Structural Changes of Cu(110) and Cu(110)-(2 × 1)-O Surfaces under Carbon Monoxide in the Torr Pressure Range Studied with Scanning Tunneling Microscopy and Infrared Reflection Absorption Spectroscopy

Baran Eren,[†] Zongyuan Liu,[‡] Dario Stacchiola,*,[§] Gabor A. Somorjai,[†] and Miquel Salmeron*,[†,‖]

[†]Materials Sciences Division, Lawrence Berkeley National Laboratory, 1 Cyclotron Road, Berkeley, California 94720, United States
[‡]Chemistry Department, Brookhaven National Laboratory, Upton, New York 11973, United States
[§]Department of Chemistry, Stony Brook University, Stony Brook, New York 11794, United States
[‖]Department of Materials Science and Engineering, University of California, Berkeley, Berkeley, California 94720, United States

ABSTRACT: The atomic structure of the clean Cu(110) and the oxygen covered Cu(110) surfaces in the presence of carbon monoxide (CO) gas in the Torr pressure range at 298 K is studied using scanning tunneling microscopy (STM) and infrared reflection adsorption spectroscopy (IRRAS). We found that the initially clean surface reconstructs to form short rows of Cu atoms along the $[1{-}10]$ direction separated by missing rows. The adsorbed CO molecules show two different C–O stretch vibration modes originating from molecules bound to Cu atoms with different coordination numbers, in the middle and at the end of the atomic rows. On the oxygen covered p(2 × 1) surface, adsorbed CO is observed only after removal of surface O atoms by reaction with CO. In the presence of 1:5 and 1:1 mixtures of O_2 and CO at 298 K, the p(2 × 1)-O reconstructed surface transforms into Cu_2O, instead of reducing to metallic Cu.
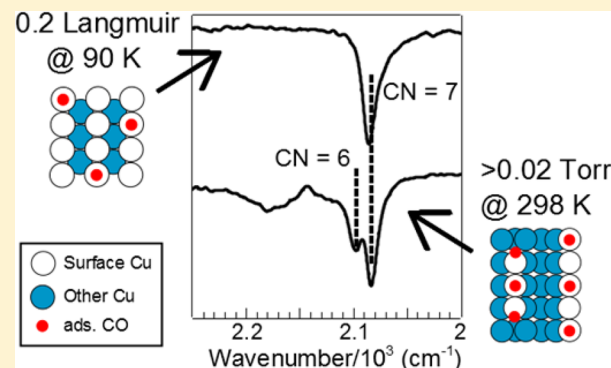
1. INTRODUCTION

Cu-based catalysts are commonly used in industry for various CO conversion reactions, such as CO oxidation,[1−3] methanol synthesis,[4,5] and water–gas shift,[6,7] with CO oxidation being considered a prototypical catalytic reaction.[8−10] This reaction has been investigated extensively on single crystal Cu surfaces, Cu films, and powders.[1,2,10−15] The development of ambient pressure surface science techniques, such as ambient pressure scanning tunneling microscopy (APSTM),[16−19] ambient pressure X-ray photoelectron spectroscopy (APXPS),[20,21] and optical techniques, such as infrared reflection adsorption spectroscopy (IRRAS)[22,23] has made possible monitoring the atomic and chemical structure of surfaces under more realistic conditions,[24] helping to bridge the "pressure gap" separating traditional surface science studies at low pressures (and typically at cryogenic temperatures), and studies under reaction conditions. APSTM provides structural information at the atomic level, while IRRAS and APXPS provide spectroscopic information to identify adsorbed species, their coverage, and the chemical state of the catalyst surface.

