In Situ Observation of the Potential-Dependent Chemical State and Structure of a Cu Monolayer Deposited on the Surface of Carbon-Supported Platinum Clusters

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A complete electrochemical oxidation−reduction cycle for a Cu monolayer on carbon-supported Pt clusters in alkaline solution has been monitored in situ by X-ray absorption spectroscopy. No desorption of Cu was observed upon oxidation. Near-range order and oxidation state of the Cu layer as a function of potential was obtained by in situ X-ray absorption spectroscopy. In contrast to bulk copper, the adsorbed copper monolayer transforms directly from the reduced state to Cu^{2+} and from the oxidized form to Cu^0. Adsorption of OH^- ions on the Cu layer was observed for potentials below those for the $Cu^0 \rightarrow Cu^{2+}$ and $Cu^{2+} \rightarrow Cu^0$ transitions.

1. Introduction

Surface reactions involving dispersed metal clusters are of great significance in various fields such as catalysis, fuel cells, and energy storage.[1,2] These reactions include adsorption and desorption of atoms and ions as well as chemical processes in which these adsorbates participate. A detailed knowledge of the reactions at metal cluster surfaces is therefore of special interest. During the last two decades new methods have been developed, particulary scanning tunneling microscopy and surface X-ray scattering, which have significantly improved our knowledge about the structure of solid surfaces and the processes occurring at the solid/ambient interfaces. Most of the published work, however, deals with the structure of bare and adsorbate-covered single-crystal surfaces.[3] Contrary to that, there exist only few reports about the structure of adsorbates deposited on the surface of metal clusters.[4−7]

A characteristic feature of metal-cluster materials is their large specific surface area of up to several 100 m²/gram. Owing to the large ratio of surface area and mass, metal clusters covered with a monolayer or even submonolayer of an adsorbate allow a unique possibility for the in situ study of adsorbed species using X-ray absorption spectroscopy (XAS). This method yields information about the near-range order of the adsorbed atoms as well as their chemical state[8] under reaction conditions. In contrast, the presence of a liquid phase next to the surface under study prevents the use of most of the techniques employed in UHV for in situ investigations.

In many cases details about reactions occurring at the metal/electrolyte interface cannot be easily determined. On the other hand, electrochemical reactions can be easily controlled by the electrode potential. Many of the reactions are also reversible, and therefore the original state of the system can be readily recovered. Types of reactions such as the oxidation and reduction of an adsorbed species are well suited as model systems for the investigation of chemical processes at the solid/liquid interface.

The oxidation of a metal surface is one of the most fundamental electrochemical phenomena. Whereas the process of oxide formation and reduction has been intensively studied with electrochemical, spectroelectrochemical, and ex situ UHV methods,[9] there exist only a few reports about the structure of oxide layers formed during the very first stages of the bulk metal oxidation, and to the best of our knowledge there are no reports in the literature on the structure and the chemical state of metal monolayers during their electrochemical oxidation and reduction. Metal overlayers in the monolayer or submonolayer range can in many cases be easily obtained using the so-called underpotential deposition (UPD). In that case, the deposition of a monolayer or submonolayer of a metal occurs at a potential more positive than the Nernst equilibrium potential.[10,11] The subject of our work is the chemical state of a Cu monolayer during oxidation and reduction in alkaline solution that was formed by UPD on highly dispersed Pt clusters. In the following we present XAS data obtained for electrochemical oxidation and reduction of a copper monolayer deposited on the surface of carbon-supported platinum clusters.

2. Experimental Section

The electrodes were fabricated using carbon-supported platinum cluster material with a mean cluster diameter of 2 nm and a platinum loading of 10 wt %. This size is given by the supplier and was checked via the effective Pt surface by electrodeposition of a monolayer of Cu. The electrode preparation procedure was similar to that published by McBreen.[5] Prior to copper deposition the electrode was cleaned by cycling in 0.5 M H_2SO_4 in the potential range between hydrogen evolution and oxygen evolution. The cycling was performed until a current−potential curve similar to that for massive polycrystalline platinum electrodes was obtained. The deposition of copper was then performed in

