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A view of surface science since 1960: Oxygen states at metal surfaces

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A Tribute to Julian Ross.

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ABSTRACT

The article describes how the application of experimental methods developed over the last 40 years (work function, photoemission, photoelectron spectroscopy and scanning tunnelling microscopy) enables our understanding of oxygen chemisorption to progress in a step-wise manner, with STM providing the ultimate atom-resolved evidence for the dynamics involved. Different oxygen states exhibit distinct reactivities and provide a stimulus for the design of catalysts with specific activities in oxidation catalysis. There is also evidence accruing that disordered oxygen states are in general more active in dehydrogenation reactions than the ordered states, with for example ammonia being ‘oxidised’ to nitrogen adatoms at Cu(1 1 0) at cryogenic temperatures.

1. Early days at Queen’s University Belfast

Julian Ross was one of a group of outstanding graduate students – Martin Quinn, Clive McKee, Brian Wells and Richard Joyner were others – who opted to pursue doctoral studies in surface science and catalysis, with Julian supervised jointly with Charles Kemball. Queen’s University was, at that time, one of the leading centres for investigating the chemisorption and catalytic reactions of hydrocarbons at metal surfaces using Kemball’s approach to elucidate the nature of the surface fragments through H_2–D_2 exchange studies and analysing the desorbed products mass-spectrometrically. The chemisorption and catalytic hydrogenolysis of neopentane at palladium and tungsten surfaces was investigated [1] by Julian with evidence for both C–H and C–C bond cleavage at relatively low temperatures (~373 K).

Gas phase analysis, either through mass-spectroscopy or gas–liquid chromatography, was the most frequently used experimental method in surface catalysis, with infrared spectroscopy providing the only direct method then available for characterising surface species and confined in the main to carbon monoxide in view of it is high extinction coefficient. The development of vibrational spectroscopy was reviewed recently by Sheppard [2].

Surface sensitive experimental methods were limited in the early 1960s and Martin Quinn and Brian Wells opted to apply work function and photoemission methods [3,4] to study oxygen chemisorption at metals. We were intrigued by the apparent instability of oxygen states at cryogenic temperatures. Surface reconstruction was implicated and questions raised as to whether and how did the chemisorbed oxygen adlayer transform to an “oxide” and would photoelectron yield and electron energy distribution data throw further light on the transition. Furthermore, how many oxygen atoms bonded to a single nickel atom constituted an oxide, and was it “NiO”? It was a problem that also intrigued others and discussions with Sir Nevill Mott at Cambridge and Walter H. Brattain at Bell Laboratories are considered later. It was, however, subsequent developments in Surface Science, some 30 years later, that enabled more precise molecular models to be developed. These we will discuss.

