivity (ca. 15–50%) to propylene oxide (PO) can be sustained as propylene conversion increases from ca. 1 to 12%, and a PO formation rate of 2.1 $\text{mmol}\,g^{-1}\,h^{-1}$ has been obtained over this catalyst. The current catalyst does not require prereduction, and the PO selectivity can be kept at a high O_2 partial pressure or a highly O_2-rich atmosphere.

Keywords: Propylene; Epoxidation; Molecular oxygen; Copper catalyst; Potassium modifier

1. Introduction

The gas-phase epoxidation of propylene to propylene oxide (PO) remains one of the most challenging chemical reactions, even though the epoxidation of ethylene by O_2 over the Ag/α-Al_2O_3-based catalyst has been commercialized for several decades. The main difficulty arises from the higher reactivity of the allylic C–H bonds in propylene. Although a few studies have reported other catalysts, including Ti-containing molecular sieves [1,2], most research efforts have focused on the epoxidation of propylene by O_2 over Ag-based catalysts, and it is now clear that with Ag-based catalysts, heavy modifications, particularly with chlorides and/or in the presence of gas-phase modifiers, such as organic chlorides, are generally required to obtain moderate PO selectivity [3–5]. Without the presence of halide additives, PO selectivity is very low over the Ag-based catalysts [4,5]. On the other hand, through a series of surface chemistry studies on Ag and Cu single-crystal surfaces under ultrahigh vacuum conditions, Lambert and coworkers [6–8] have shown convincingly that Cu surfaces are more selective than Ag surfaces for the epoxidation of higher alkenes, such as styrene and methylstyrene. It is reported that when allylic hydrogen atoms exist in the alkene molecules, epoxidation can still occur on Cu(111) surfaces, whereas the combustion of alkenes occurs mainly on Ag surfaces [6]. Thus, Cu-based catalysts may be promising for propylene epoxidation by O_2. However, it should be noted that there also exists a study pointing out that Cu may not function as an epoxidation *catalyst* requiring turnover numbers larger than 1, because the metallic Cu [i.e., Cu(0)], which is considered the active site for epoxidation, may be readily oxidized to the copper oxide under the reaction conditions [9].

Actually, only very few studies to date have reported the epoxidation of propylene by O_2 with Cu-based materials as true catalysts. Li and coworkers reported a PO selectivity of 43% at 0.19% C_3H_6 conversion over a NaCl-modified $VCe_{1-x}Cu_x$ oxide catalyst, with a maximum PO formation rate over this catalyst of 0.165 $\text{mmol}\,g^{-1}\,h^{-1}$ [10]. NaCl-modified Cu/SiO_2 showed a PO selectivity of 44% at 0.16% C_3H_6 conversion and a maximum PO formation rate of 0.187 $\text{mmol}\,g^{-1}\,h^{-1}$ (turnover frequency [TOF], ca. 0.12 h^{-1}) [11]. Lambert and coworkers [12] recently showed that Cu/SiO_2 prepared by a microemulsion technique without alkali chloride additives could also catalyze the PO formation; they obtained a PO selectivity of 53% at 0.25% C_3H_6 conversion and a PO formation rate of 0.014 $\text{mmol}\,g^{-1}\,h^{-1}$ (TOF, ca. 0.09 h^{-1}) under their reaction conditions. Over these catalysts, the increase in C_3H_6

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doi:10.1016/j.jcat.2006.04.028

conversion to >1% would cause a remarkable decrease in PO selectivity to <5%. Thus, although these studies are of interest, the reported catalysts exhibit high PO selectivity (40–50%) only at very low C_3H_6 conversion (<0.3%).

Here we report a halogen-free K^+-modified CuO_x/SBA-15 catalyst, which can catalyze the epoxidation of propylene by O_2 much more efficiently. Compared with the Cu-based catalysts reported to date, this catalyst exhibits very unique behavior, allowing reasonably high PO selectivity (15–50%) at significantly higher C_3H_6 conversion (1.0–12%).

