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Oxygen transient states in catalytic oxidation at metal surfaces

A.F. Carley, P.R. Davies, M.W. Roberts*

School of Chemistry, Cardiff Institute of Catalysis, Cardiff University, Main Building, Park Place, Cardiff CF10 3AT, United Kingdom

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ABSTRACT

Mechanistic aspects of catalytic *oxidation* at metal surfaces have involved four distinct stages of investigation which, in chronological order, are: (a) oxygen chemisorption and surface reconstruction with evidence for discrete metal and oxygen states; (b) the reactivity of specific oxygen states in oxydehydrogenation reactions; (c) the chemistry under dynamic conditions with evidence for dioxygen–reactant complexes at low temperature; (d) atom resolved evidence from scanning tunnelling microscopy.

We discuss how these studies draw attention to the advantages of dynamic studies in revealing individual steps in oxidation catalysis, the role of labile surface complexes in providing low energy pathways to products and their relevance to the theoretical calculations and experimental studies of Jerzy Haber and his colleagues.

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1. Introduction

I (MWR) first met Jerzy in 1962 at Queens' University Belfast and discussed with him a common interest we had in work function changes associated with oxygen chemisorption at metal surfaces. Jerzy moved on to oxides, defects in oxides and catalysis at oxide surfaces to become one of the leaders in selective oxidation catalysis. I continued with investigating the surface chemistry of metals but retaining my interest in oxygen chemisorption, oxidation and the role of oxygen states in controlling reaction pathways [1]. Although our goals were somewhat different there was much common ground between us for over 40 years and a close friendship which I very much enjoyed.

In 2002 Jerzy contributed an article "Molecular Description of Transition Metal Oxide Catalysts" in a special publication 'Surface Chemistry and Catalysis' [2]. He drew attention to four distinct areas that had contributed to the science of catalysis over the preceding 20 years: new materials; new surface science experimental methods; identifying active sites; quantum mechanical modelling of surface reactions and reactor design. Further emphasis was given to organic complexes of transition metals deposited at oxide supports, oxy-ions deposited at oxides to form oxide monolayer catalysts and the role of oxygen species in catalysis. This is where our interests overlapped closely, Jerzy with bulk oxides and ourselves with oxygen states at metal surfaces – with the significance of "Surface Complexes" as active sites – being a common theme. We had been involved in the development of X-ray photoelectron spectroscopy (XPS) in surface science and Jerzy was one of the first in Eastern Europe to explore what, in the mid 1970s was a new experimental method in catalysis.

We discuss in this paper how the isolation of individual steps involved in a surface catalysed oxidation reaction – albeit at a metal surface – can contribute to the understanding of more complex reactions at supported oxide catalyst surfaces where such evidence is frequently missing. We, therefore, focus in this article on the reactivity of oxygen states at metal surfaces but keeping in mind their relevance to oxidation catalysis, Haber's life-long interest in oxides and associated surface complexes (the active sites) and the views of Grasselli [3] for the "seven pillars" considered to underpin oxidation catalysis including: lattice oxygen; the metal–oxygen bond; redox states; site isolation and the multifunctionality of active sites being bifunctional and bimetallic.

2. Oxygen activation of adsorbates

There are (at least!) two different approaches to the investigation of mechanistic aspects of heterogeneously catalysed reactions: (a) designing catalysts with special sites for specific reactions and (b) breaking down the overall reactions into individual steps – chemisorption, structure, reactivity and selectivity – with model surfaces, including single crystals, and if possible with evidence at the atom—resolved level from scanning tunnelling microscopy. It was an interest in oxygen chemisorption, surface reconstruction, atom mobility and reactivity that provided an incentive during the period 1979–1981, through X-ray photoelection spectroscopy (XPS), to look for evidence for adsorbate activation. At Cu(1 1 1) the

* Corresponding author.
E-mail address: robertsmw@cf.ac.uk (M.W. Roberts).

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C–H bond in ethene, the O–H bond in water and the N–H bond in ammonia are all activated by preadsorbed chemisorbed oxygen at the sub-monolayer level ($\sim 4 \times 10^{14}\,cm^{-2}$) [4]:

$$373\,K: 2C_2H_4(g) + O(a) \rightarrow H_2O(g) + 2C_2H_3(a)$$

$$295\,K: NH_3(g) + O(a) \rightarrow H_2O(g) + NH(a)$$

$$300\,K: O(a) + H_2O(g) \rightarrow 2OH(a)$$

$$2OH(a) \rightarrow H_2O(g) + O(a)$$

Subsequently (in 1983) it was established [5] that oxygen chemisorbed at Ni(2 1 0) at 80 K was active in H-abstraction from water whereas the oxygen chemisorbed at 295 K was inactive. The former we designated as $O^{\delta-}(a)$ and the latter, accompanying surface reconstruction, as $O^{2-}(a)$, the "oxide" state (Fig. 1). The possibility that a transient, metastable, non-thermalised oxygen state formed during dioxygen bond cleavage could activate adsorbates was, however, a new concept. There was already evidence that the source of the active oxygen could also be the dissociative chemisorption of nitric oxide; when coadsorbed with water at Zn(0 0 0 1) at low temperatures [6] surface hydroxyls were formed. Cryogenic studies became important in pinning down the specific activities of what we described as metastable oxygen states in catalytic oxidation, and controlling reaction pathways [7].