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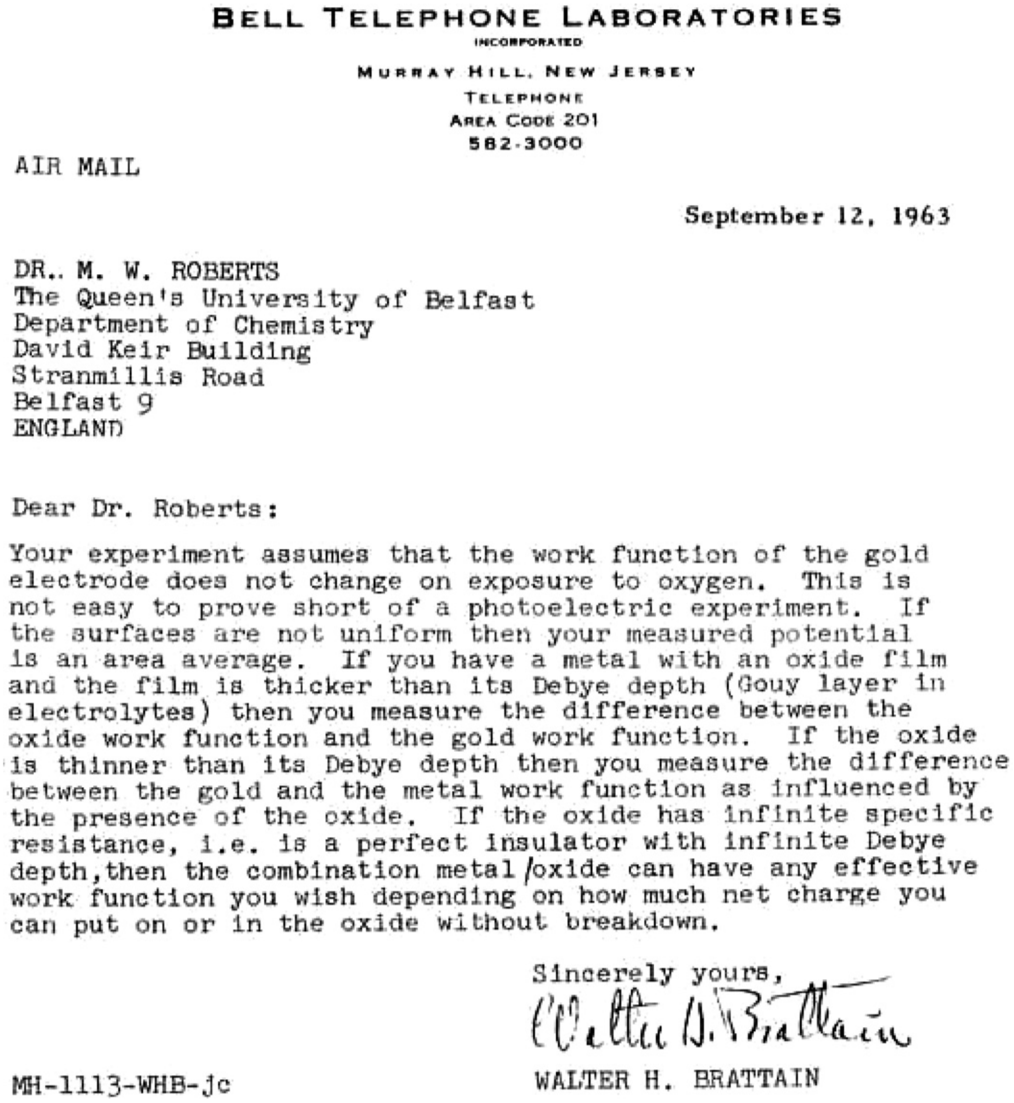

BELL TELEPHONE LABORATORIES
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AIR MAIL

September 12, 1963

DR.. M. W. ROBERTS
The Queen's University of Belfast
Department of Chemistry
David Keir Building
Stranmillis Road
Belfast 9
ENGLAND

Dear Dr. Roberts:

Your experiment assumes that the work function of the gold electrode does not change on exposure to oxygen. This is not easy to prove short of a photoelectric experiment. If the surfaces are not uniform then your measured potential is an area average. If you have a metal with an oxide film and the film is thicker than its Debye depth (Gouy layer in electrolytes) then you measure the difference between the oxide work function and the gold work function. If the oxide is thinner than its Debye depth then you measure the difference between the gold and the metal work function as influenced by the presence of the oxide. If the oxide has infinite specific resistance, i.e. is a perfect insulator with infinite Debye depth, then the combination metal/oxide can have any effective work function you wish depending on how much net charge you can put on or in the oxide without breakdown.

