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Insights into surface reactivity: formic acid oxidation on Cu(110) studied using STM and a molecular beam reactor

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Using a combination of STM and molecular beam reactor data we summarise some important features of a model reaction (formic acid oxidation on Cu(110)) which is of general significance to surface reactivity and to catalysis. Three such features are highlighted here. The first concerns the role of weakly held species (possibly physisorbed) in surface reactions. These species, although of very short lifetime on the surface, can, nevertheless, diffuse over long distances to “find” a sparse distribution of active sites. Thus a very low coverage of oxygen on the surface of Cu(110) increases the sticking probability of *all* the formic acid molecules which strike the surface to high value (0.82), even though the clean surface is relatively unreactive. The important concept here is the “diffusion circle” or “collection zone” which represents the area of surface visited by the molecule in its short sojourn in the weakly held state. The second theme concerns the concept of the “flexible surface”. We show that the involvement of surface atoms in reactions directs the structure and reactivity for a particular reaction. For formic acid oxidation the liberation of Cu atoms during the removal of oxygen as water leads to gross restructuring of the surface and can lead to “compression” of one reactant (the oxygen in this case) into a lower area, higher local coverage, unreactive state (the c(6 × 2) oxygen structure). Thirdly, and finally, it is proposed that, for many surface reactions, the surface acts in an analogous way to a solvent, supporting a “dissolved” (highly mobile and fluxional) phase of intermediates at low coverage, which crystallise out above a critical coverage (the 2D “solubility limit”).

Keywords: catalysis, combustion, oxidation, formic acid, STM, molecular beams, surface diffusion, surface reactivity, active sites, reconstruction

1. Introduction

Formic acid generally adsorbs on metal surfaces by initial dehydrogenation at the acid hydrogen. On late transition metals this produces a formate which is unstable at room temperature towards total dehydrogenation, whereas on IB metals they are stable to higher temperatures. The reaction of formic acid, therefore, makes a simple and relevant model for surface reaction processes. It is relevant because formate is a simple C1 intermediate which is involved in a variety of catalytic processes. In particular it is implicated as a selective intermediate in methanol synthesis [1], and as an intermediate in the non-selective combustion of methanol in methanol oxidation to formaldehyde [2]. We have studied this system in recent years on a Cu(110) surface in order to gain a detailed understanding of the adsorption and reaction of formic acid and of its relevance, if any, to the processes above. This paper brings this work together in a thematic way which illustrates the relationship of these specific data to more general phenomena in catalysis and surface reactivity. These include the role of weakly held (physisorbed) species in surface reactions and the large scale rearrangement of the reactive surface itself (the “flexible surface” [3,4]).

2. “Active sites”, precursor state diffusivity and the “collection zone”

The importance of precursor states in adsorption [5–7] and surface reactions [8–11] has been demonstrated previously. Formic acid adsorption represents a particular case of their significance. The term “precursor state” is used to define a species of low lifetime on a surface, but one which nevertheless is an intermediate state to the formation of the final, stable species. Thus, in principle, it can be any state (physisorbed or chemisorbed molecules) whose lifetime on the surface before desorption is short; which state is involved largely depends on temperature. By way of example let us imagine that formic acid has physisorbed and chemisorbed molecules with adsorption heats similar to the heat of vaporisation (probably an underestimate of the physisorption energy) of 40 $\mathrm{kJ\,mol^{-1}}$, and of chemisorption of 70 $\mathrm{kJ\,mol^{-1}}$. Figure 1 shows the extent of diffusion of these species at three temperatures based on the following simplistic Arrhenius type equation, where N_{H} represents the number of hops during the residence on the surface. This is derived using the approximation that the diffusion activation barrier, E_{diff}, is $1/3$ of the desorption barrier E_{des}. As can be seen in figure 1, diffusion is extensive:

$$N_{\mathrm{H}} = \tau_{\mathrm{desorption}}/\tau_{\mathrm{hopping}} = (A_{\mathrm{diff}}/A_{\mathrm{des}})\,\mathrm{e}^{-\{(E_{\mathrm{diff}}-E_{\mathrm{des}})/RT\}} \cong \mathrm{e}^{(2E_{\mathrm{des}}/3RT)}.$$

