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The development of a new concept: the role of oxygen transients, defect and precursor states in surface reactions

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Surface sensitive spectroscopies, and more recently scanning tunnelling microscopy, have provided a new insight into the dynamics of oxygen chemisorption at metal surfaces. Studies at low temperatures, using probe molecules, provided the first evidence for the role of metastable "hot" oxygen transients and molecular complexes in opening up low-energy pathways in oxidation catalysis. Progress over the past 15 years is considered, emphasizing the limitations of the classical approach in discussions of the mechanisms of surface reactions and how concepts developed through surface spectroscopies could be sustained at the atom-resolved level.

KEY WORDS: scanning tunnelling microscopy (STM); transients; oxygen; copper; ammonia; surface defects; reaction mechanisms.

1. Introduction

Concepts in science usually evolve with time and persistent inquiry rather than as the result of a single experiment, even though that experiment may have been the spark that initiated the train of thought that led to a rigorous examination of the concept.

In this paper we bring together those experiments that first led us to consider whether oxygen transients, precursor states or hot atoms were likely to have any place in controlling the dynamics of surface reactions, to establishing at the atom-resolved level the concept, and to consider the implications for traditionally held views on the mechanisms of surface reactions including catalysis.

The Chief Executive Officer of Elsevier, Derek Haank, emphasized recently how important it is for scientists to be able to link to the old literature through review articles. We discuss here some of the ideas which, over the past 15 years or so, led to the acceptance and current emphasis on how hot oxygen transients and precursor states have become an essential part of discussions of surface oxidation reactions [1]. The philosophy we adopted was "develop a model, investigate it rigorously, with atom-resolved experiments being the ultimate test".

Although precursor states have played a central role in the discussion of chemisorption at solid surfaces as formulated in the Lennard-Jones model and the kinetic analysis of Kisliuk, it is their significance as directly involved participants in chemical reaction pathways at metal surfaces we consider in this article. It is a concept that provoked much discussion and was not readily accepted, as revealed by remarks reported over the past decade at Faraday Discussions, even though Harris and Kasemo had earlier suggested that the possible existence of "hot precursors" would make it more difficult to discuss mechanisms of surface catalysed reactions as conforming to either Langmuir–Hinshelhood or Eley–Rideal mechanisms [2].

2. Some early clues from structural studies of chemisorbed oxygen at Cu(210) surfaces (1970–1980)

That oxygen chemisorption at metal surfaces involved facile reconstruction and metal mobility was established through work function studies [3] in the 1960s, with a paper in *Nature* in 1963 drawing attention to the defective nature of the chemisorbed oxygen overlayer at 295 K. These early views on the state of chemisorbed oxygen were explored further by X-ray photoelectron spectroscopy, with scanning tunnelling microscopy in the 1990s providing evidence at the atom-resolved level. However, it was low energy electron diffraction (LEED) that provided the first direct experimental evidence for surface disorder through observations of streaks, split spots, rings and high background intensity. Although there was a tendency to give most attention to analysing "perfect" diffraction patterns, surfaces exhibiting imperfect patterns were being thermally annealed to produce perfect patterns. If there is present disorder in any particular direction then streaks in diffraction features lying normal to that direction are observed. If the disorder is due to domains of small size, then all diffraction features are affected but frequently only fractional order spots are involved and oxygen island formation with antiphase domains is indicated; there

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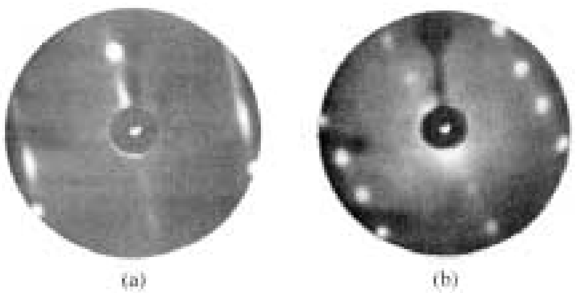


Figure 1. LEED patterns for oxygen (a) chemisorbed at 295 K at Cu(210) and (b) after heating the adlayer for 600 s at 473 K when the original disordered oxygen orders to the (2 × 1)-O state.

were many examples of oxygen chemisorption on metal surfaces where such features were observed. An approach that we found most informative [4] was to apply optical diffraction simulation of LEED patterns using matrices which had been constructed to simulate the formation of the chemisorbed oxygen adlayer. In figure 1 are shown LEED patterns for oxygen chemisorption at a Cu(210) surface at 295 K and after heating to 473 K; the half-order spots are streaked at 295 K but sharpen up after heating—indicating that the initial disordered adlayer becomes ordered at 473 K to give a (2 × 1)-O chemisorbed layer. By comparing LEED patterns with optical simulations using matrices developed from models of chemisorption it was concluded [5] that a nucleation mechanism was an essential prerequisite for developing a successful model. Furthermore correlated or semi-correlated diffusion by a hopping mechanism over quite long distances (~10 nm) is required to account for the observations. Finally, for a nucleation model there must be considerable diffusion at the molecular precursor state to account for the high sticking probability. The simulation studies supported the idea that the initial streaked (2 × 1) structure formed at 295 K is kinetically controlled and that Cu–O* complexes are the diffusing species [5]. These conclusions, reached nearly 25 years ago, provided a stimulus for our interest in this area of surface science and its possible relation to chemical reactivity.

3. The specific reactivity of oxygen states (1976–1985)

Although the common perception of chemisorbed oxygen in heterogeneous catalysis was that it inhibited the chemical reactivity of a metal surface—a catalytic poison—photoelectron spectroscopy established that specific oxygen states, designated as $O^{\delta-}(a)$ were active in dehydrogenation reactions at low temperatures. Evidence was obtained for the activation of O–H bonds in water, N–H bonds in ammonia, S–H bonds in hydrogen sulphide, and chemisorption replacement reactions (*e.g.* chemisorbed oxygen by sulphur or nitrogen) recognized as very facile, low-temperature processes [6].

