Gross rearrangement of metal atoms during surface reactions

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Abstract. We have used STM to observe changes in surface structure during the reaction of formic acid and methanol with oxygen precovered Cu(110). The reactivity pattern of oxygen on Cu(110) is strongly coverage and reactant dependent. This is partly due to the nature of the p(2 × 1) oxygen layer itself, which is an added row structure consisting of Cu–O chains in the [001] direction. Cu is unstable at the end of these chains and seeks an alternative, stable location during reactions. With methanol this location is associated with the methoxy layer itself. Formate resulting from formic acid adsorption, however, prefers to bond to the original surface layer, leaving the Cu atoms to diffuse elsewhere. If the surface is partially covered by oxygen this 'elsewhere' is the step, where Cu builds up between the diminishing O islands creating a sawtooth structure. When the surface is fully covered by the p(2 × 1) layer, however, the copper can only diffuse over the (2 × 1) layer itself, where it is converted into the higher coverage c(6 × 2) structure by rearrangement and compression of the original p(2 × 1) layer.

1. Introduction

Scanning tunnelling microscopy has a major advantage in comparison to other techniques employed for surface studies, and especially for studies of surface reactivity, namely that it is a real space technique which is also a non-averaging technique. This is of special importance for surface reactions because the 'active site' concept in catalysis often refers to specific minority sites on a surface which is where the reaction rate may far exceed that at other places. STM gives us the ability to image such sites at the atomic scale.

In this paper we focus on one aspect of surface reactivity which has come to the fore in recent years, that is, the incorporation of surface metal atoms into adsorbate induced surface structures. In particular we address the role of these metal atoms in the course of reaction on the surface. This concerns the involvement of surface metal atoms in structure formation at the surface, and longer range effects involving surface diffusion over reasonably long distances (∼100 Å or more). An advance in this direction came with the discovery by [1, 2] that the oxygen p(2 × 1) structure on Cu(110) was probably formed as an 'added row' arrangement, with chains of alternating Cu–O atoms in the [001] direction. This added row structure is comprised of Cu atoms, adsorbed on top of the original surface layer, which are thought to have come predominantly from step sites by diffusion. A model of this process is given in figure 1. A highly mobile phase of Cu atoms is present on the clean surface, which is in equilibrium with the steps edges (and perhaps mainly with kink sites). Cu atoms spend
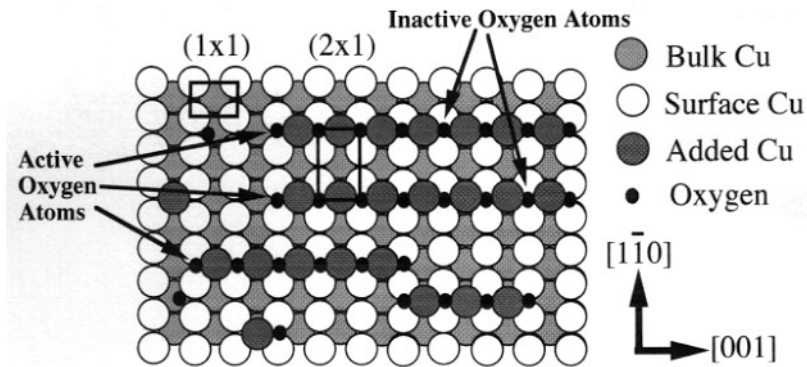
Figure 1. This shows the (1×1)-Cu(110) surface and the formation of the added row $p(2 \times 1)$ islands consisting of chains of alternating oxygen and copper atoms aligned in the [001] direction. The copper atoms which are incorporated into the growing island come from steps or terraces, the easiest route at 300 K being from steps. O–Cu chains tend to have a long aspect ratio early in the growth cycle. How the addition to the growing island occurs is uncertain. It may be by sequential addition of copper and oxygen atoms, though the authors feel it is more likely to be by addition of a diffusing Cu–O pair or higher ogliomers, one of which is illustrated in the figure. This could maintain the island with a more stable oxygen termination (see figure 2). When this oxygen structure is reacted with molecules such as methanol or formic acid, the terminal oxygen atoms at the short edge are more active than are the oxygen atoms in the island, even those in the long [001] oriented edge. This appears to be due to the lower surface coordination of these active atoms (threefold versus fourfold).