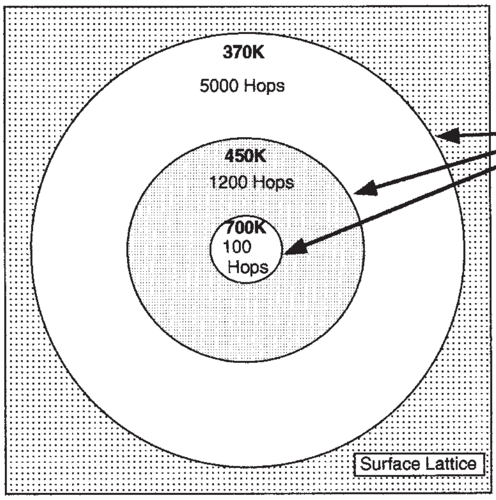

Figure 1. Diffusion circles for a molecule with either 40 or 70 kJ mol^{-1} desorption energy (10^{-13} s lifetime at infinite temperature). For the former value the extent of diffusion corresponds to temperatures as indicated in the figure. For the higher desorption energy the corresponding temperatures are 650, 790 and 1225 K.

Here τ are Frenkel lifetimes, A represents the frequency factors which, on the right-hand side of the equation, are assumed equal. The circles shown in figure 1 are simply drawn with a radius of $(N_{\mathrm{H}}/\pi)^{1/2}$ representing the sum of their hops. In reality some sites will be multiply visited. However, within the approximations involved, the circles are a good visualisation of the extent of surface diffusion by weakly held states. If the diffusing species is physisorbed it will only weakly sense the corrugation of the surface, and so is likely to exhibit the circular isotropic diffusion zone. However, if it is chemisorbed, it is likely that the molecule will exhibit anisotropic diffusion, depending on surface morphology. For instance, on Cu(110) it is likely to diffuse further, on average, along the low corrugation $\langle 1\bar{1}0\rangle$ direction than in the $\langle 001\rangle$ direction across the more severe potential corrugation.

The experimental validation of these ideas for the particular system studied here is shown in figure 2. This shows the sticking of formic acid on Cu(110) and illustrates several important facts:

(i) The clean surface is of relatively low reactivity at 300 K.

(ii) Very low coverages of oxygen enhance the sticking of formic acid to a high value of 0.82 (±0.01).

(iii) For half of the saturation coverage of oxygen (0.25 ML) the sticking of formic acid is essentially constant as the reaction proceeds, until almost all of the oxygen is lost.

(iv) When 0.5 monolayers of oxygen is adsorbed (completion of the p(2×1) structure) only half of the oxygen is consumed by the reaction; the remaining 0.25 monolayers is apparently unreactive. This is also why the initial sticking probability does not stay constant, in contrast to the result at 0.25 ML, since part of the surface becomes unavailable, as described below, reducing the total area for adsorption.

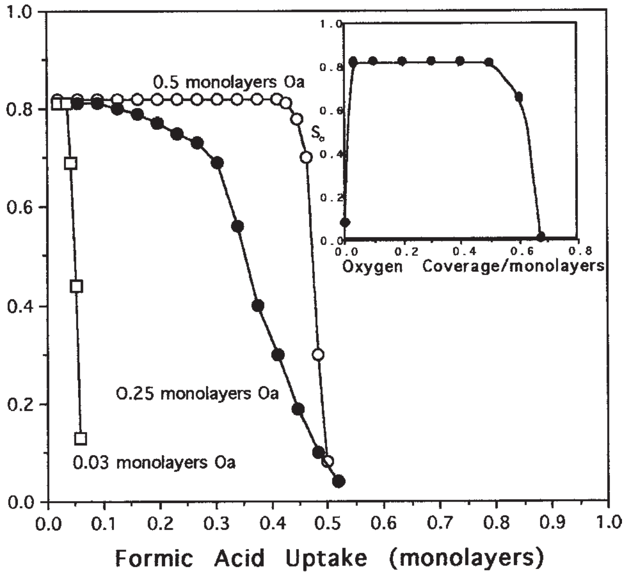

Figure 2. The sticking probability dependence on formic acid uptake (as formate) on Cu(110) at 300 K for three different pre-coverages of oxygen atoms. Note that the sticking probability on clean Cu(110) is approximately 0.07. The inset shows the initial sticking probability of formic acid and its dependence on oxygen pre-coverage, and shows that formation of the c(6×2) oxygen layer (0.67 monolayers of oxygen) results in a low reactivity surface.

(v) At 0.67 monolayers of oxygen (the c(6×2) structure) the adsorption probability is very low (at approximately 0.01). This is shown in the inset of figure 2, which displays the measurement of the initial sticking probability (S_0) of formic acid for various oxygen precoverages on the surface.

