Catalysis Letters 58 (1999) 93–97

Oxygen chemisorption at Cu(110) at 120 K: dimers, clusters and mono-atomic oxygen states

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Received 23 November 1998; accepted 12 February 1999

Three distinct states of oxygen have been observed at a Cu(110) surface at 120 K by scanning tunnelling microscopy (STM): isolated oxygen adatoms; pairs or dimers, separated by about 6 Å; and clusters of five or six atoms arranged anisotropically. There is also evidence for oxygen atoms undergoing ballistic motion as might be expected from "hot" oxygen atoms. Such states of oxygen have been central to the mechanistic models proposed earlier, and based on surface spectroscopic studies, for the oxidation of ammonia at copper surfaces under ammonia-rich conditions.

Keywords: scanning tunnelling microscopy, copper, chemisorption

1. Introduction

That transients present during the dissociative chemisorption of oxygen provided low-energy reaction pathways in surface oxydehydrogenation reactions was first established in coadsorption studies of ammonia-rich dioxygen–ammonia mixtures at Mg(0001) surfaces [1,2]. From a model proposed for the reaction mechanism, where oxygen adatoms underwent surface diffuse hopping, the life-time of the $O^{\delta-}$ transient was estimated to be of the order of 10^{-8} s at 295 K. The life-time was defined as the time oxygen adatoms were present under the reaction conditions before forming the inactive "oxide" islands. Although the main impetus for this work was to explore whether during the dynamics of oxygen dissociative chemisorption reactive oxygen transients were indeed present, it also provided an insight into selectivity in oxidation catalysis. In this case, ammonia was the "probe molecule", unreactive (not chemisorbed) at either the atomically clean magnesium surface or the chemisorbed oxide overlayer. It was, however, readily dehydrogenated when exposed to a Mg(0001) surface simultaneously active in the dissociative chemisorption of dioxygen. This led to a range of studies where this concept was shown to have wide validity: the oxidation of carbon monoxide at aluminium and magnesium surfaces [3]; the oxidation of hydrocarbons at caesiated Ag(110) surfaces [4], and the oxydehydrogenation of water [5]. Most emphasis has, however, been given to the oxydehydrogenation of ammonia at Cu(111) and Cu(110) surfaces, where a highly selective and facile reaction led to the formation of chemisorbed imide species at both Cu(111) and Cu(110) surfaces [6–8]. No evidence for chemisorbed oxygen was found using XPS during the formation of the imide overlayer and transient oxygen species undergoing rapid surface diffusion were clearly implicated in the reaction mechanism. In this paper, we consider how STM can provide more direct experimental evidence for the presence of oxygen transients during the formation of the chemisorbed overlayer at a Cu(110) surface. Since we established that the unique oxydehydrogenation activity associated with the Cu(110) surface occurred at low temperatures, the STM studies of oxygen adsorption have been carried out at 120 K, when surface reconstruction or oxidation would be anticipated to be unfavourable.

The chemisorbed oxygen overlayer formed at Cu(110) at room temperature has already been extensively studied by STM [9]; low-temperature studies are confined to those of Bradshaw et al. [10] at 4 K and Crew and Madix [11] at 150 K. The present studies of oxygen interaction at 120 K are therefore confined to low oxygen coverages and in the temperature range where the oxydehydrogenation of ammonia was reported to generate amide and imide surface species. We have reported recently [12] an STM investigation of the structural characteristics of the imide "strings" formed at a Cu(110) surface at room temperature; it is the atomic nature of the reactive oxygen species that we explore in this paper.

2. Experimental

A specially designed ultra-high-vacuum spectrometer, incorporating both STM and XPS facilities was supplied by Omicron Vacuum Physik. The single-crystal Cu(110) surface was cleaned using cycles of argon ion bombardment (600 eV, 10 μA) and annealing to 800 K. Images could be obtained over a wide range of temperature (80–800 K) using tungsten tips. The gases were spec pure and obtained from Argo International.

