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Autocatalytic water dissociation on Cu(110) at near ambient conditions

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ABSTRACT

Autocatalytic dissociation of water on the Cu(110) metal surface is demonstrated based on X-ray photoelectron spectroscopy studies carried out *in-situ* under near ambient conditions of water vapor pressure (1 Torr) and temperature (275 – 520 K). The autocatalytic reaction is explained as the result of the strong hydrogen-bond in the H₂O-OH complex of the dissociated final state, which lowers the water dissociation barrier according to the Brønsted-Evans-Polanyi relations. A simple chemical bonding picture is presented which predicts autocatalytic water dissociation to be a general phenomenon on metal surfaces.

1. Introduction

Water chemistry on metal surfaces constitutes a fundamental part of chemical processes of great economical importance, such as the hydrogen-production through steam reforming (SR), $\text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3 \text{H}_2$ and the water-gas shift (WGS) reaction, $\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$, both of which are cornerstones of today's large-scale chemical industry.¹ Other examples of the importance of water-metal chemistry include corrosion and fuel cell technology. Although a correct modeling of elementary surface reactions involving water chemistry at the gas-solid interface should consider earlier reports on hydrogen (H-) bond assisted lowering of the water dissociation barrier from ultra-high vacuum (UHV) studies^{2,3} and theory⁴⁻¹⁰, on both metal^{2,4-6} and non-metal surfaces^{3,7-10}, this is very far from common practice. The effects of lateral and attractive H-bond interactions are today still only partially known, particularly at near ambient and reaction conditions.

On Cu(110) a large variation of the dissociation barrier for water has been observed depending on experimental conditions. From kinetic measurements of the WGS reaction rate at 10 Torr H₂O + 26 Torr CO, 543 K ≤ T ≤ 653 K, Nakamura *et al.*¹¹ report a water dissociation barrier of 0.87 eV. A significantly lower dissociation barrier with a value of ~0.55 eV in the saturated water monolayer was obtained by some of the present authors under UHV conditions and low temperatures.² The difference in activation barriers can be explained by two extreme situations for water dissociation, the monomer and the saturated water monolayer.² This autocatalytic water dissociation on Cu(110) is also supported by recent calculations within the framework of density functional theory.⁴

In order to arrive at a general understanding of the autocatalytic water dissociation we extend our studies on Cu(110) using synchrotron-based X-ray photoelectron spectroscopy (XPS) to elevated water pressure (1 Torr)^{12,13} and temperatures up to ~520 K, i.e. approaching technologically relevant conditions. Autocatalytic water dissociation is argued to be a general phenomenon on metal surfaces, originating from a strong H-bond between H₂O and OH in the dissociated final state.

2. Experimental Section

Experiments were performed in the ambient pressure photoemission spectroscopy (APPEs) endstation at the undulator beamline 11.0.2 at the Advanced Light Source (Berkeley, USA).¹² The vacuum base pressure in the endstation is about 2×10^{-10} Torr. The electron spectrometer is a Specs Phoibos 150 with a custom-designed differentially-pumped electron lens. O 1s XPS spectra were recorded at a photon energy of 735 eV and a total energy resolution on the order of 350 meV.

Because both gas-phase attenuation and transmission of electrons through the electron optics are energy-dependent processes, particular care needs to be taken for a proper analysis of the data. Quantification of surface coverage is obtained by measuring the relative O 1s and Cu 3p signals for identical electron kinetic energies, obtained by choosing appropriate X-ray excitation energies, and by calibration against the O 1s to Cu 3p ratio obtained for a 0.5 monolayer of atomic O^{14,15} [1 monolayer

(ML) = 1.09×10^{15} atoms cm^{-2} for Cu(110)]. Similarly, through reference measurements of adsorbed, as well as gas-phase, species with well known C:O ratio the C 1s to O 1s intensity ratio for identical electron kinetic energies could be established. This was used to determine the level of C-contamination on the surface.

The Cu(110) crystal was cleaned by cycles of Ar^+ -sputtering and annealing to 850 K until a sharp 1×1 LEED pattern was observed. The temperature of the sample was monitored by a K-type (chromel-alumel) thermocouple located inside a special pocket of the sample for good thermal contact. The Milli-Q water (H_2O , $T = 295$ K) used was cleaned (degassed) by multiple freeze-pump-thaw cycles and finally by distillation right before introduction into the experimental chamber.