Points (iv) and (v) will be dealt with in section 3.2 below. The reaction of formic acid with the surface can be summarised by the following equations:

$$\mathrm{HCOOH_{(g)}} \rightarrow \mathrm{HCOO_{(a)}} + (1/2)\mathrm{H_{2(g)}} \qquad (1)$$

$$\mathrm{2HCOOH_{(g)}} + \mathrm{O_{(a)}} \rightarrow \mathrm{2HCOO_{(a)}} + \mathrm{H_2O_{(g)}} \qquad (2)$$

$$\mathrm{HCOOH_{(g)}} + \mathrm{O_{(a)}} \rightarrow \mathrm{CO_{2(g)}} + \mathrm{H_2O_{(g)}} \qquad (3)$$

The work described in this paper is mostly concerned with reaction (2) which occurs at temperatures where formate is stable on the surface; reaction (3) begins to occur above 400 K and is dominant by 600 K [12]; reaction (1), on the clean surface, has a low probability.

The reason for the observations in figure 2 and points (i)–(iii) above lies in the diffusion of a weakly held (precursor) state of formic acid. The active site for reaction (2) is the oxygen atom, and even though the vast majority of the surface is clean at low oxygen coverage with a very low ability to dissociate formic acid, nevertheless the reaction probability is already high. This shows that the diffusion is high, the average spacing between oxygen atoms at this coverage being something like five sites, and yet the

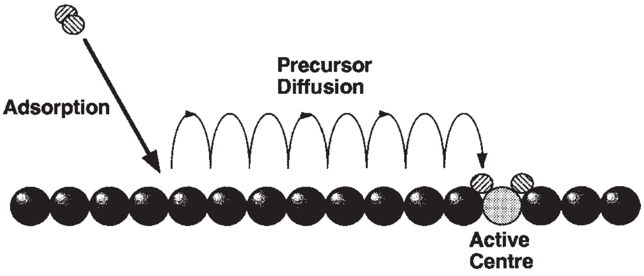

Figure 3. A schematic model of adsorption into a short lifetime precursor state at an inactive site on the surface and diffusion to find the active site for, in this case, dissociation. The active site could also be a different element on the surface or a defect.

formic acid has a 100% probability of finding them during diffusion in the weakly held state. For propan-2-ol the same kind of effect was observed but was measured to an even lower oxygen pre-coverage of 0.008 monolayers [13]. In reality "average spacing" is an incorrect concept for this system, since oxygen grows in an island fashion and, at the low coverages mentioned, tends to exist in the form of mobile strings [14,15]. The average spacing between strings is approximately 30 lattice units in one dimension. Many molecules would impinge on the surface at a site remote from the strings and, without diffusion in the weakly held state, would be reflected back into the gas phase.

This kind of diffusivity is very important for surface reactions in general and for some kinds of catalysis. Henry at Marseilles has shown that the lifetime of *all* CO molecules which first hit a MgO surface with a 1% coverage of Pd is high, even though the lifetime on clean MgO is very low (the net sticking probability on clean MgO is zero, whereas with only 1% Pd coverage it is close to unity) [16]. In effect, this makes the cross section for reaction of the incoming molecule very high. As demonstrated in figure 3, this can be significant for enabling molecules colliding with a catalyst to "find" the active centre for the reaction which might be at a minority metal particle, or at a defect centre in an oxide which may be present at very low coverage. Note that in other works this area of diffusion has been called, as here, the "diffusion circle" (figure 1) [11] or the "collection zone" as described by Boudart [8,9].

3. The "flexible surface": gross restructuring of reacting surfaces

3.1. Saw tooth formation

A major contribution of surface science has been to the understanding of local rearrangement of surface atoms during adsorption (adsorption-induced reconstruction). Well-known examples of this phenomenon are the naturally hexagonally reconstructed clean Pt(100) surface which reverts to the bulk terminated (100) upon the adsorption of many types of molecules [17] and the $(1 \times 1) \to (1 \times 2)$ missing row transition upon adsorption of oxygen [18] or CO [19] on Pd(110), for instance. Cu(110) also reconstructs in oxygen, but in a rather different way, to form an "added-row" reconstruction (figure 4) consisting of added Cu and O atoms in an island growth mode [20,21]. The nature of this layer has important consequences for the reactivity with formic acid and other molecules.