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3. Results and discussion

In figure 1(a) is shown the initial distribution of oxygen states present at the Cu(110) surface after exposure to 0.1 L oxygen (1 L $= 10^{-6}$ Torr s) at 120 K; figure 1(b) shows the same surface region imaged 5 min later. Under these conditions we would have anticipated that thermally activated surface diffusion of oxygen adatoms would not be of major significance. We draw attention to the presence of three distinct configurations, marked A, B and C on the 21.1 nm image; these are also shown expanded. A is the image of a "dimer" of oxygen adatoms, B is a cluster of three dissociated oxygen molecules and C reflects two oxygen adatoms separated by about 20 Å, one of these adatoms being present at a step. Dissociative chemisorption at the step is likely to be more exothermic than on the terrace giving rise to an enhanced translational energy component and the ballistic-type motion of one of the oxygen atoms. The oxygen adatoms within the dimer (A) are separated by about 6 Å, similarly within the cluster B. Just above the cluster (B) there are five adatoms in close proximity with one isolated adatom having diffused to a point some 20 Å away. The dissociated adatoms are anisotropically arranged, but the clustering suggests that during surface accommodation energy dissipation involves collisional events between dioxygen states leading to dissociative chemisorption. That clusters take a characteristic shape is not unusual, aggregates of CO_2 taking a T-shape configuration due to the intermolecular interaction between ionic $CO_2^{\delta-}$ and neutral CO_2 moieties and providing a pathway to dissociative chemisorption. The pairs of oxygen adatoms in T-type configurations (figure 1 (a) and (b)) may well be a consequence of an $O_2^{\delta-}\cdots O_2$ interaction leading to dissociation and a cluster of O-adatoms at 120 K.

What is also clear is that these clusters are stable over time at 120 K, images (a) and (b) (figure 1) being taken at an interval of about 5 min. On warming to 295 K the characteristic –Cu–O–Cu–O– strings form; an example is shown in figure 2. In the image shown the strings are about 100 Å long and observed after an exposure to 1 L of oxygen at 295 K.

LEED studies by us [13] of oxygen interaction with copper single crystals at low temperatures also provide evidence for metastable oxygen configurations. At Cu(100) a "4-spot" structure, not present at 80 K, is transiently present at 180 K before forming at 295 K the "stable" $(\sqrt{2} \times \sqrt{2})$ R45° associated with surface reconstruction. At Cu(210) surfaces [14] defective LEED structures observed after dissociative chemisorption at 295 K were interpreted as due to rapid surface diffusion of Cu–O* complexes, a process later confirmed by STM.

A Monte Carlo simulation of the formation of the oxide overlayer allowed a comparison to be made of the experimentally observed reactivity of preadsorbed oxygen in NH_x formation with specific oxygen sites within the oxide overlayer as a function of surface coverage [15]. It was concluded that the reactive oxygens were located at the ends of –Cu–O–Cu–O chains and, indeed, this was confirmed by Madix's STM studies [16].