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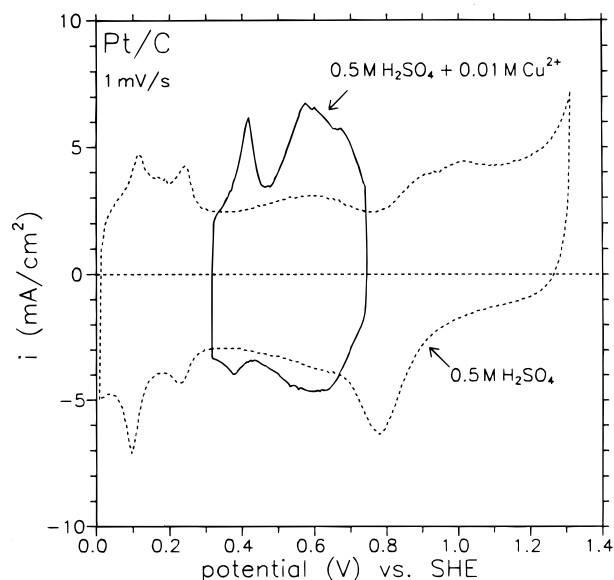
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Figure 1. Cyclic voltammograms for Pt/C electrodes in Cu-ion-free (dashed) and Cu-ion-containing (solid) 0.5 M H_2SO_4. Scan rate: 1 mV/s.

Figure 2. Cyclic voltammograms for a Pt/C electrode in 0.1 M NaOH. Dashed, electrode without adsorbate layer; solid, after deposition of a copper monolayer at +0.3 V (vs SHE) in sulfuric acid solution.

a solution of 10 mM $CuSO_4$ and 0.5 M H_2SO_4 by holding the electrode for several hours at a potential of +0.3 V vs SHE (standard hydrogen electrode), i.e., slightly positive of the Cu/Cu^{2+} equilibrium potential for a 10 mM Cu^{2+} solution. After copper deposition, the electrode was removed from the acidic solution and immediately immersed into a Cu^{2+}-free 0.1 M NaOH solution. In NaOH, the adsorbed copper ions were first reduced at negative potentials between −0.7 and −0.5 V vs SHE and then transferred into the cell for XAS measurements[12] again containing 0.1 M NaOH. During transfer the electrode was exposed to the ambient air, and as a result a full oxidation of the adsorbed copper atoms occurred. Therefore, the first X-ray measurement was preceded by a renewed reduction of the Cu adlayer at −0.6 V.

The XAS measurements were performed at the HASYLAB beam lines X1.1 and BW1 in the vicinity of the Cu K absorption edge. The intensity of the incoming X-ray beam as well as the transmitted intensity were measured using gas-filled ionization chambers. A third ionization chamber was used for a simultaneous recording of copper foil spectra. The X-ray beam from the e+ storage ring was monochromatized by a double-crystal monochromator with Si(311) or Si(111) depending on the beam line. Details about the beam lines can be found in refs 13 and 14. After the measurement at a particular electrode potential, the value was scanned to another one with 2 mV/s and the next spectrum was recorded after the electrode current decreased below 10% of its maximum value during the shift.

