Real-Time Atomic-Scale Visualization of Reversible Copper Surface Activation during the CO Oxidation Reaction

Langli Luo, Yao Nian, Shuangbao Wang, Zejian Dong, Yang He, You Han, and Chongmin Wang

Abstract: By using in situ aberration-corrected environmental transmission electron microscopy, for the first time at atomic level, the dynamic evolution of the Cu surface is captured during CO oxidation. Under reaction conditions, the Cu surface is activated, typically involving 2–3 atomic layers with the formation of a reversible metastable phase that only exists during catalytic reactions. The distinctive role of CO and O$_2$ in the surface activation is revealed, which features CO exposure to lead to surface roughening and consequently formation of low-coordinated Cu atoms, while O$_2$ exposure induces a quasi-crystalline CuO$_x$ phase. Supported by DFT calculations, it is shown that crystalline CuO$_x$ reversibly transforms into the amorphous phase, acting as an active species to facilitate the interaction of gas reactants and catalyzing CO oxidation.

Introduction

The interaction between gas molecules and catalyst surface is of fundamental importance in heterogeneous catalysis. It has been generally realized that catalysts experience both structural and chemical changes, as directly revealed by emerging in situ characterization methods,[1] which is critical to catalytic processes under reaction conditions. For noble metal catalysts such as Pt and Au, the adsorbed CO molecules can cause the metal surface atoms to restructure[2] and morphological change of supported nanoparticles has also been reported.[3] For transition-metal catalysts such as Cu, the structural and chemical change of the active species should be more vigorous because of the tendency of the valence change of metals. For instance, the Cu/ZnO catalyst for methanol synthesis has been readily reported to experience redox reaction[4] and strong interaction between ZnO support and Cu involving both structural and chemical changes.[5] For Cu as electrocatalysts, surface states of oxide-derived Cu plays a critical role in the electrochemical conversion of CO to liquid fuels but remains largely unknown.[6] Understanding surface behaviors of the transition metal catalysts especially obtaining in situ dynamic information under reaction conditions are essential to identify active sites that lead to the deciphering of the reaction mechanisms.

Specifically, the atomistic process of surface and subsurface dynamics for Cu catalysts in redox reaction remains largely unclear. Exemplified by the water gas shift (WGS) reaction and CO oxidation reaction involving either oxidizing (O$_2$ or H$_2$O) and reducing gases (CO), the valence variation of Cu plays a significant role in catalyzing the reactions. CuO$_x$ phase has been proposed to be more active than pure Cu and CuO based on the studies of nanoparticle catalysts with three phases[7] and CuO nanocrystals have been reported to undergo in situ surface oxidation during the reaction.[8] Surface oxides exist on Cu catalysts exposed to air and even after pretreatment/annealing under an O$_2$-rich reaction condition (1 at% CO in air is usually used in performance test) in accordance with in situ spectroscopy results.[9] Structurally, the reactant gases could re-arrange surface atoms of Cu that the Cu(111) surface with compact and the lowest energy surface, can be activated by CO adsorption to form mobile clusters and become activated for water dissociation in WGS reaction.[10] These observations highlight the strong interaction between Cu and CO deviated from the canonical scenario that needs further investigation. Herein, we use AC-ETEM to visualize atomic-scale dynamics on pure Cu surface under CO oxidation reaction conditions (CO + O$_2$ gas mixture and elevated temperature), where the Cu surface is activated through atomic rearrangement down to 2–3 atomic layers. We also discovered distinctive structural responses to the exposure of CO and O$_2$ on the Cu surface, and the unique role of surface CuO$_x$ species formed on the Cu surface is identified under the real gas reaction conditions. Density functional theory (DFT) calculation and ab initio molecular dynamics (AIMD) simulation corroborate the experimental observa-
tion on the nature of CuO₂ species and its implications for catalytic reactions.