most of their time at the step, but occasionally overcome the barrier to diffuse away from the step, execute a random walk for a relatively short period of time and are then recaptured by the step. When oxygen is adsorbed on the terrace, oxygen atoms act as trap sites for these diffusing Cu species and the resulting Cu–O units then diffuse effectively as a surface molecule to be finally captured at the end of a growing [001] directed chain. A second source of Cu atoms is their direct removal from the terrace by oxygen atoms. It may be that this is always the mechanism of initial Cu–O association, but the defect produced in the terrace would be rapidly healed by Cu atoms migrating from the step. At high oxygen coverage where Cu adatom diffusion from steps is suppressed, the healing of terrace defects becomes more difficult, due to a lower clean surface equilibrium concentration of Cu. This process then dominates producing distinctive trenches where Cu atoms have been removed [3].

The nature of this added row structure is very important for the way oxidation reactions proceed at the surface of Cu(110)—what happens to the added Cu when the oxygen is removed from the $p(2 \times 1)$ structure by reaction with, for instance, methanol or formic acid? This is exactly the subject of this paper and is discussed in section 3 below.

2. Experiment

STM experiments were performed using an Oxford Instruments variable temperature STM. The STM is contained within an ultra-high vacuum (UHV) chamber equipped with additional facilities for temperature programmed desorption (TPD), Auger electron spectroscopy (AES), low energy electron diffraction (LEED) and Ar$^+$ ion sputtering. The chamber was ion pumped to produce a typical base pressure of 1×10^{-10} mbar while additional pumping for high gas loads during initial stages of system bakeout were available from a

turbomolecular pump. Tips are made from W/Re wire (97% W/3% Re, 0.2 mm diameter) and are prepared by electrochemical etching using concentrated NaOH with the application of a 10 V AC bias. The sample is mounted in a molybdenum holder and heating is achieved with a tungsten filament situated close to the rear of the sample, while higher temperatures can be achieved using electron beam bombardment. The system has been described in more detail elsewhere [4]. All images presented are raw data except for a simple global plane subtraction procedure. Tip–sample bias voltages and tunnelling currents are shown in the figure captions.

Gas exposures were carried out by backfilling the chamber; exposures are quoted in Langmuirs (L) where $1 \text{ L} = 1 \times 10^{-6}$ Torr s.

The Cu(110) sample was cleaned by repeated cycles of Ar^+ ion bombardment at 710 K, cooling in the ion beam and then annealing to 670 K. These were repeated until no trace of C or S was detectable in the AES. LEED was also utilized for surface cleanliness and for determining the structures formed on the surface.

3. Results and discussion

3.1. Methanol oxidation on Cu

We have carried out a considerable amount of work on this system [5–9]. A major finding of early work was that a stable methoxy species was formed on the surface when dosing methanol onto a predosed oxygen layer. Madix was the first to propose this from TPD [10] and UPS [11] studies, while EELS [12] and IRAS [13, 14] have confirmed this proposition. Two methanol molecules react with the preadsorbed oxygen to liberate water into the gas phase. Molecular beam studies have shown the reaction to be strongly oxygen coverage dependent, the reaction probability being high (0.15) at 300 K on a surface with 0.25 monolayers of oxygen, but being immeasurably low (<0.01) on a surface with the saturation coverage of p(2 × 1) oxygen, 0.5 monolayers. This is due to the requirement for a specific active site for this reaction, and this is the oxygen atom terminating the O–Cu rows of the p(2 × 1) islands (figure 1). These oxygen atoms are removed during reaction and the reaction front propagates in the [001] direction. The one-dimensional nature of the methanol reaction is described in detail elsewhere [6], and appears to be quite general for oxidation reactions on this surface (NH$_3$, CO and HCOOH all react with the oxygen preferentially in the [001] direction [15–17]).

It appears that the Cu atoms in the oxygen p(2 × 1) island are unstable at the end of chains which therefore preferentially terminate in oxygen atoms. When a terminal oxygen atom is removed by reaction (figure 2) the exposed Cu atom is left with lower co-ordination and is free to diffuse away from the chain. The fate of this free adatom has consequences which can alter the microscopic surface geometry, significantly affect the surface reactivity and even stabilize particular types of surface intermediate.