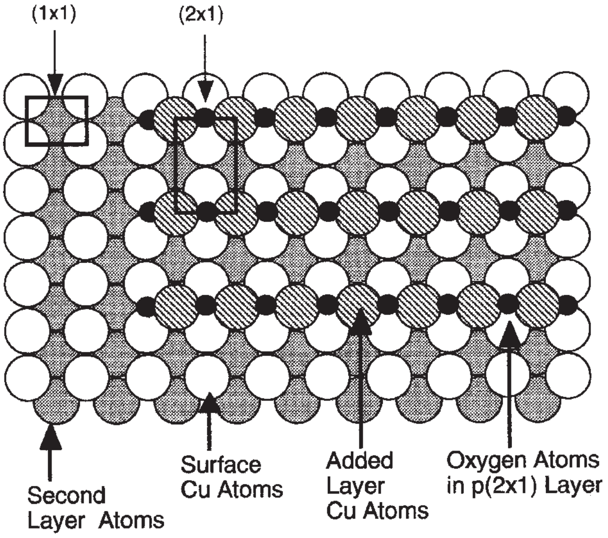

Figure 4. Model of the added row $p(2 \times 1)$ oxygen structure on Cu(110).

When formic acid reacts with a Cu(110) surface which is half covered with islands of $p(2 \times 1)$-O, then the reactivity with formic acid is high (figure 2), and all the oxygen is consumed in forming a layer with 0.5 monolayers of formate adsorbed in a well-ordered $c(2 \times 2)$ structure [12,22–24]. However, as the STM images in figure 5 show, the surface rearranges on a gross scale to form a totally new morphology with a sawtooth arrangement nucleated at the originally straight steps. This occurs due to the nature of the reaction, as illustrated in figure 6. When oxygen is reacted from the island it is left with terminal Cu atoms, which are unstable at the end of Cu–O chains, the latter preferring an oxygen termination. The evidence for this instability is several fold. Firstly, the $p(2 \times 1)$ structure has been formed predominantly by loss of Cu atoms from step edges [20], and so it might be anticipated that the reverse process could occur on removal of oxygen. Secondly, in other related work [25], we found that Cu from the $p(2\times1)$ was incorporated into methoxy islands after reaction; this was evidenced by the extension of nearby steps when methoxy islands were broken up by decomposition. Thirdly, the gross structural changes reported in detail below support loss of Cu from the islands as the oxygen is lost from them. The Cu atoms that are liberated take the "easiest" (lowest barrier) pathway to a stable (long-lived) binding site. In this case, we believe that this involves diffusion over the clean surface between the oxygen islands with precipitation at the step sites which are of higher coordination and stronger binding than the terrace sites. The reason for the sharp sawtooth then probably relates to the initiation of this step growth, which is ordered by the original oxygen islands which were fairly evenly spaced. However, as seen in the bottom left image in figure 5, and in