**Results and Discussion**

We use single-crystal Cu thin films to create low-index surfaces for atomic-scale imaging and make real-time video recording in AC-ETEM. The detailed experimental setup is described in Methods in the Supporting Information. The in situ observations are made on (100) and/or (110) surfaces of the Cu from a cross-sectional view (Supporting Information, Figure S1). Single CO or O₂ or a gas mixture of CO and O₂ with an atomic ratio CO/O₂ ≈ 2:1 at about 1 × 10⁻⁴ mbar is introduced to the Cu surface at 350°C inside the microscope column. It should be noted that we choose the stoichiometric ratio rather than CO 1%-Air for the CO oxidation reaction as we focus on the atomistic mechanisms under a thermodynamic equilibrium status while not introducing any kinetic effects.

**Cu Surface Activation under Reaction Conditions**

Real-time atomic-scale structural change on a Cu(100) surface after gas mixture introduction was captured by time-resolved high-resolution (HR) TEM images (Figure 1). First, a clean Cu(100) surface under vacuum (ca. 1 × 10⁻⁸ mbar) is shown in Figure 1a. After 201 s of exposure to the gas mixture, Cu surface atoms slightly deviate from their original positions both laterally and vertically as shown in Figure 1b. This is induced by the adsorption of CO and O₂ gas molecules, and it continues to evolve into the subsurface with increasing exposure time, leading to the atomic rearrangement of the first two atomic layers (ca. 3.6 Å) of Cu(100) surface as shown in Figure 1c. A clear interface (red dashed line) separates the activated surface atoms of disordered phase from perfect bulk Cu face-centered cubic (FCC) lattice, and this surface region finally reaches a thickness of about 4.4 Å after 824 s gas exposure (Figure 1d). The whole activation process is also illustrated by the representations in Figure 1a–d, where we hypothesize that the CO molecules drag the surface atoms out of their original position and O₂ atoms generated through O₂ chemisorption penetrate into the subsurface. We will discuss the different roles of two reactant gases in detail later. We evaluate the degree of atomic structure change on the Cu surface during the reaction by comparing the lateral strain induced by atomic rearrangement during the surface activation process. A significant increase of surface strain before and after gas exposure is found as shown in strain analysis results (Figure 1c,f), respectively. The strain caused by strong gas–metal interaction increases the total free energy of the Cu surface and should be counteracted by the gas adsorption energy and the chemical potential of the CO oxidation reaction. Another noting phenomenon is that once we remove the gas mixture, the surface restores to a perfect FCC structure (Supporting Information, Figure S2), indicating this surface activated structure is, in nature, a metastable phase, that only exists during catalytic reactions.