Here, we use these techniques to study the CO adsorption on the bare and oxygen-reconstructed Cu(110) surfaces in equilibrium with CO gas in the Torr range pressure. In line with our previous work with Cu(111),[25] we found that the

Cu(110) surface restructures, driven by the energy gained through CO adsorption on new low-coordination Cu sites that are formed at the edges of short linear clusters. IRRAS reveals two different CO vibrational states that correspond to adsorption of the molecule on high- and low-coordination sites. Furthermore, we found that on an oxygen precovered surface, which is relevant to the CO oxidation reaction, adsorbed CO can only be detected after removal of atomic oxygen from the surface by reaction to form CO_2. In the presence of both O_2 and CO (ratios 1:5 and 1:1) at 298 K, the surface oxidizes to Cu_2O.
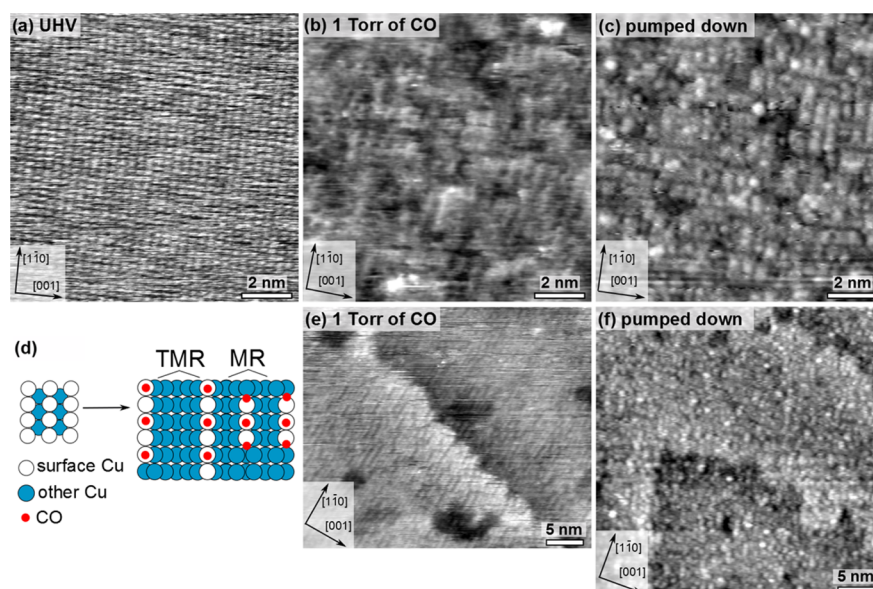
2. METHODS

The APSTM, IRRAS, and APXPS measurements were performed in three different chambers under the same reaction conditions of pressure and temperature. Auger electron spectroscopy (AES) was used in the APSTM and IRRAS chambers to monitor the surface cleanliness before and after the experiments.

Figure 1. STM images of the Cu(110) surface at 298 K: (a) in UHV, (b) and (e) in the presence of 1 Torr of CO, and (c) and (f) after evacuation of CO. Imaging parameters: I_t = 0.6 nA, V_b = 0.1 V for (a), I_t = 1 nA, V_b = 0.1 V for (b), I_t = 0.5 nA, V_b = 0.42 V for (c) and (f), and I_t = 0.8 nA, V_b = 0.1 V for (e). The surface breaks up into short (few nm) linear clusters in the [1−10] direction separated by two or three times the atomic periodicity, resembling "missing rows" (MR) and "triple missing rows" (TMR), as illustrated in the model presented in (d). After the chamber is evacuated from CO, the surface does not recover back to the initial atomically flat Cu(110) surface due to kinetic limitations although no adsorbed CO is present.

2.1. Sample Preparation.

A clean Cu(110) surface was obtained following cycles of Ar sputtering (1 keV, 15 min) and annealing (770−820 K, 10 min). To study the oxygen covered surface the clean sample was exposed to 10 L (Langmuir, 1 L = 10^{-6} Torr × sec) of O_2 at 600 K,[26] which produced a Cu(110)-(2 × 1)-O structure, also referred to as the 'added-row structure', where Cu−O chains are formed in the [001] direction, with a coverage of 0.5 monolayers (ML) of atomic oxygen.

The CO gas was leaked into the chambers starting from a base pressure of ∼1 × 10^{-10} Torr in the APSTM chamber, ∼ 5 × 10^{-10} Torr in the APXPS chamber, and ∼8 × 10^{-10} Torr in the IRRAS chamber. No nickel contamination (from potential Ni-carbonyls) was detected after the experiments.