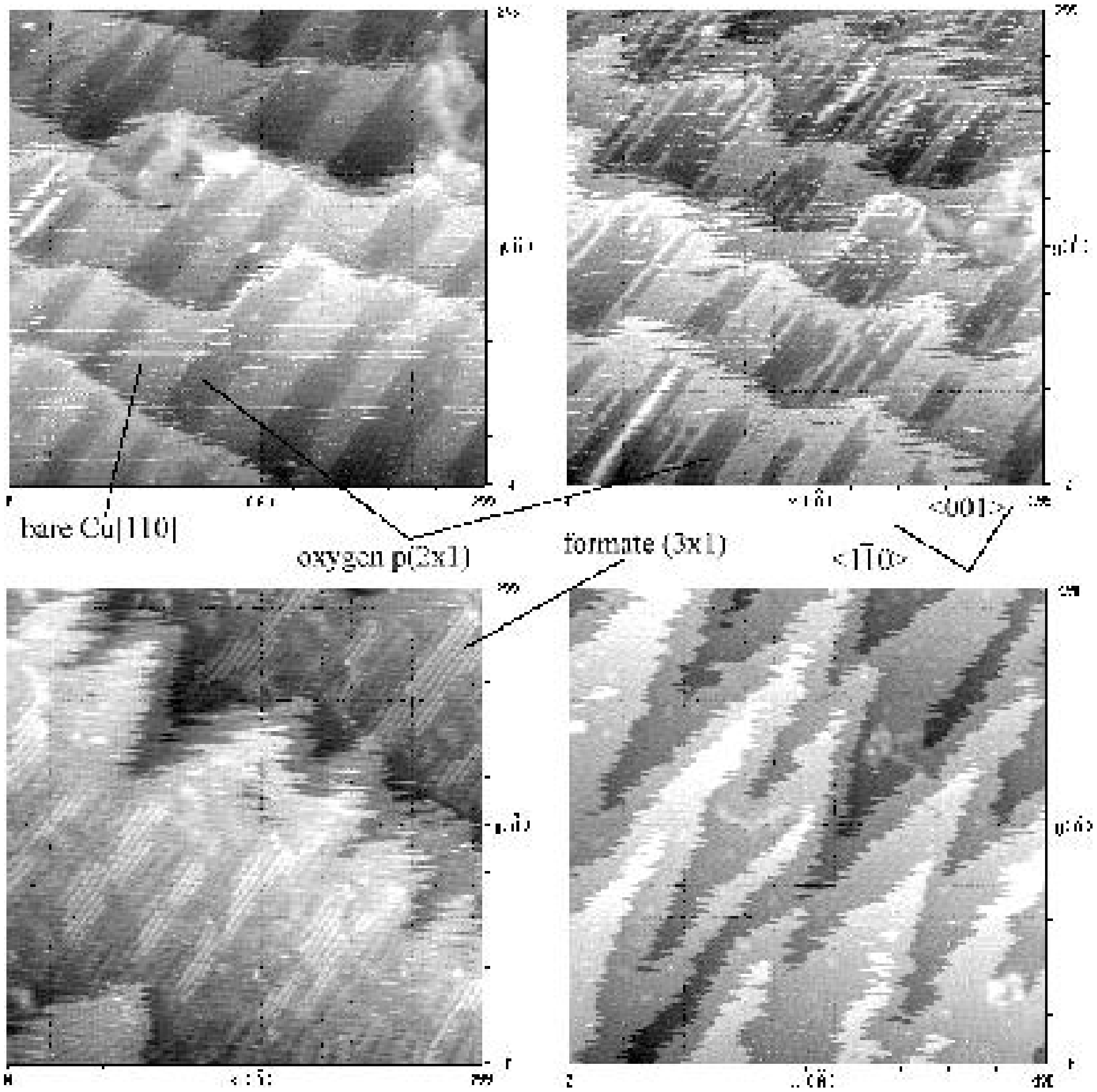

Figure 5. These STM images show the gross change in morphology of originally straight step edges when formic acid reacts with approximately 0.25 monolayers of oxygen pre-adsorbed on Cu(110), present in the form of p(2 × 1) islands. The steps change to a sawtooth shape and are decorated by formate in the c(2 × 2) structure. First image (top left): formic acid just introduced to the chamber (1 nA, −1000 mV, time = 0). Second image (top right): 1 min later showing diffusion and reaction (1 nA, −1000 mV, time = 60 s). Third image (bottom left): considerable reaction and adsorption of formate (1 nA, −500 mV, time = 600 s). Forth image (bottom right): showing sawtooth formation (1 nA, −500 mV, time = 1680 s). All images taken under 10^{-8} mbar ambient formic acid.

other high magnification images [23,24], there is formate present on the sawtooth and this may also play a role in dictating the shape of the growing sawtooth. Clearly the formate can diffuse to these sites from the reaction centres.

The behaviour of the formate is quite different from that of the methoxy formed from a similar reaction of adsorbed oxygen with methanol. In that case the liberated Cu stayed largely in the methoxy structure [26]. This is probably because methoxy binds in a single-bond fashion to only one site (which involves an added Cu atom on the original surface), whereas formate ideally requires two close packed Cu atoms which are not immediately available, except on the clean part of the Cu(110) surface. Thus, it does not bind to the individually liberated Cu atoms, which are left free to find a more stable configuration.

3.2. Adsorbate compression: p(2 × 1) conversion to c(6 × 2) by reaction with formic acid

When 0.5 monolayers of oxygen (which is saturation of the p(2 × 1) structure) is pre-adsorbed, there is no clean Cu surface available as a facile path for diffusion of Cu atoms liberated during reaction. Now the Cu atoms have to diffuse over the p(2 × 1) structure itself. This completely changes the nature of the surface rearrangement during reaction, as shown in figure 7. The molecular beam data presented in figure 2 reveal that there is still oxygen left on the surface after reaction, and this oxygen is apparently unreactive. This is due to the formation of a c(6 × 2) high coverage oxygen layer which can be seen as islands in figure 7. This structure has been discussed by others [27–29] and consists of 2/3 of a monolayer of oxygen atoms combined with 5/6