Also a significant observation in the context of the present review was that the exposure of a molecular adlayer of water to nitric oxide at a Cu(110) surface resulted in extensive hydroxylation at low temperatures (100 K). A reactive oxygen state was clearly implicated, which had been formed through the dissociative chemisorption of nitric oxide [7]. Similar chemistry was also observed for the co-adsorption of water and nitric oxide at a Zn(0001) surface and O^- was suggested to be the active species.

We were clearly dealing with reactive metastable oxygen species and further evidence was obtained for such reactive oxygen states from studies of the interaction of water with oxygen chemisorbed at 80 K at both Ni(210) and Pb(pc) surfaces [8]. In both cases a weakly adsorbed state, designated $O^{\delta-}(s)$, was active in H abstraction while the stable chemisorbed state $O^{2-}(a)$, formed at 295 K, was unreactive. The O^{2-} state was associated with surface reconstruction or "oxide" formation while the $O^{\delta-}(s)$ state was seen to be metastable and the precursor to the formation of the $O^{2-}(a)$ state. That perfect oxide surfaces (*e.g.* NiO) were relatively unreactive became more readily accepted later and reactivity was to be associated with the presence of defective states Ni^{3+} and O^-, their presence being evident in the Ni(2p) and O(1s) spectra [9].

It was to explore the proposition that the $O^{\delta-}(s)$ state was a precursor to O^{2-} formation in the dynamics of oxygen chemisorption at metal surfaces (see scheme below) that we initiated co-adsorption studies involving dioxygen–ammonia mixtures [10].

$$O_2(g) \rightarrow O_2^{\delta-}(s) \rightarrow 2O^{\delta-}(s) \rightarrow O^{2-}(a).$$

The choice of the ammonia–dioxygen system was prompted by the gas-phase reaction

$$NH_3(g) + O^-(g) \rightarrow NH_2(g) + OH^-(g)$$

being known to be facile, occurring with high collision efficiency and of low activation energy. If the transient $O^{\delta-}(s)$ had a significant surface life-time we would anticipate the formation of chemisorbed amide $NH_2(a)$ and hydroxyl species OH(a), each being recognized through their characteristic core-level N(1s) and O(1s) spectra.

The essential principles involved in the probe-molecule approach for unravelling the role of surface oxygen transients [10] were further emphasized [11] at the 8th International Seminar on Electron Spectroscopy in Poland in 1990. The central point was that for an ammonia surface coverage of say 10^{-5} each surface site will be visited several hundred times during the surface sojourn time of the ammonia molecule (~10^{-6} s). It is this that would provide the evidence for the existence of $O^{\delta-}$ species through the highly efficient reaction

$$O^{\delta-}(s) + NH_3(s) \rightarrow OH(a) + NH_2(a).$$

4. Evidence for the transient $O^{\delta-}(s)$ state: surface spectroscopy studies of co-adsorption (1986–1993)

The system chosen initially [10] was the Mg(0001)–O_2–NH_3 since both atomically clean Mg(0001) and the "oxide" overlayer, $O^{2-}(a)$, had been shown to be unreactive to ammonia at 295 K. An important aspect, but perceived initially as of secondary significance, was that co-adsorption studies hitherto unfashionable in surface science provided information relevant to unravelling the molecular pathways in heterogeneously catalysed reactions and in particular of selective oxidation.

Prompted by our earlier evidence for reactive oxygen states [6–8] present at low temperatures (80 K) we first exposed molecular (physisorbed) ammonia present at a Mg(0001) surface to dioxygen at 110 K. The N(1s) and O(1s) spectroscopic evidence was unambiguous, indicating the instantaneous formation of $NH_2(a)$, OH(a) and $O^{2-}(a)$ species. By contrast the Mg(0001)–O^{2-} overlayer formed at 295 K was unreactive to ammonia under the same conditions. It was concluded that the key species in the dehydrogenation (oxidation) reaction was an oxygen transient [10].

Through a series of co-adsorption studies involving not only dioxygen but also other sources of atomic oxygen transients (the dissociative chemisorption of NO and N_2O) and by monitoring the N(1s) and O(1s) spectra, a prima facie case for $O^{\delta-}(s)$ transients as active species in the facile dehydrogenation reaction at low temperatures was established. The following model was proposed involving a sequence of elementary steps:

transient formation:

$$\tfrac{1}{2}O_2(g) \rightarrow O^{-}(s) \tag{1}$$

formation of stable and unreactive chemisorbed state:

$$O^{-}(s) \rightarrow O^{2-}(a) \tag{2}$$

physisorbed state; the probe molecule:

$$NH_3(g) \leftrightarrow NH_3(s) \tag{3}$$

the key reaction step:

$$NH_3(s) + O^{-}(s) \rightarrow NH_2(a) + OH(a) \tag{4}$$

dehydroxylation:

$$OH(a) \rightarrow O^{2-}(a) + H(s). \tag{5}$$

The $O^{-}(s)$ transient formed in an exothermic abstractive chemisorption process (figures 2 and 3) has two possible reaction pathways: either it proceeds to form (equation (2)) the stable and chemically unreactive chemisorbed oxygen overlayer $O^{2-}(a)$ or it interacts with the probe molecule, ammonia, undergoing surface "hopping" (equation 4) and at 295 K, present at an immeasurably low coverage, its heat of adsorption being no more than 40 kJ mol^{-1} (equation (3)). Ammonia-rich mixtures were chosen in order to favour the thermodynamically

