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Ethan J. Crumlin, Cynthia M. Friend, and Miquel B. Salmeron

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Structure of the Clean and Oxygen-covered Cu(100) Surface at Room Temperature in the Presence of Methanol Vapor in the 10 to 200 mTorr Pressure Range

Baran Eren, †, Heath Kersell, †, Robert S. Weatherup, †, Christian Heine, †, Ethan J. Crumlin, ‡, Cynthia M. Friend, #, Miquel B. Salmeron, †, ¶ ,*

† *Materials Sciences Division and* ‡ *Advanced Light Source, Lawrence Berkeley National Laboratory, 1 Cyclotron Road, Berkeley, California 94720, United States,* # *Paulson School of Engineering and Applied Sciences, Harvard University, Cambridge, Massachusetts 02138, United States,* ¶ *Department Materials Science and Engineering, University of California, Berkeley, California 94720, United States*

*Phone: +1-510-486-6704 E-mail: mbsalmeron@lbl.gov

Abstract (less than 150 words)

Using ambient pressure x-ray photoelectron spectroscopy (APXPS) and high pressure scanning tunneling microscopy (HPSTM) we show that in equilibrium with 0.01 to 0.2 Torr of methanol vapor, at room temperature, the Cu(100) surface is covered with methoxy species forming a c(2×2) overlayer structure. In contrast, no methoxy is formed if the surface is saturated with an ordered oxygen layer, even when the methanol pressure is 0.2 Torr. At oxygen coverages below saturation methanol dissociates and reacts with the atomic oxygen, producing methoxy and formate on the surface, and formaldehyde that desorbs to the gas phase. Unlike the case of pure carbon monoxide and carbon dioxide, methanol does not induce the restructuring of the Cu(100) surface. These results provide insight into catalytic anhydrous production of aldehydes.

1. INTRODUCTION

Heterogeneous catalytic reactions are complex chemical processes involving many reaction steps such as adsorption of the reactants, bond-breaking, and new bond-formation on the catalyst surface. Experiments under low pressure and cryogenic temperature conditions on well-defined single crystal surfaces have until recently been the general approach for providing an atomic/molecular level understanding of phenomena related to the adsorption step, such as coverage, surface reconstructions, heat of adsorption, and the nature of adsorbed intermediates.[1,2] Although traditional surface science studies with various spectroscopy and microscopy techniques, together with theoretical calculations, constitute the basis of our current knowledge, kinetic limitations imposed by the low temperature and low pressure conditions may hinder certain dynamic processes and structures that manifest only in equilibrium with the gas phase. Over the last two decades, new experimental techniques have been developed that enable the application of surface science techniques to higher pressure and temperature conditions, thus expanding the study of model catalysts to cover a wider range of the thermodynamic phase diagram.

The ‘methanol economy’ is one of the roadmaps proposed as a sustainable alternative to the currently prevalent ‘oil economy’. Partial oxidation is one of the main approaches for chemical conversion of alcohols and is especially important for onboard hydrogen generation in fuel-cell powered vehicles because of the high reaction rate and exothermicity.[3] The Cu/ZnO_x system is especially important as it exhibits impressive activity and selectivity towards hydrogen formation, which has driven much of the research on co-adsorption of methanol (CH_3OH) and oxygen and formation of products such as surface methoxy (CH_3O-M), formaldehyde (CH_2O), and surface formate (COO-M). Early work in the literature performed on Cu surfaces under UHV includes structural studies using x-ray absorption spectroscopy (XAS), scanning tunneling microscopy (STM), and infrared reflection absorption spectroscopy (IRRAS),[4-6] as well as adsorbate identification with x-ray photoelectron spectroscopy (XPS) and other techniques.[7-9] XAS and XPS were also used under reaction conditions.[10-13] Under both UHV and ambient pressure conditions methoxy was found to be the main reaction intermediate in all cases, irrespective of whether single crystals, foils, powder catalysts or supported nanoparticles were used.[3]

