Flexibility of the Cu(110)–O structure in the presence of pyridine

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The presence of pyridine is shown by STM to have a profound effect on the structure of a Cu(110)–O surface; the spacing within the <100> directed Cu–O chains is unchanged at 3.6 Å but there is an increase in the spacing between the chains from 5.1 to 7.7 Å; the flexibility of the Cu(110)–O structure is emphasised by the observation that the change in structure is reversible when the pyridine is thermally desorbed.

Surface reactions are often discussed in the context of stable structures. However, work in Cardiff over the last 15 years has shown[1–4] that this neglects much of the interesting chemistry that goes on before the stable structures are formed. Furthermore, even when stable structures have been formed they can still be sensitive to weakly adsorbed species and this may have consequences for the chemistry that can occur at the surface.

Here, we return to the adsorption of pyridine at preoxidised copper surfaces, a system which we have previously studied[5] with XPS and HREELS. We reported that at clean Cu(111) surfaces pyridine desorbs completely below 240 K but that at preoxidised surfaces it is stable to 380 K. The HREELS data indicated that in the absence of preadsorbed oxygen, pyridine physisorbs with its ring plane parallel to the surface whereas in the presence of oxygen the orientation is different, with the ring plane perpendicular to the surface. There was also strong evidence for the formation of an N–O bond. The direct interaction between the oxygen and the nitrogen was confirmed by the XPS spectra which showed a shift of the O1s peak upwards in binding energy. The XPS also showed that the maximum concentration of pyridine adsorbed at the Cu(111)-O surface corresponded to approximately one-fifth of the preadsorbed oxygen concentration.

Here, we investigate the pyridine–oxygen interaction at the Cu(110) plane where in contrast to Cu(111)[6] there is extensive surface reconstruction[7,8] with the oxygen being incorporated into added copper–oxygen chains orientated in the <100> direction.

XPS and STM data were acquired on a combined STM/XPS instrument designed and built by Omicron Vacuum Physik. The sample was sputtered clean using argon at an energy of 0.6 kV and subsequently annealed at *ca.* 750 K for 30 min. Surface cleanliness was confirmed by XPS and the purity of the gases tested with *in situ* mass spectrometry.

Initial oxidation of the Cu(110) surface leads to the formation of copper–oxygen added rows, orientated in the <100> direction. The O–O spacing along the row is *ca.* 3.6 Å whilst the inter-row spacing is 5.1 Å giving an overall (2 × 1) unit cell. This well known structure was used to check the calibration of the STM measurements. Fig. 1(a) shows a section of a Cu(110) surface with several small islands of added oxygen–copper rows after exposure of the surface to dioxygen giving a surface coverage of approximately one-third of saturation. The (2 × 1) unit cell can be clearly made out in the image and more faintly the substrate rows that run in the $<1\bar{1}0>$ direction. The islands in Fig. 1(a) were stable over several scans and our experience from all of our work on this surface is that oxygen islands of this size are completely stable at room temperature and in the *absence*[9] of any other adsorbates.

Exposure of this surface to 1 L‡ of pyridine results in an increase in the spacing between the Cu–O chains to *ca.* 7.7 Å (three times the copper lattice dimensions), Fig. 1(b), but it is clear from the STM images that the structure within the chains maintains its original spacing. Quantification of the XPS data shows a ratio of 1:0.8 between the surface oxygen concentration and the pyridine molecule concentration. The copper substrate