2.2. APSTM Measurements.

APSTM measurements were performed at 298 K with a custom-built STM scanner using Pt−Ir tips.[18] The STM was operated in the constant current mode by applying a bias to the sample. Imaging parameters are indicated in the figure captions.

2.3. IRRAS Measurements.

IRRAS measurements were performed in a combined UHV chamber with AES and an IRRAS in a reactor cell system coupled to a commercial Fourier transform infrared (FT-IR) spectrometer (Bruker, IFS 66v/S). The spectra were collected with a resolution of 4 cm^{-1} at grazing incidence.[27]

2.4. APXPS Measurements.

APXPS easurements were performed at BL11.0.2 of the Advanced Light Source in Berkeley to determine the nature and coverage of adsorbed species. Calibration of the XPS peak intensities was done by reference to the oxygen 1s peak intensity of the Cu(110)-(2 × 1)-O surface, assigned to 0.5 ML. In this manner the total CO coverage on Cu(110) was estimated to be 0.22 and 0.32 ML under 0.2 and 1 Torr of CO respectively at 298 K.[10] More detailed information can be found in ref 10.

3. RESULTS AND DISCUSSION

3.1. Cu(110).

The images in Figure 1 show the structural changes of the surface that occur in the presence of 1 Torr of CO at 298 K. The initially flat surface (Figure 1a) restructures into short (1−3 nm) linear clusters along the [1−10] direction (Figure 1b and e) separated by 2 lattice distances along the [001] direction, although a few rows can also be seen spaced 3 lattice distances. These are called single, double, or triple missing rows. The latter has two missing rows in the first layer and one missing row in the second layer, and it is difficult to distinguish it from a double missing row in APSTM images. This structure remains kinetically unchanged after pumping the chamber down to 2 × 10^{-9} Torr, which causes desorption of all CO from the surface (Figure 1c and f). As we showed recently, the CO restructured (111) surface becomes very active and react readily with background gases, in particular water.[25] The same is true on the present (110) surface. Differences in the image contrast before and after CO evacuation can be attributed to both the lack of adsorbed CO on the surface and on the tip, and to the presence of small amounts of dissociated water from background adsorption.[25,28]

Theoretical calculations in the context of electrochemical adsorption from aqueous solutions predict CO to bind to Cu atoms with energies between 0.6 and 1 eV at 0.5 ML and below, for separations of 2 and 1 lattice constants along [1−10] on the unreconstructed Cu(110) surface, with similar energies for top or bridge sites of Cu atoms with coordination number (CN) 7. These values do not change appreciably on surfaces with missing single, double, or triple rows.[29] Electron-stimulated desorption ion angular distribution (ESDIAD) experiments at low temperature (32 K) suggest that CO adsorbs on top sites forming short rows in the [1−10] direction,[30] with the two molecules at the end tilted due to the repulsion from nearest neighbor molecules. Some tilting toward the [001] direction is also observed in longer rows.[30] Our STM

images show short Cu rows, with lengths of a few nm. The terminating Cu atoms of these short clusters have a CN = 6. The low coordination number increases the energy gained through CO adsorption.[25] Figure 1d shows proposed models of the surface forming linear nanoclusters.