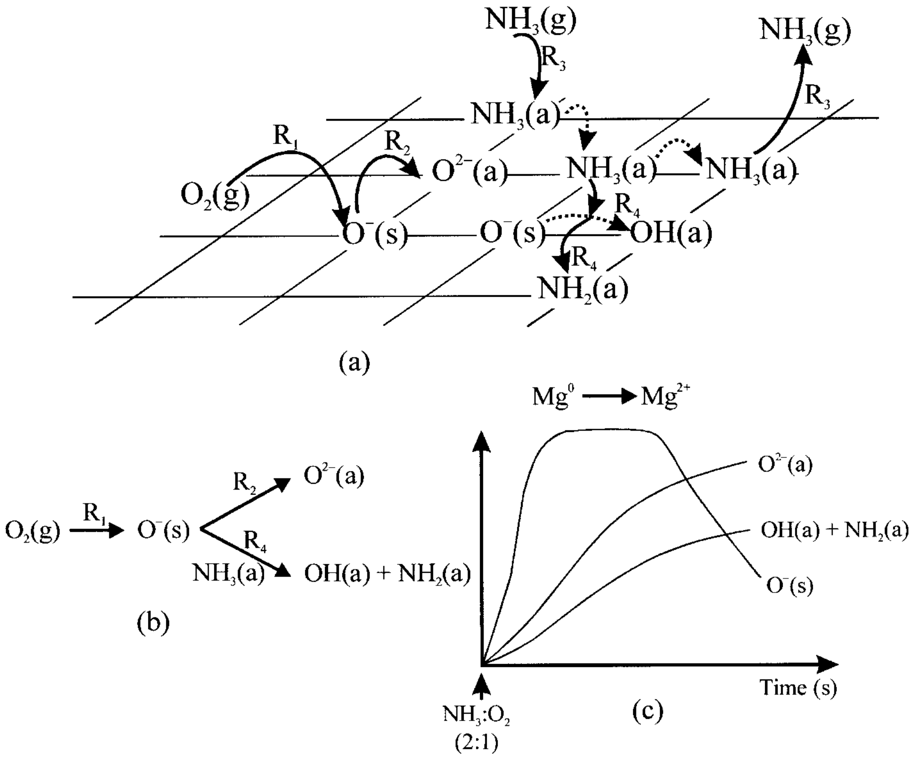


Figure 2. (a) Reaction pathways for the interaction of an NH_3–O_2 mixture with a Mg(0001) surface at 295 K. (b) The $O^{-}(s)$ transient formed in an exothermic abstraction mechanism has two pathways (i) to form the unreactive O^{2-} state (R_2) or (ii) to generate chemisorbed hydroxyl and amide species (R_4). (c) Schematic variation of the $O^{\delta-}(a)$, $NH_2(a)$, OH(a) and $O^{2-}(a)$ concentrations along the catalytic oxidation pathway. The Mg^0 to Mg^{2+} transition was observed through the chemical shift in the Mg(1s) spectrum and surface concentrations calculated from the O(1s) and N(1s) intensities.

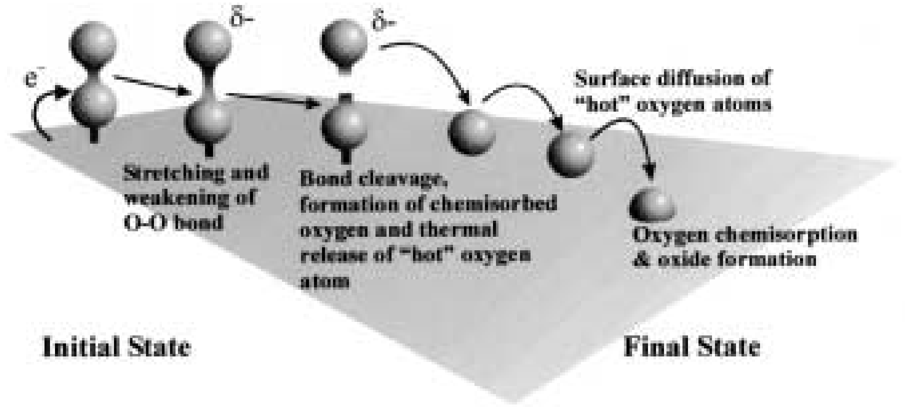


Figure 3. Cartoon model for the reaction dynamics of the dissociative chemisorption of oxygen at a Cu(110) surface via the transients $O_2^{\delta-}$(s) and $O^{\delta-}$(s).

driven chemisorbed amide route; further confirmation of the model proposed was obtained from varying the $NH_3:O_2$ ratio and for oxygen-rich mixtures formation of the oxide layer (equation (2)) dominated with no evidence for chemisorbed NH_2 or OH species.

This model (figure 2) provided the key to much of our subsequent studies aimed at a more wide-ranging exploration of the possible role of oxygen transients in the dynamics of oxygen dissociative chemisorption and also in oxidation chemistry [12]. The oxidation of carbon monoxide and propene were the next systems we studied [13]. Aluminium and magnesium substrates were chosen as we had already studied their oxidation and interaction with carbon dioxide with O(1s) and C(1s) spectra assigned to surface oxide, carbide and carbonate species. Furthermore both carbon monoxide and propene were unreactive, other than being physically adsorbed ($\Delta H \simeq 20\,\text{kJ mol}^{-1}$) at low temperatures at the clean metal surfaces. They therefore were good probe-molecules for reactive oxygen states. Evidence for carbonate, and also for facile carbon–oxygen bond cleavage, through the presence of carbidic species, was obtained from their characteristic features in the C(1s) spectra with transient oxygen states, $O^{\delta-}$(s), implicated in the mechanisms.

At the Faraday Symposium, held in 1986 at Bath, the implications of the co-adsorption of probe molecule results with Mg(0001) were discussed and attention drawn to the possible limitations of describing reaction mechanisms as conforming to either Langmuir–Hinshelhood (LH) or Eley–Rideal (ER) type kinetics [14]. As the oxidation of ammonia reaction involved a non-thermalized, hot, oxygen transient with an ammonia molecule undergoing rapid surface diffusion it could be considered as obeying neither LH nor ER mechanisms. The need to provide an alternative approach to the mechanisms of surface-catalysed reactions was a theme which gained further momentum over the next 5 years [12,19].

