Mechanistic insights into the oxidation of catalytically relevant AgCu near-surface alloy interfaces

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Abstract
Recent heterogeneous catalysis studies have demonstrated that synergy between Ag and Cu can lead to more selective partial oxidation chemistries. We performed a series of scanning tunneling microscope experiments to gain a better understanding of the AgCu system under oxidative conditions. These experiments were carried out by exposing sub-monolayer coverages of Ag on Cu(111), in the form of a near-surface alloy (NSA), to range of oxygen exposures and temperatures. This enabled us to study the initial stages of oxidation of well-defined Ag/Cu interfaces with atomic resolution and thereby understand the dynamic response of the AgCu NSA to oxygen environments. At low oxygen exposures, oxidation was observed on exposed Cu terraces and at the interface between the AgCu NSA and Cu(111). Higher oxygen exposure led to the segregation of Cu atoms up through the Ag layer and the appearance of surface adsorbed oxygen. Significant phase segregation of Cu was then observed at higher oxygen exposures at elevated temperatures, evidenced by the formation of Cu oxide patches within and on the top of the Ag layer. These results provide a more detailed picture of how AgCu NSAs interact with, and restructure in response to, oxygen.

KEYWORDS
alloy, bimetallic, scanning tunneling microscopy, segregation

1 | INTRODUCTION

The complexity and tunability of metal alloys have made their development a major focus in heterogeneous catalyst design. For example, and specific to this work, bimetallic catalysts containing small concentrations of Cu in Ag have been shown to enhance both the rate and selectivity of ethylene epoxidation without the need for promoters.[1–3] Barteau and co-workers reported that the performance of AgCu catalysts was highly correlated with reactant feed stoichiometry with increasing oxygen partial pressure leading to increased selectivity and activity, while increasing ethylene partial pressure yielded an increase in selectivity but slight drop in activity.[2,3] Schlögl and co-workers demonstrated that Ag catalysts with ~1% Cu have three times the epoxidation selectivity but half the activity of pure Ag.[11] Propylene[4–10] and butadiene[11–14] epoxidation have also been studied on Ag, Cu, and dilute Cu in Ag catalysts. More generally, both Cu and Ag are important for industrially relevant reactions including the use of Cu in methanol synthesis,[15–18] methanol partial oxidation, and the water gas shift reaction.[19] Multiple studies on Cu and Ag-based catalysts have shown oxidation state dependent selectivity and reactivity toward selective oxidation.[1,20–22] In order to understand the origins of these promising catalytic systems, one must first understand the structure of the alloys, and how they react with, and restructure in response to oxygen.

Before discussing our work on the AgCu near-surface alloy (NSA), a brief review of how the individual elements interact and react with oxygen is warranted. Molecular oxygen adsorbs dissociatively on Cu(111) above 170 K.[23,24] It is generally accepted that Cu(111) oxidation proceeds through oxygen chemisorption and nucleation until the surface oxide saturates at which point bulk oxide growth begins.[25] For the ordered surface Cu2O, careful control of the oxide formation kinetics can lead to either the "29" or "44" structures.[23,26–28] These structures are named for their respective unit cell sizes relative to the Cu(111) lattice. Oxide formation prior to the saturation of the surface oxide initiates at the step edges and defect sites in the terraces. There are two types of oxides that...
form in the terraces: terrace oxide and added oxide. Defect sites in the terrace serve as nucleation sites for terrace oxide which grows via the displacement of Cu atoms from the terrace. Displaced Cu atoms are then oxidized to form added oxide, which sits on the top of the terrace and tends to be amorphous in comparison to the terrace oxide that grows along the close-packed directions. Terrace Cu oxide prefers to grow on (100) steps and restructures (111) steps to form its preferred (100) steps.\textsuperscript{23,29}

This is in contrast to the oxidation of Ag(111), which is negligible under ultra-high vacuum conditions. Four states of oxygen desorption from Ag(111) have been identified: molecular physisorption, molecular chemisorption,\textsuperscript{30} atomic adsorption, and subsurface.\textsuperscript{31} The dissociative sticking probability of oxygen on Ag(111) has been found to be $\sim 10^{-6}$ and strongly influenced by the presence of co-adsorbates such as water.\textsuperscript{32,33} Adsorbed oxygen deforms the Ag(111) surface and eventually leads to surface reconstructions such as the widely studied p(4 × 4)-O reconstruction. The p(4 × 4)-O reconstruction forms at higher pressures and elevated temperatures with a saturation coverage of 0.375 monolayer (ML) of oxygen.\textsuperscript{33–38} The state of adsorbed oxygen and thus also the selectivity are heavily influenced by temperature and oxygen pressure.\textsuperscript{39}