In the specific case of reaction with methanol, Cu adatoms that are released become incorporated into the methoxy p(5 × 2) structure which is formed. Support for this comes from (i) lack of evidence of Cu building up on terraces or steps during adsorption and (ii) Cu build-up at steps during decomposition of the methoxy as shown in previous work [6]. The latter may be viewed as the reverse of the Cu supply process to form the O p(2 × 1) structure.

The fate of copper atoms in the reacting p(2 × 1) islands depends upon the molecule with which it reacts and very different behaviour is observed during reaction with formic acid, as outlined below.
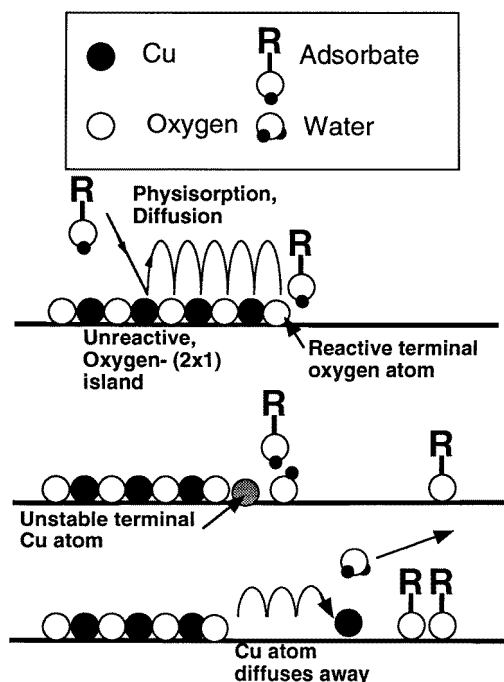
Figure 2. A schematic of the reaction of a Cu–O chain of the p(2 × 1) added row oxygen island, showing a terminal atom reacting with the hydrogens from the adsorbate to produce gas phase water and adsorbed intermediates (R_a), either methoxy or formate in the examples used in this paper. When the oxygen is removed in this way it is proposed that the terminal copper atom it reveals is in an unstable situation (see text for justification) and so it diffuses away from the terminal position across the surface, thus revealing a new, active, terminal oxygen atom to allow the reaction to proceed. The fate of the liberated Cu atom depends on the nature of the reacting molecule, as described in the text.

3.2. Formic acid oxidation on Cu(110)

The reaction stoichiometry of formic acid with oxygen is similar to that with methanol, that is, two molecules of formic acid react with one atom of oxygen at 300 K to produce water in the gas phase and two adsorbed formate units [18]. However there are several important differences:

(i) The structures formed are quite different from methoxy, and more varied (including c(2 × 2), (3 × 1) and p(4 × 1) [17–19]); the formate adsorption geometry is probably bidentate requiring two close packed Cu atoms with which to bond.

(ii) Formic acid is much more reactive having an initial reaction probability of 0.82, even on the 0.5 monolayer oxygen dosed surface.

(iii) The formate produced does not in general incorporate the Cu atoms released from the p(2 × 1) directly into its structure.