Some 14 years later, and with the advantage of the emergence of scanning tunnelling microscopy, Ertl [1], reviewing the field of reaction dynamics at surfaces, emphasized that the "ER mechanism as proposed 60 years ago hardly operates in its pure form, even in reactions involving atomic particles. Instead hot adatom processes appear to be more common (even with molecular adsorbates)".

In summary, the key factor in controlling surface reactivity that emerged from the model (equations (1)–(4)) was being able to maintain the surface oxygen in the $O^{\delta-}$ state (equation (1)) and not allow the relatively unreactive O^{2-} state, the oxide layer, to develop (equation (2)). A cartoon model reflecting these molecular events is shown in figure 3. We will discuss later how STM provided atom-resolved information that would add further confidence to what had been deduced from surface-sensitive spectroscopies (XPS, UPS and in a more limited way electron energy loss spectroscopy). There were also two further bits of experimental information, that became available somewhat later, that supported the model. Ceyer [15,16], studying the dissociative chemisorption of F_2 at silicon, found that there was a finite probability that some of the adsorption energy liberated was dissipated in kinetic/translational energy resulting in F atoms being ejected into the gas phase, while Ertl reported a similar event for oxygen chemisorption at caesium surfaces [17]. Ceyer referred to the phenomenon as "abstractive chemisorption".

Although evidence for the limited activation of NH_3 at a Cu(111)–O surface, the oxygen being pre-adsorbed, had been reported [18] in 1980 we explored whether co-adsorption of ammonia–oxygen mixtures might provide further evidence as to the state of the active oxygen; with ammonia-rich mixtures a complete monolayer of NH species was formed at 295 K and confirmed by both XPS and HREELS. Furthermore, by varying the $NH_3:O_2$ ratio and temperature the oxidation reaction pathway could be controlled to generate either N(a), NH(a) or NH_2(a) species [19]. For an oxygen-rich mixture the catalytic reaction was shut down with the formation of the relatively inactive "oxide" overlayer (equation (2)). Monte Carlo simulation studies in conjunction with experimental data suggested that for a partially oxidised Cu(110) surface the active oxygens were situated at the ends of –Cu–O–Cu– chains [20].

5. Evidence for the molecular precursor state $O_2^{\delta-}$(s) from surface spectroscopy

There was one further point to resolve in the scheme proposed (equations (1)–(5), also figures 2 and 3), and that was whether a molecular transient $O_2^{\delta-}$(s) could be isolated under favourable conditions. There were two systems that were likely to yield information on this point: oxygen chemisorption at Zn(0001) surfaces [21] where dissociative chemisorption had been shown to be a slow process (sticking probability 10^{-3} at 295 K), and oxygen chemisorption at Ag(111) where the molecular state was known to be stable [22].

At the Zn(0001) surface, co-adsorption of ammonia-rich mixtures exhibited precursor-type kinetics (figure 4) to generate NH_2, OH and O^{2-} species; the reaction was faster the lower the temperature, indicating the participation of an NH_3–$O_2^{\delta-}$ complex. It was also the first example of where the rate of dioxygen bond cleavage could be increased by nearly a factor of 10^3 by providing an alternative reaction pathway *via* a metastable dioxygen surface complex and where the adduct involved, NH_3, was on its own unreactive at the metal surface. The complex lowered the activation energy for dioxygen bond cleavage leading to dissociative chemisorption with the added thermodynamic sink of the chemisorbed products to drive the reaction forward [21].

XPS established that when an ammonia-rich dioxygen–ammonia mixture was exposed to Ag(111) there was no evidence in the O(1s) or N(1s) spectra for either oxygen or ammonia present in the adsorbed state at 200 K and above. However, as the temperature was lowered the intensity of the O(1s) peak increased and at 100 K vibrational loss features at 1488 and 1640 cm^{-1} were observed which were assigned to two different oxygen states and those at 1120 and 3390 cm^{-1} to adsorbed ammonia. On warming to 210 K there was no evidence for the two oxygen states or adsorbed ammonia but loss features assigned to OH and NH_x species had emerged. The oxygen loss feature at 1488 cm^{-1} was assigned to a $O_2^{\delta-}$–NH_3 complex which, as with Zn(0001), provided a facile route to OH and NH_x formation. We suggested that the oxygen within the complex, $O_2^{\delta-}$, is distinctly different from the peroxo species which, when pre-adsorbed, does not form the complex on exposure to ammonia [22]. The state of the oxygen in the complex is clearly determined by the co-adsorbate, ammonia, in a synchronous process. Thornburg and Madix [23] reported very similar conclusions for the Ag(111)–oxygen–ammonia system.

The principal aim of our co-adsorption or probe molecule studies was to search for oxygen transients and how they might participate in the chemistry of dioxygen at metal surfaces. The progress up until 1992 was reviewed at the Tokyo meeting [12] where added impetus for the concept came from Gerhard Ertl who, in his Plenary address, described STM results [24] for oxygen chemisorption at Al(111) showing that subsequent to dissociation oxygen adatoms may be separated by as much as 80 Å. In his 2000 review Ertl [1] contrasted schematically the dynamics of the Langmuir model for adsorption involving strong coupling with the surface and the hot precursor or transient model where the oxygen (say) exchanges its energy with the surface in a step-wise manner through travelling across the surface before coming to rest. This was the central tenet (figure 2) of the probe molecule approach [10–12] using