STM studies (in 2004) of the activation of some amines offered further evidence for the difference in behaviour between oxygen in a chemisorbed state and oxygen that is coadsorbed with the reactant [8]. The chemisorption of aniline at preoxidised ($\theta_O < 1$) Cu(1 1 0) surfaces for example resulted in the formation of a phenyl imide with the surface covered in a mixture of three ordered domains with structures described by the $\begin{pmatrix} 4 & 0 \\ 2 & 2 \end{pmatrix}$, $\begin{pmatrix} 4 & 0 \\ -1 & 2 \end{pmatrix}$ and $\begin{pmatrix} 4 & 0 \\ 1 & 2 \end{pmatrix}$ unit meshes and an aniline surface concentration of $2.8 \times 10^{14}\,cm^{-2}$. A 300:1 aniline/oxygen mixture at 293 K however, resulted in a much higher packing density with much greater surface order (Fig. 2). A surface concentration of 3.4×10^{14} molecules cm^{-2} was obtained with the STM images showing a highly ordered biphasic structure characterized by $\begin{pmatrix} 3 & 0 \\ -1 & 2 \end{pmatrix}$ and $\begin{pmatrix} 3 & 0 \\ 1 & 2 \end{pmatrix}$ domains.

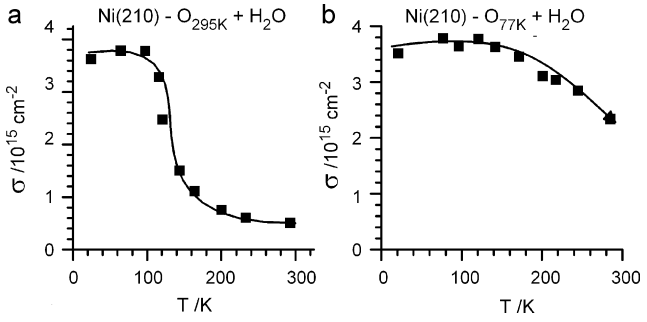

Fig. 1. Reactivity of oxygen states at Ni(2 1 0) to water; oxygen is preadsorbed at 295 K and at 77 K; water is then adsorbed at 77 K and the adlayer warmed to 295 K. The oxygen chemisorbed at 295 K is unreactive, the water having desorbed at 160 K, whereas the oxygen preadsorbed at 77 K is reactive forming surface hydroxyls. The total "surface oxygen" concentration, σ, is calculated from the O(1s) spectrum.