This latter point is the one of focus here. Figure 3 shows a sequence of images obtained as about 0.25 monolayers of oxygen are reacted rapidly with formic acid. The monatomic steps grossly change their shape during this process to leave, at the end of the sequence, a sawtooth structure which has formate adsorbed on it in the c(2 × 2) structure. The reason for this relates to the instability of Cu at the end of the chains during reaction (figure 2).
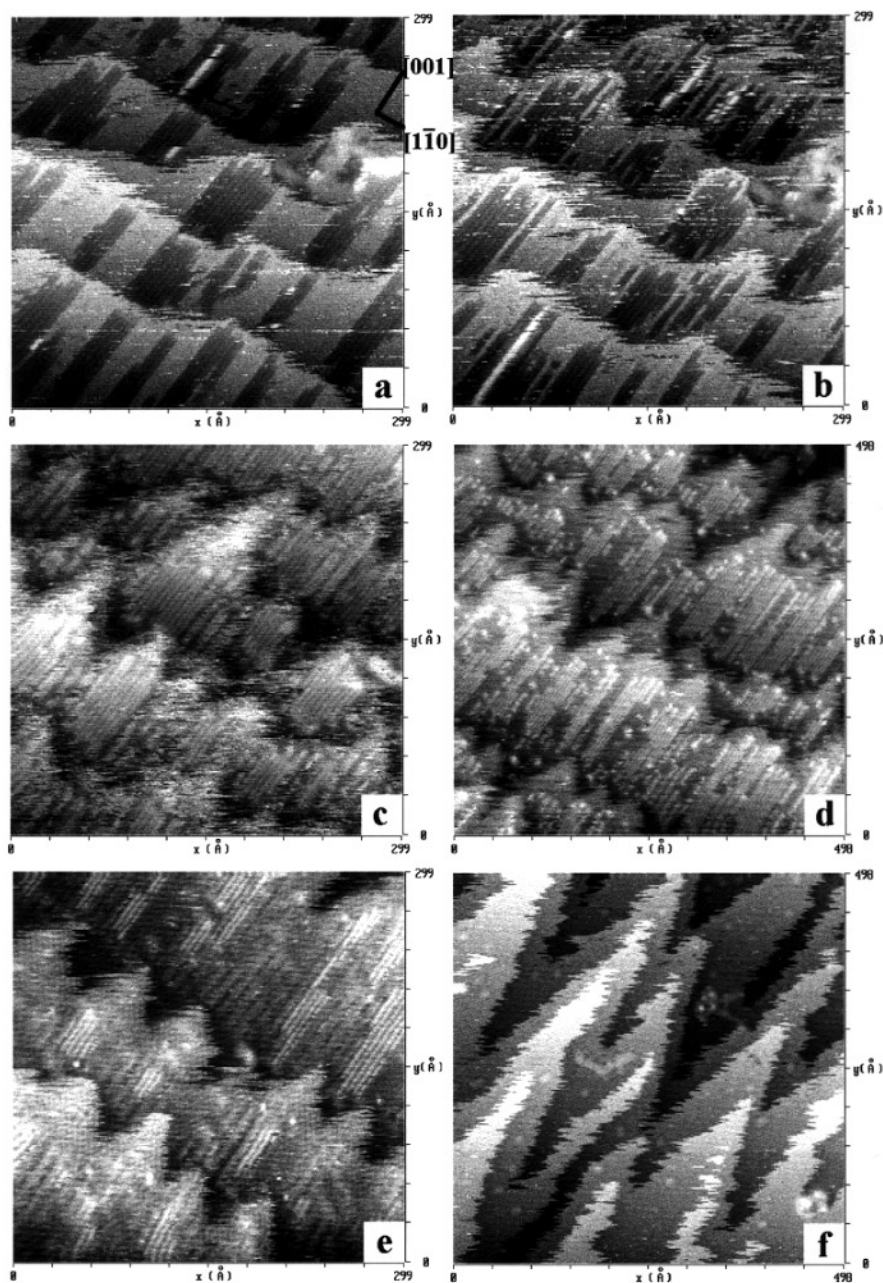
Figure 3. Successive STM images taken during the exposure to 2×10^{-8} mbar formic acid of Cu(110) predosed with $\sim$0.25 ML oxygen. The original surface (a) contains areas of clean surface and O-(2×1), the latter being the darker regions on a terrace. The sample was maintained at 300 K throughout. STM