In this work, we investigate the initial oxidation of an AgCu NSA to determine the influence of Ag on the oxidation of both the AgCu NSA and exposed Cu. Our studies focus on sub-monolayer amounts of Ag on Cu(111) enabling us to study the oxidation of both the AgCu NSA, which consists of an adlayer of single-atom-thick Ag layer on the Cu surface, and exposed pristine Cu(111) under identical conditions. We find that the oxidation of the exposed Cu regions follows the typical mechanism for Cu(111) oxidation on terraces, including the formation of terrace and added oxide patches. In the NSA regions, as oxygen exposure is increased, small amounts of Cu segregate up through the Ag layer, and eventually formation of ordered Cu oxide patches is observed. Further oxidation of this surface leads to the growth of a thin film of Cu oxide on the AgCu NSA beneath. Our scanning tunneling microscope (STM) results also reveal that this dynamic AgCu NSA allows Ag to resist oxidation even when using ozone as an atomic oxygen source. These results provide valuable information relevant to the oxidation of Cu-based alloys and the impact of alloying with Ag.

2 | EXPERIMENTAL

An Omicron Nanotechnology variable-temperature STM was used in an ultra-high vacuum chamber with a base pressure of $<5 \times 10^{-11}$ mbar. All images were acquired at room temperature with an etched W tip. A Cu(111) single crystal was cleaned by successive cycles of Ar\textsuperscript{+} sputtering (1.5 keV, 15 $\mu$A) followed by annealing at 875 K in a preparation chamber with a base pressure of $<1 \times 10^{-10}$ mbar. The Cu(111) sample was transferred between the preparation chamber and STM chamber under vacuum. Cleanliness of the crystal was monitored with STM and X-ray photoelectron spectroscopy (XPS). A precision leak valve was used to introduce O\textsubscript{2} (Airgas, 99.994% purity) into the chamber. All O\textsubscript{2} doses were performed at a pressure of $1 \times 10^{-6}$ mbar for varying amounts of time depending on the desired Langmuir dose (1 L = 1.0 × $10^{-6}$ Torr sec). A homebuilt deposition source consisting of an Ag wrapped W filament was used to deposit Ag at a deposition rate of $\sim 0.01$ ML min\textsuperscript{-1}. Ag coverage was calibrated using both STM and XPS. For all experiments, the overall coverage of Ag on the Cu(111) surface was 0.15 ML. A Del Ozone LG-7 ozone generator was used for ozone experiments.

Temperature programmed desorption experiments were performed in an ultra-high vacuum chamber with a base pressure of $<1 \times 10^{-10}$ mbar. A Cu(111) single crystal was cleaned by successive cycles of Ar\textsuperscript{+} sputtering (1.5 keV, 15 $\mu$A) followed by annealing at 750 K. A Hidden Hal RC 201 mass spectrometer was advanced to less than 1 mm of the crystal face during experiments. A linear temperature ramp of 1 K sec\textsuperscript{-1} was used for all experiments. A precision leak valve was used for O\textsubscript{2} deposition. Deposition of Ag was performed using an Ag wrapped W filament at a deposition rate of $\sim 0.01$ ML min\textsuperscript{-1}. Ag coverage was calibrated via carbon monoxide (CO) desorption and low-energy electron diffraction (LEED).