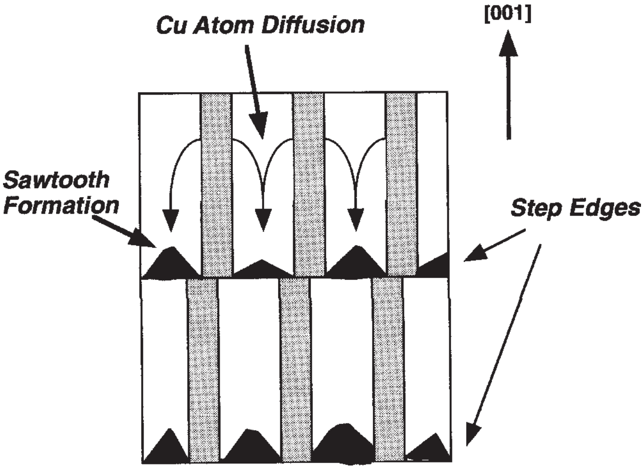

Figure 6. A schematic diagram illustrating the formation on the sawtooth structures at the Cu(110) surface. This occurs by reaction of formic acid with the Cu–O islands (shaded areas) followed by the diffusion of Cu atoms liberated from the islands to their most stable position which is at the step edge. The growing Cu sawteeth are shown as solid black areas. This is proposed because (i) sawteeth seem to grow out from the original steps, and (ii) diffusing species are usually reflected at down steps but can adsorb at upstep sites.

monolayers of Cu in a double-layer structure. This structure is relatively unreactive to formic acid, as shown by independent measurements on a complete c(6×2) oxygen layer [30], and as illustrated in the inset of figure 2. The c(6×2) can only be formed by oxygen dosing after very high exposures to gas (20,000 L at 600 K) whereas the p(2×1) is saturated after only 10 L. However, the c(6×2) can be formed with formic acid dosing after only 10 L of oxygen and 10 L of formic acid. It is interesting to note that if the surface shown in figure 7 is heated to 600 K to decompose the formate then only a lower local coverage oxygen layer, the p(2×1), is left partly covering the surface and this can be completely reacted off by a further dose of formic acid [11].

The c(6×2) is formed by the diffusion of Cu atoms over the p(2×1) layer, together with oxygen displacement from the p(2×1). In effect, the p(2×1) layer is *compressed* into the c(6×2). The reason for this is that the p(3×1) formate layer which is formed occupies a bigger area than the oxygen it removes into the gas phase as water:

$$\begin{aligned}&\text{O-p}(2 \times 1) + 2\text{HCOOH}_{(g)}\\&\quad\rightarrow 2\text{HCOO}_{(a)}\text{-p}(3 \times 1) + \text{H}_2\text{O}_{(g)}\end{aligned} \tag{4}$$

We consider that the p(3×1) layer has a local formate coverage of $2/3$ of a monolayer [31]. This structure has, therefore, removed one oxygen atom per formate unit cell formed which contains two formate intermediates, but that unit cell occupies three substrate unit cell areas, whereas the oxygen only occupied two in the p(2×1). This is incompatible with area conservation and so oxygen and Cu are displaced from the p(2×1) layer, together with the Cu atom removed by the oxygen loss to the gas phase. Given that 0.5 monolayer of formate is adsorbed upon completion of the reaction (figure 2), and that it is in the p(3×1) structure, the fractional area of surface covered by formate, AF, is approximately given by the formula $0.5\text{ML} = (2/3)\text{ML} \times \text{AF}$ giving $3/4$ or 75% coverage, in reasonable agreement with STM measurements (figure 7): this relates the total half monolayer of formate formed to the proposed local coverage ($2/3$ monolayer in the formate (3×1) structure) and the fraction of surface it occupies. However, this would leave only one quarter of the surface to be occupied by the c(6×2) oxygen layer, giving an oxygen coverage of $2/3 \times 1/4 = 1/6$, i.e., 0.17 monolayers of oxygen. This is a lower amount of residual oxygen remaining on the surface after the reaction than would be predicted from the uptake of formic acid in the $2:1$ stoichiometry regime (0.25 monolayers). In fact, the c(6×2) areas vary from one image to another [12,22,31] between 20 and 34%, indicating that perhaps a little more than half the original oxygen is removed in such an experiment. The STM dosing procedure is not as well defined as the molecular beam and so the reaction may go somewhat beyond the titration point in figure 2. It is possible to further slowly react the c(6×2) with very high doses of formic acid [32]. Also more Cu is released from the oxygen reaction than is incorporated into the c(6×2) and this is likely to cause the formation of the bright (3×1) formate rows in figure 7. These are higher level formate rows, probably incorporating some of the Cu lost from the p(2×1) islands, thus raising them above the formate strings binding to the original surface layer.