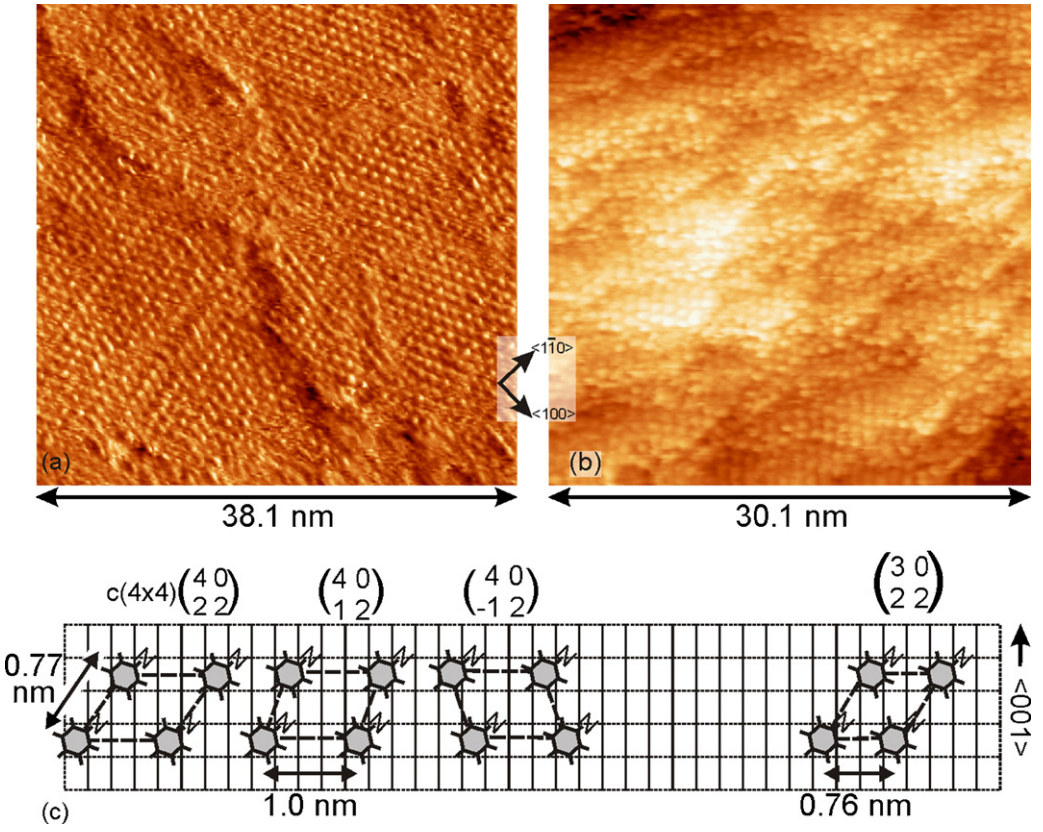

Fig. 2. A comparison of phenyl imide adsorption from preadsorbed and coadsorbed oxygen. Note the higher degree of order and closer packing in the coadsorbed case. (a) Cu(1 1 0) surface with an initial oxygen concentration of $2.4 \times 10^{14}\,cm^{-2}$ exposed to 200 L aniline at 293 K, $V_S = 0.95$ V, $I_T = 1.93$ nA. (b) Clean Cu(1 1 0) surface exposed to 200 L of a 300:1 aniline/dioxygen mixture at 293 K, $V_S = 0.95$ V, $I_T = 2.04$ nA. (c) Shows a schematic comparing the three structures observed in (a) with the close packed structure in (b).

3. Oxygen transient states

Prompted by the activation of adsorbates such as NH_3, H_2O and C_2H_4 by oxygen, we examined in 1986 the proposition that an O^- state could conceivably be present as a short-lived surface transient, when dioxygen, nitric oxide or nitrous oxide were dissociatively chemisorbed at Mg(0 0 0 1) and had a sufficiently long surface life-time to control reaction pathways in catalytic oxidation. This led to the probe molecule approach which can distinguish between the chemistry associated with a transient oxygen state and the 'oxide' O^{2-} state at metal surfaces. In view of the known high reactivity of $O^-(g)$ with $NH_3(g)$ in the gas phase – a low activation energy and high collision efficiency homogeneous reaction – we chose ammonia as the probe molecule for studies at a Mg(0 0 0 1) surface [9].

$$O^-(g) + NH_3(g) \rightarrow OH^-(g) + NH_2(g) \quad (1)$$

The methodology was discussed at the 8th International Seminar on Electron Spectroscopy in Zakopane in 1990 [10]; the essential point is that each surface site is visited by the probe molecule (NH_3) several hundred times during its surface sojourn time (10^{-6} s) at 295 K. There is, therefore, a high probability that it traps an O^- transient (Eq. (1)) if present. The details and background as to how the method evolved is discussed elsewhere [11].

Ammonia-rich mixtures containing O_2, NO or N_2O established that at Mg(0 0 0 1), oxygen adatom transients were present and provided a low energy pathway to surface amide NH_2(a) under conditions where the chemisorbed 'oxide' state was inactive [9]. The reactive $O^{\delta-}$ (or O^--like) state formed by dissociative chemisorption had sufficient translational kinetic energy to undergo surface hopping (diffusion), but with increasing surface coverage nucleate to form the unreactive oxide O^{2-} state. The possible limitations of Langmuir–Hinshelwood and Eley–Rideal mechanisms were discussed but not readily accepted at Faraday Discussion Meetings [9,12], with the classical model of dissociative chemisorption of oxygen resulting in the two oxygen atoms funnelling into two adjacent surface sites being also unrealistic. We discuss later how STM has provided confirmation of the model that was set up to examine whether transient states were present in the dynamics of oxygen dissociative chemisorption but which also provided a different view of oxidation catalysis.