2. Experimental

SBA-15, a typical mesoporous silica with a surface area of 760 $m^2\,g^{-1}$ and pore diameter of 5.8 nm, was synthesized with a procedure described elsewhere using Pluronic P123 triblock copolymer (EO_{20}–PO_{70}–EO_{20}) as the surfactant template and tetraethyl orthosilicate (TEOS) as the silicon source [13,14]. Copper was introduced into the SBA-15 through an impregnation method. After undergoing calcination at 823 K, powdery SBA-15 was immersed into an aqueous solution of copper nitrate, and the slurry was dried at 333 K for ca. 4 h under continuous stirring. After further drying at 373 K for 12 h, the powdery sample was calcined at 823 K in air for 6 h to obtain the CuO_x/SBA-15. The K^+-modified CuO_x/SBA-15 was prepared by impregnating the CuO_x/SBA-15 with an aqueous solution of potassium acetate, followed by drying and calcination at 823 K in air. The catalysts were characterized by powder X-ray diffraction (XRD), diffuse reflectance ultraviolet–visible (UV–vis) spectroscopy, and H_2 temperature-programmed reduction (H_2-TPR) measurements. Catalytic reactions were carried out using a fixed-bed reactor operated at atmospheric pressure. Note that the catalyst before reaction was pretreated in the quartz reactor with a gas flow containing He and O_2 at 823 K and was not subjected to any reductive treatments. The products along with the unreacted reactants were analyzed using two on-line gas chromatographs.

3. Results and discussion

As confirmed by XRD, the ordered hexagonal mesoporous structure of SBA-15 was sustained after the incorporation of Cu and K. No crystalline copper oxide phases were observed for the samples with Cu content <10 wt%. Diffuse reflectance UV–vis spectroscopic measurements for the 1 wt% CuO_x/SBA-15 with and without K^+ modification showed one strong absorption band at ca. 235 nm along with a weak shoulder at ca. 330 nm, which could be assigned to the charge-transfer transitions of the ligand O^{2-} to metal center Cu^{2+} for the isolated Cu(II) ions and small Cu(II)O clusters, respectively [15]. The absorption band near 800 cm^{-1} assignable to the d–d transition of CuO particles was very weak. As shown in Fig. 1, the H_2-TPR profile for the 1 wt% CuO_x/SBA-15 had two reduction peaks, at 503 and 829 K, compared with the single peak at 569 K for crystalline CuO; these two reduction peaks likely can be attributed to the reduction of the Cu(II)O clusters and the isolated Cu(II) ions, respectively. The modification with K^+ shifted both peaks to higher temperatures, indicating that the presence of K^+ stabilized the high oxidation state of copper. These characterizations suggest that copper species in the catalyst with a low Cu content (e.g., 1 wt%) are located mainly in the mesoporous channels of SBA-15 and likely exist as small Cu(II)O clusters and isolated Cu(II) ions.

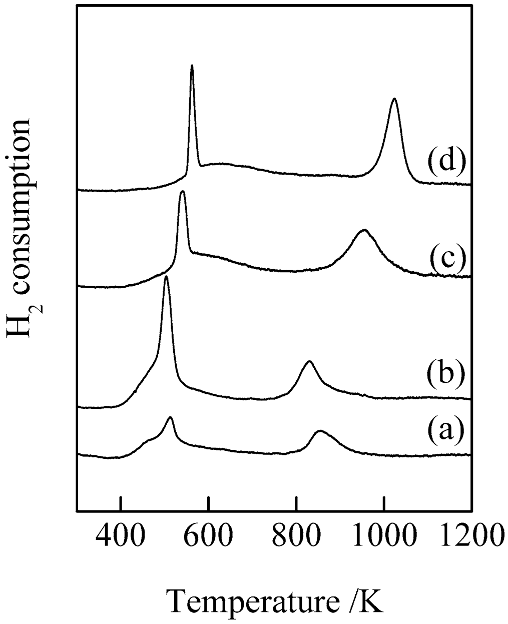

Fig. 1. H_2-TPR profiles. (a) 0.5 wt% CuO_x/SBA-15, (b) 1 wt% CuO_x/SBA-15, (c) K^+–1 wt% CuO_x/SBA-15 (K/Cu = 0.7), (d) K^+–1 wt% CuO_x/SBA-15 (K/Cu = 2.0).