The surface cleanliness before water adsorption was ≤ 0.03 ML O. This remaining small amount is most likely due to a small percentage of highly reactive defects on which H_2O dissociates at 1×10^{-7} Torr, the base pressure after evacuation from experiments at 1 Torr H_2O . We believe that these small amounts of atomic O are not affecting the results obtained at pressures 7 orders of magnitude higher that produce large amounts of dissociated H_2O . Although no C was observed (< 0.001 ML) before water adsorption, a small amount was detected after water exposures, reaching ≤ 0.03 ML in the experiments at 1 Torr H_2O . In order to keep C-contamination at this low level, each data point at 1 Torr H_2O was obtained after a cleaning procedure and thus corresponds to an experiment on a freshly prepared clean Cu(110) surface. In all cases rapid data acquisition was essential. Starting from vacuum ($\sim 10^{-7}$ Torr) a 1 Torr H_2O environment was reached within ~ 30 s and acquisition of the O 1s XPS spectrum, with an acquisition time of 60 s, then immediately started.

Regarding the issue of X-ray and electron-induced water dissociation,^{2,16} a comparative ambient pressure XPS study of Cu(111) and Cu(110),¹⁷ recorded under X-ray irradiation and water pressure conditions identical to those reported here, resulted in no observable dissociation products on the chemically more inert Cu(111) surface unless pre-dosed with atomic O. We take this as proof that possible X-ray and electron-induced water dissociation, in the gas-phase and at the surface, does *not*

influence our results. The Cu(111) results also rule out possible O₂-contamination in the water vapor. We also performed blank experiments on Cu(110) to investigate water dissociation in the absence of the X-ray beam. Introduction of water up to pressures of 1 Torr was followed by evacuation down to $\sim 1 \times 10^{-7}$ Torr and then recording the spectra. Equally large amounts of water dissociation products were observed as when the X-ray beam was present during water dosing. Water dissociation on Cu(110) at 1×10^{-7} Torr was negligible compared to high-pressure exposures. We are therefore confident that our results are not affected by X-ray or electron-induced dissociation.

3. Results and discussion

3.1 Autocatalytic water dissociation: the observations

In order to discuss the water chemistry on the Cu(110) surface at near ambient conditions we first identify the species corresponding to the various peaks in the XPS O 1s region. In Fig. 1 we show spectra taken in 1 Torr pressure of H₂O at three different temperatures (275, 348 and 453 K). Three different adsorbed species can be distinguished. Molecular H₂O produces a peak in the 532.65 – 533.0 eV range, depending on the coverage, with the highest binding energy value at the lowest total (H₂O + OH) coverage. Two different types of OH species are observed: one hydrogen-bonding with H₂O (OH_{wmix}) with a binding energy at 530.95 eV and another at 530.45 eV which is assigned to a pure OH phase (OH_{pure}). All three species compare well with previous measurements of adsorbed H₂O and OH on Cu(110) under ultra-high vacuum (UHV) and low temperature conditions.^{2,18-20} No statistically significant amounts of atomic O was observed under 1 Torr H₂O in the 275-520 K range. A more detailed account of our data together with an extensive comparison to previous UHV results is available elsewhere.²¹