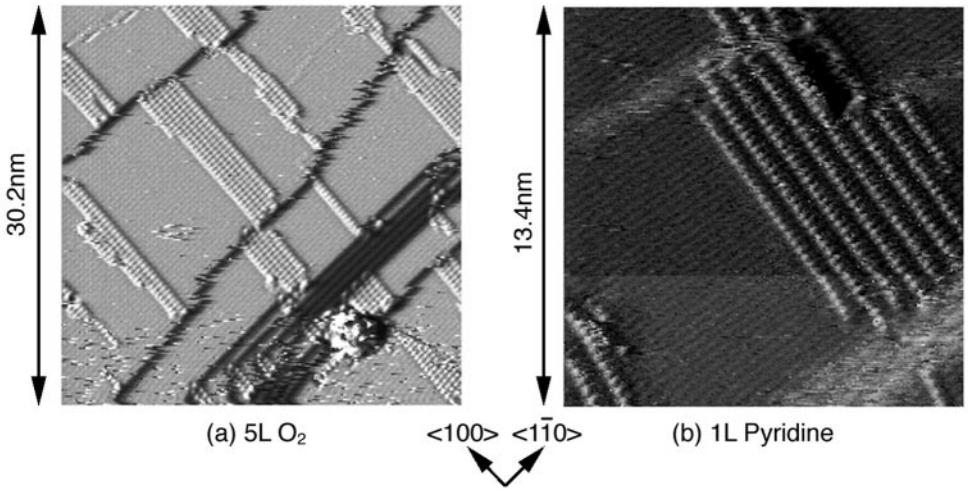

Fig. 1 The effect of pyridine on preadsorbed oxygen at a Cu(110) surface. (a) Cu(110) surface after exposure to 5 L O_2 at 290 K. The added Cu–O rows are *ca.* 5.1 Å apart and are orientated in the <100> direction giving a (2 × 1) structure. Imaging conditions: sample bias = −0.94 V, current = 3.1 nA. (b) Close up view of a section from (a) after exposure to pyridine at room temperature, the inter-row spacing is now 7.7 Å but the maxima within the rows are still spaced at 3.6 Å. Imaging conditions: sample bias = −0.12 V, current = 3.1 nA.

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structure is very clearly resolved in STM images taken under these conditions, possibly because of the adsorption of pyridine molecules on to the imaging tip. One can see that the brightest features in the restructured chains are exactly in line with the bright rows visible on the substrate. In the original (2 × 1)O structure, the copper rows line up with the positions of the oxygen atoms in the copper–oxygen chains,[7,8] Fig. 2(a). We would expect these features in the restructured chains to be the sites where pyridine is adsorbed and therefore the image adds further weight to the earlier XPS and HREELS evidence from Cu(111) that the pyridine interacts directly with the oxygen atoms within the chains. This is also consistent with the structure of pyridine *N*-oxide.

On heating the surface to *ca*. 380 K for 40 minutes the structures orientated in the < 100 > direction revert to the interchain separation of 5.1 Å typical of the (2 × 1) oxygen structure.

We deduce that the pyridine molecules adsorb on the Cu–O chains at the oxygen sites and are responsible for forcing the rows apart. The reason for the increase in the inter-row spacing can be understood when one considers that the internal structure along the rows retains its 3.6 Å spacing. The pyridine molecule is *ca*. 5 Å in diameter and the XPS shows close to a 1 : 1 pyridine/oxygen ratio. This implies that the pyridine ring must be orientated perpendicular to the surface with its plane lying in the $<1\bar{1}0>$ direction, in other words at right angles to the direction of the Cu–O chain, Fig. 2(b). Because of the diameter of the ring, steric hindrance would prevent pyridine adsorption on adjacent rows. It seems however, that the formation of the pyridine–oxygen complex provides sufficient energy to break up the existing structure forcing the chains apart and thereby enabling further pyridine adsorption.

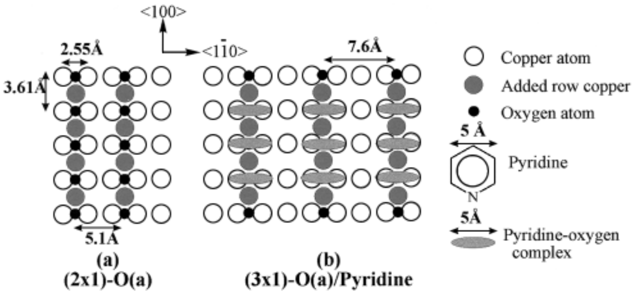

Fig. 2 (a) Structure of the (2 × 1)O(a) added row reconstruction on Cu(110); (b) proposed structure for pyridine adsorbed at the preoxidised Cu(110) surface.

Comparing the adsorption of the pyridine at the (111) and (110) surfaces we note that five times as much pyridine will adsorb onto the surface of the latter. We believe this is due to the flexibility of the particular structure formed by oxygen on Cu(110) in which the oxygen atoms are present in the added chains which are capable of moving over the surface with a low energy cost.[9] In contrast, the adsorbed state of oxygen on Cu(111) involves no large scale reconstruction[6] and the oxygen atoms are embedded within the substrate lattice effectively immobilising them.

The relevance of the observations here to the reactivity of a surface in the presence of a 'co-adsorbate' is obvious. They show that even weakly adsorbed species may influence the structure of the surface in such a way as to increase (or decrease) the availability of adsorption and reaction sites at the surface. Clearly, this must cast doubt on conclusions reached about reaction mechanisms based on structures observed in the absence of other reactants.

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Notes and references

‡ 1 L = 10^{-6} Torr s.

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