tunnelling conditions; (a)–(d) 1 V, 1 nA; (e)–(f) -500 mV, 1 nA. The images were taken after exposure to formic acid for time (t) of: (a) $t = 0$, (b) $t = 30$ s, (c) $t = 2$ min, (d) $t = 7$ min, (e) $t = 10$ min, (f) $t = 15$ min.
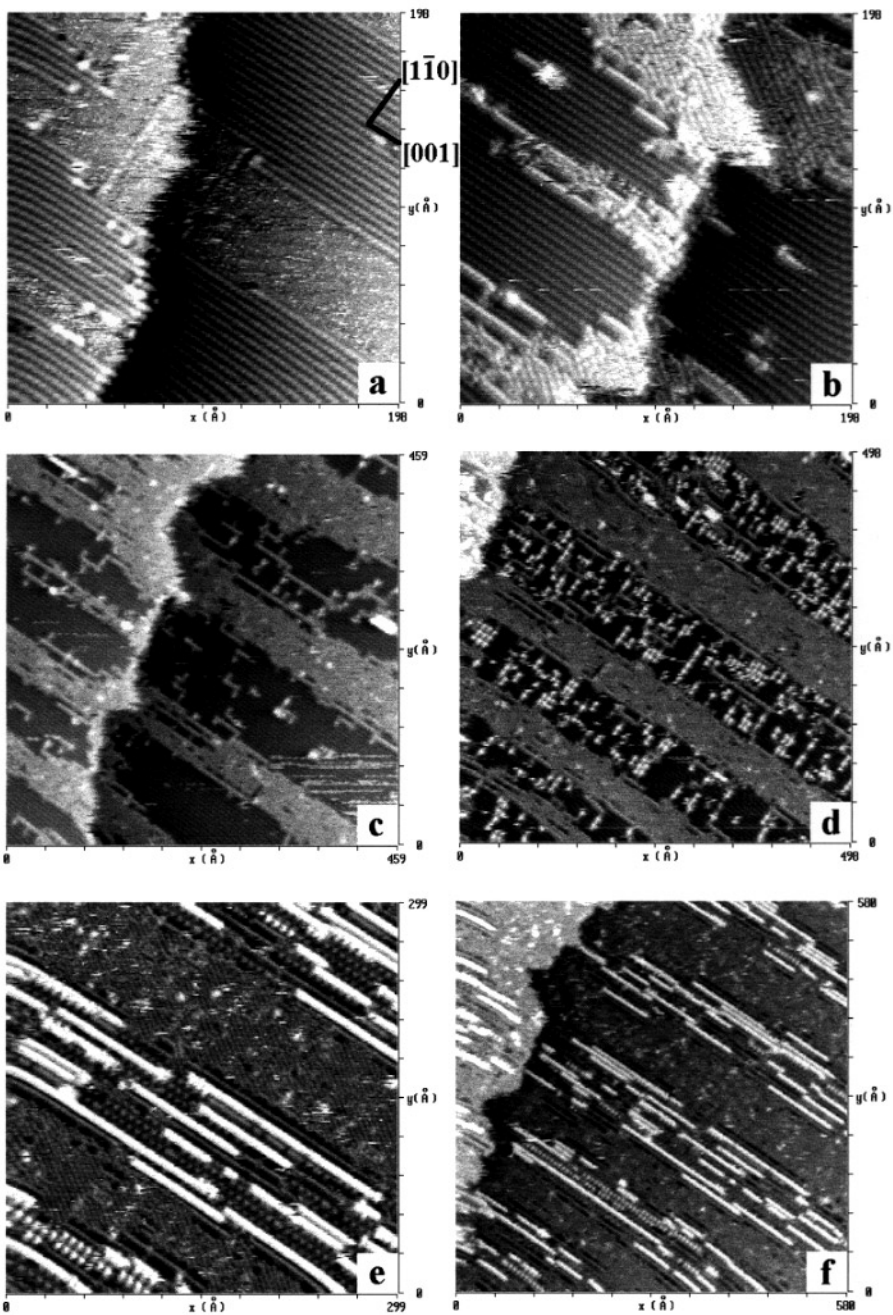
Figure 4. Successive STM images taken during the exposure to 5×10^{-9} mbar formic acid of Cu(110) predosed with $\sim$0.25 ML oxygen. The sample was maintained at 300 K throughout. Note that the background pressure of formic acid was considerably lower than in figure 3. STM tunnelling conditions; (a)–(d) 100 mV, 1 nA; (e)–(f) 100 mV, 0.1 nA. The images were taken after exposure to formic acid for time (t) of (a) $t = 0$, (b) $t = 22$ min, (c) $t = 26$ min, (d) $t = 32$ min, (e) $t = 43$ min, (f) $t = 44$ min.