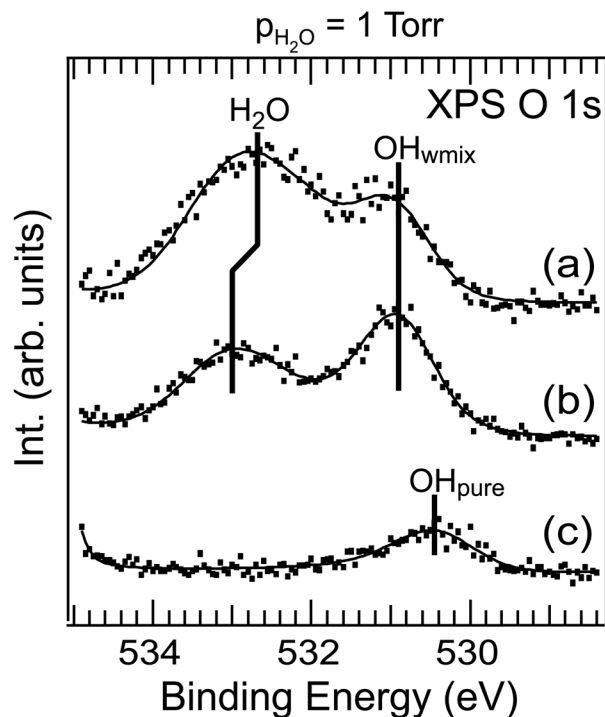


Figure 1. O 1s X-ray photoemission from Cu(110) recorded in the presence of 1 Torr partial pressure of H_2O at: (a) 275 K, (b) 348 K and (c) 453 K. The two spectral features OH_{wmix} and OH_{pure} correspond to OH-species bonding with H_2O and isolated OH groups, respectively. The spectra are normalized with respect to coverage and the result of a least-squares peak-fitting procedure after background subtraction is shown as a solid line for each spectrum. The gas-phase peak of H_2O located above 535 eV is not shown.

The saturation (maximum) coverage of OH on the surface was established to be 0.35 – 0.4 ML under our experimental conditions. In Fig. 2 we show the total OH coverage observed at 1 Torr H_2O as a function of surface temperature. Indicated in the figure is also the temperature (~ 430 K) up to which significant amounts of H_2O could be detected by XPS (≥ 0.03 ML). We observe that above 380 K the total OH coverage starts to drop significantly below its saturation coverage. This is a result of either kinetic limitations on the rate of OH production (by H_2O dissociation) or a decrease of OH equilibrium coverage. Resolving this issue would have required time-resolved results, i.e. sequential spectra, which unfortunately at 1 Torr was not feasible due to increased surface contamination in spectra beyond the

first. Irrespective of the actual situation we show that our data, when compared to prior measurements,^{2,11} are fully consistent with autocatalytic water dissociation taking place at near ambient conditions.

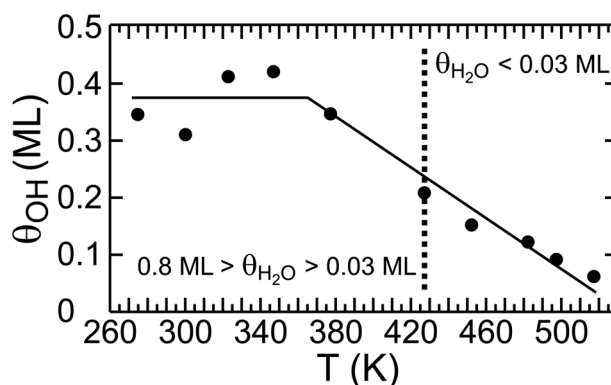


Figure 2. Total OH coverage (θ_{OH}) as a function of temperature on Cu(110). The solid line is shown to emphasize the trend for the observed OH coverage changes. The vertical dashed line marks the highest temperature (428 K) at which molecular water can still be observed by XPS (≥ 0.03 ML).

Based on the total OH coverage after exposure of the sample to 1 Torr H_2O for 60 s (the XPS spectrum acquisition time), the dissociation probability per H_2O collision with the surface (P_{diss}) can be calculated. Whether the obtained P_{diss} represents an absolute value or a lower limit depends on whether the observed OH coverage is the result of limitations in the H_2O dissociation rate or simply represents a thermodynamic equilibrium. Either way we find that it does not affect our conclusions.

In the temperature range 470 – 520 K, the water coverage is well below our detection limit (i.e. $\ll 0.03$ ML). Under these conditions we find P_{diss} to be $\geq 0.5 - 0.2 \times 10^{-8}$. These results compare very well with Nakamura *et al.*¹¹ who established, under low water coverage conditions, P_{diss} to be $\geq 0.5 \times 10^{-8}$ at 473 K. Equally good agreement is deduced from the obtained WGS data in the same study by Nakamura *et al.* (Fig 2 in Ref 11); extrapolation down to the 470-520 K range indicates a P_{diss} of $1 - 5 \times 10^{-8}$. Our results in the 470-520 K range ($P_{\text{diss}} \geq 0.5 \times 10^{-8}$) are hence in good agreement with the different values extrapolated from Nakamura *et al.*¹¹ data ($P_{\text{diss}} 0.5 - 5 \times 10^{-8}$) even though there are considerable differences in reaction conditions and in the way P_{diss} is extracted. The agreement

indicates that possible contaminants in our system (e.g. CO and H₂) have only a small impact on our results.