To decipher different roles of reactant gases in the activation process, we expose Cu surface to CO and O₂, respectively, under the same gas partial pressure and temperature (350°C). Similarly, under high vacuum, the Cu surface shows gradually curved atomic steps forming a smooth surface (Figure 2a). Upon CO exposure (ca. 6.5 × 10⁻⁵ mbar), the smooth Cu surface becomes rough and exposes more low-coordinated surface atoms (Figure 2b). An enlarged HRTEM image (upper, Figure 2e) shows that surface atoms and some of the subsurface atoms largely re-arranged themselves under CO gas. The atomic positions of these atoms are deviated from the original positions in FCC structure and more steps and kinks are seen on reconstructed Cu(001) surface. This perturbation of atomic arrangement in the surface region is induced by strong CO adsorption and bonding with Cu atoms. This finding is in accordance with recent reports that strong interaction between Cu and CO leads to the formation of protonated surface structure.[10] In distinct contrast, the O₂ exposure leads to lattice expansion near the step edges on a stepped Cu(001) surface (from Figure 2d to 2e). When introducing O₂ gas at a pressure of about 3.5 × 10⁻³ mbar, the Cu(002) plane distance increases from 1.81 Å to 2.1 Å (upper, Figure 2f), and a metastable surface oxide appears near the step-edge (labeled by the white arrow in Figure 2e). It is noted that the lattice expansion is more prominent near the...
The surface decreases in pure CO gas environment (h) which induces top surface lattice expansion. A recent study shows that the metallic Cu phase is only maintained under conditions where close to full oxygen conversion is achieved in the CO oxidation reaction. We have also found such surface oxides in our gas experiments given that we have removed native oxides by annealing in H$_2$ gas. The existence of these surface oxides may largely affect the catalytic behaviors of Cu catalysts in terms of altering the gas adsorption and mass/electron transfer. Thus, we further study the structural dynamics of surface oxides on Cu under different gas environments. Figure 3a shows a few layers of surface oxide at the step-edge (white arrows) have a crystalline phase (labeled as c-CuO) with an expanded lattice space (ca. 2.1 Å) compared with that of Cu substrate (002) space (ca. 1.8 Å) and is considered as the product of O$_2$ chemisorption induced surface reconstruction as that shown in Figure 2e. Upon gas mixture (CO + O$_2$) exposure, this c-CuO$_x$ experiences vigorous structural change and transforms into an amorphous phase within a minute as shown in Figures 3b and c. The whole atomic-scale dynamic process is captured by the Supporting Information, Supplementary Video S1, depicting a gradual transition from crystalline to amorphous phase through a layer-by-layer process. As shown in Figure 3b, this phase transition first takes place on the oxide covering step-edge (dashed-line arrow) and after it finishes the phase transition, the oxide on the terrace still possesses a crystalline phase to some extent (solid white arrow), which indicates the phase transition is kinetically dependent on local structures (for example, steps). After 47 s, c-CuO$_x$ decreases by size in pure CO gas environment (h).

**Role of Surface Oxide in CO Oxidation**

Under real CO catalytic reaction conditions, especially the O$_2$-rich gas environment (1 vol% CO balanced with air), the surface oxidizes and the Cu is covered with surface oxides. As shown in the Supporting Information, Figure S3, once in contact with air, the Cu thin film deposited in UHV evaporation apparatus has been covered with a considerable amount (ca. 5 nm in thickness) of native oxide (Cu$_2$O). Even at a very low oxygen pressure, the Cu surface can have O$_2$ chemisorption and surface oxide can be readily formed through a step-edge growth mechanism. A recent study shows that the metallic Cu phase is only maintained under conditions where close to full oxygen conversion is achieved in the CO oxidation reaction. We have also found such surface oxides in our gas experiments given that we have removed native oxides by annealing in H$_2$ gas. The existence of these surface oxides may largely affect the catalytic behaviors of Cu catalysts in terms of altering the gas adsorption and mass/electron transfer. Thus, we further study the structural dynamics of surface oxides on Cu under different gas environments. Figure 3a shows a few layers of surface oxide at the step-edge (white arrows) have a crystalline phase (labeled as c-CuO) with an expanded lattice space (ca. 2.1 Å) compared with that of Cu substrate (002) space (ca. 1.8 Å) and is considered as the product of O$_2$ chemisorption induced surface reconstruction as that shown in Figure 2e. Upon gas mixture (CO + O$_2$) exposure, this c-CuO$_x$ experiences vigorous structural change and transforms into an amorphous phase within a minute as shown in Figures 3b and c. The whole atomic-scale dynamic process is captured by the Supporting Information, Supplementary Video S1, depicting a gradual transition from crystalline to amorphous phase through a layer-by-layer process. As shown in Figure 3b, this phase transition first takes place on the oxide covering step-edge (dashed-line arrow) and after it finishes the phase transition, the oxide on the terrace still possesses a crystalline phase to some extent (solid white arrow), which indicates the phase transition is kinetically dependent on local structures (for example, steps). After 47 s, c-CuO$_x$ decreases by size in pure CO gas environment (h).
transition and being activated. This a-CuO$_x$ keeps a dynamically evolving atomic structure (Supporting Information, Video S1 and Figure S8). This phenomenon is firstly observed here for a surface Cu oxide, as illustrated in Figure 3d.