4. The two dimensional gas model: ammonia oxidation at Cu(1 1 0)

Subsequent to the evidence [9] in 1986 for hot transient, reactive oxygen adatoms present at Mg(0 0 0 1) we returned to the Cu(1 1 0) and Cu(1 1 1)—0 systems where *preadsorbed* chemisorbed oxygen had been shown to be partially active in ammonia, hydrocarbon and water activation [4]. Three distinct regimes of oxygen reactivity were delineated at 295 K: for the fractional surface oxygen atom coverage $\theta_0 = 1.0$ the surface was inactive; for $\theta_0 = 0.5$ there was partial reactivity and for an ammonia-rich NH_3–O_2 mixture a complete monolayer of imide NH(a) formed "instantaneously" [13] but with *no evidence for surface oxygen during their formation*. For $\theta_0 = 0.5$ it was oxygens at the periphery of clusters (islands) that were active [11]. By varying the temperature and NH_3:O_2 ratio, oxidation could be controlled, and we observed NH_2(a) and NH(a) at lower temperatures and N(a) at higher temperatures.

These spectroscopic (XPS and HREELS) studies had by 1993 established that to maintain high oxidation reactivity it is advantageous to ensure that multi-oxygen atom nuclei or cluster formation (nucleation) is limited since this favours surface reconstruction and the development of the inactive oxide O^{2-} state. Three distinct oxygen states were delineated at Cu(1 1 0): mobile hot oxygen adatoms $O^{\delta-}$(s); isolated oxygen adatoms $O^{\delta-}$(a) and the reconstructed or oxide state O^{2-}(a) [11,14].

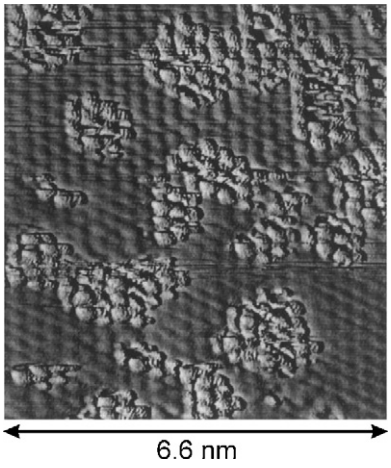

Fig. 3. STM image of oxygen chemisorption at Al(1 1 1) at 295 K indicating the nucleation of oxygen patches.
Reproduced from Ref. [17].

A similar approach for oxygen chemisorption at Ni(1 0 0) provided evidence for $O^{\delta-}$(a) at low coverage with the onset of O^{2-}(a) with increasing coverage accompanied by evidence from the Ni(2p) spectra for $Ni^{2+,3+}$ states [15]. However, only at low surface coverage was the oxygen state active in the oxidation of ammonia and water [16].

In 1992 the first STM evidence for hot oxygen adatoms was obtained by Ertl's group for oxygen dissociative chemisorption at Al(1 1 1) [17] where the hot atoms travelled up to 10 nm across the surface before coming to rest (Fig. 3). What then could be learnt from STM regarding the two dimensional gas model [18] for catalytic oxidation? We returned [19] to the oxidation of ammonia at Cu(1 1 0) with STM coupled with *in situ* XPS—providing both structural and chemical information in the temperature range 80–500 K. At cryogenic temperatures oxygen dissociation resulted in atom states which were disordered, well separated from each other and mobile, but which with increasing temperature became well ordered to form the (2×1) structure associated with chemisorption at room temperature (Fig. 4) and established by the earlier studies of Ertl and Besenbacker. Surface mobility of both the copper and oxygen states was facile. The coadsorption of ammonia rich NH_3–O_2 mixtures at 295 K resulted in well ordered NH states running in the ⟨1 0 0⟩ direction. When coadsorbed at 60 K followed by warming to 295 K, very surprisingly we observed the formation of N(a) states which were accompanied by surface "poisoning" as the disordered mobile oxygen states ordered to form the unreactive (2×1)O state, Fig. 5. A very similar picture for the oxidation reactivity of oxygen states at Cu(1 1 0) was also evident from the studies of Madix at Stanford [20]. A more complete discussion is given elsewhere [11].

For metals where dioxygen bond cleavage is "slow", as at Zn(0 0 0 1) and Ag(1 1 1) at 295 K, a dioxygen transient state $O_2^{\delta-}$(s) forms a complex with ammonia at low temperatures to provide a low energy route to oxidation [21]. It is in effect a *precursor assisted cleavage of the dioxygen bond*, a description given to it by van Santen and Niemantsverdriet [22]. It is driven thermodynamically by the formation of surface amide and 'oxide' species.