Cu-based catalysts are used for several important conversion reactions, including CO oxidation ($2CO+O_2\rightarrow 2CO_2$),[14-17] water gas shift and reverse water gas shift ($CO+H_2O\leftrightarrow CO_2+H_2$),[18-19] methanol synthesis ($CO_2+3H_2\rightarrow CH_3OH+H_2O$),[20-21] partial oxidation ($2CH_3OH+O_2\rightarrow 2CH_2O+2H_2O$, and $2CH_3OH+O_2\rightarrow 2CO_2+4H_2$),[3] anhydrous formaldehyde formation from methanol ($CH_3OH\rightarrow CH_2O+H_2$), steam reforming ($CH_3OH+H_2O\rightarrow CO_2+3H_2$),[22] and auto-thermal reforming (combination of $CH_3OH+H_2O\rightarrow CO_2+3H_2$ and $2CH_3OH+3O_2\rightarrow 2CO_2+4H_2O$) of methanol.[22] The combination of ambient pressure XPS

(APXPS),[23-24] and high pressure STM (HPSTM)[25-28] has proven to be a powerful way to understand various processes occurring at surfaces. Using this approach we have recently shown that low Miller index Cu surfaces can break up into nanoclusters in the presence of CO,[29-31] or CO_2,[32] a result that we explained in terms of their different binding energies on steps and terraces.

Among the alcohol oxidation reactions, anhydrous formaldehyde formation is the most desirable because H_2 is the valuable product, and the undesired water by-product does not need to be separated with an additional expensive process. For these reason, the reaction of CH_3OH on Cu(100) to form methoxy, the first step for formaldehyde formation, is investigated in the present work. We found that: a) the Cu surface does not break up into clusters of Cu atoms but remains intact in equilibrium with CH_3OH vapor at room temperature (298 K); b) more than 90% of the surface is covered with methoxy species arranged in an ordered c(2×2) structure (equivalent to $(\sqrt{2}\times\sqrt{2})R45°$); c) when the surface is fully pre-covered with an ordered layer of atomic oxygen with $(2\sqrt{2}\times\sqrt{2})R45°$ structure no significant amounts of methanol or methoxy are observed on the surface; d) if the Cu surface is only partially covered by oxygen, a rapid reaction that removes oxygen and produces methoxy, formate, and gas phase formaldehyde takes place.

2. EXPERIMENTAL

The HPSTM and APXPS measurements were performed in two different chambers with a base pressure of 1×10^{-9} Torr. The Cu(100) surface was prepared by cycles of Ar^+ sputtering (1 keV, 15 min), and annealing (823 K, 10 min). The oxygen saturated Cu(100)-$(2\sqrt{2}\times\sqrt{2})R45°$-O surface was prepared by dosing 1000 Langmuir O_2 at 520 K.[33] Methanol gas was introduced from the vapor/liquid phase in a container through a leak valve. Dissolved air in liquid methanol was removed by several freeze-pumping cycles. The purity of the methanol gas was checked with mass spectroscopy. As explained in the Supporting Information (SI), desorption from the chamber walls and pumps upon introduction of methanol produces a small background containing water, H_2 and other components, as shown in Figure S1.

A home-built STM scanner with Pt-Ir tips was used for HPSTM measurements.[27] The images were acquired at constant tunneling current with the bias applied to the sample. Imaging parameters are indicated in the figure captions.

The APXPS measurements were performed at beamline 9.3.2 of the Advanced Light Source at the Lawrence Berkeley National Laboratory.[34] Photon energies ($E_{h\nu}$) of 785, 540, and

325 eV were used to produce photoelectrons with a kinetic energy (E_{kin}) of 250 eV in the O 1s, C 1s, and Cu 3p regions, respectively. The binding energy scale was set by assigning the origin to the Fermi level in the spectra acquired for each photon energy. Coverage estimations were done using the O 1s to Cu 3p peak intensity ratio for each surface species and using the peak ratio for the Cu(100)-(2√2×√2)R45°-O surface as reference for 0.5 ML coverage.

3. RESULTS AND DISCUSSION

3.1 Chemical Analysis with APXPS

The APXPS peaks in the C 1s and O 1s regions are assigned to methanol derivatives at different CH_3OH pressures (Figure 1a and b lower panels), based on the literature.[8,12,13] All the peak positions are summarized in Table S1. An important consideration is that surface reconstruction (e.g., formation of Cu clusters) induced by the high coverage under ambient pressures can alter XPS peak positions due to adsorption at low coordinated sites. However, in contrast to the case of CO and CO_2,[29-32] in the present case with CH_3OH we did not observe Cu reconstruction, as we will show later by HPSTM.