The features and the wavenumbers in the infrared spectrum of adsorbed CO are very sensitive to the nature of the adsorption sites and their CN.[31] Our IRRAS measurements in the presence of CO at various pressures are shown in Figure 2a.
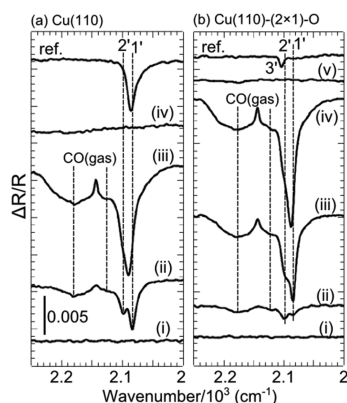
Figure 2. IRRAS spectra of CO adsorption at 298 K on (a) bare Cu(110), and (b) oxygen covered Cu(110)-(2 × 1)-O surfaces. In (a): (i) in UHV, (ii) in the presence of 0.02 Torr of CO, (iii) in the presence of 0.5 Torr of CO, (iv) after evacuation of CO. Top: reference spectrum after dosing 0.2 L of CO with the sample at 90 K. In (b): (i) in UHV, (ii) in the presence of 0.01 Torr of CO, (iii) in the presence of 0.1 Torr of CO, (iv) in the presence of 0.5 Torr of CO, (v) after evacuation of CO. Top: ref spectrum after dosing 0.2 L of CO with the sample at 90 K. CO adsorption peaks are marked with primed numbers: 1′ at 2084−2086 cm⁻¹ due to CO on Cu with CN = 7; 2′ at 2099 cm⁻¹ from CO on Cu with CN = 6; and 3′ at 2104 cm⁻¹ (in b-ref.) from CO on intact Cu(110)-(2 × 1)-O. The absence of this feature in other spectra in (b) is due to the negligible amount of adsorbed CO, due to its low adsorption energy on the oxygen-covered surface. In this surface CO adsorbs only on vacant Cu sites created by the CO + ¹/₂O → CO₂ reaction. Scale bar is the same for (a) and (b).

Apart from the gas phase features, at 0.02 Torr the spectra contain two peaks around 2084 and 2099 cm⁻¹, which we attribute to CO bound to top site Cu atoms with CN = 7 and CN = 6, respectively.[32] In the presence of 0.5 Torr of CO, the spectrum appears as a single feature at around 2091 cm⁻¹ due to the superposition of the previous two peaks, suggesting an increase in the density of clusters with increasing pressure. Once CO gas is evacuated from the chamber, CO desorb completely from the surface as shown in spectrum (iv). A reference spectrum taken at 90 K after a 0.2 L exposure (Figure 2a top spectrum) shows only the 2084 cm⁻¹ feature, appearing slightly shifted to 2086 cm⁻¹ (the literature value at this coverage is 2088 cm⁻¹).[32,33] A similar observation was previously made in experiments on Cu(100), where the CO peak appeared at 22 cm⁻¹ higher wavenumber at ambient pressures relative to that at cryogenic temperatures.[34]

3.2. Cu(110)-(2 × 1)-O. On Cu(110) oxygen forms a p(2 × 1) structure with 0.5 ML of chemisorbed oxygen (see Figure 3a inset for the ball model). Previous STM studies at cryogenic temperatures by other authors suggest that CO adsorbs on top sites of the Cu atoms in the Cu−O added rows chains, slightly displacing them from their initial positions.[35] Also using STM it was proposed that around 400 K the Cu−O chains become
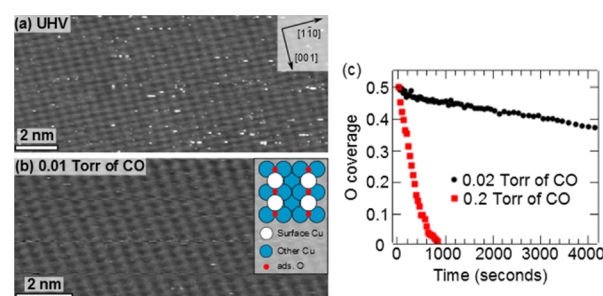

Figure 3. STM images of the Cu(110)-(2 × 1)-O surface (a) in UHV and (b) after ∼1 h in 0.01 Torr of CO. Imaging parameters: I_t = 0.8 nA, V_b = 1.4 V. (c) Variation of the atomic oxygen coverage due to reaction to form CO₂ in the presence of 0.02 and 0.2 Torr of CO measured with APXPS.[10]

mobile, forming defects that serve as active sites for CO to react and remove O from the surface.[36,37] Furthermore, thermal desorption spectroscopy showed a CO desorption peak around 120 K, substantially lower than the 210 K value found on bare Cu(110).[38] The oxygen binding energy on this structure was calculated to be 2.0−2.1 eV,[39] which makes the activation energy for the CO + ¹/₂O₂ → CO₂ reaction higher on this surface than on Cu(100) or Cu(111).[10]