Fig. 2 compares the temperature dependence of catalytic performance for the oxidation of C_3H_6 by O_2 over the 1 wt% CuO_x/SBA-15 and the K^+–1 wt% CuO_x/SBA-15 (K/Cu = 0.7) catalysts. Without K^+ modification, C_3H_6 conversion was higher but PO selectivity was lower (e.g., only 6.9% at a C_3H_6 conversion of 0.77% at 498 K), and the main partial oxidation product was acrolein. Although a part of acrolein may come from PO, we have observed that decreasing contact time increases the selectivity of both acrolein and PO, indicating that acrolein and PO are likely formed in parallel. Thus we believe that acrolein should result mainly from the allylic oxidation of C_3H_6. It is highly significant that after the modification with K^+, PO, not acrolein, becomes the main partial oxidation product. PO selectivity over K^+–CuO_x/SBA-15 was 59% at 498 K and 46% at 523 K, and C_3H_6 conversion was 0.40% at 498 K and 0.95% at 523 K. The apparent activation energy changed from 92 to 72 $kJ\,mol^{-1}$ after the K^+ modification. Thus, it is reasonable to consider that the modification with K^+ shifted the main reaction route from allylic oxidation to epoxidation. More interestingly, different from the observation that over other reported Cu-based catalysts, the increase in C_3H_6 conversion to >1% caused a big drop in PO formation [10–12], moderate PO selectivities (ca. 15–50%) were sustained over our modified catalyst as C_3H_6 conversion was increased from ca. 1 to 12% by increasing the reaction temperature from 523 to 623 K. A PO yield of 1.8% was achieved at 623 K.

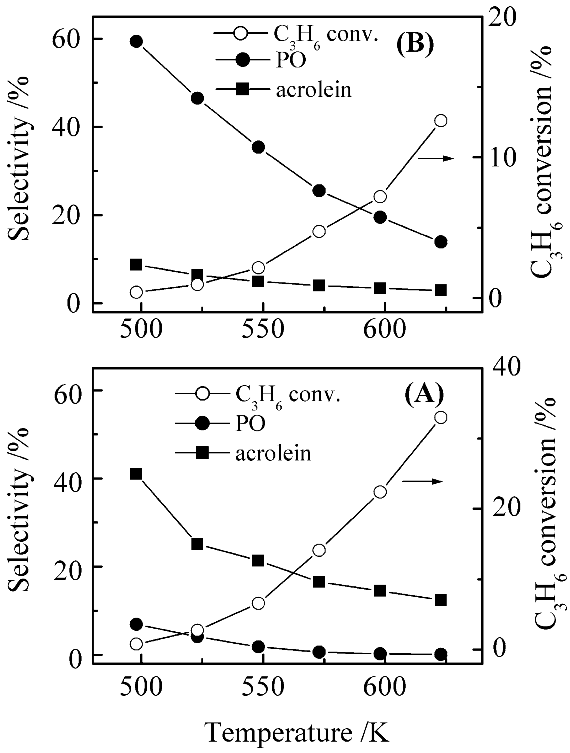

Fig. 2. Temperature dependences of catalytic behaviors of the 1 wt% CuO_x/SBA-15 (A) and the K^+–1 wt% CuO_x/SBA-15 (K/Cu = 0.7) (B) for the oxidation of C_3H_6 by O_2. The other products were mainly CO and CO_2. Catalyst, 0.2 g; $P(C_3H_6)$, 2.5 kPa; $P(O_2)$, 98.8 kPa; total flow rate, 60 mL min^{-1}.