The dioxygen bond is weakened through complex formation, and with decreasing temperature the concentration of the dioxygen–ammonia complex at Zn(0 0 0 1) increases, leading to enhanced surface oxidation and amide formation. The rate of O_2 bond cleavage is a factor of nearly 300 greater at low temperature

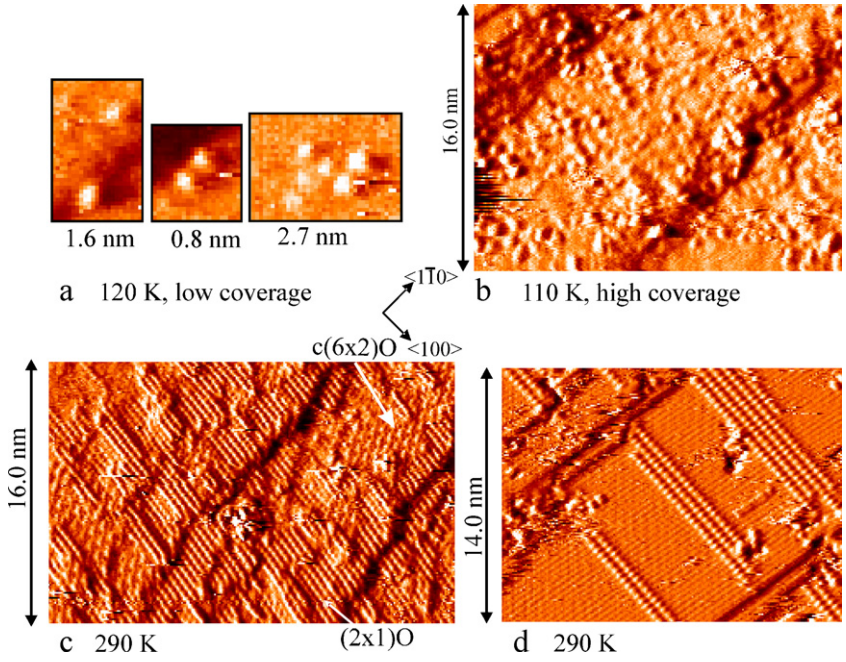

Fig. 4. STM images of oxygen chemisorption at Cu(1 1 0) revealing the oxygen states involved in the formation of the chemisorbed overlayer (a) low oxygen coverage at 120 K, (b) high coverage at 110 K, (c) (2 × 1) and c(6 × 2) oxygen states on warming (b) to 295 K, and (d) (2 × 1)O strings for oxygen chemisorption at 295 K.

via the complex compared with oxygen dissociation at 295 K [21]. Of particular significance was that the rate of oxidation increased as the ammonia to oxygen ratio increased at low temperatures, due to the increased surface concentration of physisorbed ammonia and the consequent increase in the concentration of the complex, Fig. 6. At Ag(1 1 1) very similar chemistry is observed, where the oxygen state $O_2(s)$, a precursor of the peroxo O_2^- state, forms the complex [23]. At low temperatures the complex is "frozen out" and the oxygen state may thus be characterized by XPS and vibrational spectroscopy, where we observe a band at a frequency of 1490 cm^{-1}. What is important is that these oxygen states, at both Ag(1 1 1) and Zn(0 0 0 1), would not be observed in spectroscopic studies in the absence of the coadsorbate (reactant) ammonia, and are only present in significant concentrations at low temperature.

$$O_2(g) \rightarrow O_2(s) \quad (2)$$

$$O_2(s) \rightarrow O_2{}^{\delta-}(a) \quad (3)$$

$$O_2(s) + NH_3(s) \rightarrow (O_2{}^{\delta}\cdots NH_3) \quad (4)$$

$$(O_2{}^{\delta-}\cdots NH_3) \rightarrow O(s) + OH(a) + NH_2(a) \quad (5)$$

$$O(s) + NH_2(a) \rightarrow OH(a) + NH(a) \quad (6)$$

$$OH(a) \rightarrow O(a) + \tfrac{1}{2}H_2(g) \quad (7)$$

(2)	Surface accommodation of dioxygen; (s) signifies transient
(3)	Peroxide formation is a kinetically slow route; (a) signifies chemisorbed state
(4)	Charge transfer complex formation at low temperatures involving the dioxygen transient
(5, 6, 7)	Facile dissociation of complex, driven thermodynamically by formation of hydroxyl, amide/immide and 'oxide'; an example of precursor assisted dioxygen bond cleavage

The intermolecular forces within the NH_3–O_2 complex, resulting in the weakening of the dioxygen bond are likely to be of similar magnitude to the dispersion forces involved in the complex–metal interaction. There is, therefore, a thermodynamically driven low energy pathway for complex breakdown to products mediated by

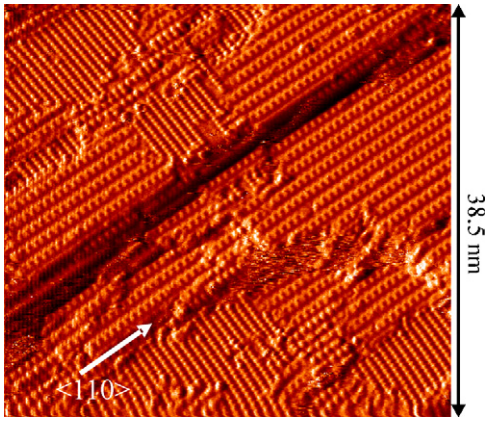

Fig. 5. Formation of (2 × 3) nitrogen adatoms and (2 × 1)O strings running in the ⟨1 1 0⟩ and ⟨1 0 0⟩ directions respectively when a 1:1 NH_3–O_2 mixture is exposed to Cu(1 1 0) at 60 K and warmed to 295 K. Evidence for the high activity of mobile oxygen states prior to becoming inactive with the formation of the stable (2 × 1)O reconstructed state.

