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Article

Selective Epoxidation of 1,3-Butadiene on AgCu Near-Surface Alloys

Laura A. Cramer, Avery S. Daniels, Volkan Çinar, Prashant Deshlahra, and E. Charles H. Sykes*

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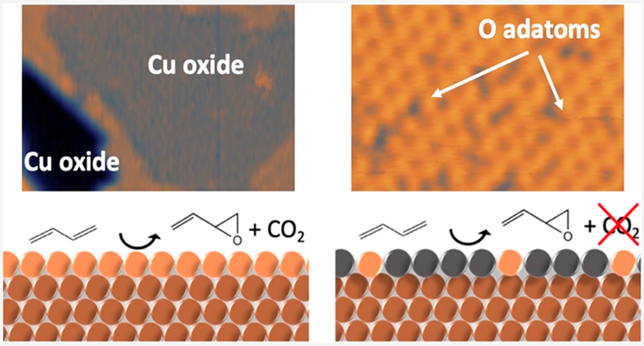
ABSTRACT: Bimetallic AgCu catalysts have gained considerable interest, as both metals have demonstrated ability to perform selective oxidation reactions. Many of these studies have shown increased selectivity arising from the combination of Ag and Cu, but the mode of selectivity enhancement for Cu in Ag remains unclear. The AgCu near-surface alloy provides a well-defined model system with which to study selective oxidation reactions. By using a combination of high-resolution scanning tunneling microscope imaging and temperature-programmed reaction studies, we demonstrate that the addition of a single monolayer of Ag to Cu increases the overall selectivity for the epoxidation of 1,3-butadiene to 3,4-epoxy-1-butene from ∼40% on Cu(111) to 100% on the complete monolayer. Specifically, the near-surface alloy undergoes dynamic restructuring that brings Cu atoms into the surface layer, which enhances oxygen dissociation on the Ag surface, but the Ag overlayer inhibits the formation of extended Cu oxide domains that also catalyze the combustion pathway. Together, these results indicate that high-surface-area catalysts comprised mostly of Ag with very small amounts of Cu may exhibit promising selective epoxidation chemistry.



■ INTRODUCTION

Epoxides are important chemical intermediates in the production of numerous value-added commodity chemicals, and as such, alkene epoxidation reactions are of significant interest both academically and commercially. Ag-based catalysts are the industrial standard for many selective oxidation reactions including ethylene epoxidation and formaldehyde production via partial methanol oxidation.[1−7] Atomic oxygen on Ag has been identified as the active species in ethylene epoxidation, and promotors such as Cl and alkalis such as Cs have been shown to increase the selectivity, and sometimes the activity, of the catalyst.[6,8] Though Ag is uniquely suited for selective oxidation reactions, it has several limitations. The reactions are often operated at suboptimal temperatures to avoid total combustion and formation of the thermodynamically favored product CO_2.[9,10] Another significant limitation of Ag is the relatively high oxygen activation barrier on the surface, which when coupled with the lower operating temperatures that avoid total combustion, leads to low conversion to products.[11−13] There is therefore great interest in methods that can modify both the intrinsic activity and selectivity of Ag and, in particular, promote the activation of molecular oxygen on the Ag surface.

In addition to ethylene, the epoxidation of higher olefins such as 1,3-butadiene to form 3,4-epoxy-1-butene has also gained much attention because epoxybutene is an important precursor in the production of value-added chemicals.[14] 1,3-Butadiene is similar to ethylene in that it is an unsaturated hydrocarbon with no allylic hydrogen atoms, and epoxidation proceeds through the addition of an oxygen atom to one of the C=C double bonds. Single crystal studies on Ag(110) have shown that 1,3-butadiene reacts with oxygen on the preoxidized surface to yield mostly 2,5-dihydrofuran and furan.[7] While Ag catalysts have exhibited increased selectivity and activity after the addition of Cs promotors,[15] isotope studies have demonstrated that the rate-limiting step for 1,3-butadiene epoxidation on Cs-promoted Ag catalysts is still the activation of molecular oxygen.[16] Related to this point, Cu has gained attention in the realm of selective oxidation reactions for its ability to more easily activate molecular oxygen than Ag.[17−20] For example, the epoxidation of styrene has been demonstrated on Cu(111),[19] and the addition of Cs to the surface led to an increase in conversion that was attributed to the inhibition of oxide formation on Cu, the formation of which prevented the reactant styrene from adsorbing.[19] Furthermore, the epoxidation of styrene has been demonstrated on Ag single crystals through the use of an atomic oxygen source.[21−24] This demonstrates the ability of Ag to