3. Results and Discussion

3.1. Electrochemical Results. Figure 1 shows cyclic voltammograms (CV) recorded for a carbon-supported Pt electrode in 0.5 M H_2SO_4 with and without Cu^{2+} ions in the solution. The curve for Cu^{2+}-free H_2SO_4 closely resembles that for a polycrystalline platinum electrode. The main difference is the significantly larger current density in the double-layer region (0.4−0.7 V) due to contributions of the active carbon substrate to the total current.[7] In the Cu^{2+}-containing solution copper deposition and dissolution is observed between +0.75 and +0.3 V. The deposition was started at 0.75 V, and after reaching 0.3 V the potential was held constant for about 30 min. Subsequently, a positive-going potential scan was applied. The
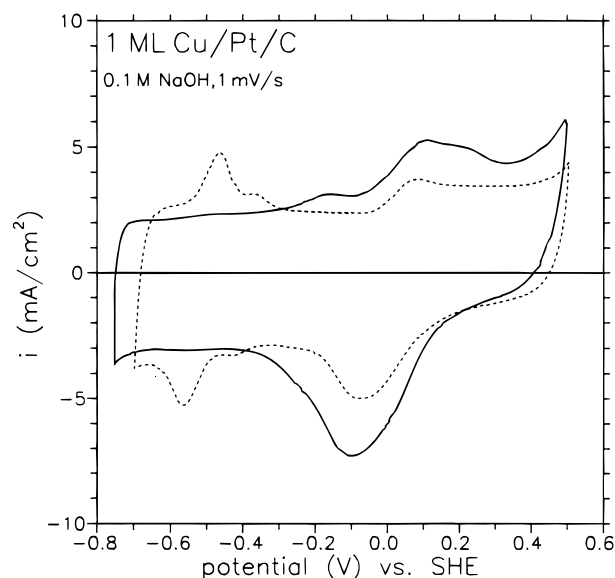
somewhat larger overall current density during the anodic scan may reflect the fact that metal deposition on a highly porous substrate often suffers from diffusion limitation and deposition of a full monolayer can only be achieved after some time has elapsed. The desorption curve is very similar to that for Cu UPD on a polycrystalline Pt substrate,[15] which again appears to be a superposition of curves characteristic for the single crystalline Pt faces[16] including edge and corner positions as well. This is a consequence of the equilibrium shape for small fcc metal clusters consisting mainly of (111) and (100) faces as well as edge and corner positions.[17]

In 0.1 M NaOH, the most characteristic feature in the CV for the Pt/C electrode after Cu UPD is the total absence of the hydrogen adsorption and desorption peaks between −0.3 and −0.65 V, which are present in the curve for the bare Pt/C electrode (Figure 2). This strongly suggests that, after electrode transfer to the alkaline solution, the Pt clusters are still completely covered with the Cu monolayer or at least that all hydrogen adsorption places are blocked by Cu atoms. The current density in the oxide formation and reduction region (around +0.1 and −0.1 V, respectively) increased significantly, and for the positive going scan a new, weak peak appears at −0.2 V.

Let us compare now the behavior of the Cu-covered Pt/C electrode in alkaline solution with that of polycrystalline copper in the same solution. Figure 3 shows a typical CV at a scan rate of 10 mV/s. The two anodic (A1 and A2) and the two cathodic peaks (C1 and C2) correspond to the formation of a copper oxide layer and its subsequent reduction, respectively. Peak A1 can be assigned to the formation of Cu(I) oxide, peak A2 to the formation of a Cu(II) oxide/hydroxide layer.[18] The cathodic peaks C1 and C2 are usually assigned to the reduction steps $Cu^{2+} \rightarrow Cu^{1+}$ and $Cu^{1+} \rightarrow Cu^{0}$, respectively. For a potentiodynamic surface oxide formation at scan rates of 10 mV/s or more, the oxide layer formed on the copper surface is only some few nanometers thick. However, at scan rates below 5 mV/s, a significantly thicker oxide/hydroxide layer is formed and the reduction curves reveal a more complex structure.[19] Owing to the many layers of Cu involved in the bulk oxide layer formation, the latter situation is not comparable to the oxidation/reduction behavior of a copper monolayer.
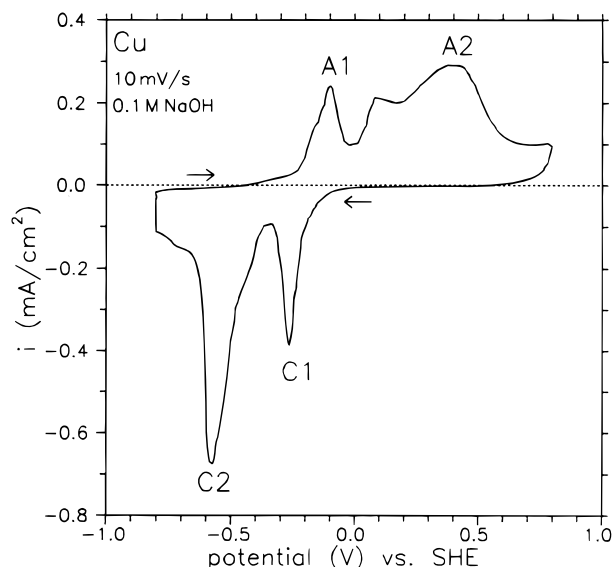
Figure 3. Cyclic voltammograms for polycrystalline bulk copper in 0.1 M NaOH. A1 and A2 mark the oxidation peaks, C1 and C2 the oxide reduction to Cu^{1+} and Cu^0, respectively.