Sincerely yours,
Walter H. Brattain

MH-1113-WHB-jc WALTER H. BRATTAIN

Mignolet [5] at Liége, Belgium, and Tompkins and Culver [6] at Imperial College, London, had set out in the 1950s to determine the surface potential (change in work function) for molecules adsorbed at metal surfaces and thereby obtain information on the nature of the adsorbate-surface bond. For a given crystal plane the surface potential at full coverage was considered to be characteristic of any given adsorbate. This was, however, not the case for oxygen chemisorption at nickel and some other metal surfaces [3]. At nickel the work function change was dependent on the oxygen pressure and temperature and was time dependent [4]. There was no single value of the surface potential that was characteristic of the nickel–oxygen system and we reported variations of greater than 1 eV. We proposed [3,4] that the chemisorbed oxygen adlayer – no more than two monolayers at 295 K – was an "oxide", but was it "NiO"? (Fig. 1). Very similar work function changes were observed for oxygen chemisorption at aluminium in the temperature range 80–295 K [4], the activation energy for the transformation from chemisorption to 'oxidation' being less than 3 kcal mol^{-1}. But what was being measured by the capacitor method for determining the work function change? Did the 'oxide' overlayer have semiconductor properties, was it an "insulator" or did it retain its "metallic" characteristics. Following the publication of a paper in Nature in 1963 concerning the defective nature of the 'oxide' overlayer at nickel we had discussions with Walter Brattain who shared the Nobel Prize in Physics with Bardeen and Shockley in 1956. This letter (see above) stimulated us to explore further how we might establish whether or not an 'oxide' overlayer formed on a nickel surface when exposed to oxygen at 10^{-6} Torr at 295 K, and that it could be distinguished experimentally from a "chemisorbed adlayer."

Photoemission was an attractive approach to pursue this in view of the contribution it was making to semiconductor surface physics [7] in the early 1960s and in 1963 we constructed [8] an ultra-high vacuum system incorporating a photocell to investigate, under dynamic conditions, the electron energy distribution and photoelectron yield ($h\upsilon = 5.76$ eV) when a nickel surface was exposed to oxygen at both 120 and 295 K (Fig. 2).

The photoelectrons escape with a range of energies, the distribution of which can be determined by applying a negative potential to the (gold) collector until the photocurrent ceases. This "stopping potential" V_0 is the same for all metals but different for semiconductors V_0^1, so that

$$eV_0^1 = eV_0 + \delta; \quad \text{since } eV_0 = {}_{c} - h\upsilon \text{ and } eV_0^1 = {}_{c} - h\upsilon + \delta$$

If the surface of the emitter (nickel) is transformed to a semiconducting oxide adlayer when exposed to oxygen at

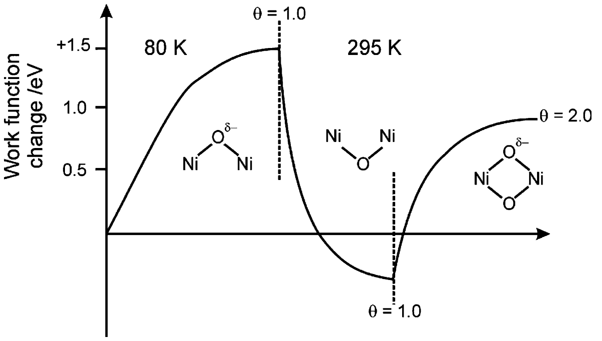


Fig. 1. Work function change for oxygen adsorption at a nickel surface at 80 K, warmed to 295 K and further exposed to oxygen. Evidence for three oxygen states: chemisorption, surface reconstruction and 'oxidation' [3,4].

10^{-6} Torr at 295 K there will exist different electron energy states so that photoemission need not occur from the metal's Fermi level since the highest filled states can be $\pm\delta$ eV from it. The proposition we put forward was that a change in V_0 to V_0^1 will indicate 'oxide' formation provided that the electron escape depth lies within the 'oxide' [4,8]. However, if the escape depth is much greater than the oxide thickness, then V_0 will not appear to shift. The experimentally observed shift [8] in V_0 was therefore taken to indicate oxide formation and significantly that the photoelectron escape depth was "about 10 Å." It was a conclusion that led us to follow Siegbahn's pioneering work and develop an ultra-high vacuum photoelectron spectrometer for studying chemisorption and reactions at atomically clean metal surfaces in 1969. Allen and Gobeli [7] at Bell Laboratories had also established in 1964 that "95% of the photoelectrons from silicon are trapped by an oxide layer 20 Å thick."

The photoelectric yield showed characteristics analogous to the work function changes observed by the capacitor method—a decrease, followed by a recovery and a further decrease (Fig. 2). These were interpreted as chemisorption, followed by reconstruction and finally oxidation. But how to proceed to establish this?

