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Hydroxyl-Induced Wetting of Metals by Water at Near-Ambient Conditions

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We report different wetting properties of Cu(110) and Cu(111) at near-ambient conditions using in situ photoemission spectroscopy. At near-ambient conditions of pressure (1 Torr) and temperature (295 K), the Cu(110) surface is covered with a mixed OH and H_2O layer, whereas the Cu(111) surface remains clean and adsorbate-free. We show that wetting is controlled by the presence of OH groups on the surface, acting as anchors for water adsorption. Hydroxylation of the Cu(110) surface is facilitated by a lower activation barrier for water dissociation compared to Cu(111).

1. Introduction

Wetting by water is ubiquitous on solid surfaces in nature and technology. The degree of wetting, wettability, depends on the physical and chemical nature of the surface, whether it is *hydrophilic* or *hydrophobic*. The wettability of a metal surface has a strong influence on interfacial chemistry in electrocatalysis and atmospheric corrosion in humid environments. The wettability of a surface has traditionally been characterized by the contact angle of water droplets at ambient conditions, which gives little microscopic insight into the interaction of water with surfaces.[1] In contrast, surface-science studies in ultrahigh vacuum (UHV) and at low temperatures have provided detailed information on the interaction of water with surfaces at a molecular level.[2,3] Yet most processes of interest in real systems take place at ambient or higher pressures and elevated temperatures. Hence, it is very important to carry out molecular-level studies of the wetting water layer on metals under realistic ambient conditions.

Here we have investigated the wetting of water on two different Cu surfaces of (110) and (111) orientations at near-ambient conditions ($p(H_2O) = 1$ Torr, $T = 268−333$ K), using an in situ X-ray photoemission spectroscopy (XPS) setup developed recently.[4,5]

2. Experimental Section

The experiments were performed using a specially designed photoemission spectrometer that can operate at near-ambient pressures (i.e., up to several Torr) located at the undulator beamline 11.0.2 at the Advanced Light Source (Berkeley, USA). O 1s XPS spectra were measured at a photon energy of 735 eV with a total resolution better than 450 meV. Each O 1s XPS spectrum shown here is normalized with respect to the recorded Cu 3p peak intensity.

The Cu(110) and (111) surfaces were cleaned in UHV by cycles of argon sputtering and annealing until a sharp 1×1 low-energy electron diffraction (LEED) pattern was observed and then exposed to water vapor of near-ambient pressures. The oxygen-covered Cu(111) surface was prepared by dosing 1×10^{-6} Torr O_2 at 300 K followed by heating the sample to 573 K.

The surface cleanliness before water exposure and under near-ambient pressure water vapor was checked using XPS. The coverage of O residue before water dose was less than 0.03 monolayer (ML) on Cu(110) and below the detection limit of XPS (<0.001 ML) on Cu(111). No C species were observed before water dose neither on Cu(110) nor on Cu(111). Under 1 Torr H_2O, the coverage of C contaminations that contribute to the O 1s region (i.e., CH_3O-, $HCOO-$, and $-CO_3^{2-}$) was less than 0.03 ML. However, the coverage of C contaminations on the oxygen-covered Cu(111) under 1 Torr H_2O was 0.07 ML. A monolayer (ML) is defined as one molecule per unit cell, that is, 1.08×10^{15}/cm^2 for Cu(110), and 1.77×10^{15}/cm^2 for Cu(111), respectively. The coverage of surface species on Cu-(110) and Cu(111) in UHV was calibrated by comparing the O 1s XPS intensity to that in the $p(2 \times 1)$-O/Cu(110) (0.5 ML) reference system.[6,7] The O 1s/Cu 3p ratio for the above system was used as reference to obtain the coverage under near-ambient conditions because the peak attenuation by gas-phase molecules and lens transmission function were cancelled out by taking the ratio of two XPS peaks measured with the same kinetic energy. We estimate the error in the coverage calibration to be less than 10%.

