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On the nature of the active site in catalysis: the reactivity of surface oxygen on Cu(1 1 0)

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ABSTRACT

The nature of the 'active site' remains a subject of continual fundamental and applied interest in catalysis. In this paper we review the reactivity of oxygen on a well-defined copper surface to emphasize that not all sites on a surface are active sites, and that oxygen in different environments, even on such a well-defined material, has very different reactivities. By combining the use of molecular beam methods and STM imaging of surface reactions, it is generally found that the oxygen atoms which terminate islands on the (1 1 0) surface have much higher reactivity than those in the centre of the island. However, some molecules (formic acid, for instance) show high reactivity, even with these latter atoms. We show that the reactivity pattern is of acid–base character and that the oxygens terminating the islands are stronger bases than those in other locations. These, then, are effective for reactions with weak acids such as methanol or methyl mercaptan, whereas stronger acids such as formic acid appear to be able to react effectively with the more weakly basic oxygen in the centre of the islands.

1. Introduction

Ben Nieuwenhuys has published extensively in the field of catalysis, imaginatively blending surface science studies on single crystal substrates with more applied catalytic approaches and always seeking to elucidate reaction mechanisms by identifying intermediates and reaction pathways [1–7]. Often avoiding the *usual* substrates studied by others, Ben's philosophy is exemplified by his approach to methanol oxidation where, as he stated in 2005 [8], he aims:

> "to obtain a broader understanding on the role of the structure of sites on the surface ... on the activation of C–O and O–H bonds of methanol."

This philosophy has much in common with our own approach to studying catalysis; we use surface science techniques to explore fundamental reaction pathways of relevance to catalytic processes.

Surface science has had a significant impact on the understanding of catalysis at a number of levels, but especially at the atomic scale. Major advances in understanding include the recognition of the importance of surface reconstruction ([9] for one of the earliest examples) and flexibility [10,11], especially during adsorption and reaction, the structure sensitivity of many reactions (for the classic, and Nobel Prize-winning example see [12,13]) and the nature of the adsorption states involved in surface reactions and catalysis. This work on fundamental adsorption and reaction processes contributes to an understanding of industrial catalytic processes.

In a compliment to Ben's work, in this article we explore the nature of the active site in selective oxidation, a topic to which Ben has contributed significantly over the years. We focus here, entirely on the reactions of oxygen at a Cu(1 1 0) surface, which we have studied using a variety of different approaches over recent years. It is an interesting system because of the pronounced anisotropic reactivity of the chemisorbed oxygen, first shown clearly for methanol reaction with oxygen by molecular beam and STM studies [14–17], but also for reaction with ammonia on the basis of XPS data and Monte Carlo modelling [18] and subsequently by STM [19]. The root cause of this behaviour can be traced to the anisotropic nature of the chemisorbed oxygen structure at coverages below $\theta_O = 0.5$. It has been shown by a number of authors that oxygen forms strings in the [0 0 1] direction, which consist of alternating copper and oxygen atoms, and that these strings tend to cluster due to attractive interactions between the rows, into islands of p(2 × 1) structure [20]. The islands, at low coverages tend to have a high aspect ratio of the [0 0 1]:[1 1 0] dimensions, with the [1 1 0] sides much longer than the side [0 0 1] edges, as shown in Fig. 1. STM is an invaluable tool in such surface reactivity studies and its application to methanol reactivity, and to that of other systems, has recently been reviewed [21]

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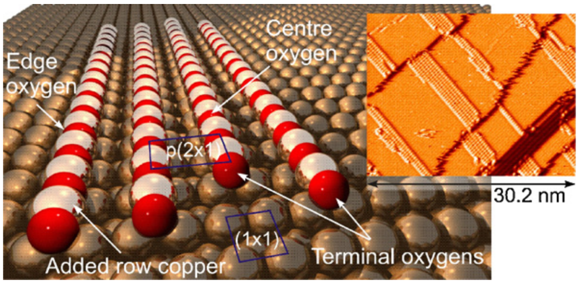

Fig. 1. Oxygen adsorbed on Cu(1 1 0), showing the island structure of the adsorbate, which consists of rows of Cu–O strings in the [0 0 1] direction, which group together to form islands in the [1 1 0] direction.

In this article we compare the behaviour of a number of different reactants with O/Cu(1 1 0) highlighting aspects of the selective oxidation mechanism that are perhaps not evident from considerations of the reactivity of a single molecule type. We start with methanol, for which we have clear evidence about its reactivity from diverse experimental methods, and then consider some analogues for which gas phase acidities differ.