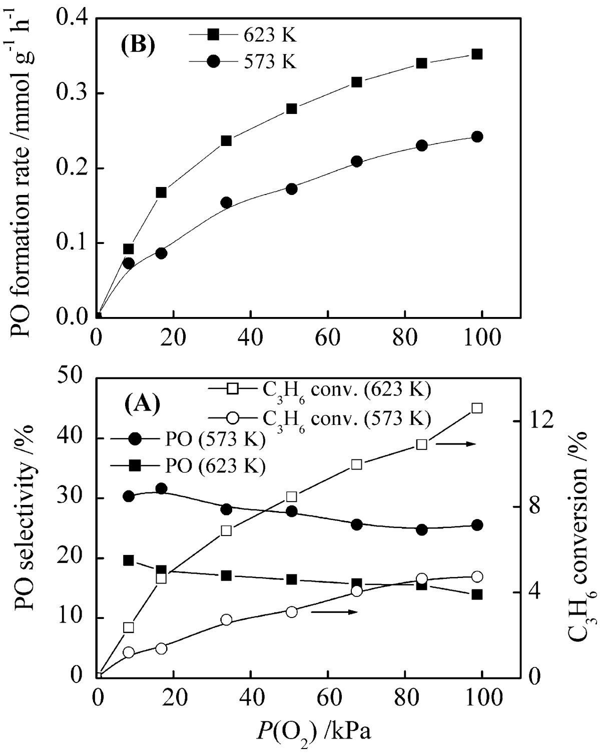

Fig. 3. Effect of O_2 partial pressure on catalytic behaviors of the K^+–1 wt% CuO_x/SBA-15 (K/Cu = 0.7) for the oxidation of C_3H_6 by O_2. (A) PO selectivities and C_3H_6 conversions at 573 and 623 K. (B) PO formation rates at 573 and 623 K. Catalyst, 0.2 g; $P(C_3H_6)$, 2.5 kPa; total flow rate, 60 mL min^{-1}.

The prereduction of a Cu-based catalyst before reaction is always carried out in the literature, because it is generally accepted that metallic Cu species are needed for the epoxidation of alkenes by O_2 [10–12,16]. In our case, the catalyst was pretreated in O_2-containing flow, and thus the Cu was in an oxidized state before reaction. Moreover, the catalytic reactions shown in Fig. 2 were carried out in a highly O_2-rich atmosphere [$P(O_2) = 98.8$ kPa]. This leads us to speculate that the highly dispersed copper species in oxidized states modified by K^+ may be responsible for the C_3H_6 epoxidation by O_2 over our catalyst. To gain further insight into this point, we have investigated the effect of O_2 partial pressure on catalytic behavior over the K^+–1 wt% CuO_x/SBA-15 (K/Cu = 0.7). Figs. 3 and 4 summarize the catalytic results obtained at lower and higher partial pressures of C_3H_6 ($P(C_3H_6) = 2.5$ and 50.7 kPa), respectively. With increasing $P(O_2)$, C_3H_6 conversion increased significantly, and became slightly lower only at higher $P(O_2)$ (42.4 and 50.7 kPa) in the case of high $P(C_3H_6)$ (50.7 kPa) and high temperature (623 K) (Fig. 4). It is of interest that PO selectivity does not undergo a significant decrease with increasing $P(O_2)$ under both the higher $P(C_3H_6)$, where O_2 is deficient, and the lower $P(C_3H_6)$, where O_2 is excessive. Thus, the rate of PO formation increased remarkably with $P(O_2)$ in both cases, and could reach 2.1 mmol g^{-1} h^{-1} (the TOF for PO formation based on Cu was 17.5 h^{-1}), which was one to two orders higher than the Cu-based catalysts such as the NaCl-modified $VCe_{1-x}Cu_xO_y$ [10], NaCl–Cu/SiO_2 [11], and Cu/SiO_2 [12] reported to date. Moreover, our observation that the PO selectivity

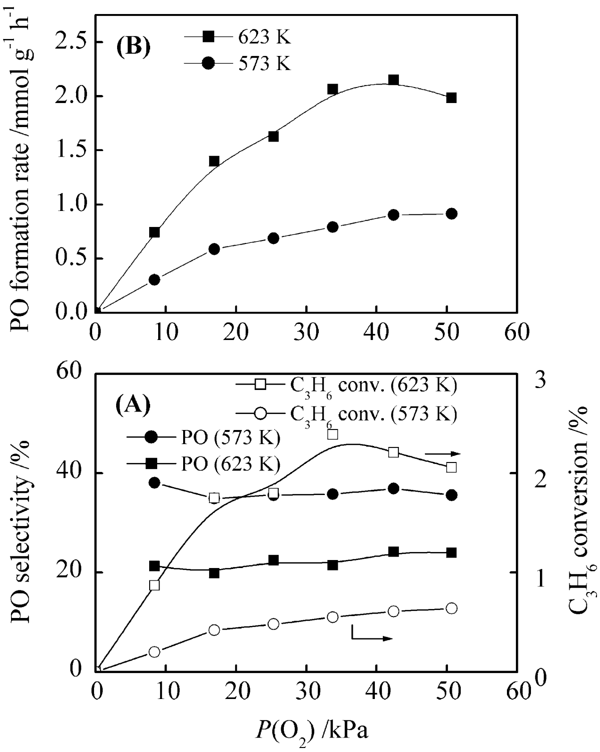

Fig. 4. Effect of O_2 partial pressure on catalytic behaviors of the K^+–1 wt% CuO_x/SBA-15 (K/Cu = 0.7) for the oxidation of C_3H_6 by O_2. (A) PO selectivities and C_3H_6 conversions at 573 and 623 K. (B) PO formation rates at 573 and 623 K. Catalyst, 0.2 g; $P(C_3H_6)$, 50.7 kPa; total flow rate, 60 mL min^{-1}.