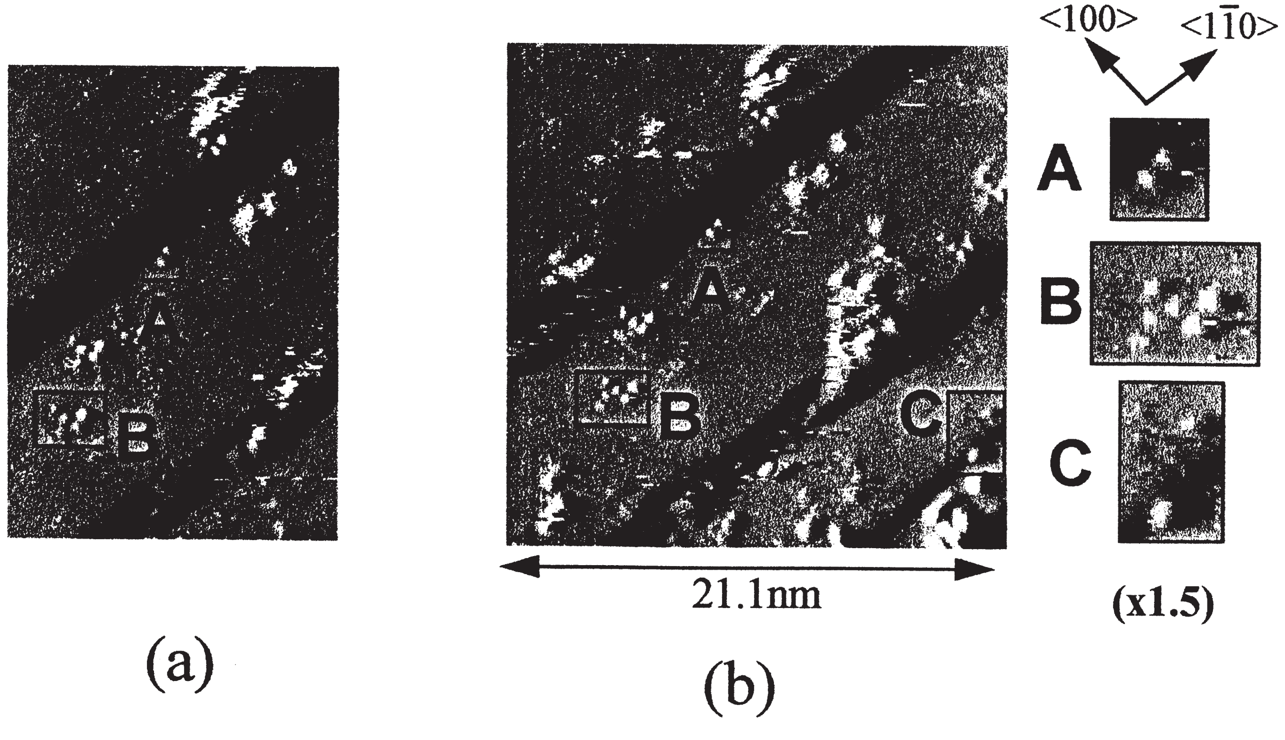

Figure 1. (a) Clusters of oxygen atoms observed at a Cu(110) surface after exposure to 0.1 L of dioxygen at 120 K. Sections of the image expanded by a factor of 1.5 are shown on the side of the main image. Tunneling conditions: sample bias 2.04 V, tunneling current 2.94 nA, scan speed 564 nm s^{-1}. (b) An image taken 5 min later establishing the stability of the clusters at 120 K.

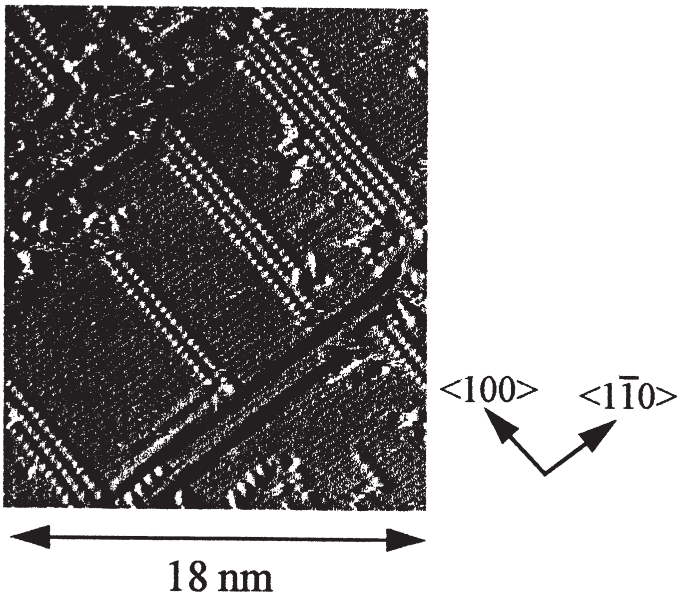

Figure 2. Copper–oxygen chains orientated in the $\langle 1\bar{1}1\rangle$ direction formed after the exposure of a Cu(110) surface to 1 L of dioxygen at 295 K. Tunneling conditions: sample bias 2.275 V, tunneling current 3.17 nA, scan speed 422 $\mathrm{nm\,s^{-1}}$.