3 | RESULTS AND DISCUSSION

We begin by briefly discussing the alloying mechanism of Ag with Cu(111) which is vital in understanding the oxidation of the AgCu NSA. Vapor-deposited Ag atoms traverse large distances (>100 nm) on Cu(111) until they encounter a step edge and nucleate. Classic Frank–van der Merwe layer-by-layer growth continues outward from the step edge in a single monolayer, and multilayer growth begins once the Ag monolayer becomes saturated.\textsuperscript{40} The large lattice mismatch of $\sim 13\%$ between Ag and Cu (bulk $d_{\text{Cu}} = 0.256$ nm, bulk $d_{\text{Ag}} = 0.289$ nm) leads to the formation of a 9 × 9 reconstruction in the topmost Cu(111) layer underlying Ag to minimize lattice strain.\textsuperscript{41,42} The ejection of Cu atoms and shift of approximately 20% of underlying Cu atoms from their native fcc to hcp sites accompany the formation of this reconstruction. The shift of these Cu atoms leads to the formation of triangular dislocation loops in the topmost Cu layer and the resulting in the 9 × 9 reconstruction. STM images of the monolayer Ag on Cu(111) NSA demonstrate the characteristic triangular pattern due to this dislocation loop (Figure 1A). At sub-monolayer Ag coverages, the AgCu NSA forms very large domains on the surface, and is stable to elevated temperatures due to the lower surface free energy of Ag making it favorable to reside on the top of the reconstructed Cu(111) surface. This AgCu NSA has been modeled with density functional theory (DFT) calculations in our previous work.\textsuperscript{14} The atomic resolution image in Figure 1B shows the initial stages of NSA formation with a monolayer-high Ag layer (right) growing out from a Cu step edge on the left-hand side of the image. The resolution of this image also demonstrates the larger size of the Ag atoms relative to the Cu atoms. Figure 1C shows a model of the AgCu NSA where the grey circles represent Ag atoms on the surface, brown-colored circles represent Cu atoms, orange circles represent hcp-shifted first layer Cu, and the blue rhombus outlines the 9 × 9 unit cell.

In order to examine the effect of oxidation on both the Ag and Cu components of the NSA, sub-monolayer deposition of Ag on Cu(111) was performed in order to study samples with
FIGURE 1  (A) Large-scale room-temperature scanning tunneling microscope (STM) image of a region of the AgCu NSA. (B) Low-temperature, atomically resolved STM image of the AgCu interface with the $9 \times 9$ AgCu near-surface alloy (NSA) (right) growing out from an existing Cu step edge. (C) Model of the $9 \times 9$ reconstruction of AgCu. Unit cell is outlined by blue rhombus. Scale bar for panel (A) is 10 nm and (B) is 1 nm.

FIGURE 2  Scanning tunneling microscope (STM) images of sub-monolayer Ag on Cu(111) near the interface between AgCu near-surface alloy (NSA) and exposed Cu after exposure to O$_2$ at the given conditions (A) 0 L, 300 K, (B) 100 L, 300 K, (C) 300 L, 300 K, (D) 500 L, 300 K, (E) 500 L, 375 K, (F) 1500 L, 500 K. Arrows point toward Ag added into lower Cu terrace. Grey triangle shows the close-packed, (100)-type steps. Scale bars are 10 nm.

large domains of pristine AgCu NSA (see e.g., Figure 1A) and the interface of the NSA and exposed Cu(111) (see e.g., Figure 1B). Figure 2 shows the initial stages of oxidation of both the AgCu NSA and exposed Cu(111) at oxygen exposures ranging from 0 to 1500 L and temperatures from 300 to 500 K. Oxidation of the Cu(111) terraces proceeded as expected with the formation of both added and terrace oxide. These structures can be seen in Figure 2C–E corresponding to exposures of 300 L and 500 L at 300 K and a 500 L exposure at 425 K. Terrace oxide nucleates at defect sites in the Cu(111) terrace and appears in STM images as large depressions with well-defined edges Figure 2D,E.$^{[23,28,29]}$ Formation of terrace oxide occurs after the ejection of Cu atoms from the terrace, and its formation follows the close-packed directions with (100)-type steps.$^{[23,28,29]}$ Terrace oxide has three preferred edges with (100)-type steps as indicated by the grey triangle in Figure 2E. Added oxide occurs when the ejected Cu atoms become oxidized on top of the Cu terrace, resulting in the formation of amorphous added oxide islands. The arrows in Figure 2C,D indicate an interesting consequence of the oxidation of the AgCu NSA Cu terraces where a region of ejected Cu atoms has been filled in with Ag, as identified by the NSA $9 \times 9$ reconstruction, rather than forming terrace oxide. This indicates that the migration of Ag atoms competes with the formation of Cu oxide upon the ejection of Cu atoms along the step edge.

In terms of oxidation of the AgCu NSA, the presence of individual oxygen adatoms appeared in STM images as random depressions on the $9 \times 9$ Ag regions (Figure 2D,E). The concentration of these individual depressions increased with increasing oxygen exposure as previously demonstrated.$^{[43]}$ Cu oxide patches appeared within the Ag overlayer at sufficiently high oxygen exposures and temperatures. For example, a 1500 L oxygen dose at 500 K leads to the appearance of regions of Cu oxide within the Ag overlayer as seen in Figure 2F. This demonstrates that surface oxygen reverses the segregation energy for AgCu, stabilizing reverse-segregated Cu atoms in the Ag surface layer.

