



# On the nature of the active site in catalysis: the reactivity of surface oxygen on Cu(1 1 0)

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## ABSTRACT

The nature of the 'active site' remains a subject of continual fundamental and applied interest in catalysis. In this paper we review the reactivity of oxygen on a well-defined copper surface to emphasize that not all sites on a surface are active sites, and that oxygen in different environments, even on such a well-defined material, has very different reactivities. By combining the use of molecular beam methods and STM imaging of surface reactions, it is generally found that the oxygen atoms which terminate islands on the (1 1 0) surface have much higher reactivity than those in the centre of the island. However, some molecules (formic acid, for instance) show high reactivity, even with these latter atoms. We show that the reactivity pattern is of acid–base character and that the oxygens terminating the islands are stronger bases than those in other locations. These, then, are effective for reactions with weak acids such as methanol or methyl mercaptan, whereas stronger acids such as formic acid appear to be able to react effectively with the more weakly basic oxygen in the centre of the islands.

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## 1. Introduction

Ben Nieuwenhuys has published extensively in the field of catalysis, imaginatively blending surface science studies on single crystal substrates with more applied catalytic approaches and always seeking to elucidate reaction mechanisms by identifying intermediates and reaction pathways [1–7]. Often avoiding the *usual* substrates studied by others, Ben's philosophy is exemplified by his approach to methanol oxidation where, as he stated in 2005 [8], he aims:

“to obtain a broader understanding on the role of the structure of sites on the surface ... on the activation of C–O and O–H bonds of methanol.”

This philosophy has much in common with our own approach to studying catalysis; we use surface science techniques to explore fundamental reaction pathways of relevance to catalytic processes.

Surface science has had a significant impact on the understanding of catalysis at a number of levels, but especially at the atomic scale. Major advances in understanding include the recognition of the importance of surface reconstruction ([9] for one of the earliest examples) and flexibility [10,11], especially

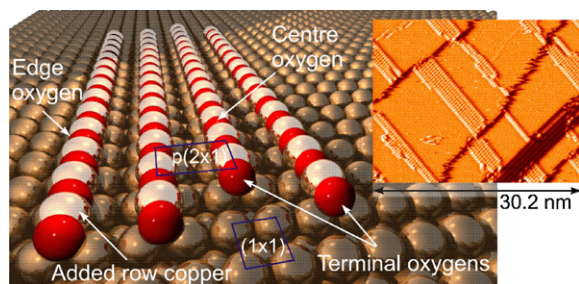
during adsorption and reaction, the structure sensitivity of many reactions (for the classic, and Nobel Prize-winning example see [12,13]) and the nature of the adsorption states involved in surface reactions and catalysis. This work on fundamental adsorption and reaction processes contributes to an understanding of industrial catalytic processes.

In a compliment to Ben's work, in this article we explore the nature of the active site in selective oxidation, a topic to which Ben has contributed significantly over the years. We focus here, entirely on the reactions of oxygen at a Cu(1 1 0) surface, which we have studied using a variety of different approaches over recent years. It is an interesting system because of the pronounced anisotropic reactivity of the chemisorbed oxygen, first shown clearly for methanol reaction with oxygen by molecular beam and STM studies [14–17], but also for reaction with ammonia on the basis of XPS data and Monte Carlo modelling [18] and subsequently by STM [19]. The root cause of this behaviour can be traced to the anisotropic nature of the chemisorbed oxygen structure at coverages below  $\theta_o = 0.5$ . It has been shown by a number of authors that oxygen forms strings in the [0 0 1] direction, which consist of alternating copper and oxygen atoms, and that these strings tend to cluster due to attractive interactions between the rows, into islands of  $p(2 \times 1)$  structure [20]. The islands, at low coverages tend to have a high aspect ratio of the [0 0 1]:[1 1 0] dimensions, with the [1 1 0] sides much longer than the side [0 0 1] edges, as shown in Fig. 1. STM is an invaluable tool in such surface reactivity studies and its application to methanol reactivity, and to that of other systems, has recently been reviewed [21]

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**Fig. 1.** Oxygen adsorbed on Cu(1 1 0), showing the island structure of the adsorbate, which consists of rows of Cu–O strings in the [0 0 1] direction, which group together to form islands in the [1 1 0] direction.

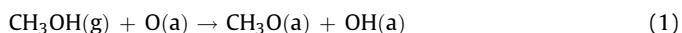
In this article we compare the behaviour of a number of different reactants with O/Cu(1 1 0) highlighting aspects of the selective oxidation mechanism that are perhaps not evident from considerations of the reactivity of a single molecule type. We start with methanol, for which we have clear evidence about its reactivity from diverse experimental methods, and then consider some analogues for which gas phase acidities differ.