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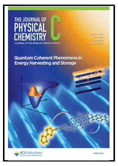

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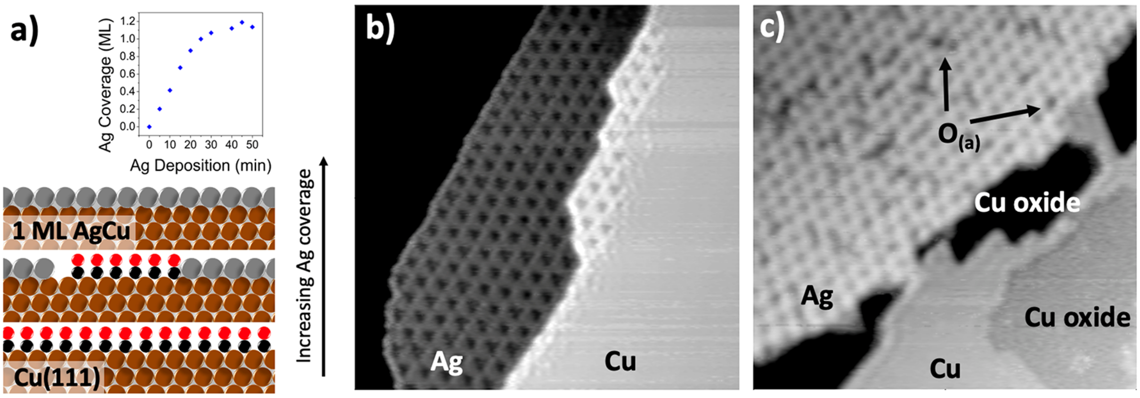

Figure 1. (a) Schematics showing layer-by-layer growth of Ag on Cu(111) and adsorption of CO exclusively on exposed Cu. Brown circles represent Cu, gray represent Ag, and black and red represent CO. The graphical inset shows Ag deposition time on Cu(111) versus Ag coverage in monolayer (ML), as calibrated via CO TPD. (b) STM image of the sub-ML AgCu NSA showing areas with exposed Ag and Cu. (c) STM image showing regions of oxidized Cu and isolated oxygen adatoms on the Ag layer after exposing the NSA to 500 L of O_2 at 300 K.

perform selective epoxidation reactions and motivates the addition of Cu to enable facile oxygen activation.

Given that oxygen activation is more facile on Cu than Ag, but Cu is prone to deep oxidation, we focus this study on a combination of the two metals in an attempt to harness the selectivity of Ag while using Cu to increase oxygen activation. Such bimetallic AgCu catalysts have gained considerable interest, as both metals have demonstrated ability to perform oxidation reactions.[21−28] Many of these studies have shown increased selectivity using a combination of Ag and Cu, but the mode of selectivity enhancement for Cu in Ag remains unclear, which has motivated studies on well-defined single crystals.[9,10,25−31] When Cu is deposited on Ag(111), the Ag tends to cap the exposed Cu.[32] Therefore, we focused on the AgCu near-surface alloy (NSA), which is composed of a single-atom-thick monolayer (ML) of Ag on Cu(111). We have previously shown using model single-crystal studies that Ag remains on the surface of the AgCu NSA after exposure to oxygen at room-temperature.[33] Importantly for the current work, this alloy dynamically restructures upon oxygen exposure, and the appearance of isolated oxygen adatoms on Ag is linked with Cu that is able to reverse segregate to the Ag surface where it aids molecular oxygen dissociation.[33] In this study, we perform model single-crystal experiments combining high-resolution imaging and quantitative temperature-programmed reaction (TPR) studies in order to relate the atomic-scale structure of AgCu model catalysts to their activity and selectivity for the epoxidation of butadiene. Specifically, in our TPR studies, reactants are adsorbed on the crystal surface at low temperature, and then the sample temperature is ramped, and both reactants and products are observed desorbing by quantitative mass spectrometry, thus enabling us to report yields of epoxide and CO_2 and the overall reaction selectivity. This surface science approach to building structure−function relationships in model systems that then inform catalyst design has previously contributed to the discovery of new selective hydrogenation catalysts.[34,35] The results presented herein demonstrate that the addition of Ag to Cu in the form of a NSA increases the overall selectivity for the epoxidation of 1,3-butadiene to 3,4-epoxy-1-butene.