Identification of adsorbed species: In the presence of 1×10^{-7} – 0.4 Torr of CH_3OH, the dominant adsorbed species is methoxy which produces peaks (marked ξ) around 530.2-530.4 eV and 285.2-285.5 eV in the binding energy scale.[8,12] This is consistent with a recent sum frequency generation study showing spontaneous methanol dissociation and formation of a methoxy covered Cu surface in the presence of 1 Torr of methanol at room temperature.[35] Since the methoxy peaks overlap only moderately with peaks from other species, particularly in the O 1s region, it makes their assignment unequivocal (Table S1). Gas phase methanol peaks are observed at 288.0 and 534.2 eV (marked β),[12-13] with the exact position depending on sample work function. Peaks from adsorbed molecular methanol, observed at cryogenic temperatures, would appear at 533.8 and 287.4 eV in the binding energy scale,[36] which might be superimposed to gas phase methanol and surface formate peaks in the O 1s and C 1s regions, respectively. The presence of a small peak at around 533.8 eV in the presence of 1×10^{-7} Torr of methanol, with no gas phase peaks detectable at this pressure, and the formate peak in the O 1s region separated by more than 2 eV from the adsorbed methanol peak, indicates that only a negligible amount molecular methanol could be present on the surface. The area of this peak would correspond to a coverage around 0.02 ML. Unfortunately it is not possible to make a coverage estimation at higher pressures due to superimposition with the gas phase methanol peak.

In spite of the low base pressure in the measurement chambers (1×10^{-9} Torr), the spectra acquired in UHV show small contributions from atomic oxygen (~529.6 eV), hydroxyl (~531.1 eV), and molecular H_2O (~534 eV) with a total coverage of less than 0.05 ML. As a result we also observe small amounts of surface formate once methanol is introduced into the chamber, with XPS peaks at around 531.4 eV and 287.5 eV (marked γ),[8,12] even with no oxygen in the gas phase. We propose that the surface oxygen originates from segregation of O dissolved in the subsurface region of the Cu crystal. Adsorbed methanol reacts with the adsorbed O to form methoxy which in turn forms CH_2O, visible as a gas species with peaks at ~290 and 534.5 eV (marked α).[12-13] CH_2O can also originate from the dry dehydrogenation reaction, i.e., from reaction of methoxy on clean Cu. In the O 1s region, this peak cannot be easily distinguished from the gas phase methanol peak due to their similar positions.[13] The energy resolution in the C 1s region at beamline 9.3.2 is currently higher than in the O 1s region,[32] making peak assignments easier and more accurate in the C 1s spectrum. In addition water and hydroxide, with XPS peak energies close to those of CH_3OH(gas) and formate, respectively, make assignment of reaction products and intermediates less accurate in the O 1s region.

Thermal desorption spectroscopy measurements of methanol on low Miller index Cu surfaces performed under UHV conditions show a methanol desorption peak below 150 K, and a formaldehyde peak in the 350-380 K range.[7,37] The latter peak indicates that the first dehydrogenation to form methoxy has likely occurred below room temperature while the second dehydrogenation reaction to form formaldehyde occurs above 350 K. The formation of methoxy under such UHV conditions is likely to occur at the step edges where it remains bound.[38,39] In the present case at room temperature, it is possible that methoxy formed at step edges spills over to the terraces to cover the entire surface. However due to the much higher methanol pressure, it is also possible that direct dehydrogenation on the terraces at room temperature provides enough methoxy after a short exposure time. It is important to mention that under UHV conditions, water was found to enable methoxy formation on a Cu(111) surface.[40] Since the amount of water impurities is likely higher at ambient pressures it can also play a role in the present work.