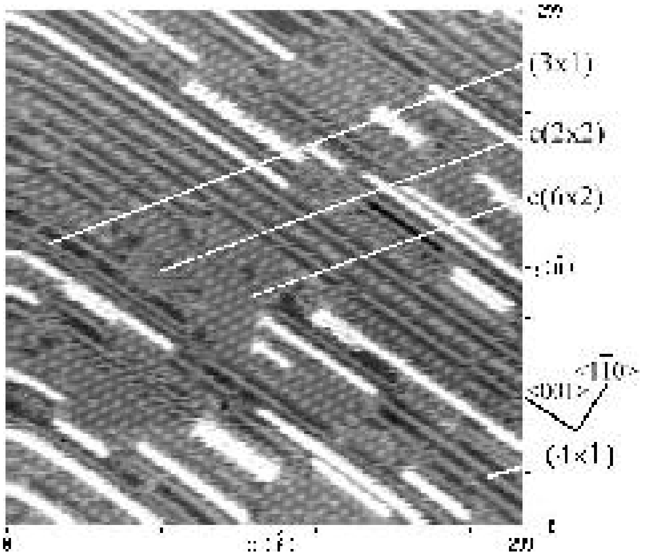

Figure 7. An STM image of a surface of Cu(110) which was pre-covered with a full layer of p(2×1) oxygen and then reacted with 3.6 L of formic acid and gently annealed. Two new structures are formed – the p(3×1) formate structure and the c(6×2) high coverage oxygen structure. The latter is formed, in effect, by "compression" of the p(2×1) oxygen and remains on the surface because it is much less reactive to the formic acid than the p(2×1). Some other formate structures are present in the image such as the c(2×2) and (4×1), the latter due to the slight annealing of the surface.

This example is probably a manifestation of a more general phenomenon in surface reactivity. Other examples include the compression of O on Cu(110) by C_{60} adsorption [33] and the compression of layers of S, shown