Previous studies have shown that Cu(111) step edges refacet to their preferred (100) orientation for the formation
of terrace oxide.[29] This preference leads to triangular terrace oxide patches and “saw tooth” like step edges due to re-facing. In contrast, in the AgCu NSA, the decoration of the Cu(111) steps with Ag allowed the terrace oxide to deviate from this preference and form oxide along (111)-type steps (Figure 2E). This is clear by the termination of terrace oxide, where the ascending edge does not align with the grey triangle in Figure 2E.

A detailed characterization of the oxidized AgCu NSA near the interface with exposed Cu oxide, including measurements of topographic line profiles along the white lines in the STM images and side-view diagrams reflecting interpretations about elemental composition, is shown in Figure 3. Figure 3A shows the surface after exposure to 300 L oxygen at 300 K with a line profile bisecting a terrace oxide region and the associated side-view diagram. The apparent height difference between the terrace oxide and the terrace depended on the STM tip state but averaged ~0.25 nm. Figure 3B shows the surface after exposure to 500 L oxygen at 300 K with patches of terrace oxide and regions of Ag added into the descending terrace, resulting from the ejection of Cu atoms during terrace oxide formation. A 0.03 nm height difference between the Cu(111) terrace and Ag in the lower terrace matched that expected from the difference in monoatomic step height between Ag (0.24 nm) and Cu (0.21 nm) when measuring from the height of the Ag (x-axis distance of 25 nm) to the clean Cu terrace beyond the added oxide region (x-axis distance of 10 nm). Figure 3C shows a region of the AgCu NSA after exposure to 500 L oxygen at 475 K where the Ag grew outward from what was Cu(111) step before Ag deposition. Prior to oxidation, this interface between the native Cu(111) step and the AgCu NSA would have been almost flat with only an ~0.03 nm height difference coming from the different sizes of Cu and Ag as mentioned (Figure 1B), and the undulations of the 9 × 9 reconstruction. After exposure to 500 L oxygen at 475 K, there are now regions of added and terrace oxide along the AgCu interface. The native Cu(111) terrace is easily identified in the diagram associated with the line scan. The terrace oxide appears darker in the STM image due to it being formed one Cu step height lower than the Cu terrace.

Figure 4 shows STM images and line profiles of the AgCu NSA after 1500 L exposure to oxygen at 500 K. The patches of Cu oxide within the 9 × 9 Ag overlayer are visible in Figure 4A. The line profile reveals an apparent height difference between the Ag layer and Cu oxide patch of ~0.11 nm. These oxide patches have an ordered structure similar to that of the ordered oxides found on Cu(111) such as the "29" or "44" oxides.[26,28,44] Due to the small size of the patches, it was difficult to determine the exact unit cell of these features; however, they exhibited a regular lattice spacing within the ordered oxide regions of ~0.6 nm. This spacing is similar to that previously reported for added oxide where the distance between row features is 0.55–0.70 nm and in line with the 0.6 nm lattice constant of Cu₂O.[26,28,44] Figure 4B
shows a region of the surface with Cu oxide growing over the previously Ag-terminated AgCu NSA. This is apparent from the faint $9 \times 9$ lattice spacing associated with the AgCu NSA, combined with the ordered row structure of the Cu oxide. The line profile gives a step height of 0.21 nm between the oxide covered $9 \times 9$ terraces, consistent with what is expected based on the observed structure of Cu oxide on the AgCu NSA with the overall step height determined by the underlying Cu(111) surface. This result is consistent with the findings of Schweinar et al. who identified the formation of a metastable 2D oxide on the surface of a dilute Cu in Ag alloy in an oxidizing atmosphere. Previous work has also demonstrated the phase segregation of Cu to the surface on AgCu alloys in the presence of oxygen.