Steady-state gas mixture: When O_2 is added into the gas mixture (XPS spectra shown in Figure 1 upper panels), a peak due to gas phase O_2 appears at 539 eV (marked χ). The paramagnetic O_2 doublet is not resolved due to the relatively low energy resolution in that region, as mentioned above. There are two more important observations: 1- We do not observe gas phase CO_2(gas) (peak positions: 292.8 eV and 536.5 eV),[32] indicating that there is no oxidation of formate; 2-There is no significant peak at 529.6 eV associated with atomic oxygen. This is in part due to the proximity to the intense methoxy peak that it makes difficult to detect O with coverage below 0.05 monolayers (ML). These results are consistent with atomic oxygen immediately reacting with methoxy to form CH_2O (290 eV) and formate (287.5 eV and 531.4 eV) (Figure 1b). Carbonate, which can form due to beam induced effects, has a C 1s peak at 289.3 eV and an O 1s peak at 532 eV (both close to formaldehyde and formate peak positions, respectively).[41] Since no increase of these peaks was observed over time, we conclude that no carbonate forms on the surface.

Pressure-dependent coverage of adsorbed species: In order to determine the coverage of different species as a function of pressure we normalized the peak intensities with respect to the Cu 3p peak intensity measured at the same kinetic energy (Figure 2a and b). The methoxy and formate peak intensities vary in a similar manner in the C 1s and O 1s regions. With increasing methanol pressure, the normalized intensity of methoxy increases up to 0.01 Torr, above which it stays constant. This suggests that at 298 K saturation is already reached at this pressure. As expected, once O_2 is dosed the formate coverage increases as the methoxy coverage decreases. Similarly, Figure 1b shows that the gas phase CH_2O intensity also increases with increasing O_2 pressure in the gas mixture.

The formate coverage, determined from the normalized peak intensity, increases with increasing methanol pressure (Figure 2 lower panels). This is explained by saturation of the methoxy coverage, whilst the equilibrium coverage of formate increases with the increasing partial pressure of water impurities, i.e., methoxy is oxidized by the water impurities to form formate.

Using the O 1s to Cu 3p peak intensity ratio of the well-known Cu(100)-$(2\sqrt{2}\times\sqrt{2})R45°$-O surface structure as a reference for 0.5 ML of oxygen coverage (dashed horizontal blue line in Figure 2b), we estimate a methoxy coverage of ~0.65 ML at saturation. However, as will be shown with HPSTM below, the methoxy coverage is actually around 0.5 ML. We believe the coverage over-estimation with APXPS is due to some contribution from water and hydroxyl in the O 1s spectrum.

3.2 Surface Structure with HPSTM

Cu(100) surface covered with low coverage (disordered) oxygen: As previously discussed, at a base pressure of 1×10^{-9} Torr the surface contains small amounts of atomic oxygen and OH groups, from bulk segregation and water adsorption, which produce dark spots (depressions in STM contrast) in the images (Figure 3a). When the surface was prepared at lower base pressures (e.g., 1×10^{-10} Torr), the dark spots are much less frequent (Figure S2). At a CH_3OH pressure of 5×10^{-8} Torr, the dark spots on the surface decrease in density and completely disappear once the pressure is increased to 3×10^{-6} Torr (Figure 2b and S3). This is in line with the APXPS spectra which show no peaks of atomic oxygen on the surface, because it reacts with methanol to form methoxy or with methoxy to form formate or CH_2O. The absence of any distinguishable features in Figure 3b suggests methoxy is diffusing rapidly across the surface due to the low coverage in equilibrium with 3×10^{-6} Torr CH_3OH.

Cu(100) surface pre-covered with oxygen: Ordered oxygen structures lie between the disordered O/Cu and Cu_2O stability regions of the thermodynamic phase diagram, such as the Cu(100)-$(2\sqrt{2}\times\sqrt{2})R45°$-O surface structure which corresponds to 0.5 ML atomic oxygen.[33] In this structure, one of every fourth Cu rows is missing while oxygen occupies pseudo-hollow sites similar to the hollow sites on the bare surface but 3-fold coordinated due to the missing Cu rows (Figure S4d shows a ball model). Missing rows appear both in the [001] and [010] directions, which are equivalent on the (100) surface. Figure 3c shows an atomically resolved image of this structure. The STM contrast is explained in references 33 and 42. This structure remains intact even after 0.5 hours of exposure to 0.02-0.2 Torr of CH_3OH, as shown with the HPSTM image in Figures 3d and S4. Similarly, we observed no change in atomic oxygen intensity with APXPS during 0.5 hours under 0.02-0.2 Torr of CH_3OH (Figure S5). In a recent work, we showed that this surface structure also changes negligibly in the presence of 0.02 Torr of CO, with the atomic oxygen intensity decreasing at a slow rate of 1×10^{-4} ML/s for the first 0.5 hours.[43] In the present case with methanol, oxygen pre-adsorption at low coverages facilitates methoxy formation but not at high oxygen coverages. Wachs and Madix related this to the lower sticking coefficient of methanol on Cu(110) when the oxygen coverage if above 0.2 ML.[7] Leibsle and coworkers also observed a lower reactivity at higher oxygen-covered Cu(110) surfaces.[44] In their further work the authors intentionally used surfaces where the atomic oxygen coverage was 0.25 ML or below in order to observe methoxy and formate from the reaction, which occurs at the edges of the Cu-O added row chains.[45] We can thus conclude that methanol adsorption and reaction with the preadsorbed oxygen happens at a much lower rate when the surface is saturated (i.e., 0.5 ML coverage) with oxygen.