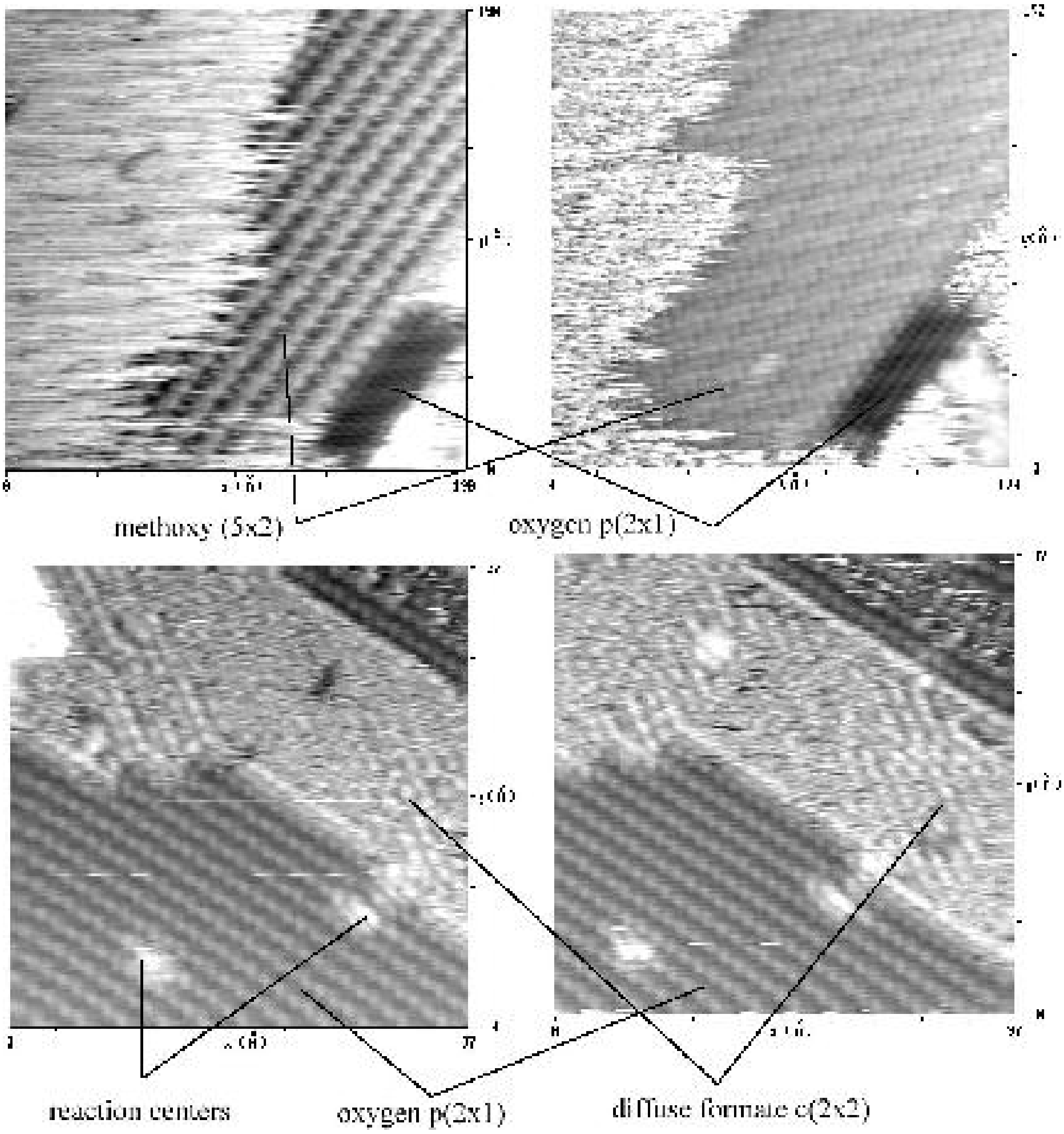

Figure 8. The upper two images show the nucleation of a (5 × 2) methoxy island on the edge of a small oxygen p(2 × 1) island. The island coexists with a dilute phase which appears as a streaky unstructured region surrounding the islands. The lower images show formate on the Cu(110) surface between islands of oxygen p(2 × 1). Again, rapidly diffusing adsorbates appear unstructured in the image whereas regions of locally higher density begin to crystallise in to the c(2 × 2) formate structure, apparently near kinks in the oxygen island structure.

by Salmeron and Dunphy [34], on Pt(111) after the post-adsorption of CO.

4. The surface as solvent: 2D crystallisation

For several adsorbates we have studied it appears that at low coverage the adsorbate is highly mobile on the surface at ambient temperature, even in the intermediate state. It is not possible to image methoxy or formate species at low coverage under such conditions because of their lack of local order and high diffusivity on the STM timescale. However, it appears that there is a critical coverage at which the adsorbate "precipitates" out of the surface solvent and crystallises. Examples of this are shown in figure 8, one for the methoxy species and the other for formate. For the former, crystallisation has occurred to form a p(5 × 2) methoxy island and nucleation has occurred at the long edge of a p(2 × 1) oxygen island [35]. We have earlier reported zero-order behaviour for the decomposition of methoxy islands and it appears that this is due to methoxy decomposition at active sites away from the islands which are themselves in equilibrium with a dilute, highly mobile methoxy phase [36]. Figure 8 also shows images for the reaction of formic acid with (2 × 1) oxygen islands on Cu(110) and the beginning of the formation of c(2 × 2) formate islands on the clean surface area between oxygen structures. These formate crystallites are fluxional between one image and the next.

Thus we feel that in many of these cases the surface acts in an analogous way to a solvent and the adsorbate–surface mix can act as a solution. This is clearly a gross analogy, since water solvation is not involved in this case. Nevertheless, when the adsorbate coverage goes above a critical level, the 2D solubility limit, then crystallisation of the adsorbate phase occurs into islands of well-defined structure. The reverse can occur upon heating and consequent reduction of the adsorbate coverage. Clearly, in the case of adsorption–desorption equilibrium the critical coverage of the adsorbate will be reached at a particular P for any particular T condition. This is, in turn, close to the observations of order–disorder transitions for simple adsorbates and the idea of the “lattice gas”.

5. Conclusions

Formic acid adsorption on clean and oxygen-covered Cu(110) acts as an excellent model system for demonstrating some important and general features of surface reactions.

Precursor states are highly mobile short-lived surface species, often physisorbed states, which can diffuse over a wide area of the surface. This enables them to “seek out” active sites and to have a high probability of finding them, even when such sites are at very low concentration. The active sites might be oxygen atoms at low coverage on Cu(110), as described here, or metal particles at very low loading on a support, or even sparsely distributed anion vacancies on an oxide catalyst, for instance.

Gross restructuring of surfaces can occur due to the implicit involvement of surface metal atoms in the reaction event itself. For formic acid on Cu(110), the reaction of formic acid to produce formate by reduction of surface oxygen to liberate gas-phase water results in mass migration of surface Cu atoms, which diffuse to their most stable sites. These are at step edges if a clean Cu diffusion pathway exists, or on top of the oxygen layer for a complete O-(2 × 1) layer. In this particular case, the production of the formate p(3 × 1) results in compression of the remaining O-(2 × 1) into an unreactive c(6 × 2) structure which is locally of $2/3$ monolayer oxygen coverage and which is very oxide-like in behaviour.

For any reaction system the surface can be considered to be a solvent for the adsorbate. Below the critical coverage (the 2D solubility limit) the adsorbate is highly mobile and unstructured, above the critical coverage 2D crystallisation occurs, with the crystallites in dynamic equilibrium with the dilute, inter-island phase.

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