Although the anodic peaks A1 and A2 in Figure 3 seem to correspond to the peaks at -0.2 and $+0.1$ V in Figure 2, respectively, the reduction of the Cu monolayer proceeds in a completely different manner compared to bulk copper. Except for the reduction peak at -0.1 V (Figure 2), we observed no other copper reduction peak comparable to that for polycrystalline bulk material. Apparently, the electrochemical behavior of a copper monolayer differs significantly from that of the bulk material.

3.2. X-ray Absorption Results. The most striking property of the copper monolayer deposited on the surface of platinum clusters is its very high stability in NaOH against dissolution. We observed no loss of the adsorbate even after several oxidation/reduction cycles within the potential range of -0.6 and $+0.5$ V (SHE) corresponding to a repeated oxidation of the copper monolayer and its subsequent reduction to the metallic form. This behavior is clearly indicated by the X-ray spectra recorded during an electrochemical oxidation/reduction cycle. Figure 4 shows EXAFS spectra for the copper adsorbate in the reduced state at the beginning of the potential cycle (-0.6 V), for the completely oxidized state at $+0.5$ V, and again for the reduced state at -0.5 V. For comparison, spectra recorded for a Cu foil, Cu_2O (cuprite), and CuO (tenorite) are also shown in Figure 4. These spectra suggest that the copper monolayer deposited on the surface of platinum clusters can be reversibly oxidized and reduced. At the most positive potential the near-range order around the copper ions is similar to that of CuO rather than Cu_2O.

The high level of electrochemical reversibility for the copper monolayer oxidation and reduction is demonstrated in Figure 5 with XANES spectra at negative potentials. Both the heights of the absorption curves and the fine structures of the absorption edges are virtually identical at the beginning and at the end of an oxidation/reduction cycle in both examples ($-0.6/-0.5$ V and $-0.2/-0.2$ V). Identical heights of the absorption edges before and after the oxidation indicate that no desorption and loss of copper ions occur during this procedure. In contrast, repeated oxidation/reduction cycles applied to a bulk copper electrode lead to a continuous dissolution (corrosion) of the metal surface and, as a result, to an enrichment of copper ions in the solution. The similarity of the fine structures suggests that the mean near-range order in this potential range is only a function of the
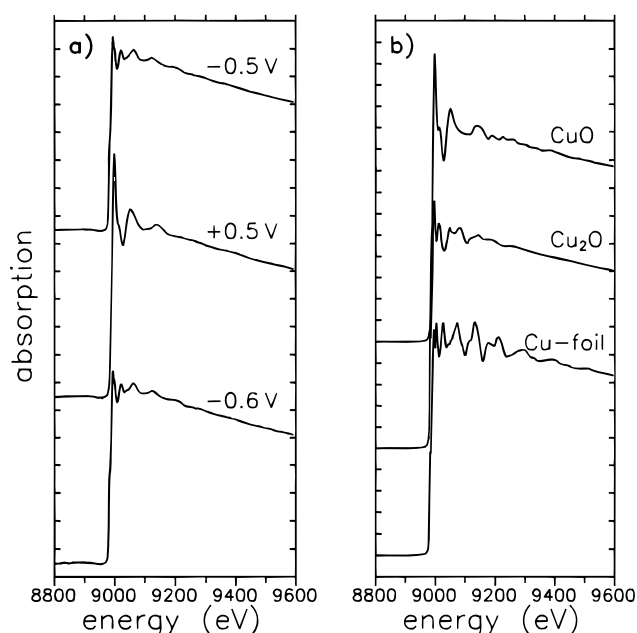