2. Oxygen on Cu(1 1 0)

Oxygen dissociates efficiently on Cu(1 1 0) with a small activation barrier of 3 kJ mol^{-1} [22]. Below 80 K no ordering takes place and the oxygen states formed have been shown to be highly reactive [23]. Above 200 K or so the characteristic anisotropic islands described above are formed; Fig. 1 shows an image of just such an island, together with a schematic diagram indicating different types of oxygen sites present within the islands. We identify four types: (i) fourfold coordinate oxygens in the centre of the island; (ii) fourfold coordinate atoms at the [1 1 0] long edge; (iii) oxygens terminating the [0 0 1] short ends of the islands (probably threefold coordinate) and (iv) “isolated” oxygen atoms which may not yet have been incorporated into the islands but may be associated with a copper atom picked up from the step edges. The latter are not observed by STM at room temperature because of their rapid movement over the surface but they have been observed at low temperatures [24] and their very high reactivity demonstrated with a number of reactants [25].

3. Methanol oxidation on Cu(1 1 0)

Cu(1 1 0) has essentially no reactivity to methanol in the absence of surface oxygen and no methanol sticking is measured in a molecular beam system at ambient temperature (the details of the molecular beam system, which can be described as a single collision reactor, are reported elsewhere [26]). However, if oxygen is pre-dosed onto the surface then the alcohol reacts readily at room temperature (Fig. 2). The surface oxygen acts as a base stripping off of the acidic (alcohol) hydrogen (1).

$$CH_3OH(g) + O(a) \rightarrow CH_3O(a) + OH(a) \quad (1)$$

where ‘g’ and ‘a’ refer to gas phase and adsorbed species respectively. The surface hydroxyl is also a base and is capable of reacting with another methanol to liberate water from the surface, it is the water formation that provides the thermodynamic driving force for the reaction.

$$CH_3OH(g) + OH(a) \rightarrow CH_3O(a) + H_2O(g) \quad (2)$$

The fact that it is only the acid hydrogens which react is conclusively shown to be the case for reaction at low temperatures (up to ~350 K) by use of CH_3OD, which results in almost exclusively D_2O evolution into the gas phase [15,27]. Wachs and Madix [27] showed this early on for the reaction at low temperatures to form the methoxy, whereas Francis et al. [15] showed this to be the case at the decomposition temperature by using the molecular beam methods referred to above.

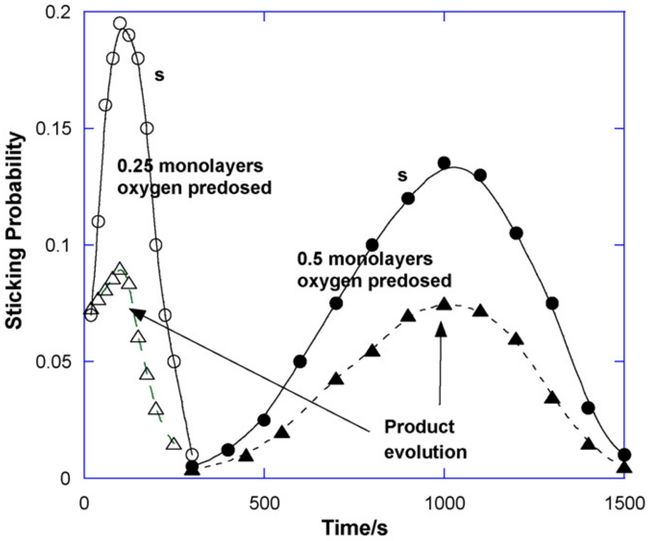

Fig. 2. Sticking probability of methanol on oxygen dosed Cu(1 1 0) at 353 K crystal temperature for two separate experiments with different oxygen precoverages. Open circles are for 0.25 mL of oxygen pre-dosed, filled circles are for 0.5 mL. Products evolve coincidently with the sticking, open triangles for 0.25 mL oxygen, filled triangles for 0.5 mL. The products are formaldehyde, hydrogen and water.

Thus adsorption is promoted by the presence of surface oxygen atoms. However, if the coverage of oxygen is too high then no reactivity is observed at ambient temperature, but if the surface is heated to 353 K, then the reactivity is very low initially and there is an induction period before reaction can proceed (Fig. 2). When these measurements are carried out much above ambient temperature, then the methoxy group can decompose at a significant rate and formaldehyde evolves into the gas phase, by the following reaction:

$$CH_3O(a) \rightarrow H_2CO(g) + H(a) \quad (3)$$

$$2H(a) \rightarrow H_2(g) \quad (4)$$

As shown in Fig. 2, formaldehyde evolution is rapid for a coverage of oxygen of 0.25 mL, but is slow when the p(2 × 1) oxygen adlayer is saturated ($\theta_O = 0.5$). Coincident with the sticking of methanol at 353 K, formaldehyde, water and hydrogen evolve into the gas phase, apparently fast compared with the adsorption which rate limits the evolution. This is because the methoxy species, which is the intermediate in this reactivity, is unstable at this temperature. Wachs and Madix showed, using TPD, that the desorption rate maximum occurs at ~350 K [27].