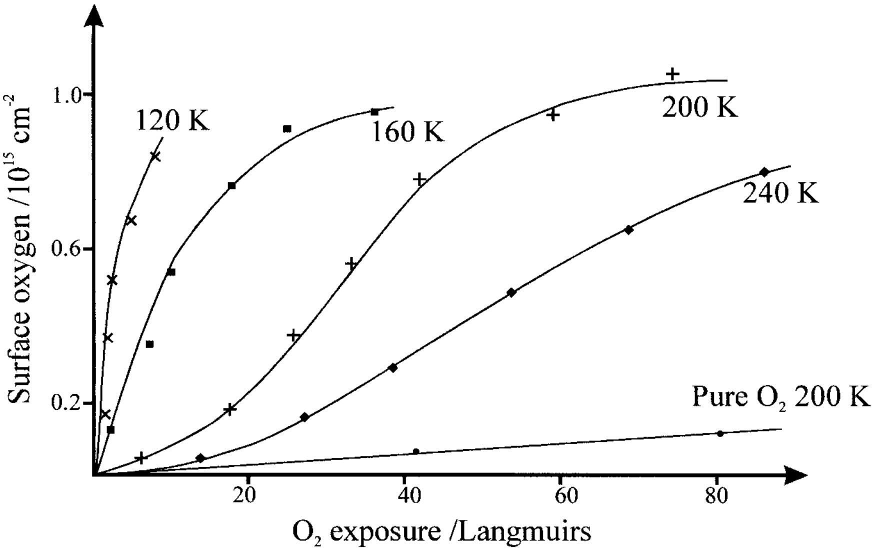


Figure 4. Evidence for the $O_2^{\delta-}$ transient at a Zn(0001) surface using a $NH_3 : O_2$ (2 : 1) mixture. Precursor-type kinetics for the dissociation of the metastable ($O_2^{\delta-}$–NH_3) complex; the complex provides a low energy pathway for the cleavage of the dioxygen bond with the products NH_2(a), OH(a) and O^{2-}(a) providing the thermodynamic driving force.

ammonia to search for oxygen transients and precursor states but then extended to other probes (water, pyridine and hydrocarbons).

Further insight into the possible role of both atomic and molecular oxygen precursors in ammonia oxidation came from the theoretical work of van Santen's group. Calculations were performed [25,26] using a Cu(8,3) cluster to mimic the Cu(111) surface. Atomic oxygen (pre-adsorbed) activated the N–H bond in ammonia but could also act as a surface poison while molecular oxygen adsorbed in the perpendicular mode could form a complex with ammonia providing a low-energy pathway for ammonia oxidation (hydrogen abstraction) leading to amide and imide species. These calculations were generally in line with what had been observed experimentally by the Cardiff group, as also were the calculations of Haber's group in Krakow [27].

It was against this background of both the experimental co-adsorption data and theoretical work that we initiated STM studies to ascertain whether the model derived from surface spectroscopic studies (figures 2 and 3) could be maintained at the atom-resolved level.

6. Atom-resolved evidence from scanning tunnelling microscopy (1992–2001)

Although Ertl's STM results provided good evidence in 1992 for "hot" oxygen transients being generated at Al(111) surfaces when oxygen was dissociatively chemisorbed at 295 K, there were no studies which could comment on their chemical reactivity and relevant to the models developed from co-adsorption studies and surface spectroscopy. Stensgaard *et al.* [28], however, in 1994 reported STM data for the interaction of ammonia with Ni(110)–O (the oxygen being pre-adsorbed). It was Madix [29] at the Faraday Discussion Meeting in 1996 who first reported STM data which confirmed that for the Cu(110)–O system the oxygens active in H abstractions were situated at the ends of the –Cu–O–Cu–O– chains, a conclusion also reached in 1994 on the basis of Monte Carlo modelling of the reaction. Bowker, at the same meeting, expressed concern at the description of oxygen species involved in co-adsorption studies (*e.g.* $NH_3:O_2$ mixtures) as "transients" and "hot" as a "buzz word" while Kasemo in the discussion drew attention to his paper with Harris [2] where the idea of "hot precursor" states had been mooted.

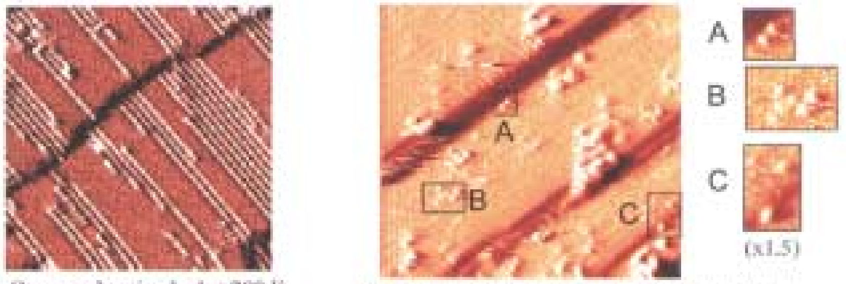
It is important to recall that the surface lifetime τ of O^-(s) transients had been defined precisely [10] for the ammonia–dioxygen co-adsorption experiments at Mg(0001). It was the time that the reactive O^-(s) species were present at the metal surface under the experimental conditions before becoming inactive as oxide O^{2-} type species (see figure 3). Clearly τ is a function of temperature, pressure, gas compositions and the metal. The oxygen adatoms were described as "hot" for three reasons; first, they had been formed as a consequence of a highly exothermic reaction; second, their reactivity simulated the gas-phase reaction $O^- + NH_3 = OH^- + NH_2$; and third, they were "radicals" undergoing rapid surface diffusion. The O^-(s) state was distinct from the two-electron oxygen state O^{2-}(a) for which a thermodynamic pre-requisite was the contribution from the "Madelung energy" associated with surface reconstruction and "oxide" formation. By contrast the $O(g) + e \rightarrow O^-(g)$ is thermodynamically favourable.

A serious disadvantage of STM is that it provides no chemical information. However, having developed models for surface reactions based on surface spectroscopies (XPS, UPS and HREELS) there was an incentive for us to test them at the atom-resolved level. By adding on an XPS facility to an ultra-high vacuum scanning tunnelling microscope, capable of operating over a wide temperature range, the possibility of combining topographic with chemical information provided us with a powerful approach to testing the models.