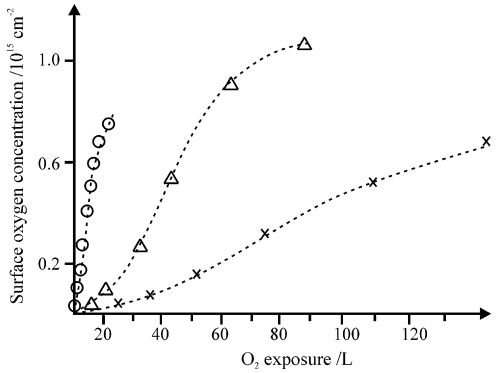

Fig. 6. Surface oxidation of Zn(0 0 0 1) when exposed to NH_3:O_2 mixtures at 200 K; the surface concentrations σ are calculated from the O(1s) intensities. (X) 66% O_2, (Δ) 34% O_2, (○) 5.9% O_2. The catalytic oxidation activity increases as the ammonia concentrations *increase* for a given oxygen exposure.

the metal substrate (Zn, Ag) with evidence for the active oxygen states being disordered, mobile and precursors of the "unreactive final chemisorbed" oxygen state O^{2-}(a).

Have we therefore isolated a reactive complex that could be relevant to catalytic reactions at high temperatures and pressures? Is a two dimensional gas model, involving weak intermolecular interactions, relevant? Witko et al. [24,25] have made considerable progress in the understanding of elementary steps in catalytic oxidation reactions using quantum mechanical methods, emphasising that the orientation of an oxygen molecule approaching (for example) a benzene ring can determine the product formed. Is it this that controls the formation of the dioxygen–ammonia complex at low temperatures? A further example where a dioxygen complex forms is with carbon dioxide at low temperature [26]; carbon dioxide has a large quadruple moment and therefore exhibits strong intermolecular interaction including the formation of the dimer (CO_2–CO_2^-) [27], and surface formate, when coadsorbed with water [28] at Al(1 1 1). Although the results we have discussed are for experiments on metal single crystals, the concepts we have developed are likely to be just as relevant to understanding oxidation catalysis at supported metal nanoparticles.

What is also clear is that focussing on the "final" stable chemisorbed oxygen state, by for example spectroscopic methods, may provide little insight into what is the "reactive site". It is the lability of the surface complex that is more likely to provide a pathway to products.

5. Oxidation of carbon monoxide

Although classical kinetic studies of CO oxidation at metal surfaces have usually been interpreted in terms of a Langmuir–Hinshelwood mechanism there is now evidence that the mechanism can be complex and facile, occurring even at cryogenic temperatures. At aluminium [29] oxygen transient states $O^{\delta-}$(s) are active at low temperatures whereas the chemisorbed 'oxide' state O^{2-}(a) is inactive at 295 K; this is supported by Ertl's evidence for hot oxygen adatoms formed by dissociative chemisorption at Al(1 1 1). Iwasawa in Tokyo also observed high activity [30] for CO oxidation at Cu(1 1 0) for oxygen states present at the unreconstructed Cu(1 1 0) surface between 150 K and 200 K, *i.e.* a precursor of the (2×1)O state. The authors associate the reactivity with oxygen states that have not formed the –Cu–O–Cu– chains observed by STM and present at room temperature. For oxygen states formed and present at 400 K at Cu(1 1 0) CO oxidation was reported by Crew and Madix [31] to be slow and occuring wholly at the periphery of oxygen islands. The authors also make a distinction between whether oxygen or carbon monoxide is preadsorbed at the Cu(1 1 0) surface.

The complexity of CO oxidation was further illustrated by Ertl's elegant STM study in real time [32] when preadsorbed chemisorbed oxygen at Pt(1 1 1) was exposed to carbon monoxide at 247 K. Initially there is improved ordering of the chemisorbed oxygen in (2×2) domains of the mixed phase while the areas between these domains are occupied by mobile CO molecules. With increasing time the (2×2) regions decrease simultaneously with the development of c(4×2) structures associated with closely packed CO molecules. The reaction proceeds not within the mixed phase but at their boundaries with the adjacent CO adlayer where the energetics are more favourable, a situation analogous to when a c(2×2)O adlayer is exposed to ammonia [11,33]. However, at least three different oxygen states have been recognised at Cu(1 1 0) (see Fig. 4), each with characteristic activities in catalytic oxidation.