We therefore distinguish four regimes of chemisorption at 120 K; dissociative chemisorption resulting in oxygen adatoms being separated from each other by about 6 Å, clustering of oxygen adatoms, oxygen adatoms isolated and at least 20 Å from the nearest oxygen adatom, and the formation of the –O–Cu–O– strings at higher temperatures.

The model we proposed to account for the high reactivity associated with ammonia-rich, dioxygen–ammonia mixtures at Cu(111) and Cu(110) surfaces is summarised below [17] and based on XPS and HREELS studies [6–8]. The advantage of XPS in providing quantitative surface concentration data is unique amongst surface spectroscopies. In the following scheme, (s) represents a transient and (a) a chemisorbed state:

(1) $O_2(g) \rightarrow O_2(s)$ Surface accommodation

(2) $O_2^{\delta-}(s) \rightarrow O^{\delta-}(s)$ Diffusing oxygen atoms $O^{\delta-}(s)$

(3) $O^{\delta-}(s) \rightarrow O^{\delta-}(a)$ Isolated oxygen adatoms $O^{\delta-}(a)$

(4) $O^{\delta-}(a) \rightarrow nO^{\delta-}(a)$ Growth of oxygen adatom clusters

(5) $nO^{\delta-}(a) \rightarrow O^{2-}(a)$ Oxidation and surface reconstruction

H-abstraction leading to amide and imide species is associated with the reactivity of either $O^{\delta-}(s)$ or $O^{\delta-}(a)$. If however, the ammonia–dioxygen mixture is richer in oxygen, then step (5) resulting in the formation of the comparatively unreactive –O–Cu–O– strings dominated the chemisorption process with the consequence that the probability of the reactive $O^{\delta-}(s)$ or $O^{\delta-}(a)$ abstracting H from NH_3 undergoing surface diffusion was negligible.

The present STM data therefore provide evidence at the atomic level for each of the steps proposed (equations (1)–(5)) to account for the surface chemistry observed during the oxidation of ammonia at Cu(110) surfaces. We also suggest that these steps are of more general relevance to the formation of the chemisorbed oxygen overlayer at metal surfaces, e.g., at Ni(110) and Ni(100) [18] and also account for catalytic oxidation reactions where there is the possibility of either selective or complete oxidation.

We discussed earlier [12] the structural aspects of imide formation when ammonia-rich dioxygen–ammonia mixtures were exposed to Cu(110) at 295 K, with no chemisorbed oxygen being observed by either STM or XPS [6,8]. Similar results were obtained with Cu(111) surfaces [7]. In figure 3 we show three sequential STM images (each image took 20 s) of small copper–oxygen strings present at Cu(110) during exposure to ammonia at 295 K. In the absence of $NH_3(g)$ the copper–oxygen strings are stable and immobile but on exposure to ammonia the shorter string marked with an arrow becomes mobile moving laterally in the $\langle 110\rangle$ direction. This movement, a precursor to the oxydehydrogenation reaction resulting in the formation of chemisorbed imide species, is presumably a consequence of the highly exothermic reaction where the oxygens at the end of the chain are replaced by an imide species, the oxygen desorbing as water.

There are some similarities between the present STM results for oxygen chemisorption at Cu(110) and those recently reported by Ertl and his colleagues for the chemisorption of oxygen at Pt(111) and Ag(110) at low temperatures [19,20]. However, it is the relationship between the atomic state of the surface oxygen at Cu(110) and its associated chemical reactivity, together with the vindication of models we have developed over the last decade for understanding surface reactivity of oxygen at metal surfaces, that we emphasise in this paper.