In a series of papers dealing with STM imaging of surface reactivity [15–17,28,29] the results show clearly why the reaction is slow at high oxygen coverage (Fig. 3) Here we see that methanol does not adsorb in the centre of the oxygen islands, but only on clean areas of the surface and there is clear phase separation between the adsorbed methoxy groups and remaining oxygen. Further, it is apparent that it is only the perimeter oxygens at the short ends of the islands which are reactive [16,17], i.e., the terminal oxygens shown in Fig. 1. In Fig. 3, it can be seen that the oxygen islands shrink from the ends since this is the location from which the oxygens are removed. We might then ask the question, why does the reaction not stop at that point, with the terminal oxygens removed? The answer is that, when the copper–oxygen

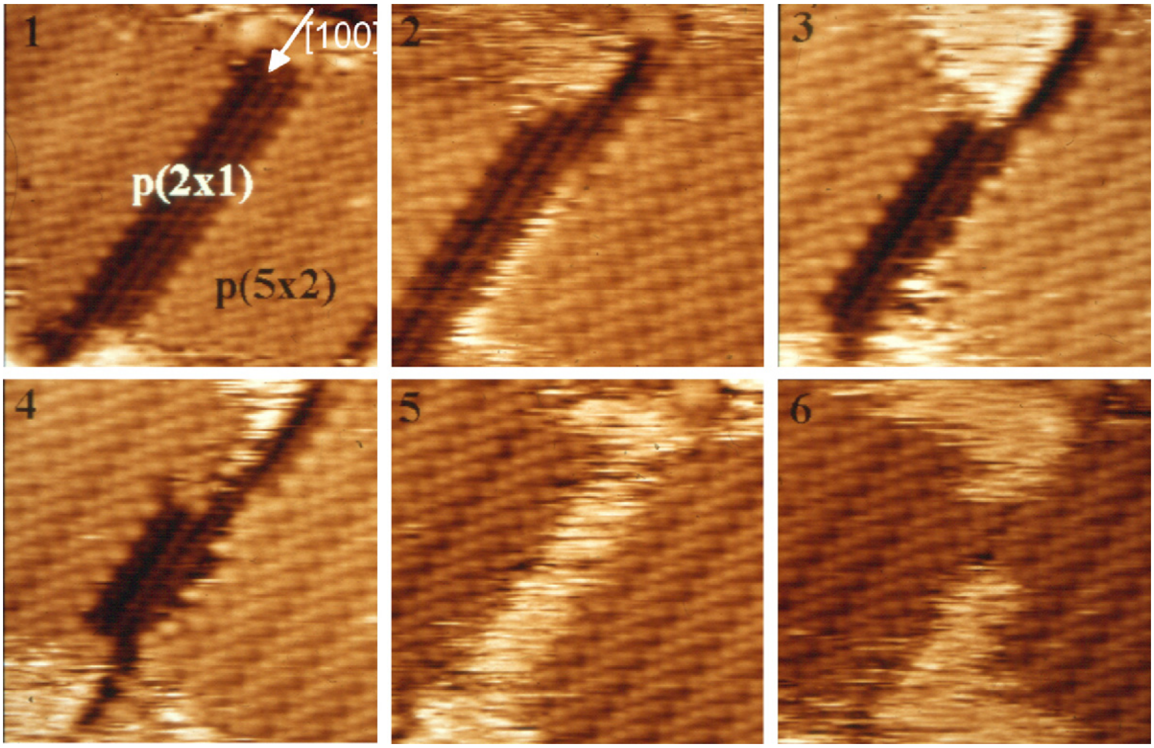

Fig. 3. The reaction of gas phase methanol with oxygen pre-dosed on the surface. Slide 1 begins part way through the reaction and shows phase separated areas of p(5 × 2) methoxy and a remaining p(2 × 1) oxygen island. The methanol does not adsorb inside the oxygen island, which reacts at the ends and shrinks in the [0 0 1] direction. The noisy areas within the island in frame 5, followed by the clear evolution of the (5 × 2) structure in 6, are probably due to diffusion of Cu atoms liberated from the Cu–O strings during reaction with the methanol.

strings shown in Fig. 1 are terminated by Cu, those atoms are unstable and diffuse away to reveal a new, active, terminal oxygen. This has been shown to be the case in a number of papers [16–18,31] (see also Fig. 8 below), generally the liberated copper atoms diffuse back to the steps.

