J. Am. Chem. Soc. **2000,** *122,* 2381−2382

Ultraselective Epoxidation of Butadiene on Cu{111} and the Effects of Cs Promotion

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Received November 29, 1999

Heterogeneously catalyzed alkene epoxidation is of great interest from both academic and technological points of view. Ethene epoxidation, for which Ag is an apparently unique catalyst, is a strategically important large-scale industrial process. As a result, elucidation of the mechanism of Ag-catalyzed epoxidation has attracted a great deal of academic research and many key features of the reaction may be regarded as well understood. Studies on single-crystal surfaces of silver have provided most of the fundamental insight, including the identification of oxygen adatoms, as opposed to adsorbed dioxygen, as the key epoxidizing agent.[1] Similarly, the mode of action of adsorbed chlorine[1] and alkali[2] promoters has been determined. A recent review is provided by ref 3. It is desirable to broaden this chemistry to the selective oxidation of certain higher terminal alkenes whose epoxides are valuable and versatile intermediates: propene[4] and butadiene are important examples. As part of this effort, one should also seek alternative catalysts to silver. Recently, using styrene as a model terminal alkene, we showed that single crystal surfaces of Cu can act as highly effective epoxidation catalysts.[5]

Here we provide the first demonstration that the clean Cu{111} surface can catalyze the epoxidation of a desired target molecule, butadiene, to 3,4-epoxybut-1-ene with extremely high selectivity: in this respect Cu far outperforms Ag. We also show that coadsorbed Cs strongly promotes the epoxidation of butadiene, without detracting from selectivity, in contrast with the behavior of alkalis in Ag-catalyzed ethene epoxidation.[2] The mechanistic implications of these findings are discussed. Epoxybutene is important because the molecule is highly functional, with each carbon atom chemically distinct. This allows manufacture of such diverse products as hydroxy ethers, glycols, and amino alcohols as well as intermediates for pharmaceutical and agricultural chemicals.

Temperature-programmed reaction (TPR) and X-ray photoelectron spectroscopy (XPS) measurements were carried out in an ultrahigh vacuum apparatus, described elsewhere.[6] Gas exposures are given in Langmuirs (1 L = 1 × 10^{-6} Torr s^{-1}) and the TPR data were acquired at a heating rate of 5 K s^{-1}. Reaction products were identified on the basis of their mass spectral fragmentation patterns. Cs[7] and O[8] coverages (θ_{Cs} and θ_O) were estimated from XPS intensities, by reference to calibrations available in the literature. These quantities are specified in fractional monolayers (ML).

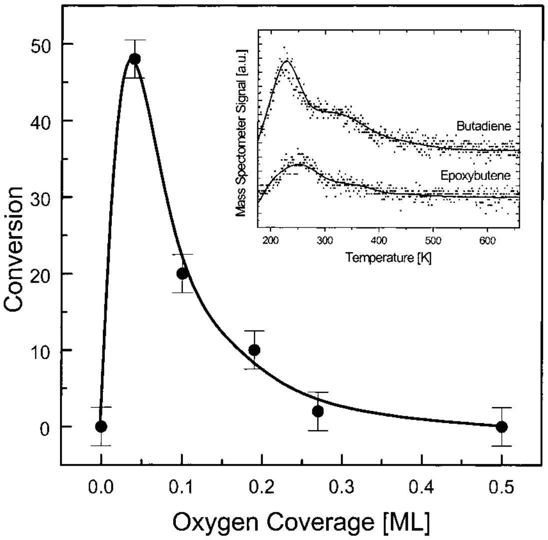

Figure 1. The conversion of butadiene to epoxybutene as a function of oxygen coverage over Cu{111}. Inset: Representative mass spectrum of butadiene and epoxybutene for $\theta_O \sim 0.04$ ML.

Thermal desorption spectra obtained following butadiene chemisorption at 170 K exhibited a maximum at ~230 K and a poorly resolved shoulder at ~350 K. Temperature-programmed reaction data were obtained by preadsorbing varying amounts of oxygen at 170 K, followed by a saturation dose of butadiene (2 L) at 170 K. The resulting spectra showed the formation of epoxybutene, detected at *m*/*z* 42, and representative results are shown in the inset to Figure 1. No CO_2, H_2O, furan, formaldehyde, 2-butenal, propenal, 2,5-dihydrofuran, nor any other products were detected under any conditions, indicating extremely efficient epoxidation with selectivity of ~100%.