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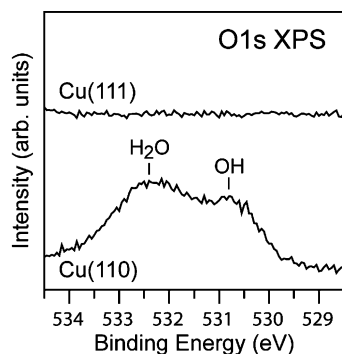[⊥] Present address: Department of Applied Physics, Chalmers University of Technology, SE-412 96 Göteborg, Sweden.

Figure 1. O 1s XPS spectra measured in the presence of 1 Torr water vapor on two different Cu surfaces at 295 K (a relative humidity of 5.0%): Cu(110) and Cu(111). The gas-phase water peak is observed around 535 eV (not shown).
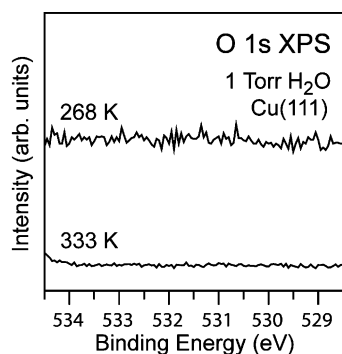

Figure 2. O 1s XPS spectra measured in the presence of 1 Torr water vapor on Cu(111) at 333 and 268 K, corresponding to 0.67 and 32% RH. The larger noise level in the O 1s XPS spectrum measured at 268 K is due to a lower flux of incident photons. The gas-phase water peak is observed around 535 eV (not shown).

3. Results and Discussion

First we show that the Cu(110) and (111) surfaces exhibit different wetting properties at near-ambient conditions. Figure 1 shows in situ O 1s XPS spectra measured on Cu(110) and Cu(111) in the presence of 1 Torr water vapor at 295 K, corresponding to a relative humidity (RH) of 5.0%. On Cu-(110), two broad peaks are observed at 530.8 and 532.4 eV binding energy, which are assigned to OH and H_2O, respectively.[8-10] The partial coverages of OH and H_2O are 0.34 and 0.68 ML, respectively. The Cu(110) surface is thus covered to saturation (i.e., 1 ML) with a mixture of OH and H_2O. In contrast, under identical conditions, the Cu(111) surface remains clean and adsorbate-free. No adsorbate is observed on Cu(111) under 1 Torr H_2O vapor in the temperature range from 333 to 268 K, corresponding to the RH range from 0.67 to 32% (see Figure 2). Therefore, the same material exhibits very different wetting properties at near-ambient conditions depending on the orientation of its exposed surface; the Cu(110) surface is much more *hydrophilic* than the Cu(111) surface under the present conditions.

In thermodynamic equilibrium, the coverage of adsorbed water on the surface is determined by the balance of adsorption and desorption kinetics. On the basis of the above result that the wetting layer on Cu(110) is formed from a mixture of OH and H_2O, we hypothesize that a strong attractive interaction between OH and H_2O slows down the water desorption kinetics dramatically, resulting in the observed large quantities of water adsorbed on Cu(110). Under UHV conditions, the stabilization of water by OH on metal surfaces has been observed as higher desorption temperatures of water from the mixed OH+H_2O layer
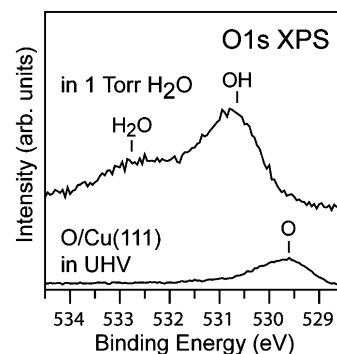

Figure 3. O 1s XPS spectra for a partially oxygen-covered Cu(111) surface ($\theta_O = 0.12$) measured in ultrahigh vacuum (UHV) and in the presence of 1 Torr water vapor at 295 K (5.0% RH). The gas-phase water peak is observed around 535 eV (not shown).