Over the last two decades CO oxidation at gold surfaces has been the most intensively studied reaction, but with little evidence for a common view on its mechanism [34], other than particle size being a significant parameter. Friend's group at Harvard has delineated how the characteristics of the oxygen adlayer at Au(1 1 1) can control the CO oxidation rate, in the degree of order within the adlayer—three different regimes of oxygen are recognised as relevant to the kinetic behaviour: chemisorbed oxygen, a surface oxide and a bulk oxide, with the highest activity being associated with the disordered low temperature chemisorbed oxygen state. There are strong similarities with the models developed for the activity of oxygen states at copper, magnesium and nickel, with surface mobility being strongly correlated with reactivity [35].

6. Hydrocarbon oxidation

Whether the oxygen transient concept, first evident in the oxidation of ammonia at Mg(0 0 0 1), had wider relevance was examined in the oxidation of propene, also at Mg(0 0 0 1). A combination of XPS for monitoring the surface reaction, with mass spectrometry to identify any gaseous products, indicated that during the initial stage C_3, C_4, C_6 and C_7 gaseous products were desorbed. However, with increasing coverage, and the emergence of O(1s) and Mg(2s) signals consistent with the development of the oxide Mg^{2+} state, the catalytic surface reaction was "poisoned" [36]. XPS indicated the formation of chemisorbed oxygen, surface carbonate and hydrocarbon species. The C_6 product was shown to be benzene and the C_7 likely to be toluene; we were also uncertain as to the nature of the C_4 gaseous product. It was evident that the role of the reactive oxygen transient was to effect H-abstraction with radical formation, carbon–carbon bond cleavage and dimerisation. This reaction was also followed using a combination of STM and XPS, providing evidence that at 295 K the catalytic oxidation reaction leading to gaseous products was confined to the oxygen transient stage, involving rapidly diffusing oxygen adatoms. The emergence of the hexagonal (2×1)O structure, revealed by STM, coincided with the loss of catalytic activity [37].

More recently Friends' group at Harvard has established through a combination of STM, mass spectrometry and vibrational spectroscopy that disordered oxygen states (generated by ozone) at Au(1 1 1) surfaces at 200 K are highly reactive in the oxidation of propene to give acrolein and acrylic acid [38]. Ordered oxygen states formed at 400 K are by comparison unreactive and form only CO_2 and H_2O (Fig. 7). The comparison with models for oxygen activation at copper and magnesium are striking, and consistent with the high reactivity of disordered mobile oxygen states at low temperatures. The authors draw particular attention to the importance of local bonding of oxygen adatoms in understanding the role of particle size in gold based catalysis involving hydrocarbons, an aspect that is closely related to the correlation between surface mobility and reactivity.

Activation of the C–H bond has been the central issue in hydrocarbon catalysis but what is surprising is that oxygen states at magnesium and lithium surfaces at cryogenic temperatures are active in methane oxidation. The disadvantage is that for the high concentrations of oxygen states present they are too active and result in carbonate formation [37]; the chemisorbed oxygen states present at 295 K are inactive.

7. Selectivity at oxide surfaces

The nature of the oxygen states present at oxide surfaces and their role as the "active sites" in selective oxidation was one of the central themes in Jerzy Harber's contribution to the fundamental understanding of catalysis at oxides. Lattice oxygen designated as O^{2-}, and adsorbed radical-type oxygen or intermediates in the reduction of O_2(g) to O^{2-}(a), have been central to the proposed mechanisms and much effort has been made to obtain spectro-