Moreover, this crystal-to-amorphous phase transition can be reversibly oscillated by alternating between CO and O$_2$ gas environments. The effect of CO and O$_2$ to surface oxides can be disentangled in catalytic reaction through in situ observations under a full cycle of various gas conditions (Figure 3e–h). First, a c-CuO$_x$ island exists on a Cu(110) surface (Figure 3e). Upon O$_2$ introduction, this c-CuO$_x$ island grows from two atomic layers to 4–5 layers within a few minutes (Figure 3f). Then, we introduce CO gas to achieve a mixture gas with an atomic ratio between CO and O$_2$ ca. 2:1, the crystalline phase starts to become amorphous and activated (Figure 3g) similar to that shown in Figure 2a–d, which can be seen as the true structure under real reaction conditions. After O$_2$ gas is removed, the surface oxides are gradually reduced with their dimension decreased (Figure 3h). Finally, we could restore the structure to c-CuO$_x$ by changing gas to pure O$_2$ gas. These in situ observations not only confirm that the crystalline to amorphous phase transition can happen in the CO + O$_2$ gas mixture but also reveal that the CO destabilize the surface oxides while O$_2$ builds up the surface oxides.

To explore the origin of these dynamic structural changes of surface oxides on Cu surface under different gas environments, we employed DFT based AIMD simulation to investigate above gas–oxide interactions. First, we start from a classic missing-row reconstructed Cu surface induced by O$_2$ chemisorption as a stable configuration which is proved by both experiments and calculations.$^{[12]}$ To reflect the configuration of multilayer surface oxide on the Cu surface (Figure 3a), two double-layer missing-row Cu$_x$O$_y$ structures on Cu(100) surface was built and misplaced here. Compared with the ordered double-layer missing-row reconstruction, the misplaced double-layer missing-row Cu$_x$O$_y$ structure is more stable (Supporting Information, Figure S4) and closer to the polygonal structure in the Cu$_x$O$_y$ observed in Figure 3a. Thus, the misplaced double-layer missing-row Cu$_x$O$_y$ on the Cu(100) surface was chosen as the Cu$_x$O$_y$/Cu(100) configuration for the following DFT and AIMD calculations.

All of the adsorption sites of reactants and corresponding adsorption energies are shown in the Supporting Information, Figure S5 and Table S1. Compared with other sites, CO prefers perpendicularly adsorbing at site 3 and O$_2$ prefers to stay at site 4 parallel to CO. The most stable configurations for CO and O$_2$ adsorption are shown in Figure 4a,b. Although their adsorption energies are almost equal with each other (−1.26 and −1.27 eV, respectively), their favorable adsorption sites are different, indicating that there is no competitive adsorption between CO and O$_2$. Both the Mulliken charge analysis (Supporting Information, Table S2) and the electron density difference (EDD) analysis (Figure 4a,b) confirm that the electrons transfer from Cu$_x$O$_y$ surface to CO and O$_2$ reactants through Cu–C and Cu–O chemical bonds.