Bare Cu(100) surface: The interaction of methanol with a clean Cu(100) surface at 298 K proceeds via O-H bond scission, yielding methoxy and hydrogen.[46,47] With the present results we cannot determine if the scission reaction occurs at the steps as suggested in the literature under UHV conditions[38] followed by diffusion of the methoxy species to fill the terraces, or if scission occurs directly on terrace sites. The hydrogen from the O-H bond scission can then desorb as H_2, as the hydrogen desorption peaks at ~330 K for Cu(110),[48] and presumably at lower temperature for Cu(100) or even below in the presence of other adsorbed species. Methoxy is relatively stable on clean Cu(100) and dissociates to formaldehyde with a rate several orders of magnitude lower than that for dissociation of methanol to methoxy.[47] Thus we expect the clean Cu(100) to be rapidly covered by methoxy, as shown by the APXPS spectra. HPSTM images taken in the presence of 0.01-0.2 Torr of CH_3OH (Figure 4), show a $(\sqrt{2}\times\sqrt{2})R45°$ overlayer (also written as c(2×2)), which we attribute to methoxy saturating the surface. Another structure can also be observed sometimes forming small patches, as that on the lower right corner of Figure 4. Co-existence of multiple structures of methanol-derivatives was previously seen in UHV-STM studies on a Cu(110) surface, with (5×2) and c(2×2) periodicities. The former was attributed to a methoxy-induced superstructure, and the latter to both methoxy and formate overlayers.[44,49] Despite the lack of similar studies on the (100) face, it has been assumed in the literature that a c(2×2) forms on Cu(100) as well.[50,51]

Methoxy adsorbs on the surface via the O ($M-OCH_3$) whereas CO adsorbs via the C atom (M-CO). This different binding makes a very substantial difference in adsorption energies: The methoxy binding energy in the c(2×2) structure was calculated to be 2.96 eV, with oxygen occupying the hollow sites.[51] This is much higher than CO in the same structure (around 0.5-0.6 eV on top sites).[30] The same study predicted the methoxy binding energy on a step edge to be 2.98 eV,[51] only slightly higher than the energy on the terrace site, which explains the lack of Cu-cluster formation in the presence of methanol.

The different ordered structure, visible as a small patch in the lower right corner of Figure 4a, (~10 nm wide), is not stable and disappears with time, being replaced by the c(2×2) overlayer structure (Figure S6). If atomic oxygen is present on the surface, hydrogen resulting from methanol dissociation can also react with oxygen to form OH, which further contributes to methanol dissociation via water formation. Methoxy can then further decompose to formaldehyde either on clean Cu sites or through interaction with or atomic oxygen or OH, yielding OH or H_2O respectively. While water adsorbs weakly on Cu surfaces, stable OH-H_2O structures have been observed at higher pressures.[52] Decomposition of methoxy to formaldehyde via C-H bond dissociation is the rate limiting step in methanol oxidation on Cu surfaces even with coadsorbed oxygen.[47] Additionally, formaldehyde adsorbs weakly to the Cu(100) surface and therefore cannot be a component of the transient structures observed by STM. Our APXPS results also show some formate present on the surface after dosing methanol. We note, however, that formate adsorbs strongly to the Cu surface. Meanwhile these structures are slowly replaced by the steady state c(2×2) structure, suggesting that they are not comprised of formate. We therefore suggest that this transient structure contains either methanol, methoxy, OH, H_2O, or a combination of these products (but not hydrogen, formate, or formaldehyde).

