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Journal of Catalysis 236 (2005) 401–404

JOURNAL OF CATALYSIS

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Research Note

Copper as a selective catalyst for the epoxidation of propene

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Received 24 May 2005; revised 14 October 2005; accepted 14 October 2005

Available online 10 November 2005

Abstract

Cu/silica catalysts show promise for the epoxidation of propene by dioxygen at atmospheric pressure. Their performance is comparable to that reported by Haruta et al. in their first paper on propene epoxidation catalysis by nanoscopic Au particles supported on TiO_2. Our materials deliver stable performance in the presence of oxygen, without the need for H_2 addition, with selectivity toward propene epoxide decreasing with increasing temperature. X-Ray photoelectron spectroscopy, Auger spectroscopy, and high-resolution electron microscopy indicate that the active phase is a highly dispersed form of Cu^0.

Keywords: Propene oxide; Cu; Cu/silica; Selective oxidation; Epoxidation

1. Introduction

Because of their versatility as intermediates, epoxides are of great value in both synthetic organic chemistry and chemical technology. The heterogeneous epoxidation of alkenes other than ethene is very difficult, however. This difficulty is often ascribed to the presence of labile allylic H atoms, whose facile abstraction results in combustion rather than selective oxidation. Propene is the protypical case; indeed, propene oxide (PO) is a more valuable intermediate than ethene oxide, the large-scale production of which is carried out using dispersed Ag as a catalyst. Silver is actually very inefficient in propene epoxidation, delivering selectivities on the order of ∼5% [1]. As a consequence, commercial production of PO proceeds by one of two homogeneous processes, both involving two stages [2,3] and leading to undesirable by-products. Clearly, a one-step, environmentally benign, heterogeneous route based on the use of dioxygen would be far preferable.

In 1998, Haruta and co-workers [4] announced the discovery of a titania-supported gold catalyst that gave propene epoxidation selectivities close to 100%, although at very low reactant conversion (1.1%). This report generated great interest and stimulated much work with both practical dispersed catalysts and single-crystal model catalysts [5]. Besides the low reactant conversions obtained, another limitation of Au/TiO_2 epoxidation catalysts is the need to co-feed a large amount of hydrogen, most of which is wastefully converted to H_2O. Incremental advances in performance have been achieved over the past decade. For example, Yap et al. [6] recently reported 60–85% selectivity at 6.5–2.5% propene conversion for Au on TS-1 with $H_2{:}O_2 \sim 1{:}1$. The nature of the active site(s) involved and the mechanism of Au/TiO_2-catalysed propene epoxidation remain controversial, there being no consensus view.

The oxidation chemistry of simple alkenes such as ethene and propene cannot be studied under vacuum conditions because of their low adsorption enthalpies—the molecules desorb before they can react. However, under such conditions, styrene and *trans*-methylstyrene can be used as mimics for ethene and propene, respectively. Our UHV studies with single crystal surfaces showed that metallic copper is intrinsically much more selective than silver in inducing the epoxidation of styrene [7,8]. Similar experiments carried out with *trans*-methylstyrene [9,10] surfaces showed that even when the alkene contains labile allylic hydrogen atoms, copper induces epoxidation, whereas silver gives rise to combustion only. Prompted by our work [7,8], Lu et al. [11] investigated propene

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doi:10.1016/j.jcat.2005.10.019

epoxidation at atmospheric pressure using a NaCl-modified $VCe_{1-x}Cu_x$ ($x = 0$–1.0) catalyst. Their best catalyst gave PO selectivities of ∼43% at 0.19% propene conversion; adding H_2 reportedly increased the selectivity to ∼70%, although conversion was not specified. Without the incorporation of a large amount of NaCl, all of their catalysts were unselective; even with added NaCl, their activity decreased substantially in the absence of co-feed H_2. The authors concluded that “coexistence of V and Ce in the catalyst plays an important role,” although the oxidation state of the PO-selective Cu component remained unclear.

Here we report on the epoxidation of propene with apparently simple Cu/silica catalysts operated at atmospheric pressure. These materials do not require promotion by alkali halide, are stable under reaction conditions (despite a substantial partial pressure of oxygen), and deliver useful selectivity toward PO formation without the need for a hydrogen co-feed. Two different catalyst preparation procedures with different Cu loadings were used to examine the possible effects of catalyst morphology.

