

Reply to comment on 'Gross rearrangement of metal atoms during surface reactions'

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REPLY**Reply to comment on ‘Gross rearrangement of metal atoms during surface reactions’**

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The incorporation of substrate atoms into an adsorbate overlayer is now widely accepted as commonplace on transition metal surfaces, and especially for oxygen adsorption on (110) planes of Cu, Ag, Pd and Ni [1–3]. Similarly, reactions on such surfaces necessarily involve the rearrangement of incorporated atoms. Of particular interest is the discovery that for some reactions on oxygen covered surfaces the active sites are the terminal atoms of the added rows [4, 5]. These points are generally accepted, including by Leibsle and Silva, and form the basis of much interesting surface chemistry. In a recent paper [6], upon which Leibsle and Silva have commented, we specifically highlighted the role of these substrate atoms in a number of reactions on the Cu(110)–O(2×1) surface.

Leibsle and Silva’s first point is regarding the methanol to methoxy reaction, that ‘... these Cu atoms are incorporated into a (5×2) methoxy structure, which represents a rare case of a molecularly-induced surface reconstruction involving added metal atoms’. We dispute that this is a rare case. For example, it has been recently reported that benzoate species are stabilized by Cu adatoms on Cu(110) to form flat lying overlayers, while on Cu(111) (where the natural coverage of Cu adatoms is lower) such flat lying species are only formed by co-deposition of Cu and benzoic acid [7]. The authors go on to suggest that this phenomena, which controls adsorbate orientation, can explain the face specificity of surface reactions and thus has general applicability.

The second point which Leibsle and Silva have difficulty with regards our suggestion that Cu termination of Cu–O rows is unfavourable; they question ‘... why the Cu–O rows should be inclined to form in the first place’. There are several possible answers to this question. On a simplistic level, just as metal surfaces prefer to be oxidised (lower surface free energy), so we might expect a Cu step site (effectively what a Cu terminus to the island would be) to be metastable in the presence of oxygen. Additionally, there is evidence in the open literature that the growth of Cu–O rows occurs by the rapid diffusion of Cu–O oligomers, in which case either Cu or O terminations provide an active site for attachment [8–10].

We fully accept Leibsle and Silva’s observation that the ends of the rows ‘sometimes’, ‘often’ and ‘occasionally’ appear different in the STM images, as has been shown previously in the literature. We also agree with the suggestion that these ‘relaxations and reconstructions ... could also explain the enhanced reactivity’; however, as the data Leibsle and Silva show are not of a reaction occurring this seems rather speculative. Furthermore, we note that relaxation of the ends of the row would be expected irrespective of Cu or O termination. The commonly observed fact that the rows break off and move laterally dictates the formation of both Cu and O terminated rows [1]. The mobility of the metal–oxygen rows has been implicated in

numerous reactions on this and similar surfaces [11–13].

Leiblsle and Silva are concerned over the fate of the liberated Cu atoms from methanol and formic acid adsorption and feel the discussion is ‘simplistic and (is) inconsistent’. However, the aim of the paper was to discuss ‘what happens to the added Cu when the oxygen is removed from the $p(2 \times 1)$ structure’, as explicitly stated in the introduction. We have clearly shown that the fate of the added Cu atoms depends on the adsorbate; methoxy incorporates the Cu, whereas the formate tends to eject it. This is a new observation. We intentionally limited ourselves to a discussion of the fate of the added Cu, as that was the aim of the paper, and we did not preclude additional Cu being incorporated within the methoxy structure. It seems peculiar that Leiblsle and Silva should query the role of Cu adatoms from the (2×1) overlayer in the methoxy structure, as Leiblsle states in the abstract of one of his papers [5] ‘Sequential STM images show the shrinking of the (2×1) Cu–O islands in the [001] direction and the formation of a (5×2) methoxy-induced reconstruction that incorporates the added-row Cu atoms of the (2×1) reconstruction’.

Similarly, we did not claim that sawtooth formation ‘utilizes only those Cu atoms released from the (2×1) O islands’; in fact, we state that the Cu adatoms released form the beginnings of a sawtooth formation. It is indeed quite likely that extra copper may be incorporated into the sawtooth structure, but there is little doubt that all of the Cu originally in the $p(2 \times 1)$ islands is incorporated here, which is the point of the paper. We proceed to show that the formation is dependent upon reaction conditions, as a slow reaction only forms a small sawtooth that decays back into the step edge. Cu atoms which cannot reach the step edge react with the $p(2 \times 1)$ to form the $c(6 \times 2)$ structure. The two reaction sequences clearly show the involvement of Cu atoms released from the oxygen in the formation of surface structures. It is rather surprising that Leiblsle and Silva have a problem with this, as Leiblsle says in his own work [14] ‘It may be argued that these structures form as a way of utilising the Cu atoms that were involved with the (2×1) O structures’.

Leiblsle and Silva’s referral to the original paper [14] is also in error, as they state in their comment that there was ‘very little oxygen’ prior to formation of the sawteeth; however, the original paper states a coverage of 0.25 ML (i.e. half the surface area). This is misleading. Furthermore, the formation of pits alluded to in the comment occurs for a different surface, one which has nitrogen atoms pre-dosed by sputtering. Leiblsle and Silva’s other observations on different systems (benzoate and acetate without pre-adsorption of oxygen), while undoubtedly interesting, have little bearing on the fate of Cu atoms released from an oxygen $p(2 \times 1)$ layer by reaction.

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