6.1. The Cu(110)–oxygen system

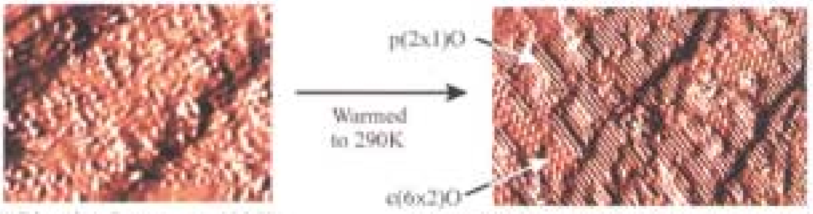
The chemisorption of oxygen at Cu(110) at 300 K had been extensively studied [30] by STM and was a model system for illustrating surface reconstruction invoking the (2 × 1)O added row concept. At very high oxygen exposures (10^5 L) and higher temperature a new structure c(6 × 2)O developed but during this period (1990–1994) STM data were confined to room temperature and above. In view of the crucial evidence we had gleaned regarding surface reactivity from experiments at low temperatures (80–200 K), and since one of the aims was to obtain evidence for oxygen states that were precursors of the "oxide" (2 × 1)-O adlayer formed at room temperature, we studied oxygen chemisorption at Cu(110) at 120 K. Three distinct configurations of oxygen adatoms were imaged [31]: isolated oxygen adatoms, pairs or dimers separated by about 6 Å and clusters of five or six atoms arranged anisotropically. These oxygen adatom configurations were present after an oxygen exposure of 0.1 L but are stable over time at 120 K. At high surface coverages, oxygen pre-adsorbed at 80 K is disordered but ordered structures develop on warming the adlayer to 295 K. In addition to the well-established (2 × 1)-O ordered structure there is also present a c(6 × 2)-O structure only previously reported for high oxygen exposures at above room temperature (figure 5).

These low-temperature experiments emphasize the variety of oxygen states that are possible at a Cu(110) surface, with a predominance of isolated or disordered oxygen adatoms at low temperatures but which undergo disorder–order transition to generate a two-phase structure (2 × 1)-O and c(6 × 2) at 295 K. It is the correlation between chemical reactivity, oxygen states and structure



(a) Oxygen chemisorbed at 290 K p(2x1)O

(b) Oxygen chemisorbed at 120K, low coverage, meta-stable, isolated atomic oxygen



(c) Disordered oxygen at 110 K: high coverage.

(d) Adsorption state at 110K, warmed to 290K, emergence of ordered p(2x1) and c(6x2) states.

Figure 5. STM images of chemisorbed oxygen states present at a Cu(110) surface at 110, 120 and 290 K.

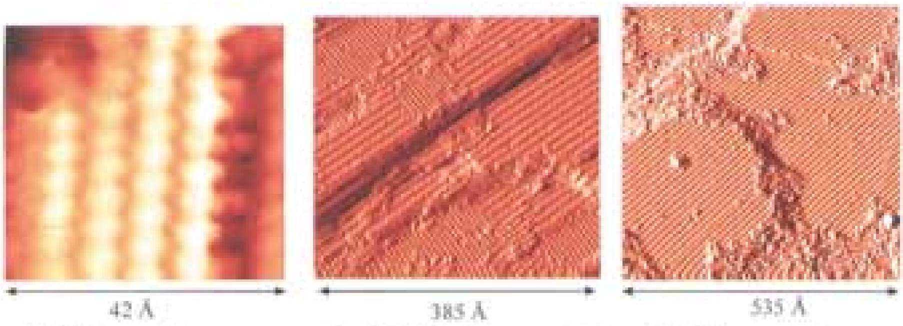
that has been the significant aspect of the STM and co-adsorption or probe-molecule studies. What still remains to be resolved is the precise electronic structure of the metastable active oxygen state which we designated as $O^{\delta-}$ or O^{-}-like, also present at the Ni(210) surface [8] at 80 K, and the key species in the dehydrogenation of ammonia at Cu(110) surfaces.

6.2. *Structure of imide strings at Cu(110): the ammonia–dioxygen system*

Following our spectroscopic studies [19], STM images were reported in 1998 for the co-adsorption of ammonia-rich dioxygen mixtures with Cu(110) and established [32,33] that a monolayer of imide species developed at 295 K which were aligned (figure 6(a)) in rows running along the ⟨110⟩ direction. There was no evidence from either XPS or STM for the presence of chemisorbed oxygen during the catalytic oxidation of ammonia, it being desorbed as water. The spacing of the units within a string is 5 Å and the strings are separated by 7.2 Å; the latter is close to twice the copper–copper spacing in the ⟨100⟩ direction. Photoelectron diffraction studies of Bradshaw *et al.* [34] indicated that imide species are in the short-bridge copper sites. The key reaction is clearly

$$NH_3(s) + O^{\delta-}(s) \rightarrow NH_2(a) + H_2O(g)$$

and involves the transient $O^{\delta-}(s)$ interacting with ammonia, present at immeasurably low concentration, but undergoing rapid surface diffusion. In 1989 a computer modelling of the ammonia oxidation reaction over magnesium indicated that the formation of chemisorbed NH_2, O^{2-} and OH species could in principle be sustained by $NH_3(s)$ concentrations as low as $10^9\,\mathrm{mol\,cm^{-2}}$ but undergoing rapid surface diffusion [12,35]. It was essentially a two-dimensional gas reaction with the Eley–Rideal mechanism ruled out. This concept was



(a) 30:1 ammonia/oxygen mixture at 290K.

(b) 1:1 NH_3/O_2 mixture at 60K, warmed to 290K.