■ METHODS

Temperature-programmed desorption (TPD) experiments were performed in a UHV chamber with a base pressure of $<1.0 \times 10^{-10}$ mbar. The chamber was equipped with a Hiden HAL 3F 301 quadrupole mass spectrometer mounted on a linear drive capable of being advanced to within 1 mm of the crystal face. A Cu(111) single crystal was cleaned via repeated cycles of Ar^+ sputtering (1.5 keV, 2 μA) and annealing to 750 K. Ag was deposited using a flux-monitored Omicron Nanotechnology EFM 3 electron beam evaporator at a constant deposition rate of 0.05 ML min^{-1} with the Cu(111) crystal at room temperature. Liquid nitrogen was used to cool the crystal to 90 K. Leak valves were used to introduce O_2 and butadiene into the chamber. A linear heating ramp of 1.5 K s^{-1} was used for the TPD experiments.

The yields of epoxybutene and CO_2 were calculated with quantitative mass spectrometry by integrating the relevant desorption peaks. The areas were then corrected for the ionization cross section, mass spectrometer quadrupole sensitivity falloff, and fragmentation pattern, consistent with the procedure from Siler et al.[36] Butadiene was tracked at $m/z = 54$, epoxybutene at $m/z = 42$, and CO_2 at $m/z = 44$, and fragmentation patterns for these molecules can be found in Table S1 in the Supporting Information. The exposures are quoted in Langmuirs (L) (1 L = 1×10^{-6} Torr·s).

STM experiments were performed on an Omicron Nanotechnology variable-temperature STM with a base pressure of $<1.0 \times 10^{-11}$ mbar. A Cu(111) single crystal was cleaned via repeated cycles of Ar^+ sputtering (1.5 keV, 15 μA) and annealing to 1000 K. The STM sputtering conditions differ from the TPD experiments because of the different sputter source, and the anneal temperature was higher to achieve a smoother surface for imaging. The TPD cleaning procedure was replicated in the STM chamber and revealed no significant changes to surface morphology. Ag was deposited at a rate of approximately 0.05 ML min^{-1} by resistively heating a Ag-wrapped W filament. O_2 was introduced into the chamber using a leak valve with the surface at 300 K.

■ RESULTS AND DISCUSSION

Ag was deposited on Cu(111) at 300 K, and the coverage was determined by CO temperature-programmed desorption (TPD), as shown in Figure 1a. These TPDs were performed by cooling the sample to ∼90 K with liquid nitrogen and then exposing it to a saturation coverage of CO. At these temperatures, CO adsorbs only on the exposed Cu(111) but not any deposited Ag, which means that any decrease in the