Figure 4. (a) EXAFS spectra of a Pt/C electrode with a Cu monolayer in 0.1 M NaOH at -0.6 V, i.e., at the beginning of the oxidation cycle, at $+0.5$ V, the most positive potential of the cycle, and at -0.5 V, after the subsequent reduction of the Cu-covered Pt/C electrode. (b) EXAFS spectra of reference compounds.
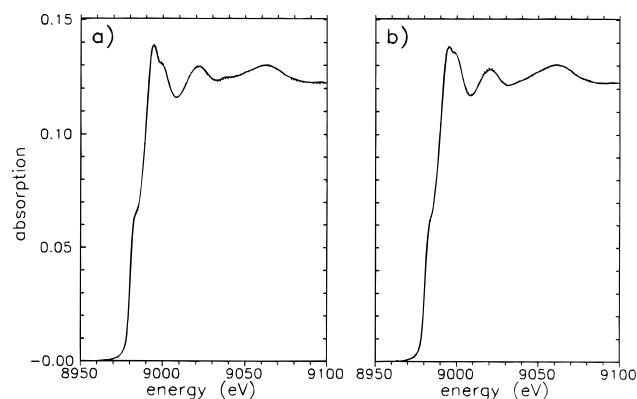

Figure 5. Near-edge absorption spectra of Cu on Pt/C in 0.1 M NaOH recorded before (solid) and after (dashed) an oxidation–reduction cycle at -0.6 and -0.5 V (a) as well as -0.2 V (b).

applied potential but not of the history of the system. This finding differs from the results obtained with purely electrochemical methods for the polycrystalline Pt surface. Measurements with single-crystal Pt electrodes suggest that the stability of the copper monolayer in NaOH strongly depends on the surface orientation.[20]

The near-edge absorption spectra for a potential series corresponding to a single oxidation/reduction cycle are shown in Figure 6. The copper atoms are in the metallic state (oxidation state 0) at the most negative potential of -0.6 V at which the first spectrum was recorded (bottom curve in Figure 6). With the potential increasing to 0.0 V, gradual changes in the form of the absorption edge due to the adsorption of OH^- ions are observed with, however, only small changes in the position of the edges. The latter suggests that no changes in the oxidation state of the Cu monolayer occur in this potential range. The position and the shape of the near edge absorption curve is indicative of the oxidation state of the absorbing atom.[8] Their changes can be better visualized by taking the first derivatives of the absorption spectra, as shown in Figure 7. At $+0.2$ V a shift of the absorption edge by ca. 5 eV relative to that for -0.6
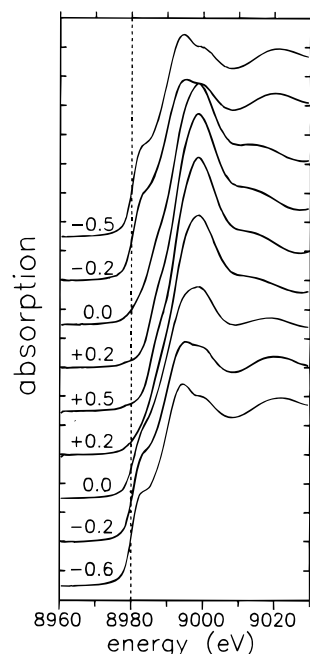
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Figure 6. Near-edge absorption spectra of Cu on Pt/C in 0.1 M NaOH for various potentials. The spectrum recorded at −0.6 V was measured at the beginning of the oxidation/reduction cycle, that at −0.5 V at its end.
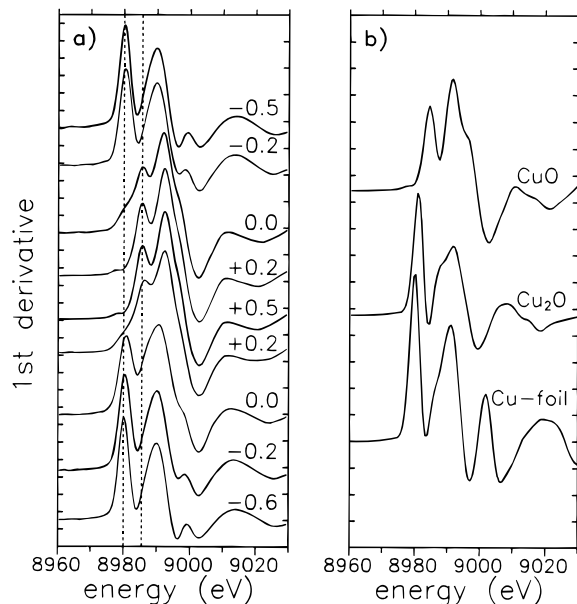