2. Surface science at the University of Bradford

In 1966 Julian joined me at the new University of Bradford initially as a Research Fellow but later as a lecturer, and played a vital role in a number of very different projects across a range of surface science. We were invited in 1967 to participate in a competition with three other Universities in the United Kingdom for funding by NASA – monitored by TRW in California – of a project to explore how novel polymer silicon films might be formed through interacting tetramethyl silane with metal surfaces [10], both in the presence and absence of electron emitting (hot) metal filaments (tungsten and rhenium). Our earlier studies [1] with complex hydrocarbons (neopentane), work function and electron emission (thermionic and photoinduced) at Queen's University [3,4] convinced two scrutineers – H.T. Mann and R.J. Salvinski from TRW – that Bradford should be funded by NASA.

Adsorption studies in the presence of an electron beam provided information on the bonding characteristics at the metal–polymer interface and therefore on its adhesion properties—an aspect relevant to TRW's space project. The surface properties of the thin polymer films were characterised by determining the critical surface tension from contact angle (wetting) studies and which Zisman suggested would reflect the nature of polymer surfaces [11].

To obtain information on the fragments (radicals) generated at the electron emitting filament in the presence of tetramethyl silane a magnetron coupled to a Quadruple Mass Spectrometer was constructed which enabled electrons and negative ions to be distinguished. Eleven different negative ions were observed: H, C, CH, CH_2, C_2H, SiH, SiH_2, SiH_3, C_3, C_3H and C_3H_2. The negative ions N^- were shown to be involved in the polymerization for a range of organic molecules [12], being most efficient for monomers with high electron affinities and low heats of adsorption (*S*) and low work function emitters (Ø):

$$\frac{\mathrm{d}N^-}{\mathrm{d}t} = A\exp\frac{\mathrm{e}(S - \ + \sqrt{\mathrm{e}E})}{kT}$$

The term $\sqrt{\mathrm{e}E}$ is the Schottky barrier term allowing for the decrease in the energy barrier for emission Ø when a field is applied between the emitter and the 'anode' where the polymer film forms. Both the Richardson equation and Kelvin methods were used to determine any changes (e.g. due to carbiding) of the work function of the emitters (tungsten and rhenium).

It was, however, the development of Low Energy Electron Diffraction (LEED) by Germer and MacRae [13] that dominated the field in the late 1960s. New diffraction features observed at metal surfaces from chemisorbates were attributed to scattering by 'heavy metal atoms' with surface reconstruction (wrongly) implicated. It took some time before it was appreciated that "light atom" adsorbates could also be effective scatterers and result in new diffraction features. Emphasis was given to obtaining evidence for ordered structures, with LEED's insensitivity to disorder being addressed later.

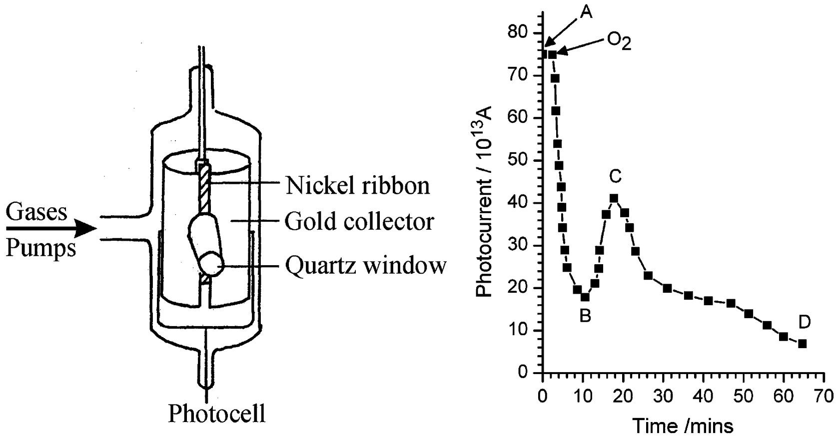


Fig. 2. Photoemission studies of oxygen interaction with a nickel surface: photoelectron yield and stopping potential measurements. Chemisorption A–B; surface reconstruction B–C; "oxidation" C–D [4,8].