CO desorption signal is directly proportional to the area of the Cu(111) surface covered with Ag (individual CO TPDs are shown in Figure S1).[37] The graph in Figure 1a shows Ag on Cu(111) as a function of Ag deposition time, as determined from the CO titration experiments. Since the Ag coverage is determined on the basis of CO adsorption on the exposed Cu, the growth appears to saturate at a monolayer; however, on the basis of previous studies, which have shown the layer-by-layer growth of Ag on Cu(111),[38−40] the surface continues multilayer growth after the Ag monolayer is saturated. The schematics in Figure 1a illustrate this and show the adsorption of CO on the exposed Cu(111), but not on regions where Ag has been deposited. Figure 1b shows a room-temperature STM image of submonolayer Ag on Cu(111), where Ag can be seen protruding outward from the step edges to form one-monolayer-high islands with a repeating triangular pattern because of the 9 × 9 reconstruction in the underlying Cu(111).[38−40] This 9 × 9 reconstruction forms in the topmost layer of Cu underlying the Ag as a strain relieving mechanism because of the large lattice mismatch between Cu and Ag. Formation of this reconstruction has been described in detail elsewhere.[33,38−42] Figure 1c shows an STM image of a AgCu NSA after exposure to 500 L of oxygen at 300 K. Regions of oxidized Cu can be seen along with oxygen adatoms on the Ag monolayer. There are two distinct features present in the Cu region, consistent with previous studies of oxide formation in Cu(111).[43−45] One type of oxide originates from the ejection of Cu atoms and follows the 3-fold symmetry of the Cu(111) surface to form structured regions with a preference for (100)-type steps.[45] This oxide appears as darker oxide portions in the STM image. A second type of oxide forms from the ejected Cu atoms that are deposited on top of the terrace. This forms the lighter colored amorphous regions of oxide. Most importantly, in the Ag region, oxygen adatoms are visible as depressions on the Ag layer, and the black arrows point to two of these features. This is due to the presence of oxygen, which reverses the segregation energy for AgCu and stabilizes Cu atoms in the Ag layer. These single Cu atoms in the Ag surface significantly lower the O_2 dissociation barrier on the AgCu NSA surface.[33]

In order to examine how the Ag and Cu content of the surface changed the butadiene epoxidation reactivity and selectivity, we performed a series of TPR measurements as a function of Ag coverage on Cu(111), as shown in Figure 2. We present the raw data in the TPR figures and then correct the mass spectrometer signals for the ionization cross section, fragmentation pattern, and mass spectrometer quadrupole sensitivity before quoting product yield and selectivities. These TPRs were recorded after exposure of different coverages of Ag on Cu(111) to 500 L of oxygen at 300 K and 0.1 L of butadiene at 90 K. The 500 L exposure to oxygen was selected to ensure that enough oxygen would be present at the surface to form a measurable amount of product while limiting the formation of Cu oxide patches in the Ag layer, which can occur at higher exposures (effects of oxygen exposure on epoxybutene yield are shown in Figure S4).[46] This oxygen exposure was also demonstrated previously to be in a regime where small amounts of Cu reverse segregate to the surface of the Ag monolayer where it significantly enhances the O_2 dissociation probability.[33] The Ag coverage varied from pure Cu(111) (black trace) to the 1 ML AgCu NSA (top trace) with the intermediate coverages of Ag corresponding to 0.20, 0.42, and 0.87 ML.

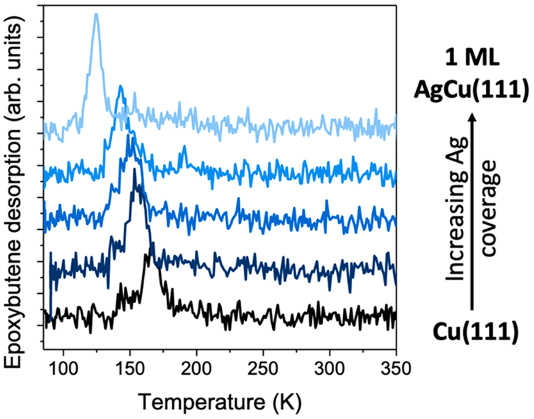

Figure 2. Epoxybutene (m/z = 42) yield from AgCu surfaces ranging from pure Cu(111) to the 1 ML AgCu NSA. All TPR experiments were performed by dosing 500 L of O_2 at 300 K and 0.1 L of butadiene at 90 K with a heating rate of 1.5 K s^{-1}. Coverages of Ag starting with the bottom (black) trace are 0, 0.20, 0.42, 0.87, and 1 ML.