4. CONCLUSION

A layer of methoxy with c(2×2) structure is formed on the clean Cu(100) surface at room temperature in equilibrium with CH_3OH gas at pressures up to 0.2 Torr. When the surface is pre-covered by oxygen, with a $(2\sqrt{2}\times\sqrt{2})R45^\circ$ periodicity, the adsorption of methanol is blocked. However, under mixtures of CH_3OH and O_2, the methanol adsorbs dissociatively forming methoxy and reacts with O to form formate and formaldehyde which latter desorbs to the gas phase. The reaction keeps the surface free of oxygen. Unlike the case of CO that induces restructuring by formation of Cu nanoclusters driven by the large adsorption energy difference on high (terraces) and low coordination sites (steps, kinks), methoxy binds more strongly but with similar binding energy on sites of different coordination number, so that the driving force for Cu restructuring is insufficient.

ASSOCIATED CONTENT

Supporting Information

Mass spectrum of methanol, additional HPSTM images and APXPS spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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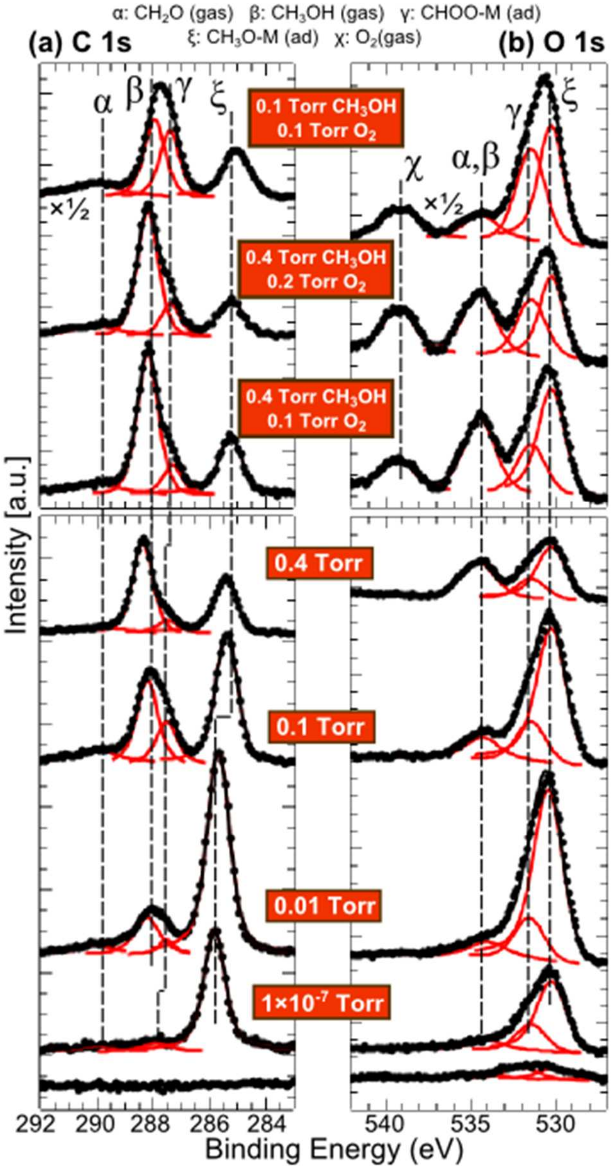


Figure 1. (a) C 1s and (b) O 1s regions of the XPS spectra of Cu(100) at 298 K in the presence of gas phase methanol (lower panels) and methanol mixed with O_2 (upper panels). The (partial) pressures are indicated inside the boxes. The adsorbed and gas phase species are indicated with Greek letters (see the top of the Figure). Black dots are the raw data, red curves are the fitted components (with Gaussian-Lorentzian functions except for methoxy fitted with Doniach-Sunjic functions). The black solid curve is the sum of the red curves. Exact peak positions are discussed in the main text. The attenuated peak intensities at higher gas pressure is due to increased scattering of photoelectrons by gas phase molecules.