Julian had immersed himself in a wide range of very different areas – chemisorption, catalysis and surface physics – but chose to pursue "real catalysis" stimulated by the opportunities that were developing from the coming on stream of natural gas from the North Sea. Steam reforming, and the design of novel nickel catalysts, were the start of a life-long journey in applied and environmental catalysis. After 15 years at Bradford Julian was appointed to a professorship at Twente University in the Netherlands where he led an excellent research group before returning to Ireland to develop catalysis at the University of Limerick.

With the rapid developments in surface science I tackled some earlier unresolved questions concerning oxygen chemisorption at metal surfaces arising from the work function and photoemission studies carried out at Queen's.

3. The emergence of photoelectron spectroscopy in surface science and catalysis

With the impact that Kai Siegbahn [14] had made in the application of X-ray photoelectron spectroscopy (XPS) to a wide range of chemistry, through the observed chemical shifts in the binding energy of core-level electrons, we applied to the Science Research Council in 1969 for the funding of an ultra-high vacuum photoelectron spectrometer, with both X-ray and UV sources of radiation, and designed for investigating adsorption and catalysis at 'clean' metal surfaces. That XPS would turn out to be surface sensitive was supported by our earlier photoemission data [8,9], the electron escape depth being estimated to be no greater than 10–20 Å at the metal oxide interface. Vacuum Generators (later VG Scientific) constructed the spectrometer and its sensitivity at the sub-monolayer level was first established [15] in 1972 for CO_2 adsorbed on Au at 80 K. Priority was given to establishing a binding energy database for surface species and being able to distinguish between molecular and dissociated states of adsorbed molecules relevant to catalysis [16] such as CO, NO, NH_3 and H_2O. That both CO and NO dissociated readily at iron and copper surfaces respectively was of particular significance in mechanistic aspects of Fischer Tropsch and environmental catalysis. We investigated both defective and stoichiometric bulk nickel oxides in order to provide a spectroscopic database prior to the study of oxygen chemisorption at nickel single crystals accompanied by improved computer-assisted data acquisition and spectra analysis [17].

The O(1s) and Ni(2p) spectra were monitored for oxygen chemisorbed at Ni(1 0 0) and Ni(2 1 0) surfaces under dynamic conditions at 295 K. The results were striking with two distinct oxygen states revealed; the initial oxygen state was not associated with any evidence for the emergence of a nickel oxidation state in the Ni(2p) spectra (Fig. 3). However, with further oxygen exposure a second oxygen state with a lower O(1s) binding energy emerged and this was accompanied by intensity developing in the Ni(2p) spectra in the 855–857 eV region, some 2 eV higher than that characteristic of Ni^0 of the atomically clean nickel surface. The initial oxygen state was assigned to O^- with an O(1s) binding energy of 531 eV and the second to the oxide-like state O^{2-} with an