2. Methods

Catalyst A was a **1 wt%** Cu/SiO_2 catalyst prepared by a microemulsion technique [12] that was expected to yield ∼5 nm copper particles of essentially uniform dispersion. It was prepared in water/oil microemulsions with *n*-heptane as the continuous oil domain. A solution of the copper precursor [0.1 M $Cu(NO_3)_2$] was added to a mixture of the oil and 16.54 wt% of surfactant, polyethyleneglycol-dodecylether (Brij 30, Fluka). The copper complexes were reduced by adding hydrazine ($Cu:N_2H_4$, 1:10) to the microemulsion. The SiO_2 support was added to the particle suspension under vigorous stirring, after which acetone was added slowly to break the microemulsion and allow the particles to deposit on the support material. The mixture was then stirred, filtered, and washed with acetone and water to remove the surfactant. After these Cu nanoparticles were deposited onto the silica support (Sigma–Aldrich; surface area 390 $m^2\,g^{-1}$), the resulting catalyst was dried in air at 60 °C for 12 h and reduced at 200 °C in 5% H_2/He for 1 h.

Catalyst B was a **5 wt%** Cu/SiO_2 catalyst prepared by incipient wetness impregnation (a procedure expected to yield large copper particles) of the same silica support with aqueous $Cu(NO_3)_2$ followed by drying in air (10 h, 120 °C), air calcination (4 h, 300 °C), and reduction in H_2 (2 h, 300 °C). Both samples were crushed/sieved to yield grain sizes in the range of 250–600 µm and were reduced in H_2 (space velocity $= 2.4 \times 10^4\ h^{-1}$) at 300 °C before testing. In the first catalytic test with catalyst A, conversion increased with time on stream until a steady state was reached after ∼2 h. In subsequent tests with the same sample, steady state was reached immediately, indicating that any residual surfactant had been burned off. Catalyst B reached steady state very quickly. All of the results reported here refer to the steady state.

The microreactor used for catalyst testing was a single-pass, fixed-bed reactor operating at atmospheric pressure with a space velocity of $2.4 \times 10^4\ h^{-1}$. Reactant and product analyses were performed using a gas chromatograph (Shimadzu 14B with Porapak and molecular sieve 5 Å columns) with thermal conductivity and flame ionisation detectors and a Siemens Ultramat NDIR CO/CO_2 detector. X-Ray photoelectron spectroscopy (XPS) measurements were performed in a VG ADES 400 UHV spectrometer using Mg-K_α radiation.

3. Results

Fig. 1 illustrates the performance of catalyst A as a function of temperature. The principal products were PO, acrolein ($CH_2{=}CHCHO$), and combustion products ($CO_2 + CO$, denoted by CO_x, and H_2O). Selectivity toward PO was greatest (53%) at 225 °C (productivity, 0.014 $mmol\,h^{-1}\,g_{cat}^{-1}$; propene conversion, 0.25%) and declined rapidly to a negligible value at ∼275 °C (propene conversion, 1.26%). Approximately constant but extremely small amounts of acetaldehyde and acetone were also observed over the whole temperature range. The results depicted in Fig. 1 were reversible with temperature, and at any given temperature the activity was constant—no changes were observable over an interval of several hours. Adding H_2 to the reactant feed (up to 5%) had no effect on the selectivity toward the various products; clearly, the reaction mechanism that characterises Cu/SiO_2 is very different from that operating on Au/TiO_2.