Note that the *global* reaction equations are as follows:

$$2CH_3OH + (1/2)O_2 \rightarrow 2H_2CO + H_2 + H_2O \quad (A)$$

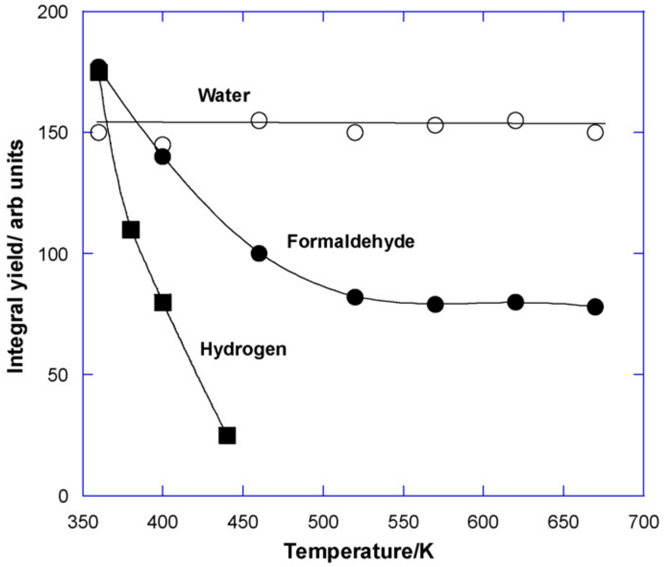

Fig. 4. The change in integral yield of products from methanol reaction with 0.5 mL of pre-dosed oxygen, as a function of reaction temperature. This illustrates the change in stoichiometry of the reaction which is discussed in the text.

This stoichiometry applies at low temperature, whereas at high temperature, the stoichiometry changes to:

$$CH_3OH + (1/2)O_2 \rightarrow H_2CO + H_2O \quad (B)$$

Fig. 4 shows this change in stoichiometry as a function of surface temperature and indicates that pathway (A) dominates at ~350 K, whereas (B) dominates above ~500 K. This stoichiometry change occurs because at high temperature, there also exists the possibility of hydrogen dissociated from the methoxy reacting with OH:

$$H(a) + OH(a) \rightarrow H_2O(g) \quad (5)$$

Once again this is proved to occur by isotopic labelling (CH_3OD), where it is shown that the dominant product above 500 K is HDO [15], whereas D_2O dominates at low temperature. The difference in reaction product distribution is due to the slow rate of methoxy decomposition at low temperature, which results in OD capture by incoming methanol before it can react with liberated H atoms on the surface. At high temperature methyl hydrogen liberation is fast compared with the methanol impingement rate and so HDO dominates. Obviously the relative rates of these processes will be a strong function of gas phase methanol pressure as well as temperature.

4. The selective oxidation of methanol analogues

Further insight into the nature of the reactivity of oxygen on the Cu(1 1 0) surface comes from a comparison of the reactivities of related molecules. Barteau and colleagues have emphasized a linear free energy relationship between gas phase acidities and surface reactivity [32–34]. Methyl mercaptan (CH_3SH) is perhaps the closest analogue to methanol but exhibits a gas phase acidity somewhat higher than that of methanol (Table 1 [35]). Experi-

Table 1
Gas phase acidities [35] of molecules used to probe the reactivity of oxygen states at a Cu(110) surface.

Molecule	Enthalpy of dissociation (kJ mol^{-1})
CH_3OH	1596 ± 4
Methyl mercaptan	1496. ± 8.4
Methylamine	1682. ± 11
HCl	1393.2 ± 1.3
NH_3	1687.8 ± 0.42
H_2O	1633.5 ± 1.7
Formic acid	1449 ± 5.0

mentally, this is evident with the observation that mercaptan, unlike methanol, reacts readily at room temperature with the clean Cu(1 1 0) surface, generating an adsorbed mercaptide ($CH_3S(a)$), Eq. (6) [30]. The hydrogen produced by this reaction presumably desorbs according to Eq. (4) although there is some TPD evidence that hydrogen may have a longer lifetime at the surface at room temperature when mercaptide is present.

$$CH_3SH \rightarrow CH_3S(a) + (1/2)H_2(g) \quad (6)$$

$$CH_3SH(g) \rightarrow CH_3SH(s) \quad (7)$$

$$2CH_3SH(s) + O(a) \rightarrow 2CH_3S(a) + H_2O(g) \quad (8)$$

$$CH_3SH(s) \rightarrow CH_3S(a) + H(s) \quad (9)$$

$$2H(s) + O(a) \rightarrow 2H_2O(g) \quad (10)$$

STM images show that the mercaptide induces significant changes in the structure of the clean surface, shortening terraces and separating bunched steps, thus indicating a very strong Cu–S