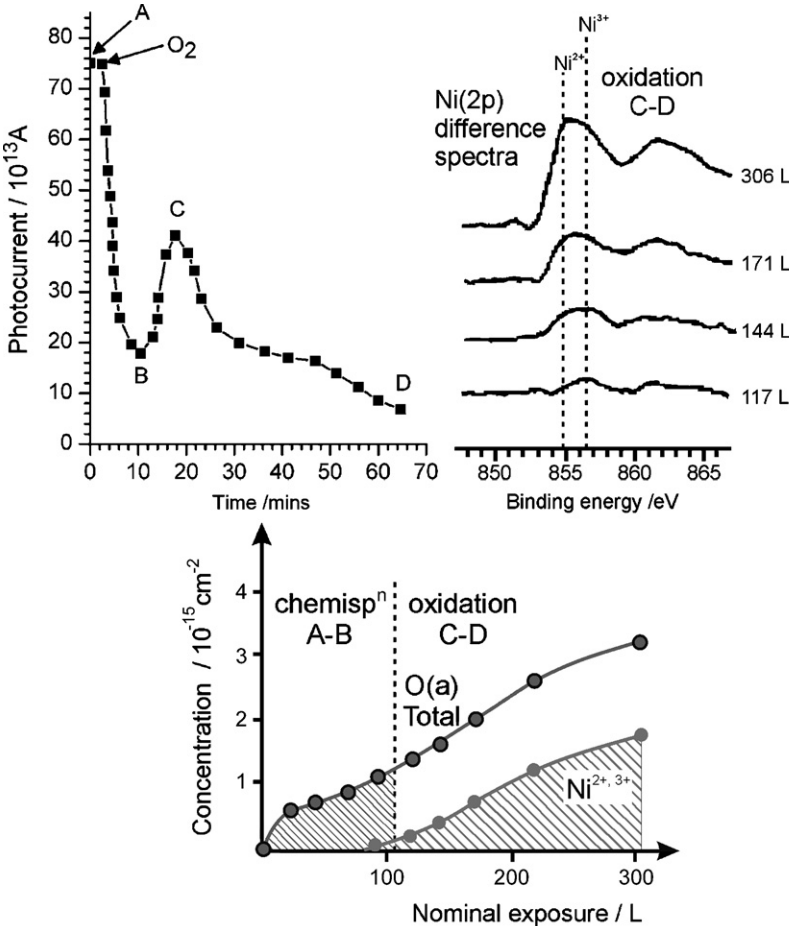


Fig. 3. Photoelectron yield (see also Fig. 2) for oxygen interaction with nickel at 295 K; Ni(2p) XPS difference spectra indicating the emergence of $Ni^{2+,3+}$ states during region C–D; surface oxygen concentration as a function of oxygen exposure at 295 K calculated from O(1s) intensifies and the emergence of $Ni^{2+,3+}$ states at an exposure of 100 L at Ni(1 0 0) (1 L ≡ 10^{-6} Torr s) [17].

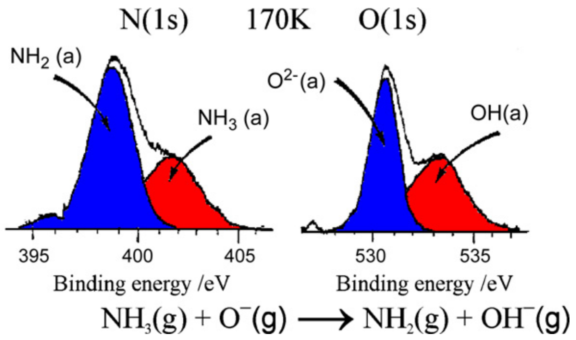


Fig. 4. N(1s) and O(1s) spectra for the coadsorption of an ammonia-rich NH_3–O_2 mixture at a Mg(0 0 0 1) surface at 170 K. The N(1s) and O(1s) spectra indicate through chemical shifts the formation of NH_2(a) and OH(a). This is analogous to the highly efficient gas phase homogeneous reaction of O^- with NH_3 [20].

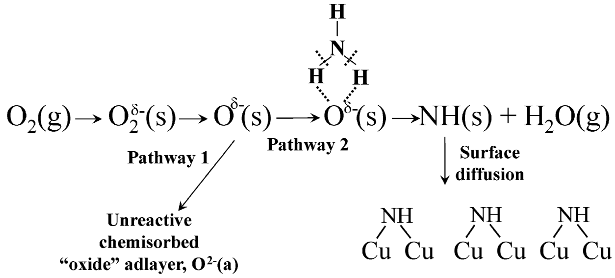


Fig. 6. Model for the coadsorption of oxygen and ammonia at Cu(1 1 0) at 295 K. Pathway 2 involves transient state $O^{\delta-}$ and NH_3 in immide formation; Pathway 1 results in surface reconstruction and oxide formation and the loss of catalytic oxidation activity [24].