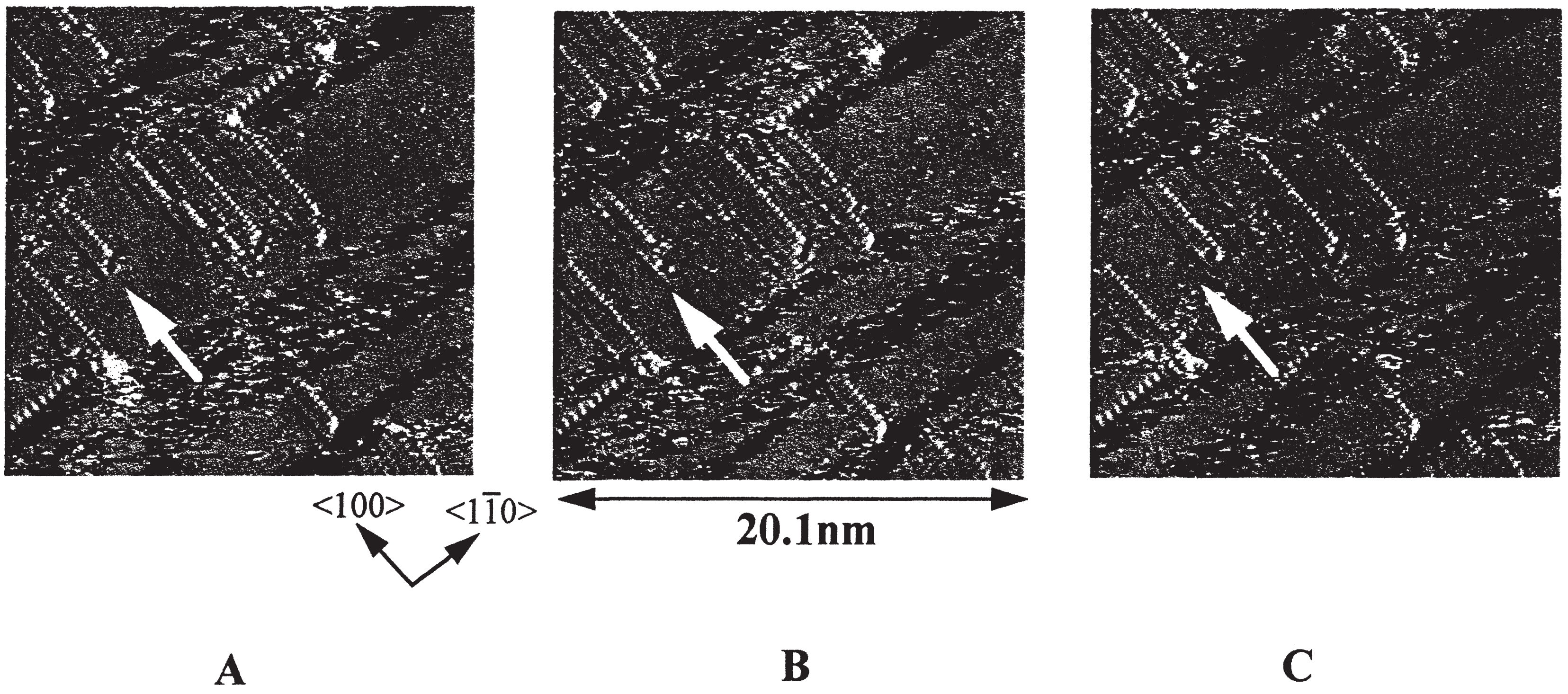

Figure 3. The influence of ammonia on copper–oxygen chains at a Cu(110) surface. The sample was imaged continously in the presence of ammonia at 1×10^{-8} mbar. The three images shown were recorded sequentially, each taking 20 s to acquire. Tunneling conditions: sample bias 0.879 V, tunneling current 2.78 nA, scan speed 500 nm s^{-1}.

Acknowledgement

We are grateful to the EPSRC for their support of this work.

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