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COMMENT

Identifying molecular species in scanning tunnelling microscopy images

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Abstract. In a recent paper by Poulston *et al* STM images of Cu(110) surfaces exposed to methanol–oxygen mixtures were presented. Regions with c(2×2) periodicities were interpreted to consist of formate molecules. This comment questions the suitability of this interpretation and subsequent conclusions in light of previously published results which show that adsorbed methoxy can also form areas with c(2×2) periodicities.

Scanning tunnelling microscopy has recently proved itself to be a useful technique for elucidating how chemical reactions proceed on surfaces [1]. Unfortunately the technique is not chemically specific and hence the assignments of features within the images to particular elements or molecules requires careful thought.

In a recent paper by Poulston *et al* [2], STM images of Cu(110) surfaces exposed to methanol–oxygen mixtures were presented. Some images of coexisting (5×2), c(2×2) and (2×1) areas were obtained and interpreted to be areas of (5×2) methoxy, c(2×2) formate and (2×1) oxygen. On the basis of the interpretation of the c(2×2) areas to consist of formate molecules, a complex mechanism was proposed to explain the generation of formate in this system. The assignment of the c(2×2) areas to be formate related and the subsequent formate generation mechanisms, while possibly correct, should be viewed with a great degree of scepticism. No supporting evidence for the validity of this assumption was presented within the study and, more significantly, results of previous work were inaccurately reported.

Figure 3(a) of Poulston *et al* shows coexisting areas of c(2×2), (5×2) and (2×1) periodicities. The assignment of the c(2×2) regions to be formate related seems to be based somewhat loosely on previous work that has shown that formate can be produced from methanol on Cu(110) surfaces [3, 4]. Poulston *et al* also claim that TPD measurements (which were not shown in the paper) are consistent with the presence of formate on the surface; however, they do not say whether the quantities of formate are consistent with the amount of surface area covered by the c(2×2) structures. The assignment of these periodicities to various adsorbates seems to be based predominantly on previous STM results. While it has been observed that partially oxygen-precovered Cu(110) surfaces when exposed to formic acid and methanol can result in the presence of c(2×2) formate and (5×2) methoxy structures respectively [5–8], Poulston *et al* inaccurately state that 'methoxy forms a single (5×2) structure'. Previous work [7, 8] has shown that, under a variety of conditions, the sequential exposure of Cu(110) surface to oxygen followed by methanol can result in coexisting areas of both (5×2) and c(2×2) methoxy areas as shown in figure 1. In fact,

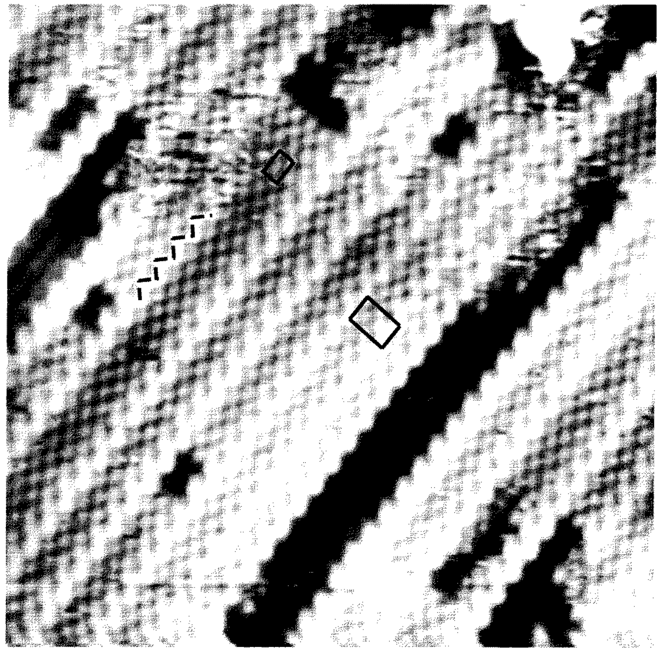

Figure 1. 200 Å × 200 Å STM image showing coexisting (2 × 1)O islands and methoxy-induced structures (from [7] and [8]). The methoxy structures take the form of zig-zag chains (dashed lines) and c(2 × 2) structures; a combination of both structures can form areas of (5 × 2) periodicity. (5 × 2) and c(2 × 2) unit cells are indicated. This image strongly resembles that obtained by Poulston *et al* in which it was claimed that the c(2 × 2) areas consisted of formate molecules. The images shown here was obtained after dosing a partially oxygen-precovered Cu(110) surface with 10 L of methanol while the sample was at 270 K. Similar images were also obtained by sequentially dosing with deuterated methanol at RT. (Sample bias −2.5 V, tunnelling current 1 nA.)

the (5 × 2) structure itself was described as consisting of 'zig-zag' chains and 'c(2 × 2)' subunits [7, 8]. It should also be noted that coadsorption studies showed that c(2 × 2) formate and methoxy structures both display protrusions centred over short-bridge sites of the underlying Cu(110) surface [5, 8]. It seems, therefore, unjustifiable to state without sufficient complementary information that the c(2 × 2) structures observed within the studies of Poulston *et al* are formate related.

In some ways, a c(2 × 2) methoxy structure may be more consistent with their findings than a c(2 × 2) formate structure. Poulston *et al* stated that continued dosing of MeOH : O_2 mixtures would eventually result in the removal of the c(2 × 2) and (2 × 1) structures with only (3 × 1) and (5 × 2) structures remaining. The (3 × 1) structure has been observed for formate [6]; however the formate coverage present in this structure is believed to be lower than that found in the c(2 × 2) formate structure. It is hard to believe that continued dosing would result in less formate on the surface. On the other hand, it was observed that c(2 × 2) methoxy structures did not remain on Cu(110) surfaces for long periods of time but evolved into (5 × 2) structures [7, 8].

In conclusion, while the interpretation of Poulston *et al* and corresponding mechanisms derived from these interpretations may be correct, their paper should not be viewed as offering reasonably convincing evidence to support their interpretations.

References

[1] For reviews of applications of STM to the study of reactions at surfaces see Murray P W, Besenbacher F and Stensgaard I 1996 *Is. J. Chem.* **36** 25
Leibsle F M, Murray P W, Condon N G and Thornton G 1997 *J. Phys. D: Appl. Phys.* **30** 741
[2] Poulston S, Jones A H, Bennett R A and Bowker M 1996 *J. Phys.: Condens. Matter* **8** L765
[3] Carley A F, Owen A W, Rajum M K, Roberts M W and Jackson S D 1996 *Catal. Lett.* **37** 79
[4] Carley A F, Davies P R, Mariotti G G and Read S 1996 *Surf. Sci. Lett.* **364** 1525
[5] Leibsle F M 1994 *Surf. Sci.* **311** 45
[6] Bowker M, Rowbotham E, Leibsle F M and Haq S 1996 *Surf. Sci.* **349** 97
Haq S and Leibsle F M *Surf. Sci.* **375** 81
[7] Leibsle F M, Francis S M, Davis R, Xiang N, Haq S and Bowker M 1994 *Phys. Rev. Lett.* **72** 2569
[8] Leibsle F M, Francis S M, Haq S and Bowker M 1994 *Surf. Sci.* **318** 46