Figure 2 clearly shows that the epoxide yield increases, and its desorption temperature decreases, with increasing Ag coverage. Specifically, we observe a 42 K shift in epoxybutene desorption from Cu(111) (167 K) to 1 ML AgCu NSA (125 K). Epoxybutene formation (monitored at m/z = 42)[18] was not observed in the absence of codeposited oxygen, thereby enabling us to rule out the possibility that it was an impurity in the butadiene sample. Furthermore, this reactively formed epoxybutene desorbed at a different temperature from chemisorbed epoxybutene, which we measured desorbing from Cu(111) at 151 K and 1 ML of Ag on Cu(111) at 168 K. The lower desorption temperature of the reactively formed epoxybutene could be related to the incomplete equilibration of an intermediate on the Ag overlayer prior to desorption. The formation of other C_4H_6O oxidation products such as 2-butenal (crotonaldehyde) and 2,5-dihydrofuran was investigated by tracking m/z = 70, 68, and 41, but these species were not observed.

Examples of the TPRs of the reaction products for butadiene epoxidation on Cu(111) and the 1 ML AgCu(111) NSA can be seen in Figure 3. Both surfaces produce the desired epoxybutene product; however, the total oxidation product of CO_2 is produced in much smaller amounts on the AgCu NSA than on Cu(111). The schematics below the TPR profiles depict the surfaces after exposure to 500 L of oxygen at 300 K. The Cu(111) surface is covered in oxide patches (seen in Figure 1c) and is indicated by the light brown circles in Figure 3a. This oxide is capable of epoxidation, but also leads to the production of CO_2 above 400 K. In contrast, under the same conditions the AgCu NSA is covered in a mixture of isolated oxygen adatoms and small, isolated Cu oxide sites, as seen schematically in Figure 3b. From these data, it is clear that the addition of a monolayer of Ag to Cu(111) enables selectivity control by shutting down the total oxidation pathway.

This point is illustrated in more detail in Figure 4, which shows the yield of CO_2 and epoxybutene as a function of Ag coverage on the Cu(111) surface. The CO_2 yields shown in Figure 4a demonstrate the decrease in total oxidation of butadiene to CO_2 as the Ag coverage increases (individual TPR traces for CO_2 are shown in Figure S3). Figure 4b shows an increasing epoxybutene yield with increasing coverage of

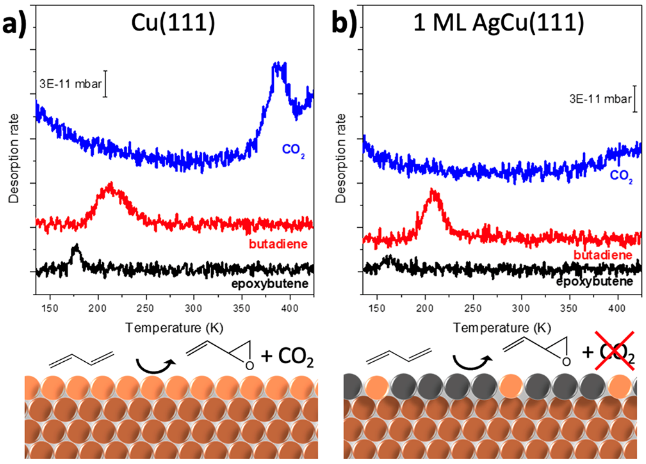

Figure 3. Butadiene (m/z = 54), epoxybutene (m/z = 42), and CO_2 (m/z = 44) desorption from 1,3-butadiene oxidation on Cu(111) and the 1 ML AgCu NSA. (a) TPR of butadiene oxidation products from oxidized Cu(111) with significant CO_2 desorption. (b) TPR of 1 ML AgCu NSA butadiene oxidation products showing a significant decrease in CO_2 production. All experiments were performed by dosing 500 L of O_2 at 300 K and 0.1 L of butadiene at 90 K with a heating rate of 1.5 K s^{-1}. Schematics show the formation of Cu oxide on the pure Cu(111) surface and Ag-capped Cu on the AgCu NSA surface with isolated Cu oxide sites. Dark and light brown and gray circles represent metallic and oxidized Cu and metallic Ag atoms, respectively.