The yield of epoxide passed through a maximum as the oxygen pre-coverage was increased; it was highest for an oxygen predose of 1L ($\theta_O \sim 0.04$ ML), reactivity eventually being quenched at $\theta_O \sim 0.5$ ML (Figure 1). This latter condition corresponds to coverage of the surface by a disordered Cu_2O-like phase.[9] The reactively formed epoxybutene exhibited a broad maximum at ~250 K tailing to higher temperatures. Note that the uptake of butadiene was not significantly affected by the amount of preadsorbed oxygen, so that the falloff in butadiene production was not due a decrease in alkene coverage.

These results indicate that minimum necessary and sufficient conditions for butadiene epoxidation on Cu{111} are butadiene molecules adsorbed on Cu metal sites in the vicinity of oxygen adatoms. The "oxidic" oxygen formed at high coverages is ineffective, even though plenty of the alkene is available. The implication is that the chemical state of oxygen is critically important, oxidic oxygen being an ineffective electrophile with respect to the adsorbed alkene. In this regard the epoxidation chemistry parallels that observed on Ag where the valence charge density on oxygen determines selectivity.[1] On Ag, the charge density on oxygen can be diminished by coadsorbed chlorine,[1] thus creating a better electrophile and favoring epoxidation. Consistent with this, alkalis have the opposite effect[2] favoring combustion over epoxidation. Cu, unlike Ag, readily forms the metal oxide, even under ultrahigh vacuum conditions. If, as seems likely, the transition from chemisorbed oxygen to Cu oxidation is accompanied by a significant change in the valence charge density on oxygen, the present results may be understood on a similar basis to that proposed for the case of Ag.[1] That is, oxygen chemisorbed on Cu is a good electrophile for the π-adsorbed alkene whereas the more highly charged oxidic oxygen (formally O^{2-}) is a poor electrophile, and therefore ineffective for epoxidation.

It is of interest to examine the effects of coadsorbed alkali on this system. Recall that in the case of Ag, added alkali strongly *decreases* selectivity toward epoxide formation, both for ethene

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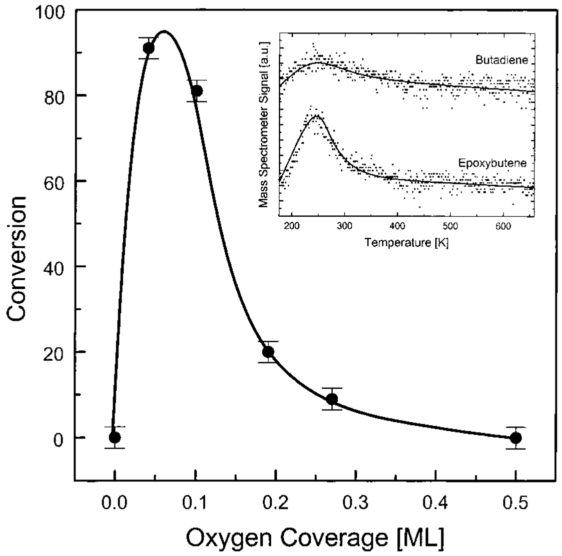

Figure 2. Conversion of butadiene to epoxybutene as a function of oxygen coverage over caesiated Cu{111}, $\theta_{Cs} \sim 0.07$ ML. Inset: Representative mass spectrum of butadiene and epoxybutene for $\theta_O \sim 0.04$ ML.

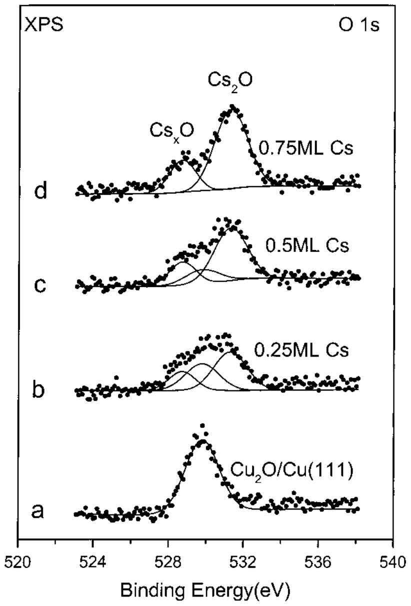

Figure 3. O 1s X-ray photoelectron spectra showing conversion of Cu_2O to Cu as a function of Cs dose: (a) no Cs; (b) 0.25 ML Cs; (c) 0.5 ML Cs; and (d) 0.75 ML Cs.