O(1s) binding energy 529.5 eV and compatible with the Ni(2p) evidence for the corresponding Ni^{2+} and Ni^{3+} states. These states were in keeping with the models based on work function and photoemission studies [3,4,8] for chemisorption, reconstruction and oxidation occurring at 295 K. That two distinct oxygen states were observed was intriguing, particularly that only one of them, assigned as O^{2-}, developed simultaneously with the development of the oxidation states of nickel; the other, designated as $O^{\delta-}$, was associated with Ni^0. In the gas phase $O(g) \rightarrow O^-(g)$ is highly exothermic, while $O^{2-}(g)$ is endothermic [18] and only stable in 'oxides' due to the Madelung term associated with the 'oxide' structure.

4. Searching for oxygen transients: the coadsorption approach

Although we had given attention by XPS to the activation of molecules (hydrocarbons, water, ammonia and hydrogen sulphide) by preadsorbed chemisorbed oxygen [19], assigned as $O^{\delta-}$ or O^- like species, we set out to explore whether such precursor states were present in the dynamics of the dissociative chemisorption of oxygen resulting in 'oxide' adlayer formation. Could such states show specific activity in the oxidation of a probe molecule such as ammonia?

That such oxygen states were present at low coverage at nickel surfaces, with no evidence for Ni^{2+} in the Ni(2p) spectra [17], provided further impetus for initiating coadsorption (mixture) studies [20], using ammonia as the probe molecule (Fig. 4) and taking note that the gas phase reaction was known to occur with:

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

low activation energy and unit collision efficiency. At Cu(1 1 0) three regimes were recognised: the Cu(1 1 0)—O monolayer was inactive to ammonia at 295 K; the partially covered Cu(1 1 0)—O adlayer showed limited activity in NH_2 formation at 170 K and NH formation at 295 K the activity being shown to be confined to oxygen states present at the ends of –Cu–O–Cu– chains. This was also the case for a complete oxygen adlayer exposed to NH_3 at 375 K. However, with ammonia-rich O_2–NH_3 mixtures at 295 K a complete monolayer of NH species was formed 'instantaneously' (Fig. 5). The following model was proposed [21], which is in effect a two-dimensional gas reaction involving the surface transients $O_{(s)}{}^{\delta-}$ and $NH_{3(s)}$, following Pathway 2. For oxygen rich mixtures Pathway 1 dominates with the formation of the 'oxide' adlayer and the catalytic oxy-dehydrogenation activity 'shuts down' (Fig. 6).

Inherent to this model is the formation of "hot" oxygen adatoms following bond cleavage; these adatoms undergo rapid surface diffusion prior to nucleation and 'oxide' formation (Fig. 7). We shall see that STM, some years later, provided proof of this at the atom-resolved level, with Ertl's study [22] of oxygen at Al(1 1 1).

5. Atom-resolved evidence from scanning tunnelling microscopy (STM)

There were many aspects of the work function, photoemission and XPS data that the availability of STM in the early 1990s might elucidate. Some 40 years ago Sir Nevill Mott (see below) was interested in what could be learnt regarding the process of oxide nucleation and how it "spreads across the surface". Both the Mg(0 0 0 1) and Cu(1 1 0)–oxygen systems illustrate how STM provided atom-resolved evidence (Fig. 8) for the chaotic behaviour of oxygen chemisorption and nucleation involving both metal and oxygen transients and disorder–order transitions at low (cryogenic) temperatures [23].

An interesting feature of these studies was that when the disordered oxygen state present at 110 K was warmed to 295 K, a disorder–order transition took place with the formation of the well

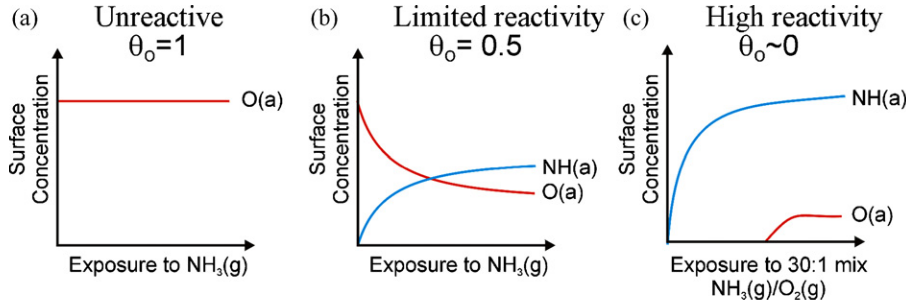


Fig. 5. Three distinct regimes of ammonia oxidation at Cu(1 1 1) at 295 K; (a) oxygen surface coverage of unity; (b) partially covered surface, $\theta = 0.5$; and (c) exposure to an ammonia-rich mixture [23,24].