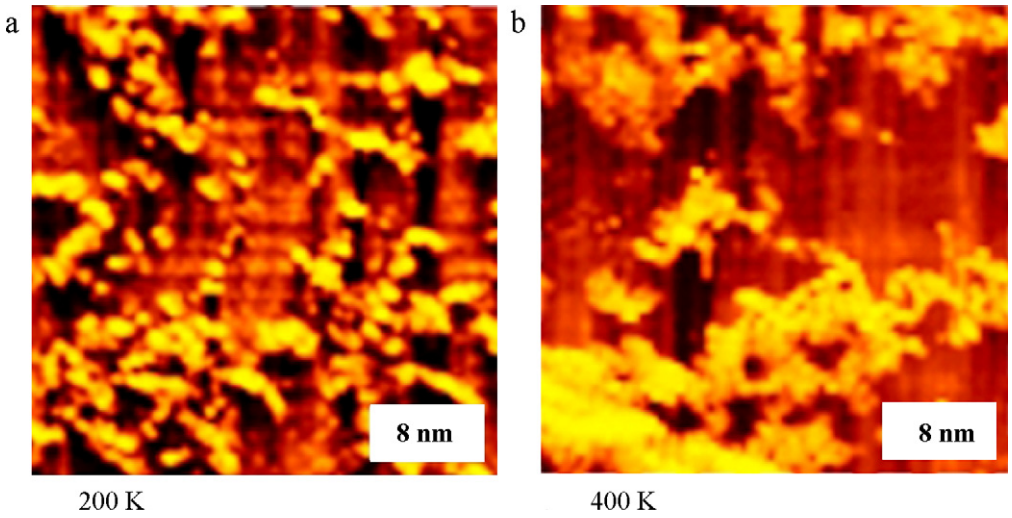

Fig. 7. STM images of oxygen/gold clusters present at Au(1 1 1) at 200 K and after heating to 400 K. The reactive metastable oxygen states at 200 K become mobile and nucleate into larger less reactive islands at 400 K [38].

scopic evidence as to how these states participate in the oxygen catalysis including extensive ESR studies by Che and Tench [39] in the 1980s. At *metal surfaces* oxygen transient states, electrophilic in character and precursors of the oxide state, could be recognised by varying the oxygen–reactant ratio. We designated these oxygen states as $O^{\delta-}$ – the precise charge was not known – but they exhibited chemistry analogous to O^- in the gas phase. STM confirmed the existence of "hot" oxygen transients [9,11,37].

At oxides the general view has been that it is the nucleophilic oxygen that is incorporated into the hydrocarbon which gives rise to selectivity, and what is required is a fast transfer of $O_2(g)$ to the $O^{2-}(a)$ state, keeping the surface of the electrophilic O^{s-} state low. How "low" and how "fast" are the crucial aspects in designing a successful catalyst. This is discussed in detail by Centi et al. [40]. The Mars-van Krevelen mechanism was generally suggested to be valid, but Centi et al. considered it to be too often accepted uncritically.

That O^--like states are active in H-abstractions from NH_3, H_2O, H_2S, C_2H_4, CH_4 and C_3H_6 is well documented [11]. Bordes [41] suggested in 1993 that H-abstraction from a terminal CH_3 group [42] is the first step in the selective oxidation of butane. Wang and Barteau [43] in 2008 concluded that under steady state consitions the Mars-van Krevelen mechanism plays a minor role in the selective oxidation of butane at vanadyl pyrophosphate and in 2009, we made the suggestion that O^--like transients could be the active oxygen state [37]. In a recent paper by Taufiq-Yap et al. [44] two oxygen states are deemed to be present at vanadium phosphate catalysts, associated with the V^{4+} and V^{5+} states. The assignment of these as O^- and O^{2-} is based on the indirect electrical conductivity studies of Hermann et al. [45]; the O^- state being responsible for the activation of butane through H-abstraction. That the O^- state is active in H-abstraction from hydrocarbon molecules is well established and recently supported by theoretical studies of the vanadium phosphate catalyst [42]; however, under steady state conditions, is it a transient O^--state (rather than the chemisorbed V^{4+}–O^- state) that is responsible for the *activity* of the catalyst? The correlation of activity and selectivity with O^--like states is well established at metal surfaces—how they might participate in the catalytic formation of maleic anhydride, with a distinction to be made between static and dynamic studies, is a pre-requisite to establish mechanism.

8. Biocatalytic oxidation: a postscript

A feature of our transient studies is that the oxygen states active in catalytic oxidation under dynamic conditions could not be observed by conventional spectroscopic methods. We have, however, provided evidence for their participation in reactions which result in bond cleavage and bond making at cryogenic temperatures, for their mobility and their radical characteristics.

The precursor assisted cleavage of the dioxygen bond in our experiments may be analogous to the mechanism associated with the cytochrome P450 system with the cysteinate ligand, as Lewis base, postulated to assist the cleavage of dioxygen. Poulos [46] has emphasised that the short life-times of the "metal-oxo" species, considered to be the key intermediates in the catalytic cycles of P450 enzymes, made them difficult to characterise by classical methods of coordination chemistry and to the elusiveness of the iron–oxygen intermediate considered to be the hydroxylating agent. There is commonality between the concepts in biocatalysis and coadsorption transient studies at metal surfaces; both systems involve radical species in the proposed mechanisms with STM providing direct evidence at metal surfaces at low temperatures. The methodology of our low-temperature transient experiments is a possible approach to elucidate further the biocatalysis system and is discussed elsewhere [47].

Acknowledgments

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