(c) 30:1 ammonia/oxygen mixture at 475 K

Figure 6. Control of reaction pathways in the oxidation of ammonia at a Cu(110) surface generating (a) c(2 × 4)-NH species; (b) (3 × 1)-N and (2 × 1)-O states; and (c)(2 × 3)-N states.

supported by the STM data for imide formation at the Cu(110) surface for ammonia-rich mixtures at 295 K, where $O^{\delta-}(s)$ are the active dehydrogenation (oxidation) species and ammonia is present at immeasurably low concentrations. The control of reaction pathways in ammonia oxidation, through varying the $NH_3:O_2$ ratio and temperature, provided further crucial evidence [33] for the role of oxygen transients in oxidation chemistry. Figure 6 shows images of ordered NH species in a c(2 × 4) structure (a); a biphasic structure consisting of (2 × 3)-N and (2 × 1)-O states (b); and a (2 × 3)-N state (c). What is significant is that oxydehydrogenation can be complete to give the (2 × 3)-N state, even at low temperatures, provided the chemisorbed oxygen is in the disordered $O^{\delta-}(s)$ state and has not formed the less reactive (2 × 1)-O state (see figure 5 images (a) and (c)).

At Aarhus University, Ruan *et al.* [28] concluded in 1994 that it was the oxygen atoms present at the ends of the short, mobile Ni–O rows at a Ni(110) surface that are active in oxydehydrogenation and that, at higher oxygen coverage, these active oxygen sites are absent, thus accounting for the oxide overlayer's relative inertness. This was, in essence, the model that had been proposed, based initially on surface spectroscopic data, for the Cu(110)–oxygen–ammonia system and supported by the Monte Carlo modelling analysis [20]. It was, however, the first STM study which provided us with direct atom-resolved evidence for the specific chemical reactivities of chemisorbed oxygen states present at low or high surface coverages and which had been distinguished as $O^{\delta-}(a)$ and $O^{2-}(a)$ in our model (equations (1)–(4) and figures 2 or 3).

6.3. Oxygen chemisorption at Pt(111) and Ag(110)

In 1997 Ertl reported STM images for oxygen chemisorbed at a Pt(111) surface [36] at low surface coverages in the temperature range 54 K to 160 K (figure 7). The atoms appear as pairs at 160 K with an average distance of separation of twice the lattice constant of the platinum surface (5.6 Å). On lowering the temperature of adsorption, different cluster shapes are observed, and at 105 K the atoms are exclusively present as chains. The authors conclude that the observations can be explained by the participation of a mobile molecular precursor with oxygen adatoms already chemisorbed acting as sites for trapping and dissociation of the precursor. In this way the dissociation probability of the dioxygen precursor is increased.

Very similar conclusions [37] were reached for the Ag(110)–oxygen system at 65 K. Only a few single adsorbates are observed but the majority are present as ensembles of two or four molecules with an interatomic distance of nearly 6 Å. The distance of twice the lattice constant along the O_2 direction is an energetically favourable configuration and even when the coverage was only 0.003 monolayers about 40% of the adparticles were present as ensembles. A hot precursor mechanism is invoked as the explanation of these observations, with the oxygen precursor being highly mobile but becoming trapped by collision with the equilibrated species with the formation of pairs or strings of molecules in the troughs of the Ag(110) surface.

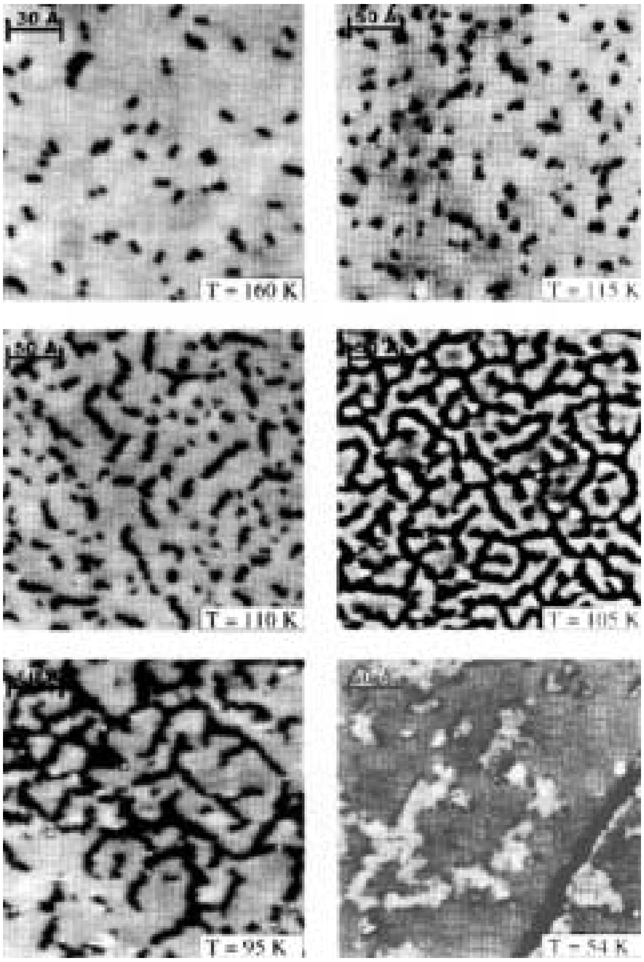


Figure 7. Temperature dependence of oxygen states at Pt(111) after an exposure of 1 Langmuir at the indicated temperatures revealing their anisotropic development [36].

7. Abstractive chemisorption and the dynamics of oxygen chemisorption

The model proposed [10] for the dissociative chemisorption of oxygen at the Mg(0001) surface (figure 3) is non-classical in the sense that the two oxygen atoms do not come to rest on adjacent sites, which would be expected from the classical Langmuir model. Ceyer drew attention to this possibility in 1995 for the dissociative chemisorption of F_2 at the Si(100) surface, where one of the fluorine atoms is "captured" by the silicon while the complementary fluorine atom either "flies along the surface as a transient species" until it becomes chemisorbed or scatters into the gas phase (desorbs). A full paper describing this work [16] was published in 1999 and the term "abstraction chemisorption" used to describe the process which was studied by scattering a F_2 beam from the Si(100) surface and detecting the scattered reaction products F and F_2. The "abstraction mechanism" is inherent to the cartoon model (figure 3) used as a representation of what was considered to reflect the individual steps in the kinetic model developed to describe the Mg(0001)–oxygen system.