could be maintained as the $P(O_2)$ changed within a wide range differed greatly from that for the prereduced NaCl-modified Cu/SiO_2 catalyst, where an increase in the O_2/C_3H_6 ratio above 0.1 caused a big drop in PO selectivity, and the higher O_2 concentration was speculated to possibly lead to the oxidation of Cu(0) into Cu(I) or Cu(II), which could not catalyze the epoxidation of C_3H_6. Therefore, the K^+-modified CuO_x/SBA-15 behaves very uniquely for the epoxidation of C_3H_6 by O_2. These unique behaviors imply that the current catalyst may represent a novel-type Cu-based epoxidation catalyst whose active site is not the metallic Cu species.

We have clarified that the peculiar result that moderate PO selectivity can be maintained in a highly O_2-rich atmosphere over the K^+-modified CuO_x/SBA-15 stems from the presence of K^+ modification. Without K^+ modification, although a PO selectivity of 9% could be obtained under C_3H_6 and O_2 pressures of 50.7 kPa at 573 K over the 1 wt% CuO_x/SBA-15, it dropped significantly to 0.9% as $P(C_3H_6)$ was decreased to 2.5 kPa. In contrast, PO selectivity decreased from 35 to 29% if the same change in the $P(C_3H_6)$ occurred under the same circumstance over the K^+–1 wt% CuO_x/SBA-15 ($K/Cu = 0.7$).

Fig. 2 clearly shows that acrolein is the main partial oxidation product over the CuO_x/SBA-15 without K^+ modification, whereas PO is the main partial oxidation product over the K^+-modified catalysts. The H_2-TPR results shown in Fig. 1 suggest that the reactivity of the lattice oxygen associated with the Cu(II) oxide clusters or the Cu(II) ions in SBA-15 has been inhibited by the interaction of K^+ with the copper species. We speculate that this may correspond to the inhibition of acrolein formation, because it is generally accepted that the lattice oxygen is responsible for allylic oxidation. Over the K^+-modified CuO_x/SBA-15 catalyst, our results suggest that it is not the Cu(0), but rather the copper in an oxidized state that accounts for the C_3H_6 epoxidation by O_2. Although both Cu(I) and Cu(II) species are possible active sites, it seems more likely that the Cu(I), which may be formed on the surface of the catalyst during the reaction, plays a crucial role in C_3H_6 epoxidation, because an electrophilic-type oxygen species generated from O_2 is required for epoxidation, and the Cu(I) may activate O_2 to such an oxygen species.

Regarding the nature of the accelerating effect of K^+ on the epoxidation, several possible mechanisms may exist. One possibility is that K^+ may favor the formation of Cu(I) species on the surface or stabilize this species during the reaction. K^+ also may stabilize the electrophilic-type active oxygen species, such as peroxide or superoxide, responsible for the epoxidation on the catalyst surface. Further investigations into the nature of the active sites and the active oxygen species are underway.

4. Conclusion

We have found an interesting halogen-free K^+-modified CuO_x/SBA-15 catalyst that exhibits significantly better catalytic performance for PO formation than the Cu-based catalysts reported to date for the epoxidation of propylene by O_2. The rate and the TOF for PO formation can reach 2.1 mmol g^{-1} h^{-1} and 17.5 h^{-1}, respectively, both significantly higher than values for other known Cu-based catalysts. It is also of interest that the current catalyst does not require prereduction and that the high PO selectivity can be sustained at a high O_2 partial pressure or a highly O_2-rich atmosphere. The copper species in oxidized states, especially Cu(I) on the surface, modified by K^+ may be responsible for the epoxidation.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (grants 20433030, 20273054, 20373055 and 20021002), the National Basic Research Program of China (grants 2003CB615803 and 2005CB221408), and the Program for New Century Excellent Talents in University of China (grant NCET-04-0602).

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