Figure 3a and b shows the STM images of the Cu(110)-(2 × 1)-O surface in UHV and under 0.01 Torr of CO. Using APXPS we found a removal rate of atomic oxygen at 298 K by gas phase CO to be around 0.1 ML/h at 0.01 Torr, as shown in Figure 3c. The IRRAS at 0.01 Torr of CO (Figure 2b-ii) shows the features related to CO at similar positions as on Cu with no preadsorbed oxygen. Since the CO adsorption energy is very low on the oxygen covered surface, we conclude that the observed features are due to CO molecules adsorbed on empty sites created by reaction of the chemisorbed O with CO to form CO₂. The chemisorbed CO can then drive Cu to reconstruct into linear nanoclusters, as on the clean surface. This is indeed in line with both the thermal desorption studies in ref[38] and our STM images showing only intact Cu(110)-(2 × 1)-O structure at this pressure (Figure 3b−compare with Figure 3a measured in UHV), during the initial stages of O removal. IRRAS data acquired after a few minutes at 0.2 Torr and above shows only the features of CO adsorbed on bare Cu (Figure 2b-iii and (iv)). In summary, in the presence of only CO in the gas phase, the Cu(110)-(2 × 1)-O surface reduces gradually to the reconstructed metallic Cu(110) surface with chemisorbed CO.

Figure 4 shows the IRRAS spectra when both CO and O₂ are present in the gas phase. At a O₂:CO ratio of 1:5, the main CO adsorption feature (labeled 4′) is found at 2116 cm⁻¹ and is due to CO on Cu₂O.[31] This feature becomes dominant with time as steady state is reached. No feature due to CO on CuO (2148 cm⁻¹) is apparent. Another prominent feature (5′) is visible at 2133 cm⁻¹, which might be due to CO coadsorbed with atomic oxygen on a Cu₂O surface, a precursor phase to full oxidation of Cu. When the CO:O₂ ratio is 1:1, this feature increases slightly in intensity while the feature at 2116 cm⁻¹ slightly loses intensity because more atomic oxygen adsorbs near CO. These spectra show that the addition of O₂ to the gas phase oxidizes the Cu(110)-(2 × 1)-O surface to Cu₂O even in a O₂:CO ratio of 1:5.
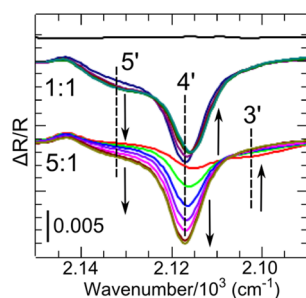
Figure 4. IRRAS spectra on the Cu(110)-(2 × 1)-O surface in the presence of CO and O_2 as a function of time. The lower set of spectra were acquired at a total pressure of 0.12 Torr, and the central spectra were acquired at a total pressure of 0.2 Torr with O_2:CO ratios as 1:5 and 1:1, respectively. The spectrum at the top is obtained after evacuation of the chamber. Three IRRAS features exist: 3′ at around 2104 cm^{-1} from CO on intact Cu(110)-(2 × 1)-O, 4′ at around 2116 cm^{-1} from CO on Cu_2O,[31] and, 5′ at around 2133 cm^{-1} from CO on Cu_2O together with coadsorbed atomic oxygen. The 5′ feature overlaps with a gas-phase feature. No feature related to CO on CuO at 2148 cm^{-1} is apparent.[31] Arrows indicate the time evolution, which shows that Cu(110)-(2 × 1)-O surface reacts with gas phase O_2 and transforms to Cu_2O, indicating that even at O_2:CO ratios of 1:5 oxidization is favored. When the partial pressure of O_2 is increased, a decrease in the intensity of the 2116 cm^{-1} takes place together with a slight increase in the intensity of the 2133 cm^{-1} feature. Once the chamber is pumped down, no CO remains adsorbed on the surface (upper spectrum).