Based on the analysis of CO and O$_2$ adsorption on the Cu$_x$O$_y$/Cu(100) surface, the mechanism that the structural changes of Cu$_x$O$_y$ crystal under CO and O$_2$ reaction conditions observed in the experiments were performed by AIMD simulations. Monolayer coverage with two CO and two O$_2$ molecules on the Cu$_x$O$_y$/Cu(100) surface is considered as the initial configurations for the AIMD calculations (Figure 4c). After about 1.76 ps evolution, the first O$_2$ molecule dissociates with two of O atoms bonding to surface Cu atoms. With the help of enough vacancy produced by the upward displacement of surface Cu atom bonding to CO molecule, the dissociated O$_6$ atom migrates and bonds to the subsurface Cu atoms (Supporting Information, Video S2). The dissociation process of the second O$_2$ molecule occurs at about 3.25 ps and the dissociated O$_3$ atom bonds to surface Cu atoms while dissociated O$_4$ atom migrates and bonds to the subsurface Cu atoms (Supporting Information, Video S3). The length changes of O$_3$–O$_4$ and O$_5$–O$_6$ bonds (Figure 4d) further confirmed the O$_2$ dissociation. Due to the diffusion of the dissociated O atoms in the Cu$_x$O$_y$ structure, the original lattice O atom is forced to migrate to the interface of Cu$_x$O$_y$ and Cu(100), resulting in the partial oxidation of Cu metal. These processes lead to the crystal distortion in the Cu$_x$O$_y$/Cu(100) configuration and further result in the amorphization of the Cu$_x$O$_y$ crystal as observed in the experiments.

After the dissociation of the adsorbed O$_2$ molecules, the dissociated O$_3$ atom which bonds to surface Cu atoms gradually migrates to the vicinity of CO and bonds to CO to form CO$_2$. The change of C1–O3 distance and O1–C1–O3 angle with the simulation time (Figure 4d) further confirmed the formation of CO$_2$ product. Once the CO$_2$ molecule is formed, it desorbs easily from the catalyst surface (Supporting Information, Video S4). Therefore, the reaction mechanism
of CO oxidation on the active Cu₆O catalyst is not the same as the Mars-van-Krevelen (MvK)¹,² mechanism that happened on the Cu₆O surface. For the MvK mechanism, the CO first reacts with the lattice O atom to produce CO₂, which would produce an oxygen vacancy at the Cu₆O surface. Then, the O₂ molecule dissociates at the O vacancy. Whereas on the active Cu₆O surface, the O₂ molecules dissociate firstly into the lattice due to the unsaturated coordination of Cu atoms in the Cu₆O crystal. Then, the adsorbed CO get a lattice O atom to produce CO₂. In general, the strong chemical interaction between CO and Cu at Cu₆O surface could help the dissociation of O₂ molecule and the migration of dissociated O atoms into the Cu₆O lattice, facilitating the CO oxidation reaction while we observed the amorphization process of the c-Cu₆O.

**Conclusion**

We have observed real-time surface dynamics on Cu at atomic-scale under CO oxidation reaction conditions by AC-ETEM. While pure CO induces surface roughening and O₂ tends to incorporate with surface atoms resulting in surface lattice expansion, the Cu surface can be activated down to two atomic layers upon CO + O₂ gas mixture exposure. Under CO oxidation reaction conditions, the universally existing surface oxide can be activated with a dynamic evolving atomic structure, vigorously interacting with CO and O₂ molecules, which reflects the true structure of active species on the Cu surface. We rationalize these observations with the aid of DFT calculation and AIMD simulation, highlighting the role surface oxides in catalytic CO oxidation reaction, which may be extended to other catalytic redox reactions.

**Acknowledgements**

The authors appreciate the support from the National Natural Science Foundation of China (Grant No. 21873069 and No. 11504162). C.M.W. is supported by the laboratory directed research at Pacific Northwest National Laboratory. Part of the work was conducted in the William R. Wiley Environmental Molecular Sciences Laboratory (EMSL), a DOE User Facility operated by Battelle for the DOE Office of Biological and Environmental Research. Pacific Northwest National Laboratory is operated for the DOE under Contract DE-AC05-76RL01830.

**Conflict of interest**

The authors declare no conflict of interest.

**Keywords:** atomic scale · CO oxidation · copper · electron microscopy · environmental TEM

**How to cite:** Angew. Chem. Int. Ed. 2020, 59, 2505–2509
Angew. Chem. 2020, 132, 2526–2530


Manuscript received: November 25, 2019
Accepted manuscript online: December 9, 2019
Version of record online: December 30, 2019