It appears that the formate prefers to bind to the original surface layer (probably due to the bidentate bond requirement for two adjacent Cu atoms) leaving the released Cu adatoms to diffuse over the surface. These adatoms traverse the clean surface (preferentially along the troughs) to hit the step sites between the p(2 × 1) islands, thus beginning to build the sawtooth structure which protrudes out from the upper terrace. The p(2 × 1) islands, which are continuous over many step edges, act to channel Cu atoms rapidly to the step edge to form the sawtooth.

The situation, however, is strongly dependent on reaction conditions and becomes quite different when a similar layer of oxygen (2 × 1) is reacted slowly as can be seen in figure 4. Again the reaction proceeds initially from the ends of the oxygen rows, which are seen to retreat from the step edge, producing adsorbed formate which aggregates in the channels of clean surface between the oxygen islands. The step edge becomes rough and a small sawtooth begins to form. Eventually the area between the oxygen islands becomes covered with formate in the c(2 × 2) structure (figure 4(b)) and the Cu adatom flux to the step is reduced. Interestingly the reaction enters a second phase where oxygen atoms at the centre of the island are reacted with formic acid. Again these progress along the row after initiation. Crucially, however, the liberated Cu cannot diffuse over the clean surface since there is no clean surface. Instead diffusion occurs over the p(2 × 1) oxygen layer where it appears to become trapped. Evidence for the presence of these atoms is given in figure 4(d) where they are shown as the bright superlayer atoms in a local (4 × 2) structure on top of the original p(2 × 1). These then rearrange over a short period of time to form a new structure, the c(6 × 2) structure (figure 4(e), (f)) which consists of a high local coverage of oxygen atoms (0.67 monolayers) and added copper (0.83 monolayers) as shown in figure 5. This structure is relatively unreactive to formic acid and it remains on the surface blocking subsequent formic acid adsorption.
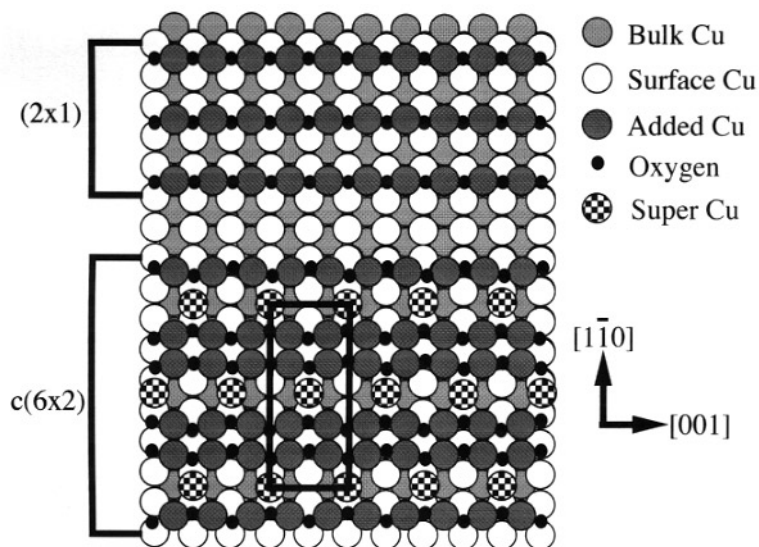

Figure 5. Schematic diagram showing the structure of the c(6 × 2) and p(2 × 1) adsorbate structures for oxygen on Cu(110). The unit cell of the c(6 × 2) structure is marked.