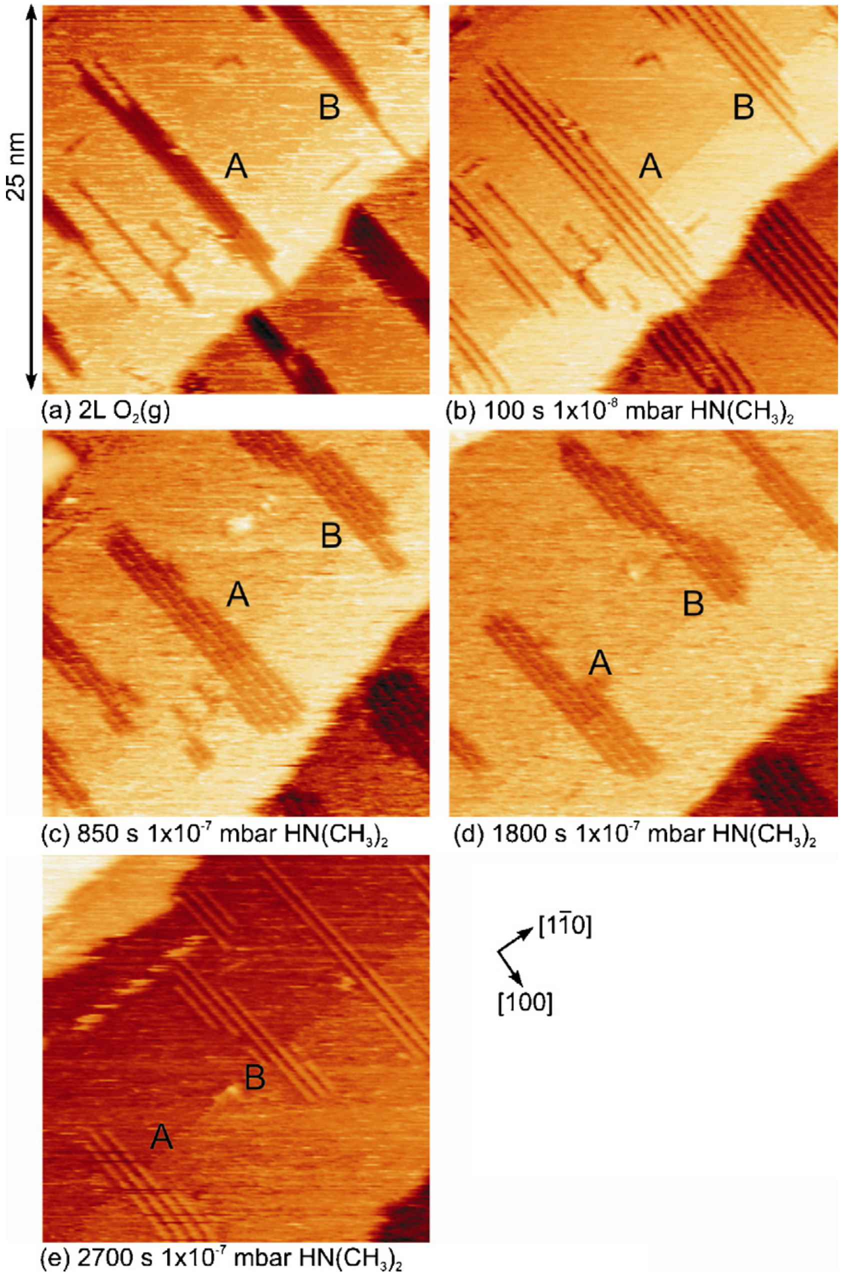

Fig. 5. STM images showing the reaction of gas phase dimethylamine with oxygen pre-dosed on the Cu(1 1 0) surface to form water and an amide which both desorb [7]. The p(2 × 1) oxygen islands in (a) are rapidly converted to a (3 × 1) structure in (b) before the "unzipping" reaction commences. Images (c)–(e) show the shrinking of the (3 × 1) islands in the [1 0 0] direction as the exposure to dimethylamine continues. Labels A and B identify the same two islands which appear to shift position in the frame because of thermal drift of the STM tip.