than from the molecularly intact water layer. Examples include Cu(110),[11,12] Ag(110),[13] Ni(110),[14] Pt(111),[15] Ru(0001),[16,17] and Rh(111).[18] On Cu(110), for instance, the peak desorption temperatures of water in the mixed OH + H_2O layer are 190 and 230 K in UHV,[11,12] which are higher than the desorption temperature of 170 K in the molecularly intact water layer.[10-12] Hence, the mixed OH + H_2O layers are more stable than the pure water layers. This is further corroborated by total-energy calculations based on density functional theory (DFT), which find that a mixed OH + H_2O layer is energetically favored over a pure water layer on Cu(110)[19] and Ru(0001).[20,21] Karlberg and Wahnström[22,23] have clarified the nature of H bonds in the stable OH + H_2O layer on Pt(111) using DFT calculations: the donating H bond from H_2O to OH is ~0.2 eV stronger than that between two water molecules.

The different wettability on two Cu surfaces, (110) and (111), thus originates from a difference in the activation barrier for water dissociation (E_a^{diss}), that is, $E_a^{diss}(110) < E_a^{diss}(111)$. The lower dissociation barrier on Cu(110) compared to Cu(111) is demonstrated by the present experiments at near-ambient conditions from the fact that OH species are present on Cu-(110) but not on Cu(111) (see Figure 1). It is also supported by previous UHV studies showing that thermally induced water dissociation occurs on Cu(110)[8,10,12,24] but not on Cu(111).[25] The absence of OH groups on Cu(111) in the present experiments ($p(H_2O) = 1$ Torr, $T = 268-333$ K) indicates that water dissociation is kinetically hindered on Cu(111) under these conditions. The dissociation barrier in the low coverage limit has been determined experimentally from kinetic measurements of the water–gas shift (WGS) reaction on Cu(110) and Cu-(111) to be ~0.87 eV[26] and ~1.17 eV,[27] respectively. These values are in good agreement with the calculated dissociation barriers of water monomers on Cu surfaces using DFT calculations.[28] The difference in dissociation barriers of water on the two Cu surfaces can be explained by the linear Brønsted–Evans–Polanyi (BEP)[29,30] relationship between activation energies and enthalpy changes for dissociative adsorption:[31] a larger thermodynamical driving force (ΔH) leads to a lower activation barrier for similar reactions. The water dissociation reaction is exothermic ($\Delta H < 0$) on Cu(110)[19] but thermoneutral ($\Delta H= 0$) on Cu(111).[32,33] The different wetting properties on two Cu surfaces at near-ambient conditions are thus well-correlated with information on the thermodynamics (stability of mixed OH + H_2O layers) and kinetics (activation barrier for water dissociation) for water on metal surfaces obtained in UHV studies.

In the following, we use preadsorbed oxygen to show that wetting is indeed controlled by OH groups on the surface. Figure 3 shows O 1s XPS spectra for a partially oxygen-covered Cu-

(111) surface measured in UHV and in the presence of 1 Torr water vapor at 295 K. The preadsorbed atomic O ($\theta = 0.12$) on Cu(111) reacts with 1 Torr water vapor ($H_2O + O \rightarrow 2OH$) to form a mixed OH and H_2O layer. The partial coverages of OH and H_2O are 0.26 and 0.17 ML, respectively. The hydrophilicity of the Cu(111) surface is thus generated by the formation of OH groups that stabilize water molecules through strong hydrogen bonds, similar to what we observe on the Cu-(110) surface.

4. Conclusions

In conclusion, the wetting properties of Cu(110) and Cu(111) surfaces are different at near-ambient conditions ($p(H_2O) = 1$ Torr, $T = 295$ K); the OH-covered Cu(110) surface is much more *hydrophilic* than the clean Cu(111) surface, which can be characterized as *hydrophobic* under these conditions. The Cu-(111) surface, however, becomes *hydrophilic* by the formation of OH groups induced by preadsorbed oxygen. Wetting of metals at near-ambient conditions is thus controlled by the presence of OH groups on the surface that stabilize water molecules via strong hydrogen bonds. The different wettability on the clean Cu surfaces originates from a lower activation barrier for water dissociation on Cu(110) compared to Cu(111). Our results clearly indicate that water chemistry, through the formation of OH groups, plays a decisive role in the wetting of metal surfaces at near-ambient conditions.

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