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REPLY TO COMMENT

Identifying molecular species in scanning tunnelling microscopy images

S Poulston, A H Jones[†], R A Bennett and M Bowker

Reading Catalysis Research Centre, Department of Chemistry, University of Reading, Whiteknights, Reading RG6 6AD, UK

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Abstract. In a recent paper we employed STM to identify differences in the development of overlayer structures during co-dosing and sequential dosing of methanol and oxygen on Cu(110). We attributed these differences to the production of formate in the co-dosing experiment, the formate being associated with $c(2 \times 2)$ and (3×1) structures. Here, in response to the previous comment we outline our reasons for associating the $c(2 \times 2)$ structure with formate.

We are grateful to Leibsle for his interest in our work and welcome this opportunity to clarify the points he has raised. First we would like to emphasize that the main theme of our paper concerned differing overlayer development for the case of co-dosing compared with sequential dosing of methanol and oxygen on Cu(110). In particular we noted the significantly increased production of formate in the co-dosing case. In his comment, Leibsle raises no objection to our assignment of (3×1) structures to formate, but questions whether the $c(2 \times 2)$ structure in our images is indeed formate. It is certainly the case that care has to be taken in the interpretation of STM images and with the assignment of structures to particular chemical species, since topographic STM is generally not a molecule-specific technique. However, in this case we have done a considerable amount of work involving a wide range of surface science techniques on both methanol and formic acid adsorption to back up the current work [1–5]. The findings of these efforts can be summarized as follows and are related to the current discussion regarding the $c(2 \times 2)$ structure.

(i) STM shows the only stable structure for methoxy on Cu(110) at around 300 K from sequential dosing is the $p(5 \times 2)$; small areas of $c(2 \times 2)$ have been shown to be unstable [6] with respect to $p(5 \times 2)$ formation as also restated by Leibsle in his comment. No $c(2 \times 2)$ structure was reported for methoxy under these conditions using LEED [1, 6]. In contrast, the $c(2 \times 2)$ areas reported in our paper are both long lived and of significantly larger size (see for example our figure 3 in [7]), being up to 20 unit cells wide in the $[1\bar{1}0]$ direction in our co-dosing experiments and only four unit cells at maximum in the sequential dosing experiments [6].

(ii) STM shows a variety of structures for formate produced by formic acid dosing on this surface, most significantly the $c(2 \times 2)$, (3×1) and (4×1) [2, 8]. For the co-dosing experiment of methanol and oxygen we see (3×1) appear after $c(2 \times 2)$ and Leibsle seems to acknowledge that the (3×1) is associated with formate.

(iii) Formate is characterized by a CO_2/H_2 coincident desorption peak at ~ 470 K [9], which we did observe following the STM experiments outlined in our previous paper. For a

[†] Now at Oxford Instruments, Chesterton Mills, French's Road, Cambridge CB4 3NP, UK.

surface with $c(2 \times 2)$ present in the STM image, the desorption amount compares well with the coverage indicated by STM as calibrated with respect to a complete half monolayer of $c(2 \times 2)$ formate produced by formic acid dosing.

Further evidence for $c(2 \times 2)$ being formate comes from the recent work of Carley *et al* who show by XPS that both methoxy and formate are produced by co-dosing methanol and oxygen on Cu(110) under similar conditions to those we employed [10].

On balance, we propose that the stable $c(2 \times 2)$ structures we observe with STM are due to adsorbed formate species, though further work in this area would be welcome. The use of IR or EELS especially would be advantageous when the $c(2 \times 2)$ structure is present, since methoxy and formate are readily detected and discriminated by these techniques [5, 11–13].

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