Hasselbrink *et al.* [38] returned to the Al(111)–oxygen chemisorption system in 2000 and concluded that an abstraction mechanism is responsible for the observation of single oxygen adatoms by STM. These authors state that "there remains no reason to invoke hot atom motion as its origin". It should however be explained that the term "hot oxygen atoms", first used in 1986, was to make a distinction between the chemical reactivity of what were isolated metastable oxygen adatoms and the "oxide" overlayer which was by comparison inert [10]. How "hot" atoms were formed was not considered, but that they were likely to be well separated from each other on the metal surface at low coverages was inherent to the model. Both the work of Ceyer with fluorine and Hasselbrink's study of the chemisorption of oxygen at Al(111) report atoms being ejected into the gas phase during chemisorption, as also did Ertl for the chemisorption of oxygen at caesium surfaces. It is these observations that provide the supporting evidence for the development of models (figures 2 and 3) for chemisorption, and the various reaction channels available in the chemistry of dioxygen at metal surfaces.

8. Summarizing comments

The concept of oxygen transients, defect and precursor states, and their role in controlling reaction pathways at metal surfaces, has developed over the past 15 years and its general relevance reflected by evidence which is now wide ranging (see for example table 1). The probe-molecule or co-adsorption approach first used by us in the mid 1980s provided a new insight to surface reactivity with Bowker emphasizing in 1996 its advantages over the more traditional approach with the following comment [42]: "Most surface science studies involving the reaction of two or more adsorbates have predominantly focussed on the interaction of reactants dosed sequentially. However, there is a growing sentiment that a such an approach is limited and that co-dosing by the simultaneous introduction of reactants may lead both to alternative reaction pathways and to a more realistic model of catalytic activity."

The oxidation of ammonia over Cu(110) surfaces [19,33] is an example of this where during the formation of a monolayer of chemisorbed imide species there was no evidence from XPS and STM for either chemisorbed oxygen or adsorbed ammonia during the reaction. Although four distinct states of oxygen have been revealed by STM, the oxygens active in the facile oxidation of ammonia are transient and not detected by either XPS or STM. Iwasawa [39] in 1999 drew attention to what he described as a "new aspect of catalysis" where reactions "are assisted by gas phase molecules undetectable at the surface", ammonia oxidation at Cu(110) and Mg(0001) being examples [19,10]. Furthermore, any evidence from studies of the surface reactivity of the individual molecules, ammonia and oxygen, would not have predicted the observed catalytic activity, an aspect that prompted the need to reconsider the more traditional views on reaction mechanisms.

The co-adsorption studies suggest that when oxygen chemisorption is highly exothermic the transient participating in oxidation catalysis is atomic, $O^{\delta-}(s)$. This is the case for magnesium, aluminium, nickel and copper at 295 K, with oxydehydrogenation being an efficient and the favoured reaction pathway. For weaker oxygen chemisorption, and when oxygen bond cleavage is "slow", as with silver and zinc, the molecular oxygen transient $O_2^{\delta-}(s)$ is the oxidizing species; the dioxygen, via the formation of a precursor complex, $O_2^{\delta-}$–X, providing a low energy pathway to products.

Table 1
Surface chemistry mediated *via* oxygen transients: evidence from surface spectroscopy (1986–1999)

Mg(0001)	$O_2:NH_3$	Facile H-abstraction [10]
Mg(0001)	$O_2:C_3H_66$	C–H activation and H-abstraction [13(b)]
Al(pc)	$O_2:CO$	Low energy pathway to C–O bond cleavage [13(a)]
Zn(0001)	$O_2:C_5H_5N$	Facile route to dioxygen bond cleavage [44]
Cu(110)	$O_2:NH_3$	Selective oxydehydrogenation reactions giving N, NH or NH_2 species [19]
Cu(110)	$O_2:CH_3OH$	Selectivity for HCHO or surface formate [45]
Ag(110)	$O_2:NH_3$	Dioxygen states stabilized in the presence of NH_3(a) [22]
Zn(0001)	$O_2:CH_3OH$	C–O bond cleavage at 80 K [40]
Cu(111) Zn(0001)	$O_2:H_2O$	Facile surface hydroxylation [46]
Ni(110)	$O_2:H_2O$	Surface hydroxylation at low temperatures [47]
Ni(110)	$O_2:NH_3$	Oxydehydrogenation to give NH species [48]
Cu(100) Ag(111)	$O_2:H_2O$	Facile hydroxylation at low temperatures [49]

Although the stimulus for exploring whether O^--like species existed transiently during the dynamics of oxygen chemisorption had come initially from XPS evidence for their presence at defective metal-oxide overlayers, it was the established gas-phase chemistry of the O^- ion that prompted us to search for evidence from co-adsorption studies. Bohme and Fehsenfeld [41] in 1969 had shown that hydrogen abstraction by O^- ions from a range of molecules, hydrocarbons and ammonia, occurred with high probability, in the range 0.1 to 0.63, so that the co-adsorption of ammonia and oxygen at a catalytically unreactive sp-metal (magnesium) [10] was an ideal system to explore the hypothesis. Such experiments also turned out to provide an insight into the limitations of kinetic studies invoking ER or LH mechanisms [10,14] with Kasemo more recently [43] discussing models for the mechanism of transient formation. It is, however, the atom-resolved information from STM studies that has re-emphasized and demonstrated clearly the complexities of what hitherto were regarded as inherently simple catalytic reactions with evidence for the participation of metastable or non-thermalized oxygen states in surface reactions.

Acknowledgments

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