interaction. Interestingly, despite the high reactivity of mercaptan with clean copper, a 2:1 stoichiometric reaction is observed when methyl mercaptan is reacted with oxygen preadsorbed at the Cu(1 1 0) surface and this 2:1 stoichiometry is maintained until the oxygen is completely removed or the reaction is halted by the lack of free sites. This suggests a relatively long lived methyl mercaptan intermediate preceding the dissociation reaction that has a high chance of finding a reactive oxygen site before dissociating Eq. (6); an alternative model in which the methyl mercaptan dissociates and the hydrogen diffuses to the reactive sites cannot be ruled out altogether though one would expect that in this case hydrogen recombination, Eq. (4) would result in a significant lowering of the 2:1 stoichiometry. STM images show that despite its higher acidity, methyl mercaptan, like methanol, reacts with the chain ends rather than the chain sides [31]. Furthermore, at the extremes of oxygen coverage mercaptan also behaves very similarly to methanol. Reaction is limited at a saturated surface with an initially low sticking probability whereas when oxygen is prevented from forming the unreactive oxygen islands very high reaction rates and closely packed adlayers of mercaptide can be generated. Coverages of $\theta_S = 0.71$ were achieved after exposures of <100 L, for example, which significantly exceeds the maximum coverage achieved through reaction with preadsorbed oxygen where methyl mercap-

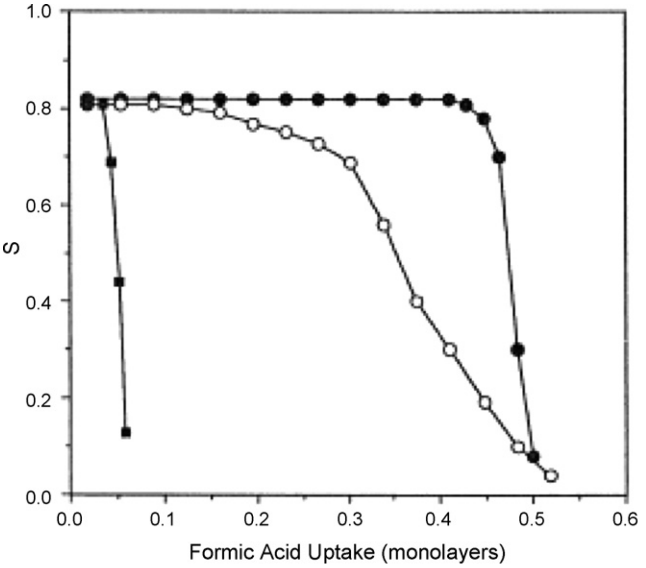

Fig. 6. The adsorption probability of formic acid on Cu(1 1 0) for three precoverages of oxygen, 0.5 (open circles), 0.25 (filled circles) and 0.03 (squares) monolayers. Note that the initial sticking probability on the clean surface is ~0.07.