In order to investigate the fate of the oxygen, the oxidized AgCu NSA was annealed in ultra-high vacuum (UHV), and both STM and temperature-programmed desorption (TPD) were used to investigate the desorption or diffusion of oxygen. Figure 5 shows the AgCu NSA after annealing the surface to 650 K. This experiment was performed by annealing in 50 K increments and imaging between each 50 K anneal. Only after the 650 K anneal was a significant change observed on the AgCu NSA. Fewer random depressions associated with oxygen within the Ag patches were observed post-anneal, indicating that the anneal caused the oxygen to either desorb from or diffuse off Ag and onto the exposed Cu. The TPD results in Figure 5C indicate that the oxygen does not desorb from the oxidized NSA; therefore it must diffuse from the AgCu NSA to Cu(111) regions where it binds irreversibly as indicated by the lack of an oxygen desorption feature in the TPD experiment.

Additional experiments in which ozone was used as an atomic oxygen source were performed in order to both confirm the presence of adsorbed oxygen and investigate the effect of harsher oxidation environments on the AgCu NSA. Ozone exposures from 5 to 100 L were investigated along with annealing the surface to 650 K and re-exposing it to 20 L ozone. Figure 6A shows the AgCu NSA after exposure to 5 L ozone at 300 K. The random depressions within the Ag $9 \times 9$ reconstruction closely resemble those seen...
after exposure to molecular oxygen at 300 K, confirming the presence of adsorbed atomic oxygen on the Ag regions arising from exposure to both small amounts of ozone or larger amounts molecular oxygen. Figure 6B shows the surface after exposure to 20 L ozone with more of the randomly arranged depressions appearing within the 9 × 9 reconstruction as expected from a larger dose of ozone. The 100 L exposure of ozone resulted in heavily disrupted 9 × 9 reconstructed Ag patches surrounded by Cu oxide (Figure 6D). However, annealing this surface to 650 K reformed the large and ordered domains of the 9 × 9 reconstructed Ag that were free of any depressions associated with adsorbed oxygen and surrounded by ordered Cu oxide. The zoomed in region of Figure 6D shows the ordered Cu oxide with the same ~0.6 nm lattice spacing seen after larger doses of molecular oxygen at elevated temperatures. Figure 6D,E shows that Ag prefers to remain in domains, but their formation competes with the formation of Cu oxide domains, and they no longer grow out exclusively from the Cu step edges as they do in the absence of oxygen. Patches of Cu oxide surrounded by 9 × 9 reconstructed Ag formed hexagonal domains (Figure 6D,E) contrary to their formation on Cu(111), where they have a strong preference for (100)-type steps resulting in triangular terrace oxide domains. Re-exposing the surface from Figure 6D leads to the formation of more individual depressions within the 9 × 9 reconstructed Ag patches shown in Figure 6E. There is also 9 × 9 reconstructed Ag present in the Cu terrace demonstrating that the Ag is highly mobile on the surface and able to fill in the regions of ejected Cu.

4 | CONCLUSIONS

Our STM data provide a visualization of the dynamic nature of the AgCu NSA upon exposure to oxygen. After exposure up to 500 L oxygen at 300 K, randomly distributed depressions were observed on the 9 × 9 reconstructed Ag, consistent with Cu atoms that had segregated up through the Ag layer and become oxidized. Increasing the oxygen exposure to 1500 L at a higher sample temperature of 500 K disrupted the AgCu NSA through the preferential oxidation of Cu and formation of Cu oxide patches. This also led to the formation of regions of ordered Cu oxide capping the 9 × 9 reconstructed Ag, consistent with oxygen-induced segregation of Cu leading to formation of a thin Cu oxide on Ag. With submonolayer deposition of Ag on Cu(111), the step edges on the AgCu surface have monolayer Ag on the ascending step and a Cu terrace on the descending step. Cu ejected from descending step edges in the presence of oxygen can be filled in by either Cu oxide or Ag from the ascending step edge. This led to the formation of Ag patches on the lower step edge seen with oxygen deposition from 300 to 1500 L. These Ag regions also resisted oxidation under harsher oxidation conditions using ozone demonstrating that the Ag is resistant to oxidation, and if extended regions of 9 × 9 Ag are disrupted by the emergence of Cu that segregates through the Ag and forms oxide patches, Ag can reform extended 9 × 9 regions through thermal annealing. Together, this work provides insight into the dynamic nature of the AgCu NSA under oxidative conditions which is of particular interest because AgCu alloys have shown promising properties for use as a heterogeneous selective oxidation catalyst.

CONFLICT OF INTEREST
The authors declare no conflict of interest.

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DATA AVAILABILITY STATEMENT
The original data that support the findings of this study are available by reasonable request to the corresponding author.

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