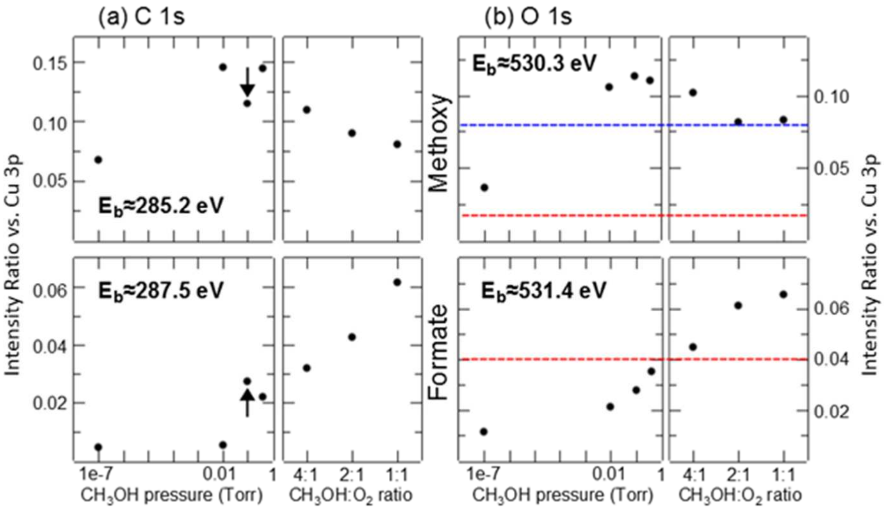


Figure 2 Trends in the coverage of adsorbed species estimated from the C 1s (a) and O 1s (b) peaks normalized to Cu 3p intensity, all spectra measured with E_{kin}=250 eV. Both show a similar trend except the C 1 spectrum at 0.1 Torr of methanol. The arrows indicate the expected position with respect to the O 1s spectrum acquired at same pressures. Horizontal red and blue dashed lines in (b) mark the 0.125 and 0.5 ML coverage estimated using the O 1s to Cu 3p ratio of the well-known $(2\sqrt{2}\times\sqrt{2})R45°$-O surface structure. The coverage of formate is overestimated because its peak position coincides with that of adsorbed molecular methanol in the C 1s region and of hydroxyl groups in the O 1s region.

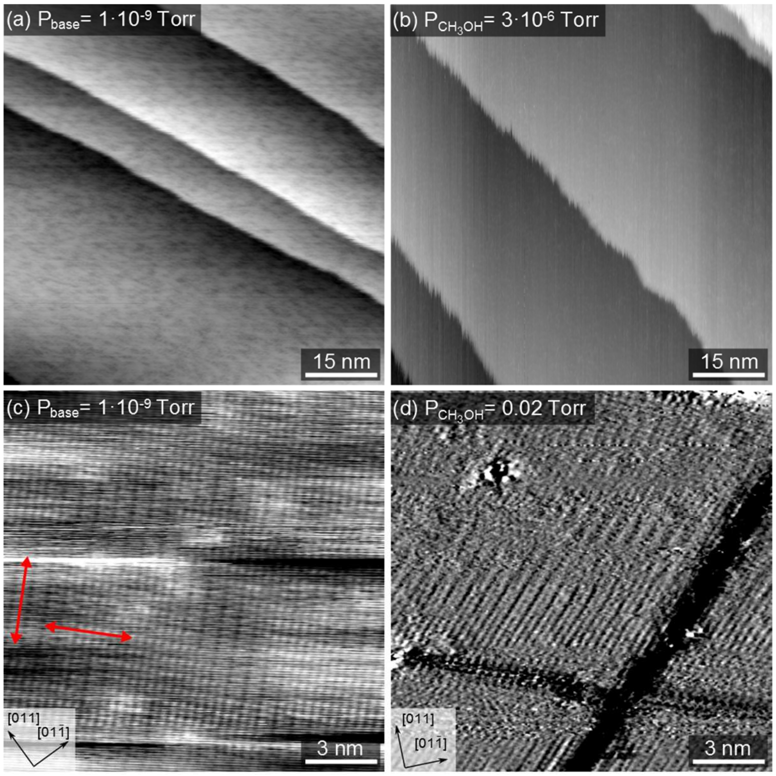


Figure 3 STM images of the Cu(100) surface at 298 K: (a) after preparation at a base pressure of 1×10^{-9} Torr (mostly water in the background), and (b) in the presence of 3×10^{-6} Torr of gas phase methanol, respectively. (a) was scanned horizontal direction, whereas (b) was scanned in the vertical direction. As the pressure is increased, black spots due to atomic oxygen and OH are removed from the surface by reaction with methanol leading to methoxy and formate formation, which are both mobile on the surface. Atomically resolved images of the Cu(100)-(2√2×√2)R45°-O surface (c) at UHV and (d) in the presence of 0.02 Torr CH_3OH. As indicated by the arrows in (c), this structure is found along the two equivalent <001> directions. (d) is shown in the derivate mode to enhance the contrast on terraces (original image shown in Figure S4). Imaging parameters are V_s=0.5 V and I_t=0.5 nA for all the images.