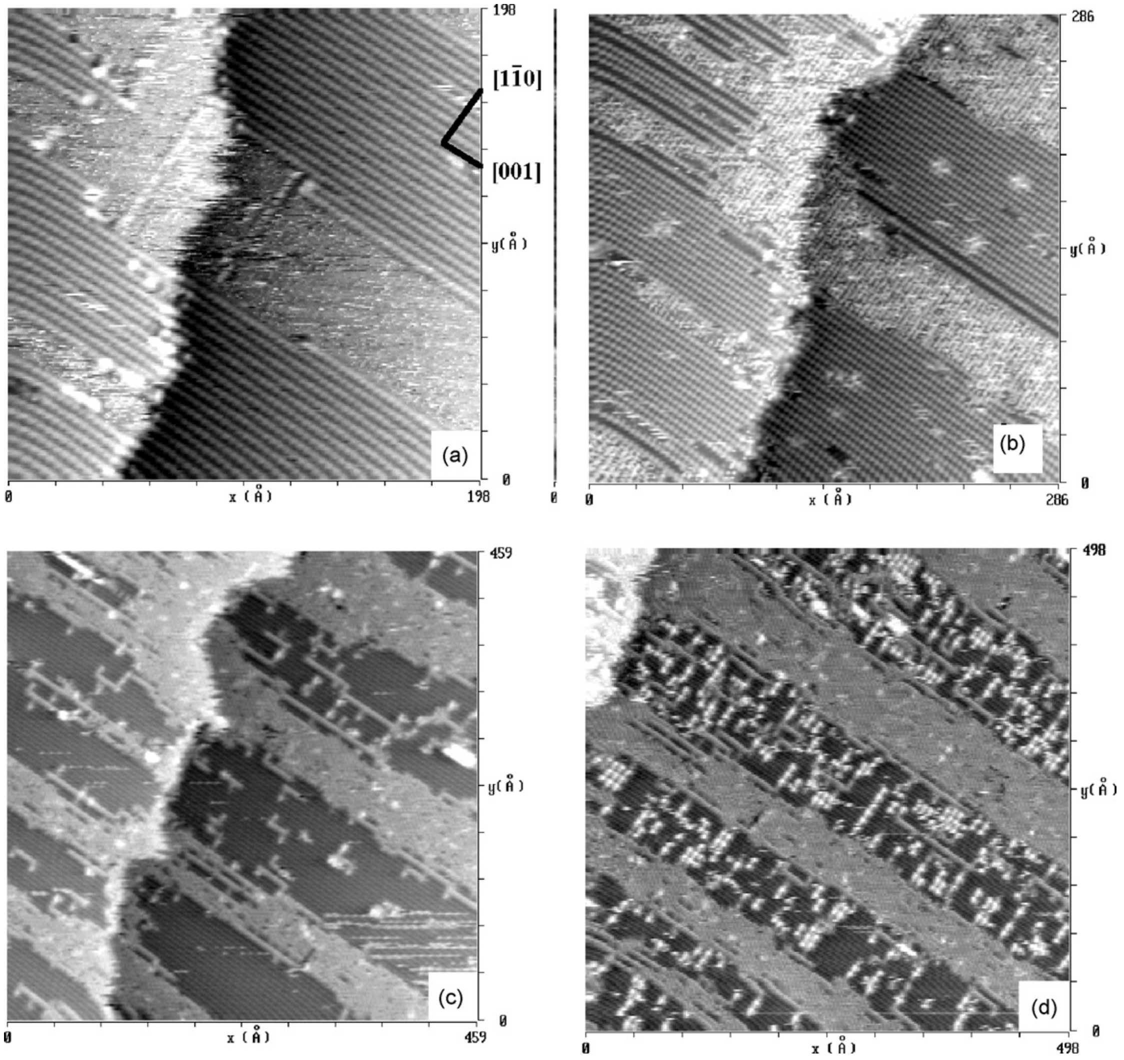

Fig. 7. Formic acid reacting with the Cu(1 1 0) surface pre-dosed with 0.25 mL of oxygen atoms. (a) Before reaction; (b)–(d) during reaction, showing reaction occurring within the original (2 × 1) oxygen islands, in contrast to the other simple molecules reported here. Image sizes: (a) 19.8 nm × 19.8 nm; (b) 28.6 nm × 28.6 nm; (c) 45.9 nm × 45.9 nm; (d) 49.8 nm × 49.8 nm.

tan exposures of over 10^3 L gave a maximum coverage of $\theta_S \sim 0.6$ [31]

The nitrogen analogue of methanol, methylamine (CH_3NH_2) introduces another dimension to the reaction with its Lewis base character in addition to the Bronsted acidity of the hydrogens on the nitrogen. The reaction of a number of amines with oxygen at Cu(1 1 0) surfaces has been investigated in a series of papers which confirm the pattern of reactivity discussed above for the methanol [37–39]. Reaction of the p(2 × 1) O(a) islands proceeds primarily by stripping of the Cu–O chains in the [1 0 0] direction; generally it appears to be strings at the edges of the islands that are removed fastest, thus islands get progressively thinner, as well as shorter. In all cases, the saturated surface is much less reactive, with reaction being initiated at step edges, defects and grain boundaries. On the other hand, as in the case of methyl mercaptan very high rates of reaction are achieved, with remarkably high selectivity, when the oxygen is prevented from forming islands by coadsorbing the oxygen with the amine reactant. In this case, as we have discussed previously [23] we propose that it is type (iv) oxygens that dominate the surface. In addition, however, a strong relationship between the basicity of the amine group and the reduction mechanism has been established which sheds an interesting light on the details of the reaction intermediates [39]. Strong bases such as pyridine and dimethylamine form complexes with the Cu–O chains with XPS showing a 1:1 N:O ratio. DFT calculations suggest that the complex involves a "dative" type bond between the nitrogen group and the copper atoms in the chain. For several amines, the reduction of the oxygen islands is preceded by the formation of a (3 × 1) structure which develops by sequentially forcing the Cu–O chains apart from the sides of the islands—a sort of island "unwrapping" that precedes the chain "unzipping" (Fig. 5). This behaviour was most clearly observed in the cases of pyridine and dimethylamine [38], the strongest bases of the amines studied and seems to be driven by steric interactions between the amine groups adsorbed on the chains and not the presence of adsorbates between the chains since STM showed no signs of such adsorbates being present, and DFT calculations showed that this is a relatively unfavourable environment. Weak bases such as ammonia and aniline do not show the (3 × 1) structure and the importance of the basicity was clearly demonstrated by replacing ethylamine with 2,2,2-trifluoroethylamine which is a much weaker base [38]. Whereas ethylamine reacts very rapidly with oxygen via a short lived (3 × 1) structure the oxygen islands maintain the p(2 × 1) structure when exposed to 2,2,2-trifluoroethylamine undergoing a slow "unzipping" reaction along the Cu–O chains. A further very interesting observation is that after an exposure of ∼20,000 L at room temperature, 2,2,2-trifluoroethylamine did not react significantly with a saturated p(2 × 1) adlayer on Cu(1 1 0), whereas the more basic ethylamine removed all traces of oxygen from the surface within 180 L. Clearly the strong adsorption of the basic ethylamine on the Cu–O chains enables a much more efficient reaction.