4. CONCLUSION

Using APSTM we have shown that the clean Cu(110) surface exposed to 1 Torr of CO at 298 K reconstructs to form missing row structures separated by 2 and 3 atomic periods along the [001] direction. The rows are not continuous but appear in segments a few nm long. APXPS indicated the coverage of CO at this pressure to be 0.32 ML. After CO evacuation the structures remain due to kinetic limitations.

IRRAS revealed that two types of CO adsorption sites exist characterized by features at frequencies corresponding to adsorption on Cu atoms with CN of 7 (in the middle of the Cu chains) and 6 at the end of the chain clusters. The extra adsorption energy of CO to the lower-coordinated Cu atoms at the chain ends explains the formation of short Cu atom clusters.

We also found that on the oxygen covered Cu(110) p(2 × 1)-O surface CO adsorbs only on the vacancies created by the reaction of the chemisorbed O with CO. When both O_2 and CO are present in the gas phase, the surface further oxidizes to Cu_2O, even at a O_2:CO ratio of 1:5.

AUTHOR INFORMATION

Corresponding Authors

*Phone: +1-631-344-4378. E-mail: djs@bnl.gov.
*Phone: +1-510-486-6704. E-mail: mbsalmeron@lbl.gov.

Notes

The authors declare no competing financial interest.

REFERENCES

(1) Szanyi, J.; Goodman, D. W. CO Oxidation on a Cu(100) Catalyst. *Catal. Lett.* **1993**, *21*, 165−174.

(2) Domagala, M. E.; Campbell, C. T. The Mechanism of CO Oxidation over Cu(110): Effect of CO Gas Energy. *Catal. Lett.* **1991**, *9*, 65−70.

(3) Royer, S.; Duprez, D. Catalytic Oxidation of Carbon Monoxide over Transition Metal Oxides. *ChemCatChem* **2011**, *3*, 24−65.

(4) Klier, K. Methanol Synthesis. In *Advances in Catalysis*; Eley, D. D., Pines, H., Weisz, P. B., Eds.; Academic Press: New York, 1982; Vol. 31, p 243.

(5) Graciani, J.; Mudiyanselage, K.; Xu, F.; Baber, A. E.; Evans, J.; Senanayake, S. D. Highly Active Copper-ceria and Copper-ceria-titania Catalysts for Methanol Synthesis from CO2. *Science* **2014**, *345*, 546−550.

(6) Newsome, D. S. The Water-Gas Shift Reaction. *Catal. Rev.: Sci. Eng.* **1980**, *21*, 275−318.

(7) Stacchiola, D. J. Tuning the Properties of Copper-Based Catalysts Based on Molecular in Situ Studies of Model Systems. *Acc. Chem. Res.* **2015**, *48*, 2151−2158.

(8) Wintterlin, J.; Völkening, S.; Janssens, T. V. W.; Zambelli, T.; Ertl, G. Atomic and Macroscopic Reaction Rates of a Surface-Catalyzed Reaction. *Science* **1997**, *278*, 1931−1934.

(9) Freund, H.-J.; Meijer, G.; Scheffler, M.; Schlögl, R.; Wolf, M. CO Oxidation as a Prototypical Reaction for Heterogeneous Processes. *Angew. Chem., Int. Ed.* **2011**, *50*, 10064−10094.

(10) Eren, B.; Lichtenstein, L.; Wu, C. H.; Bluhm, H.; Somorjai, G. A.; Salmeron, M. Reaction of CO with Preadsorbed Oxygen on Low-Index Copper Surfaces: An Ambient Pressure X-ray Photoelectron Spectroscopy and Scanning Tunneling Microscopy Study. *J. Phys. Chem. C* **2015**, *119*, 14669−14674.

(11) Eren, B.; Heine, Ch.; Bluhm, H.; Somorjai, G. A.; Salmeron, M. Catalyst Chemical State during CO Oxidation Reaction on Cu(111) Studied with Ambient-Pressure X-ray Photoelectron Spectroscopy and Near Edge X-ray Adsorption Fine Structure Spectroscopy. *J. Am. Chem. Soc.* **2015**, *137*, 11186−11190.