## 2. Oxygen on Cu(1 1 0)

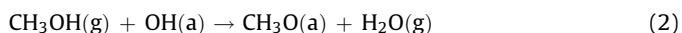
Oxygen dissociates efficiently on Cu(1 1 0) with a small activation barrier of  $3 \text{ kJ mol}^{-1}$  [22]. Below 80 K no ordering takes place and the oxygen states formed have been shown to be highly reactive [23]. Above 200 K or so the characteristic anisotropic islands described above are formed; Fig. 1 shows an image of just such an island, together with a schematic diagram indicating different types of oxygen sites present within the islands. We identify four types: (i) fourfold coordinate oxygens in the centre of the island; (ii) fourfold coordinate atoms at the [1 1 0] long edge; (iii) oxygens terminating the [0 0 1] short ends of the islands (probably threefold coordinate) and (iv) “isolated” oxygen atoms which may not yet have been incorporated into the islands but may be associated with a copper atom picked up from the step edges. The latter are not observed by STM at room temperature because of their rapid movement over the surface but they have been observed at low temperatures [24] and their very high reactivity demonstrated with a number of reactants [25].

## 3. Methanol oxidation on Cu(1 1 0)

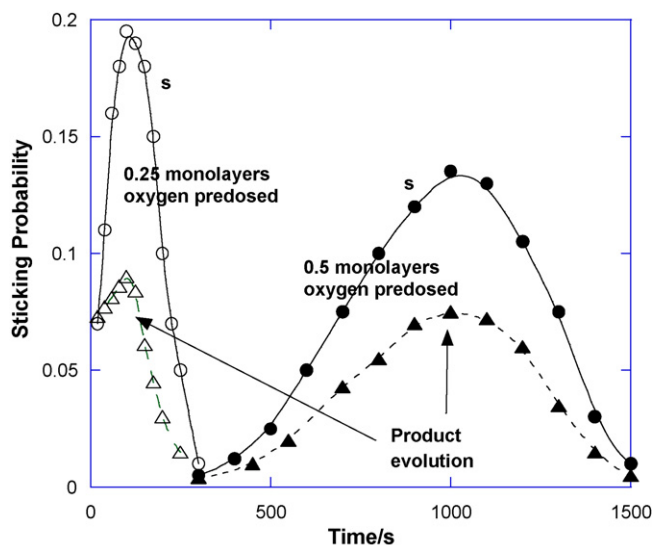
Cu(1 1 0) has essentially no reactivity to methanol in the absence of surface oxygen and no methanol sticking is measured in a molecular beam system at ambient temperature (the details of the molecular beam system, which can be described as a single collision reactor, are reported elsewhere [26]). However, if oxygen is pre-dosed onto the surface then the alcohol reacts readily at room temperature (Fig. 2). The surface oxygen acts as a base stripping off of the acidic (alcohol) hydrogen (1).



where ‘g’ and ‘a’ refer to gas phase and adsorbed species respectively. The surface hydroxyl is also a base and is capable of reacting with another methanol to liberate water from the surface, it is the water formation that provides the thermodynamic driving force for the reaction.



The fact that it is only the acid hydrogens which react is conclusively shown to be the case for reaction at low temperatures (up to  $\sim 350 \text{ K}$ ) by use of  $\text{CH}_3\text{OD}$ , which results in almost



**Fig. 2.** Sticking probability of methanol on oxygen dosed Cu(1 1 0) at 353 K crystal temperature for two separate experiments with different oxygen precoverages. Open circles are for 0.25 mL of oxygen pre-dosed, filled circles are for 0.5 mL. Products evolve coincidentally with the sticking, open triangles for 0.25 mL oxygen, filled triangles for 0.5 mL. The products are formaldehyde, hydrogen and water.

exclusively  $\text{D}_2\text{O}$  evolution into the gas phase [15,27]. Wachs and Madix [27] showed this early on for the reaction at low temperatures to form the methoxy, whereas Francis et al. [15] showed this to be the case at the decomposition temperature by using the molecular beam methods referred to above.

Thus adsorption is promoted by the presence of surface oxygen atoms. However, if the coverage of oxygen is too high then no reactivity is observed at ambient temperature, but if the surface is heated to 353 K, then the reactivity is very low initially and there is an induction period before reaction can proceed (Fig. 2). When these measurements are carried out much above ambient temperature, then the methoxy group can decompose at a significant rate and formaldehyde evolves into the gas phase, by the following reaction:



As shown in Fig. 2, formaldehyde evolution is rapid for a coverage of oxygen of 0.25 mL, but is slow when the  $p(2 \times 1)$  oxygen adlayer is saturated ( $\theta_0 = 0.5$ ). Coincident with the sticking of methanol at 353 K, formaldehyde, water and hydrogen evolve into the gas phase, apparently fast compared with the adsorption which rate limits the evolution. This is because the methoxy species, which is the intermediate in this reactivity, is unstable at this temperature. Wachs and Madix showed, using TPD, that the desorption rate maximum occurs at  $\sim 350 \text{ K}$  [27].

In a series of papers dealing with STM imaging of surface reactivity [15–17,28,29] the results show clearly why the reaction is slow at high oxygen coverage (Fig. 3) Here we see that methanol does not adsorb in the centre of the oxygen islands, but only on clean areas of the surface and there is clear phase separation between the adsorbed methoxy groups and remaining oxygen. Further, it is apparent that it is only the perimeter oxygens at the short ends of the islands which are reactive [16,17], i.e., the terminal oxygens shown in Fig. 1. In Fig. 3, it can be seen that the oxygen islands shrink from the ends since this is the location from which the oxygens are removed. We might then ask the question, why does the reaction not stop at that point, with the terminal oxygens removed? The answer is that, when the copper–oxygen

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