In the interval 225–275 °C, the decrease in PO selectivity correlates with initial increases in selectivity to acrolein, suggesting that the former is the precursor of the latter. In the interval 275–325 °C, PO production is effectively quenched, acrolein production continues to rise, and CO_x production actually falls. This suggests acrolein is more resistant to combustion than PO. Eventually, at 325 °C and above, CO_x production rises again as acrolein combustion becomes more important. Rodriguez et al. [13] carried out in situ XRD studies of the oxidation state of copper as a function of temperature under conditions of oxygen partial pressure that were very close to those used here. They found that Cu^0 was the predominant species at temperatures below ∼ 250 °C, followed by Cu_2O at interme-

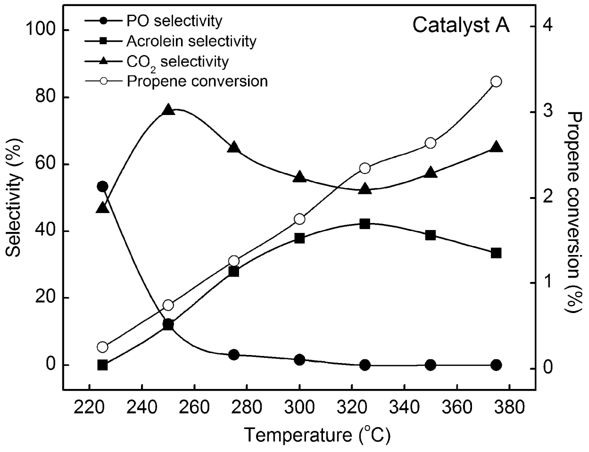

Fig. 1. Effect of temperature on selectivity to major products (left axis) and propene conversion (right axis) for the oxidation of propene (Catalyst A). Gas feed 5% C_3H_6, 5% O_2, 90% He; total flow is 50 $ml\,min^{-1}$; 0.1 g catalyst.

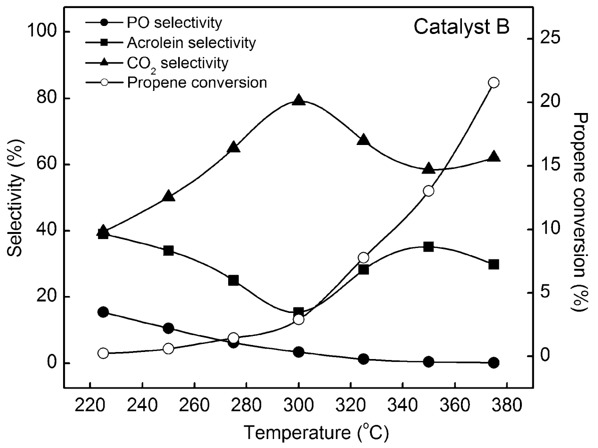

Fig. 2. Effect of temperature on selectivity to major products (left axis) and propene conversion (right axis) for the oxidation of propene (Catalyst B). Gas feed 5% C_3H_6, 5% O_2, 90% He; total flow is 50 ml min^{-1}; 0.1 g catalyst.

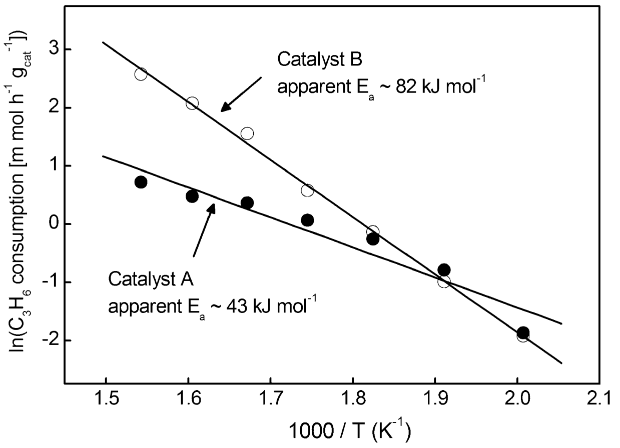

Fig. 3. Arrhenius plots for the oxidation of propene over catalyst A (●) and catalyst B (○). Gas feed 5% C_3H_6, 5% O_2, 90% He; total flow is 50 ml min^{-1}; 0.1 g catalyst.

diate temperatures, with onset of CuO formation at ∼350 °C. Comparing their results with other published data [14] suggests that CuO catalyses combustion of propene, whereas Cu_2O favours partial oxidation to acrolein. However, for present purposes, the most significant finding is that the XRD results of Rodriguez et al. demonstrate that Cu^0 survives in the temperature regime within which we observe PO formation.