The relative unreactivity of the c(6 × 2) surface manifests itself during STM and molecular beam experiments on the p(2 × 1) saturated surface [4]. These studies show
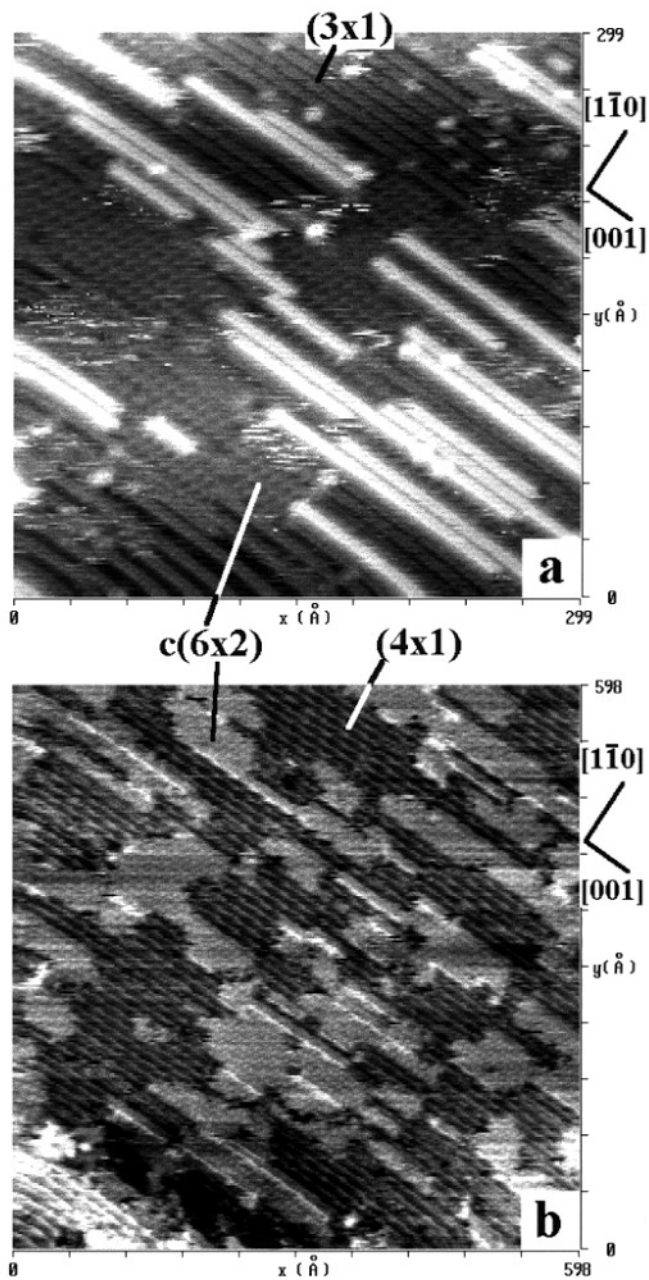
Figure 6. STM images taken following the exposure of an O-(2 × 1) presaturated surface with formic acid (a) at 300 K, −0.5 V, 1 nA, (b) with both the formic acid adsorption and the STM imaging carried out with the sample maintained at 360 K, 0.5 V, 1 nA. Regions of formate (3 × 1) and (4 × 1) and O-c(6 × 2) are indicated.

that although the initial reactivity of the p(2 × 1) saturated surface is high, the reaction terminates after only half the oxygen has been used up at room temperature. The remaining

oxygen is compressed up into the $c(6 \times 2)$ [17–19]. Notably the majority of the surface is covered by formate $p(3 \times 1)$, some of which appears raised on the terrace due presumably to incorporation of Cu atoms released in the reaction. An STM image of such an overlayer is shown in figure 6(a). The molecular beam studies accurately determine total formate uptake at this temperature (0.5 ML) and lead to the conclusion that the main structure for formate within this layer is a 2/3 monolayer coverage $p(3 \times 1)$ [4].

Interestingly, for the identical reaction undertaken at elevated temperature (340–440 K) the total uptake of formic acid drops to $\sim$0.15 ML [18]. This reduction has been shown to be due to the production of the formate (4×1) structure consisting of alternate rows of formate and oxygen–copper chains with a local formate coverage of 0.25 ML. Figure 6(b) shows an overlayer generated from the reaction of formic acid with an O-(2×1) presaturated surface at $\sim$360 K. The overlayer contains both formate (4×1) and oxygen $c(6 \times 2)$. The formate regions only occupy one height on a terrace and so does not incorporate added Cu into the formate other than that remaining in the O–Cu chains. The surfeit of Cu released in the reaction with formic acid is again responsible for the formation of large areas of $c(6 \times 2)$, this time covering $\sim$40% of the surface. The oxygen tied up in the (4×1) and $c(6 \times 2)$ is relatively unreactive, resulting in the very much reduced uptake in this temperature window.

4. Conclusions

The added row structure of oxygen adsorbed on Cu(110) has a strong influence on the way reactions take place at the surface, as demonstrated by STM imaging. It is proposed that Cu atoms are not the stable termination of these islands at 300 K, which therefore terminate in oxygen atoms. The fate of the incorporated copper atoms which are then released in oxidation reactions depends strongly on the reaction involved. For methanol, the liberated Cu atoms are mainly incorporated into the growing $p(5 \times 2)$ structure, whereas formate prefers to bind to the original surface layer, ejecting the added row Cu to other locations. With formic acid at low oxygen predoses, the other locations are steps where they can construct a large scale sawtooth structure. At saturation oxygen precoverage (complete $p(2 \times 1)$) the released copper diffuses onto the $p(2 \times 1)$-O layer to help reconstruct and compress it to the $c(6 \times 2)$ structure which has a high density of Cu atoms present. This structure remains on the surface since it is very unreactive to formic acid.

Acknowledgments

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