Figure 7. First derivatives of (a) the near-edge spectra in Figure 6 and (b) the reference compounds. The left dashed line in (a) corresponds to the edge position of the Cu adsorbate in the reduced state (8980 eV); the right one marks the edge position for the completely oxidized state (8986 eV).

V is observed with a simultaneous change of its shape corresponding to the formation of Cu^{2+} species. The oxidation state does not change with the subsequently applied potentials of +0.5 and +0.2 V. At 0.0 V a slight shift of the edge position toward lower energy is detectable. At more negative potentials shape and position of the edge match exactly those corresponding to potentials at the beginning of the series (Figure 5). The near-edge spectra suggest a direct transition from Cu^0 with and without OH^- adsorption to Cu^{2+} during the anodic part of cycle as well as a direct reduction of the oxide layer to the metal ($Cu^{2+} \rightarrow Cu^0$) during the reverse potential scan. In contrast, oxidation and reduction of the bulk copper occurs at least in
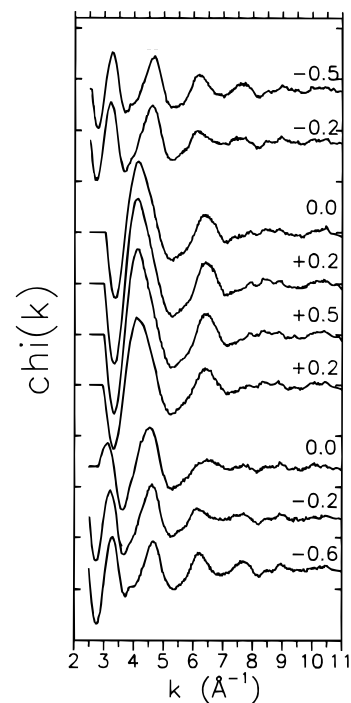

Figure 8. Fine structure of the spectra above the absorption edges corresponding to near-edge spectra in Figure 6.

two steps (Figure 3). Additionally, the reduction of the bulk oxide layer to metallic copper occurs at a significantly more negative potential compared to the metal monolayer deposited on the surface of platinum clusters.

The fine structure in the spectra above the absorption edge (EXAFS) for the whole series of potentials is shown in Figure 8. This fine structure is closely related to the near-range order in the vicinity of the scattering atom. Similar to the near-edge spectra, we observe characteristic changes in the oscillatory structure of the spectra during the anodic and the cathodic scan. The most obvious changes occur between 0.0 and +0.2 V as well as between 0.0 and −0.2 V indicating significant changes in the near-order structure around the copper atoms. As first pointed out by Sayers et al.,[21] the Fourier transform of EXAFS yields a nearest-neighbors distribution function correlated to the near-order structure around that scatterer. Figure 9 depicts the magnitudes of the Fourier transforms for the potential-dependent EXAFS data corresponding to the spectra of Figure 8. With increasing potential, a continuous growth of the peak at 1.5 Å is clearly visible. Simultaneously, the peak at 2.2 Å corresponding to the nearest Cu^0–Cu^0 distance disappears. The peak at 1.5 Å corresponds to the Cu–O distance of about 1.9 Å. Its appearance at the relatively low potential of −0.2 V, i.e., before the shift of the absorption edge to a position corresponding to Cu^{2+} occurs, is an indication for the adsorption of OH^- ions on the Cu monolayer at these potentials. Reversing the potential scan at a potential below the Cu^{2+} formation leads to a reversible change of the absorption spectra. This suggests a weak bonding of the OH^- ions to Cu atoms below −0.2 V. The Fourier transforms do not significantely change with the next potential steps after the first +0.2 V value until reduction potentials below 0.0 V are reached. The amplitude of the Cu–O peak reaches a maximum at +0.5 V and remains at this value for the following potential of +0.2 V. Below 0.0 V, the FT spectra closely match those measured at the beginning of the CV cycle indicating again a full reversibility of the adsorbate structure and oxidation state.