(12) Yang, F.; Choi, Y. M.; Liu, P.; Hrbek, J.; Rodriguez, J. A. Autocatalytic Reduction of a CuO/Cu(111) Surface by CO: STM, XPS, and DFT Studies. *J. Phys. Chem. C* **2010**, *114*, 17042−17050.

(13) Baber, A. E.; Xu, F.; Dvorak, F.; Mudiyanselage, K.; Soldemo, M.; Weissenrieder, J.; Senanayake, S. D.; Sadowski, J. T.; Rodriguez, J. A.; Matolin, V.; et al. In Situ Imaging of CuO2 under Reducing Conditions: Formation of Metallic Fronts by Mass Transfer. *J. Am. Chem. Soc.* **2013**, *135*, 16781−16784.

(14) Jernigan, G. G.; Somorjai, G. A. Carbon-Monoxide Oxidation over Three Different Oxidation-States of Copper: Metallic Copper, Copper (I) Oxide, and Copper (Ii) Oxide - A Surface Science and Kinetic-Study. *J. Catal.* **1994**, *147*, 567−577.

(15) Huang, T.-J.; Tsai, D.-H. CO Oxidation Behavior of Copper and Copper Oxides. *Catal. Lett.* **2003**, *87*, 173−178.

(16) McIntyre, B. J.; Salmeron, M.; Somorjai, G. A. A Variable Pressure/Temperature Scanning Tunneling Microscope for Surface Science and Catalysis Studies. *Rev. Sci. Instrum.* **1993**, *64*, 687−691.

(17) Laegsgaard, E.; Osterlund, L.; Thostrup, P.; Rasmussen, P. B.; Stensgaard, I.; Besenbacher, F. A High-pressure Scanning Tunneling Microscope. *Rev. Sci. Instrum.* **2001**, *72*, 3537−3542.

(18) Tao, F.; Tang, D.; Salmeron, M.; Somorjai, G. A. A New Scanning Tunneling Microscope Reactor Used for High-pressure and High-temperature Catalysis Studies. *Rev. Sci. Instrum.* **2008**, *79*, 084101.

(19) Besenbacher, F.; Thostrup, P.; Salmeron, M. The Structure and Reactivity of Surfaces Revealed by Scanning Tunneling Microscopy. *MRS Bull.* **2012**, *37*, 677−681.

(20) Salmeron, M.; Schlögl, R. Ambient Pressure Photoelectron Spectroscopy: A New Tool for Surface Science and Nanotechnology. *Surf. Sci. Rep.* **2008**, *63*, 169−199.

(21) Salmeron, M. Physics and Chemistry of Material Surfaces under Ambient Conditions of Gases and Liquids: What's New? *MRS Bull.* **2013**, *38*, 650−657.

(22) Hoffmann, F. M. Infrared Reflection-absorption Spectroscopy of Adsorbed Molecules. *Surf. Sci. Rep.* **1983**, *3*, 107−192.

(23) Zaera, F. New Advances in Infrared Absorption Spectroscopy for the Characterization of Heterogeneous Catalytic Reactions. *Chem. Soc. Rev.* **2014**, *43*, 7624−7663.

(24) Tao, F.; Salmeron, M. In Situ Studies of Chemistry and Structure of Materials in Reactive Environments. *Science* **2011**, *331*, 171−174.

(25) Eren, B.; Zherebetskyy, D.; Patera, L. L.; Wu, C. H.; Bluhm, H.; Africh, C.; Wang, L.-W.; Somorjai, G. A.; Salmeron, M. Activation of Cu(111) Surface by Decomposition into Nanoclusters Driven by CO Adsorption. *Science* **2016**, *351*, 475−478.

(26) Ling, W. L.; Takeuchi, O.; Ogletree, D. F.; Qiu, Z. Q.; Salmeron, M. STM Studies on the Growth of Monolayers: Co on Cu(110) with One half Monolayer of Preadsorbed Oxygen. *Surf. Sci.* **2000**, *450*, 227−241.