In the temperature regime 275 – 380 K water is observed in large quantities on the surface (0.8 – 0.2 ML). Under these conditions we determine P_{diss} to be $\geq 1.5 \times 10^{-8}$, a value several orders of magnitude greater than expected as discussed below. From measurements near 285 K and exposures to 1×10^{-2} and 0.1 Torr, P_{diss} was established to be as high as $1 - 5 \times 10^{-7}$. P_{diss} could possibly be higher in 1 Torr at this temperature. Specifically, the determination of P_{diss} at 0.1 Torr was obtained by ~5 s exposure at 285 K without X-rays present, followed by evacuation to 1×10^{-7} Torr and recording of the XPS spectra, which confirmed an OH_{pure} coverage of 0.2 ML. From extrapolation of the previously obtained low water coverage WGS data¹¹ down to 275 K a P_{diss} of about 5×10^{-12} is expected, however we obtain a several orders of magnitude higher P_{diss} ($\geq 1.5 \times 10^{-8}$) under 1 Torr H₂O. The value could possibly be larger than 5×10^{-7} based on the P_{diss} obtained at the lower pressure of 0.1 Torr. Our finding that at lower temperatures, corresponding to high water coverage, the H₂O dissociation rate is much faster than expected based on measurements obtained at higher temperatures, i.e. low water coverage, is fully consistent with autocatalytic water dissociation taking place at near ambient conditions.

3.2 Autocatalytic water dissociation: the origin

So far we have shown that the barrier (rate) to H₂O dissociation on Cu(110) depends strongly on whether H₂O is in monomeric form or H-bonding with other water molecules. Although a faster H₂O dissociation rate is expected at elevated temperatures this may be more than offset by the concomitant decrease in the concentration of H₂O-H₂O bonded species due to the lower H₂O coverage. In the following we discuss the driving force behind the autocatalytic water dissociation on Cu(110).

Considering the water monomer adsorption energy, i.e. in our case the desorption barrier E_{des} , which has been calculated to 0.38 eV on Cu(110)⁴ we find that there are remarkably large amounts of water adsorbed on the Cu(110) surface under our experimental conditions, e.g. 0.04 ML at a temperature of

428 K under 1 Torr H₂O. Simple adsorption-desorption equilibrium kinetic considerations show that the monomer adsorption energy is much too low to lead to the observed quantities of adsorbed H₂O. Likewise, the E_{des} for water from a pure water monolayer is only about 0.52 eV². Although higher than in the monomer case, this value is still too low to explain the large amounts of water on the Cu(110) surface. In order to account for the observed large quantities of water on Cu(110) we need to add an attractive interaction for water at the surface of approximately 0.2 eV above that provided by the H₂O-H₂O interaction. This extra stabilization of water at the surface can only be provided by existing OH groups with which H₂O forms a stable H₂O(donor)-OH(acceptor) complex (see section 3.3).

We regard the stability of the H₂O-OH complex on Cu(110) as the driving force for the lowering of the H₂O dissociation barrier. Considering water dimer (trimer) formation at the surface, possibly facilitated by high H₂O concentrations around already present OH, H-bonding configurations which result in a stabilization of OH after H₂O dissociation by accepting one (two) H-bonds from H₂O are possible. The stronger H₂O-OH bond (final state) compared to the H₂O-H₂O bond (initial state) should lead, following Brønsted-Evans-Polanyi relations^{22,23} for water dissociation²⁴ and the effect of a considerable decrease in reaction enthalpy (ΔH), to a significantly lower activation barrier (i.e. faster rate) for dissociation in, e.g., a water dimer compared to a monomer on Cu(110).

3.3 Autocatalytic water dissociation: metal surfaces in general

We propose that the enhanced stability of the H₂O-OH complex over H₂O-H₂O observed on Cu(110) is a general phenomenon on metal surfaces, and that this provides a general mechanism for water dissociation.