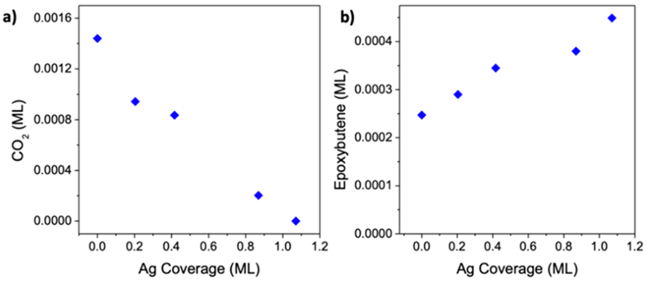

Figure 4. (a) CO_2 (m/z = 44) and (b) epoxybutene (m/z = 42) desorption products as a function of Ag coverage on Cu(111). All experiments were performed by dosing 500 L of O_2 at 300 K and 0.1 L of butadiene at 90 K with a heating rate of 1.5 K s^{-1}.

Ag. These trends illustrate that Ag increases both the selectivity toward epoxybutene and the epoxybutene yield in a single TPR cycle, and the epoxide yields in Figure 2 give a selectivity to epoxybutene of ∼40% on Cu(111) that rises to 100% at a full 1 ML of Ag coverage. Table S2 provides the full selectivity data as a function of Ag coverage. Furthermore, the presence of Ag in the current system appears to mirror the behavior of the Cs promotor that previous studies have attributed to Cs preventing the formation of extended oxide patches on Cu,[19] which have been linked to unselective total oxidation.[20] Taken together, these results suggest that small amounts of Cu in the Ag surface aid in the selective epoxidation reaction by facilitating O_2 activation[33] and, because of their small size, in keeping the adsorbed oxygen in a form that is highly selective for epoxidation over combustion to CO_2.

■ CONCLUSIONS

We have shown that the addition of Ag to Cu(111) increases the selectivity of the butadiene epoxidation reaction and leads to a higher yield of epoxybutene than Cu(111). It appears that Ag on Cu(111) inhibits the formation of extended Cu oxide domains that also catalyze the combustion pathway. Oxygen activation on the AgCu NSA is facilitated by the reverse segregation of small amounts of Cu atoms to the surface layer where O_2 dissociates to leave oxygen atoms but not extended Cu oxide domains.[33] In this way, the AgCu NSA is active in the selective oxidation of butadiene and enhances the selectivity of the reaction over pure Cu. These results indicate that high-surface-area catalysts comprised mostly of Ag with small amounts of Cu may exhibit promising epoxidation chemistry without the need for additives like Cs.[31,47]

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpcc.2c01912.

> Additional experimental details including CO TPDs used to calculate the Ag coverage on Cu(111); 1,3-butadiene and CO_2 desorption; TPR traces for epoxybutene desorption; fragmentation patterns for 1,3-butadiene partial oxidation products; and selectivity to epoxybutene (PDF)

■ AUTHOR INFORMATION

Corresponding Author

E. Charles H. Sykes − *Department of Chemistry, Tufts University, Medford, Massachusetts 02155, United States;* orcid.org/0000-0002-0224-2084;
Email: Charles.Sykes@tufts.edu

Authors

Laura A. Cramer − *Department of Chemistry, Tufts University, Medford, Massachusetts 02155, United States*
Avery S. Daniels − *Department of Chemistry, Tufts University, Medford, Massachusetts 02155, United States*
Volkan Çinar − *Department of Chemistry, Tufts University, Medford, Massachusetts 02155, United States*
Prashant Deshlahra − *Department of Chemical and Biological Engineering, Tufts University, Medford, Massachusetts 02155, United States;* orcid.org/0000-0002-1063-4379

Complete contact information is available at:
https://pubs.acs.org/10.1021/acs.jpcc.2c01912

Notes

The authors declare no competing financial interest.

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