(27) Hrbek, J.; Hoffmann, F. M.; Park, J. B.; Liu, P.; Stacchiola, D.; Hoo, Y. S.; Ma, S.; Nambu, A.; Rodriguez, J. A.; White, M. G. Adsorbate-Driven Morphological Changes of a Gold Surface at Low Temperatures. *J. Am. Chem. Soc.* **2008**, *130*, 17272−17273.

(28) Yamamoto, S.; Andersson, K.; Bluhm, H.; Ketteler, G.; Starr, D. E.; Schiros, T.; Ogasawara, H.; Pettersson, L. G. M.; Salmeron, M.; Nilsson, A. Hydroxyl-Induced Wetting of Metals by Water at Near-Ambient Conditions. *J. Phys. Chem. C* **2007**, *111*, 7848−7850.

(29) Shaw, S. K.; Berná, A.; Feliu, J. M.; Nichols, R. J.; Jacob, T.; Schiffrin, D. J. Role of Axially Coordinated Surface Sites for Electrochemically Controlled Carbon Monoxide Adsorption on Single Crystal Copper Electrodes. *Phys. Chem. Chem. Phys.* **2011**, *13*, 5242−5251.

(30) Ahner, J.; Mocuta, D.; Ramsier, R. D.; Yates, J. T., Jr. Adsorbate−adsorbate Repulsions - The Coverage Dependence of the Adsorption Structure of CO on Cu(110) as Studied by Electron-stimulated Desorption Ion Angular Distribution. *J. Chem. Phys.* **1996**, *105*, 6553−6559.

(31) Xu, F.; Mudiyanselage, K.; Baber, A. E.; Soldemo, M.; Weissenrieder, J.; White, M. G.; Stacchiola, D. J. Redox-Mediated Reconstruction of Copper during Carbon Monoxide Oxidation. *J. Phys. Chem. C* **2014**, *118*, 15902−15909.

(32) Pischel, J.; Pucci, A. Low-Temperature Adsorption of Carbon Monoxide on Gold Surfaces: IR Spectroscopy Uncovers Different Adsorption States on Pristine and Rough Au(111). *J. Phys. Chem. C* **2015**, *119*, 18340−18351.

(33) Woodruff, D. P.; Hayden, B. E.; Prince, K.; Bradshaw, A. M. Dipole coupling and chemical shifts in IRAS of CO adsorbed on Cu(110). *Surf. Sci.* **1982**, *123*, 397−412.

(34) Truong, C. M.; Rodriguez, J. A.; Goodman, D. A. CO Adsorption Isotherms on Cu(100) at Elevated Pressures and Temperatures Using Infrared Reflection Absorption Spectroscopy. *Surf. Sci.* **1992**, *271*, L385−L391.

(35) Feng, M.; Cabrera-Sanfelix, P.; Lin, C.; Arnau, A.; Sánchez-Portal, D.; Zhao, J.; Echenique, P. M.; Petek, H. Orthogonal Interactions of CO Molecules on a One-Dimensional Substrate. *ACS Nano* **2011**, *5*, 8877−8883.

(36) Crew, W. W.; Madix, R. J. A Scanning Tunneling Microscopy Study of the Oxidation of CO on Cu(110) at 400 K: Site Specificity and Reaction Kinetics. *Surf. Sci.* **1996**, *349*, 275−293.

(37) Crew, W. W.; Madix, R. J. CO Adsorption and Oxidation on Oxygen Precovered Cu(110) at 150 K: Reactivity of Two Types of Adsorbed Atomic Oxygen Determined by Scanning Tunneling Microscopy. *Surf. Sci.* **1996**, *356*, 1−18.

(38) Hirschwald, W.; Schneider, T. Adsorption States of Carbon Monoxide on Oxygenated Cu(110) Faces. *Catal. Lett.* **1992**, *16*, 335−343.

(39) Duan, X.; Warschkow, O.; Soon, A.; Delley, B.; Stampfl, C. Density Functional Study of Oxygen on Cu(100) and Cu(110) Surfaces. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2010**, *81*, 075430.