This can be understood by the fact that the metal-OH bond is strong and of mainly ionic character.²⁵ The large electron affinity of OH gives rise to a near-closed-shell electronic structure,²⁵ with significant OH⁻ character, while H₂O donates electron density to the metal substrate mainly via its oxygen^{26,27} thus enhancing its ability to donate H-bonds. Moderate strength H-bonds, such as H₂O-OH (and H₂O-H₂O),

are predominantly of electrostatic nature.²⁸ OH (δ^-) adsorbed on metal surfaces therefore has a Brønsted base character, i.e. a better H-bond acceptor but worse H-bond donor towards H₂O (δ^+) than H₂O is to itself (i.e. H₂O-H₂O). The strong H-bond at metal surfaces is therefore the H₂O(donor)-OH(acceptor) bond while the reverse situation yields a very weak bond. This is analogous to the situation of OH⁻ in solution²⁹ and consistent with theoretical results for OH donor-acceptor properties towards H₂O on Pt(111)^{27,30} and Rh(111).³¹ Based on our simple chemical bonding model, we propose that such stronger H₂O(donor)-OH(acceptor) H-bond interactions compared to H₂O-H₂O applies to other metal surfaces as well.

Besides the results presented here for autocatalytic water dissociation on Cu(110), previous theoretical work has come to the same results for the H₂O + O reaction on Pt(111)⁶ and H₂O on Ru(001),⁵ in all three cases the water dissociation barrier is lowered by 0.2 – 0.4 eV.^{2,4-6} The theoretical findings on Pt(111) and Ru(001) are in line with thermal desorption spectroscopy (TDS) studies of water from these surfaces under UHV conditions. Significantly higher water desorption temperatures from these surfaces are observed when OH groups are present,^{16,32-34} demonstrating the greater H-bond stability of H₂O-OH compared to H₂O-H₂O also on these metal surfaces. At present, the full range of examples on the greater H-bond stability of H₂O-OH compared to H₂O-H₂O on metal surfaces from TDS studies under UHV conditions include Pt(111),³² Ru(001),^{33,34} Pd(111),³⁵ Rh(111),³⁶ Ag(110),^{37,38} Ni(110)³⁹ and Cu(110).^{40,41} From near ambient XPS studies the stability of the H₂O-OH complex has also recently been demonstrated for the Cu(111) surface.¹⁷ All of these results, consistent with the chemical bonding picture presented, strongly suggest autocatalytic water dissociation to be a general phenomenon on metal surfaces.

In closing, we emphasize that the H-bonding configuration of the dissociating water molecule is expected to strongly affect the dissociation barrier to OH_{ads} + H_{ads}. Here we give a general description of the (initial state) configurations proposed to be mainly responsible for the autocatalytic water dissociation.

The water molecule can be involved in one, two or three H-bonds with other waters at the metal surface. For a reaction enthalpy lowering to occur compared to the monomer case, and hence a dissociation barrier lowering (i.e., autocatalysis), the total H-bond strength in the final state must be higher than in the initial state. Based on our simple chemical bonding model this means that the number of H₂O(donor)-OH(acceptor) (OH(donor)-H₂O(acceptor)) bonds in the final state should be maximized (minimized) because these bonds are significantly stronger (weaker) than H₂O-H₂O. This favors initial state configurations where the dissociating water accepts two (one) H-bonds in case of a trimer (dimer) water cluster. Furthermore, because OH can only donate one H-bond, by excluding cases where the dissociating water donates two H-bonds to other waters in the initial state, the complete loss of a H₂O-H₂O H-bond can be avoided.

In summary, the initial state configurations responsible for autocatalytic water dissociation at metal surfaces are expected to be those where the dissociating molecule accepts as many (and donates as few) H-bonds from (to) other water molecules as possible. This is consistent with the finding that the lowest dissociation barrier to OH_{ads} + H_{ads} in the saturated water monolayer on Cu(110)⁴ and Ru(001)⁵ is that for a H-down configuration, accepting two and donating only one H-bond to water in the initial state.

4. Conclusions

We have shown the autocatalytic role of water in water dissociation on Cu(110) under near ambient water pressures by means of *in-situ* XPS. Under the conditions explored the water dissociation rate decreases with increasing temperature, i.e. with decreasing water coverage. We argue that the greater stability of the H₂O-OH final state complex compared to the H₂O-H₂O in the initial state provides the driving force for the autocatalytic water dissociation, in accordance with the Brønsted-Evans-Polanyi relations. The initial state configurations expected to be mainly responsible for autocatalytic water dissociation at metal surfaces are those where the dissociating water molecule accepts as many (and donates as few) H-bonds from (to) other waters as possible.

The results show that the inclusion of H-bonding effects is crucial for a complete understanding of the observed water chemistry and this is likely to be true in general for surface chemical kinetics in systems with adsorbates capable of H-bond formation.

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