According to the EXAFS data and the near-edge spectra, the copper monolayer is reduced below −0.5 V and completely
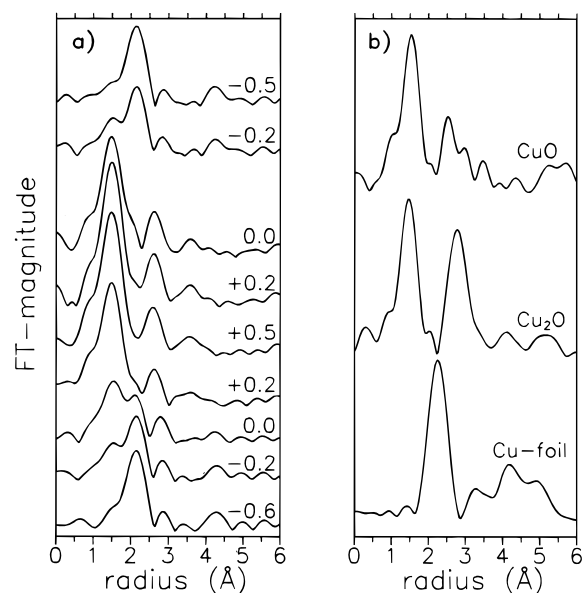
Figure 9. Magnitudes of the Fourier transforms (a) for the EXAFS spectra related to Figure 8 and for the reference compounds (b). The k-range for the Fourier transform was $3-10$ Å^{-1}; the k-weighting factor was 2.

TABLE 1: EXAFS Data

coordination shell	R (Å)	N	σ (Å)	ΔE_0 (eV)
Electrode Potential -0.6 V				
Cu−O	1.96	0.3	0.05*	20.8
Cu−Cu	2.51	4.3	0.13	−6.7
Cu−Pt	2.90	0.2	0.09	14.1
Cu−Cu	3.25	0.6	0.08	−11.2
Electrode Potential $+0.5$ V				
Cu−O	1.90	3.1	0.05	−6.8
Cu−Pt	2.52	6.3	0.15	−8.5
Cu−Cu	2.96	2.4	0.15	3.4

oxidized at $+0.5$ V down to $+0.2$ V during the cathodic scan. At all other potentials, the copper monolayer is probably either only partially oxidized or only partially covered with weakly adsorbed OH$^-$ ions. This most likely reflects the heterogeneity of a Pt particle surface on different parts of which the monolayer adsorbs differently. For a mean Pt particle size of 2 nm as used in our study, the surface of a particle has been suggested to be composed of 5% (100) faces and 50% (111) faces, the remainder being edge and corner atoms.[17] Depending on the applied potential, the adsorption of the OH$^-$ ions and the following oxidation of the Cu atoms will start at the most active sites of the Pt particle.

For the two cases of a reduced and a completely oxidized monolayer, the structural parameter characterizing the near-order structure in the vicinity of Cu atoms can be extracted from the EXAFS data that are summarized in Table 1. The results of the best fits and the original, backtransformed data for these two potentials are shown in Figure 10. Except for Cu and Pt, also O had to be taken into account in order to obtain the best fit for -0.6 V shown in Figure 10a. As shown in Figure 10b, the neglect of oxygen neighbors resulted in a worse fit. This suggests that even at the most negative potential the Cu monolayer is partially covered with OH$^-$ ions. The number of nearest copper neighbors at -0.6 V (4.3) is significantly lower than in bulk copper (12) as is expected for the nearly two-dimensional structure of a monolayer. The very low Pt coordination number (0.2) is more difficult to explain. Probably, the Pt contributions to the total Cu−Pt signal from different adsorption sites cancel
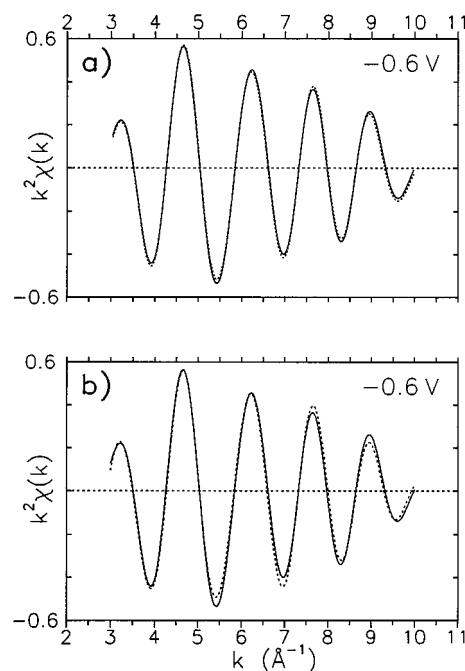