Earlier studies on single-crystal surfaces of Cu under vacuum conditions showed that metallic copper efficiently catalyses epoxidation of styrene and butadiene [7,8,15]; that is, the active site is associated with Cu^0. This work also showed that epoxidation is inhibited by the onset of Cu oxidation. More significantly, the same general behaviour was found for the oxidation of *trans*-methyl styrene (a phenyl propene containing allylic H atoms) on Cu(111) [9]. Therefore, we may tentatively infer that the results shown in Fig. 1 imply that propene epoxidation is associated with the presence of Cu^0.

The corresponding results obtained with catalyst B under the same conditions used for testing catalyst A are shown in Fig. 2. Once again, adding H_2 to the reactant gas has no effect. The behaviour with respect to PO and CO_2 production is broadly similar to that of catalyst A, although PO selectivity is significantly lower (∼15% selectivity at 225 °C with propene conversion of 0.24%, the latter being similar to that of catalyst B at this temperature). This suggests that a morphological or some other difference may exist between catalysts A and B. The difference in behaviour between the two catalysts with respect to acrolein production tends to support this view. We could attempt to rationalise this difference by speculating about possible differences in the relative importance of direct and indirect routes to acrolein formation (dehydrogenation of propene followed by oxidation of the resulting allylic species vs. isomerisation to butanal followed by dehydrogenation), but this would detract from our principal purpose—understanding PO formation.

To determine whether the fall-off in PO production with increasing temperature was associated with further epoxide conversion, a series of control experiments was carried out. Accordingly, PO (0.5%) was fed to the catalyst at a reaction temperature of 225 °C; the major product was propanal (75%), plus acetone (13%), acetaldehyde (3%), and CO_x (9%). When the catalyst was fed with PO and O_2 (0.5% and 5%, respectively, at 225 °C), the major products were acrolein (21%) and CO_x (48%), accompanied by propanal (12%), acetone (5%), and acetaldehyde (14%). Repeating both types of experiments with pure silica showed that the support was completely inert under all conditions. The implication is that in the absence of oxygen, the copper component of the catalyst promotes isomerisation of PO to propanal. Then, when oxygen is present, the propanal undergoes oxidative dehydrogenation to acrolein. We may therefore conclude that production of acrolein during propene oxidation is at least partly due to the formation and further reaction of PO.

Fig. 3 shows Arrhenius plots for the rate of propene consumption. These yield apparent activation energies of ∼43 kJ mol^{-1} for catalyst A and ∼82 kJ mol^{-1} for catalyst B.

Finally, in view of the findings of Lu et al. [11] in regard to NaCl-promoted selectivity, the effects of a range of alkali and chlorine additives on catalyst B were examined. 5 wt% NaCl-modified and 5 wt% Cl-modified catalysts were prepared by impregnating the as-prepared Cu/SiO_2 with NaCl and NH_4Cl aqueous solutions, respectively. Chlorine was also incorporated into the reaction in the form of 1,2-dichloroethane, supplied to the propene/oxygen feed gas at a concentration of 5 ppm. We found that all additives had a detrimental effect on the selectivity toward PO formation.

XPS and Auger spectroscopy were used to establish the oxidation state of the Cu in the epoxidation-active catalysts. In principle, discrimination between bulk Cu, Cu_2O, and CuO can be achieved by examining the Cu 2p XP spectra and the Cu L_3VV Auger spectra [16]; however, this is a nontrivial task with samples such as ours, which contain only very small amounts of copper. Fig. 4 shows postreaction (225 °C) XP and Auger spectra of catalyst A (the more selective of the two catalysts) and corresponding standard spectra acquired with samples of pure CuO, Cu_2O, and Cu. Based on the measured binding energies and the absence of shake-up satellite peaks at 943 eV and 962 eV, the Cu 2p spectra establish that the PO active site is not

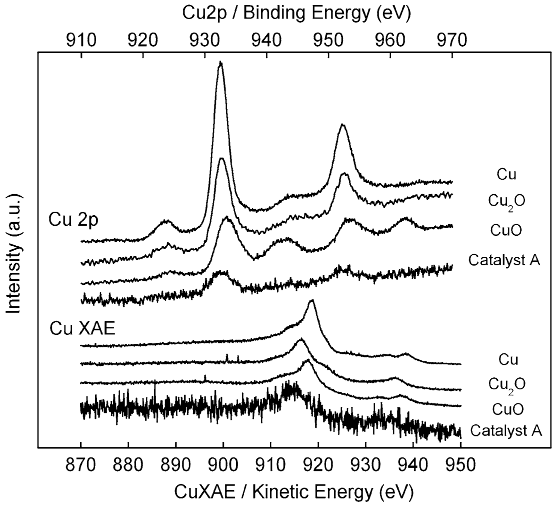

Fig. 4. Copper 2p XPS and Cu XAE spectra of catalyst A and three reference samples.