It is interesting to compare the high reactivity of the strongly basic ethylamine with that of formic acid and the even more acidic HCl. Fig. 6 shows the adsorption probability of formic acid on 0.5 monolayers of oxygen to be very high, 0.82, even at ambient temperature [36,40,41]. This clearly implies that the requirement of clean sites is not necessary for formic acid, a conclusion confirmed by STM images showing that formic acid can react with all oxygens in the oxygen islands. Fig. 7 shows formic acid reacting *within* the p(2 × 1) O island at the points indicated and goes on to react with most of the oxygens in the island. This reaction also involves considerable mobilisation of the Cu within the islands as shown in Fig. 8—where it is evident that the copper adatoms have added to the step edges after removal from the (2 × 1) islands. We have recently reported detailed kinetic modelling of this reaction [42]. Although formic acid is clearly more acidic than methanol it is evident that this is not the only factor that accounts for its reactivity since recent experiments show that HCl, which is clearly more acidic than either methanol or formic acid (Table 1) also prefers to react with the oxygen island edges [39]. As with mercaptan the HCl reacts readily with the clean surface but in the presence of preadsorbed oxygen a reaction stoichiometry of 2:1 is found, implying reaction with oxygen before reaction with the clean surface. STM images show that again the chain unzipping mechanism dominates with the copper that is released by the reaction initially trapped between the oxygen islands and subsequently adding to step edges to extend terraces or reacting with further HCl to form a novel $CuCl_2$ surface structure. Once again, reaction clearly takes place at the end of islands—there is no evidence for reaction at the centres of islands. The apparently anomalous behaviour of HCl might be related to this fact—the Cl needs a gross rearrangement of surface atoms to enable it to adsorb, and this requires vacant, metallic sites to be initially adjacent to the oxygen areas.

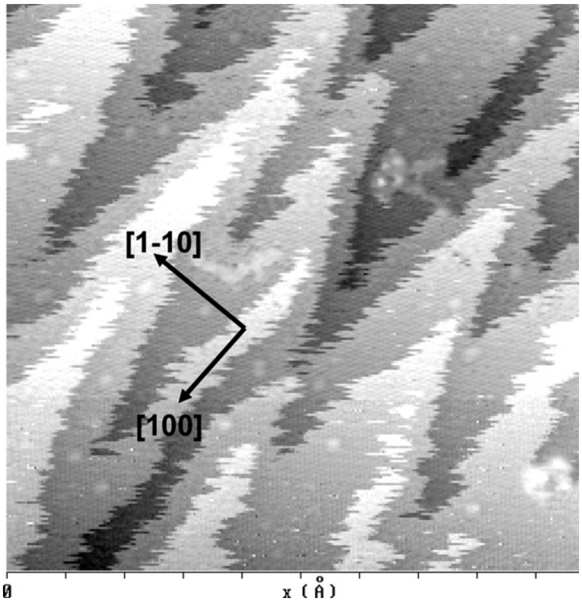

Fig. 8. A grossly reconstructed Cu(1 1 0) surface after adsorbing formic acid onto the surface with 0.25 mL of oxygen pre-dosed. The sawtooth structures correspond with what were originally linear steps on the surface and the formate is adsorbed in the (2 × 2) half monolayer structure on the flat areas of the surface. Image size 48 nm × 48 nm.

5. Conclusions

The reactivity of oxygen on copper is strongly anisotropic reflecting the varying basicity of the atoms in locations within the islands. With weakly acidic reactants like methanol, reactivity is dominated by the highly basic ends of the [0 0 1] chains on the surface. If there are few of these sites around (as on the full half monolayer structure) then reactivity is very low. Presumably the oxygen in the middle of the islands is less basic. On the other hand if the experiment is carried out in such a way that all the oxygen adatoms are effectively chain ends (in other words by coadsorbing reactants with oxygen) very high reactivities have been observed in every case. The more acidic formic acid provides a very interesting contrast to methanol since it reacts even with the island centres efficiently. However, it is not only the gas phase acidity which appears to drive the reactivity, since more acidic HCl appears to react less readily than formic acid. It may be that the site requirement for the adsorbed Cl is more demanding than for formate formation.

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