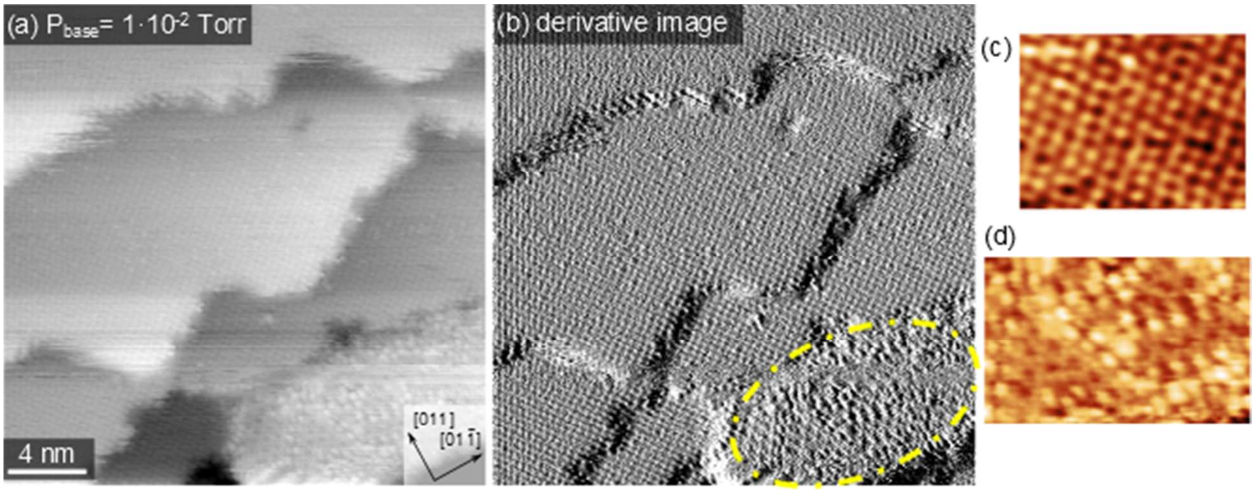
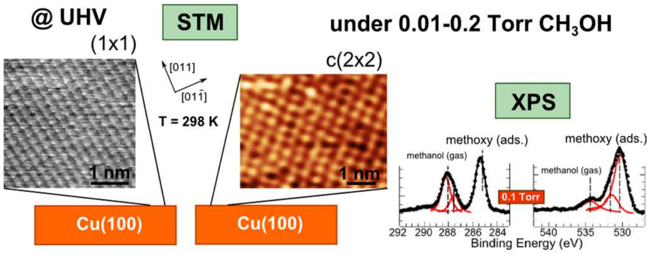


Figure 4 (a) Cu(100) surface in the presence of 0.01 Torr CH_3OH at 298 K. It consists of two regions: Most of the surface has a c(2×2) structure, except the lower-right region which has a structure not yet determined (enclosed by a yellow broken line). (b) is the derivative image of (a) to enhance the STM contrast on the terraces. (c) and (d) are expanded images from the two different regions in (a). The c(2×2) structure remains intact and covers most of the surface in the pressure range up to 0.2 Torr. Imaging parameters are V_s= 0.5 V and I_t= 2 nA.

TOC graphic:


@ UHV
STM
under 0.01-0.2 Torr CH_3OH
(1x1)
[011]
[01$\bar{1}$]
T = 298 K
c(2x2)
1 nm
1 nm
Cu(100)
Cu(100)
XPS
methoxy (ads.)
methanol (gas)
methoxy (ads.)
methanol (gas)
0.1 Torr
292
290
288
286
284
540
535
530
Binding Energy (eV)