associated with Cu^{2+}. The 2p binding energies of Cu^+ and Cu^0 are very similar and do not permit discrimination between these species; here the Auger spectra are of use. The L_3VV Auger spectrum of Cu_2O lies at substantially lower electron kinetic energy than that of metallic Cu. On this basis, the Auger spectrum of catalyst A cannot be associated with Cu_2O and must be due to metallic copper. However, comparison with the Auger spectrum of metallic copper shows that the high-kinetic energy component is strongly attenuated in our catalyst compared with bulk copper metal. This is a very unusual observation, although not without precedent. Espinós et al. [16] found very similar anomalies in the L_3VV Auger spectra of zirconia-supported Cu^0 at very small metal loadings, comparable to those used here. Although these authors did not identify the cause of this phenomenon, they concluded in a general sense that it is due to the small size of the Cu entities. Theoretical calculations [18] suggest that this anomalous spectral line shape may be associated with "atomic-like" copper as opposed to large copper particles, which would have a well-developed band structure. Earlier studies have used the Auger parameter to characterize very small Cu clusters deposited on oxide supports [16,17]. In agreement with these studies, we find that the Auger parameter characteristic of catalyst A ($\alpha_{\text{catalyst A}} = 1847.3$ eV) is substantially lower than that of bulk copper ($\alpha_{\text{bulk}} = 1851.1$ eV), indicative of very small particle size [16,17]. Consistent with the notion of highly dispersed copper, we found no XRD-visible particles (>5 nm) in either used catalyst; hence we examined them by means of HREM. Surprisingly, we found no discernible copper particles present on the silica surface in either freshly prepared or used catalyst. Thus the spectroscopy and microscopy findings suggest that the active species for propene epoxidation consists of a highly dispersed nanoscopic metallic phase with an electronic structure, and thus chemical properties, significantly different than those of mesoscopic or macroscopic copper.

A comment on the relationship between our catalysts and the NaCl-modified $VCe_{1-x}Cu_x$ materials studied by Lu et al. is in order. Notable differences between the two cases are the need for (i) heavy NaCl promotion (for useful selectivity) and (ii) H_2 addition (for stable operation) in the case of NaCl-modified $VCe_{1-x}Cu_x$. Neither of these is required in the present case, where NaCl actually *decreases* selectivity and H_2 has no effect. It seems likely that (ii) reflects the tendency of the V/Ce mixed-oxide component to oxidise the Cu^0 component [19,20] and that the role of H_2 is to counteract this. The fact that H_2 has no effect on the performance of our catalysts could reflect the range of temperatures used for testing. For the purpose of direct comparison with the work of Lu et al., these measurements were made at ~215 °C. Under such conditions, with an irreducible support such as silica, we would expect the predominant species to be Cu^0 [13] in the *absence* of H_2; hence added hydrogen should have little effect, as we observe. The reason for the very different response of the two types of catalyst to NaCl is unclear. It may be speculated that in the case of $VCe_{1-x}Cu_x$, sodium acts to neutralize sites that lead to PO isomerisation, thus inhibiting combustion, whereas with Cu/silica, the support is catalytically inert.

In summary, we have shown that an inexpensive base metal catalyst is effective for propene epoxidation without the need for a hydrogen co-feed. The active phase appears to be a highly dispersed form of metallic copper, and the performance of these materials is comparable to that reported by Haruta et al. [4] in their first paper on propene epoxidation catalysed by Au/TiO_2.

Acknowledgments

The authors thank Dr. D.A. Jefferson for performing the electron microscopy. O.P.H.V. and G.K. acknowledge the award of research studentships by the U.K. Engineering and Physical Sciences Research Council.

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