Figure 10. Comparison of the best fits to the data obtained at -0.6 V (dashed line) with the backtransformed experimental data (solid line): (a) four-shell fit including Cu−O, Cu−Cu, and Cu−Pt contributions; (b) three-shell fit without the Cu−O contribution.
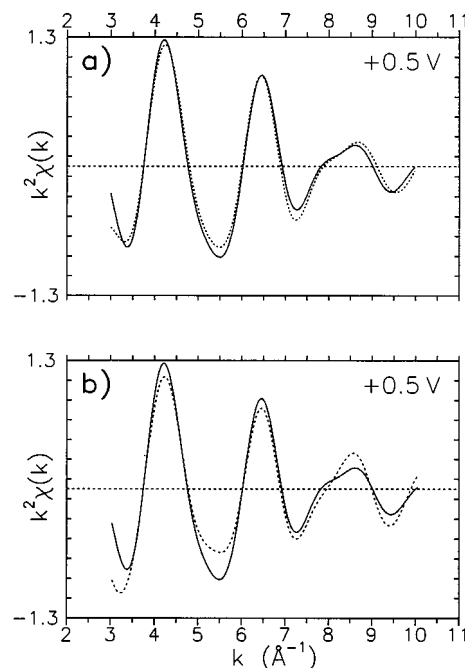

Figure 11. Best fits to the EXAFS data obtained at $+0.5$ V (dashed line) and the backtransformed experimental data (solid line): (a) three-shell fit including Cu−O, Cu−Pt, and Cu−Cu contributions; (b) two-shell fit without the Cu−Pt contribution.

each other as a result of the averaging of the signal (similar result were obtained for the Cu/Au(111) system[22]).

Owing to the limited k-range of the spectra presented in this work, only three nearest neighbors could be determined for $+0.5$ V (Figure 11a). The Cu−O distance and the number of oxygen atoms found in the vicinity of copper are compatible with the oxidation state of $+2$ concluded from the near-edge spectra. The high number of Pt nearest neighbors suggest that at the most positive potentials the copper oxide monolayer is incorporated into the Pt surface oxide formed at these high potentials.

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For comparison, much worse fit for a two-shell model (without Pt as a neighbor) is shown in Figure 11b supporting this interpretation.

4. Conclusion

Using transmission mode X-ray absorption spectroscopy, we observed in situ, under reaction conditions the near-range order and the variation of the oxidation state of a copper monolayer in alkaline solution adsorbed on the surface of platinum clusters. Since the experiments were performed in alkaline solution, Cu oxidation yielded an adsorbed oxide layer rather than Cu^{2+} ions in solution as is the case for an acidic medium. The metal monolayer was found to be very stable during several oxidation/reduction cycles. The near-range order in the reduced state depends only on the potential and not on the history of the system. A direct transformation from Cu^0 to Cu^{2+} and Cu^{2+} to Cu^0 was observed. However, significant adsorption of OH^- ions at the most negative potential has also been detected. At $+0.5$ V a near-range structure similar to that in tenorite was found with indications of the incorporation of the copper oxide into the surface platinum oxide/hydroxide layer. The results show that X-ray absorption spectroscopy is a powerfull tool for the in situ investigation of chemical and electrochemical reactions occurring at the interface between a highly dispersed metal and its liquid environment.

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