itself[2] and for the model alkene styrene.[10] The clean surface was pre-dosed with varying amounts of oxygen, followed by a fixed ~0.07 ML dose of Cs and then a (saturating) butadiene dose of 2 L. The results are illustrated in Figure 2 along with typical TPR spectra, which are shown in the inset. Again, no products other than epoxybutene were detected. Thus in contrast with Ag-catalyzed epoxidation, alkali has no effect on selectivity, which remains very high (effectively 100% within the accuracy of our measurements). Instead, for any given oxygen coverage, Cs strongly increases the amount of butadiene conversion to epoxybutene (cf. Figures 1 and 2). For $\theta_O \sim 0.1$, ~90% of the adsorbed butadiene is epoxidized. It is important to note that the increased yield of epoxide is not due to increased butadiene adsorption: this is hardly affected by to the presence of ~0.07 ML of Cs. For oxygen pre-coverages >0.08 ML, conversion decreased progressively, being fully quenched at 0.5 ML, just as in the case of the alkali-free surface. However, as inspection of Figures 1 and 2 shows, for any given oxygen pre-coverage the effect of Cs was to (approximately) double the yield of epoxide.

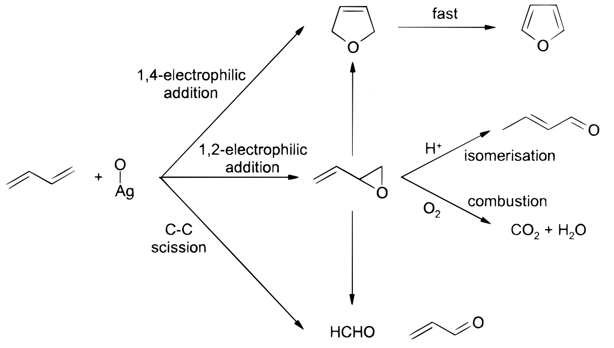

Figure 4. Reaction scheme proposed for butadiene epoxidation over Ag.

To understand how Cs modifies the catalytic behavior of the copper/oxygen system, we carried out XPS measurements to examine the chemical state of the system as a function of Cs coverage. This was achieved by depositing varying amounts of Cs on a pre-oxidized Cu_2O-like surface and monitoring the changes observed in the O 1s region. The Cu_2O-like surface was prepared by exposing the clean surface to 10^5 L of O_2 at 670 K.[9] Figure 3 shows the resulting curve-fitted O 1s spectra for different Cs loadings. The Cu_2O-like surface (spectrum a) exhibited a single peak at 529.8 eV. Addition of 0.25 ML and then another 0.25 ML of Cs to this surface led to the progressive growth of two new features at 528.7 and 531.3 eV, while the intensity of the 529.8 eV feature decreased (spectra b and c). At $\theta_{Cs} = 0.75$ ML the feature at 529.8 eV was undetectable, while the other two features became more prominent. O 1s emissions at 528.7 and 531.3 eV are associated with Cs_xO and Cs_2O, respectively.

Thus the results clearly show that Cs leads to the reduction of oxidic copper sites to metallic copper sites, yielding a mixture of Cs_2O and Cs_xO.

We may therefore write:

$$Cu_2O + Cs \rightarrow Cu + Cs_2O + Cs_xO$$

It thus appears that Cs acts to prevent the formation of copper oxide, which according to our results is catalytically inert.

It is interesting to compare Cu with Ag in regard to butadiene-selective oxidation. Single-crystal studies on Ag{110} showed no evidence for epoxide formation, the preferred products being dihydrofuran and furan formed via a 1,4-cycloaddition.[11] Butadiene can be selectively oxidized to epoxybutene over supported silver catalysts[12] but at only 1% conversion and 50% selectivity. The failure to observe epoxidation in the single-crystal case was attributed[12] to further conversion of the epoxide; the relevant processes are summarized in Figure 4.

We conclude that under TPR conditions butadiene may be selectively oxidized to epoxybutene over Cu{111} at high conversion and with close to 100% selectivity. The reaction occurs between oxygen adatoms and butadiene molecules adsorbed on Cu metal sites. Over-oxidation of the metal suppresses catalytic activity and Cs acts to enhance the reaction yield, without decreasing selectivity, by a clean-off reaction which regenerates Cu metal sites.

Acknowledgment. J.J.C. acknowledges the award of an EPSRC CASE studentship and additional support from BP-AMOCO Chemicals plc. A.K.S. acknowledges support from BP-AMOCO Chemicals plc. Financial support from the UK Engineering and Physical Sciences Research Council under Grant GR/M76706 is gratefully acknowledged.

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