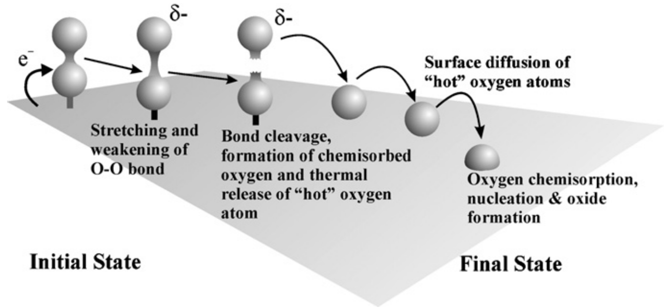
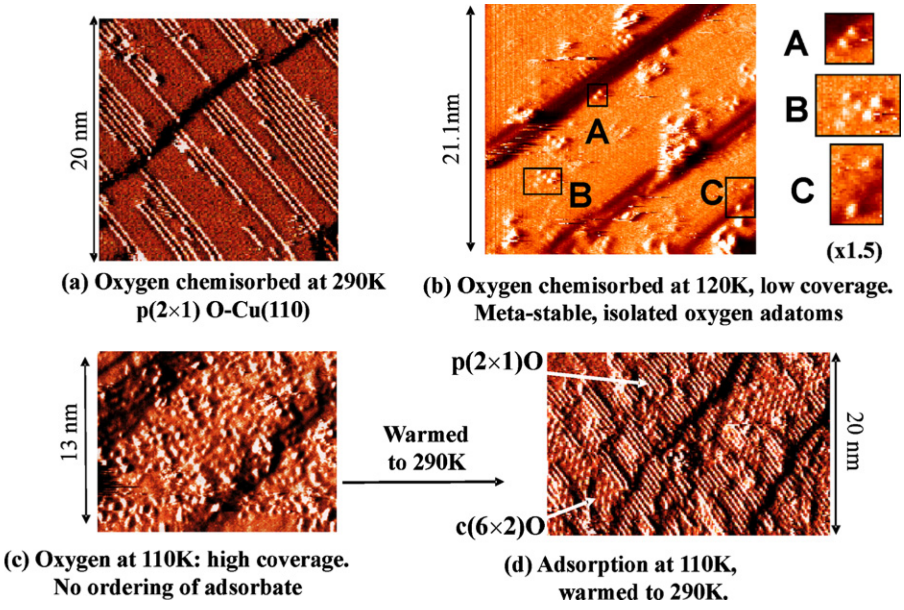


Fig. 7. 'Cartoon model' for the dynamics of oxygen dissociative chemisorption at copper and magnesium surfaces based on spectroscopic studies [23,24].

ordered Cu(2 × 1)O structure accompanied by a minor component, the C(6 × 2)O structure (Fig. 8). But what was surprising was that when the disordered state underwent the transition in the presence of NH_3(a), there were two competing reactions (Fig. 9): the complete stripping of the H-atoms from NH_3 with the formation of the nitrogen adatom (2 × 3) N-state and the transformation of the disordered state to the ordered (2 × 1)O state. The high oxy-dehydrogenation activity resulting in nitrogen adatoms is associated with the disordered transients; the ordered (2 × 1) state of the reconstructed 'oxide' structure is inactive at 290 K. A further example [23] is the coadsorption of oxygen and propene at a Mg(0 0 0 1) surface where the oxygen transients present prior to nucleation and oxide formation are the active sites in the formation of C_4 and C_6 hydrocarbons. The STM observations of



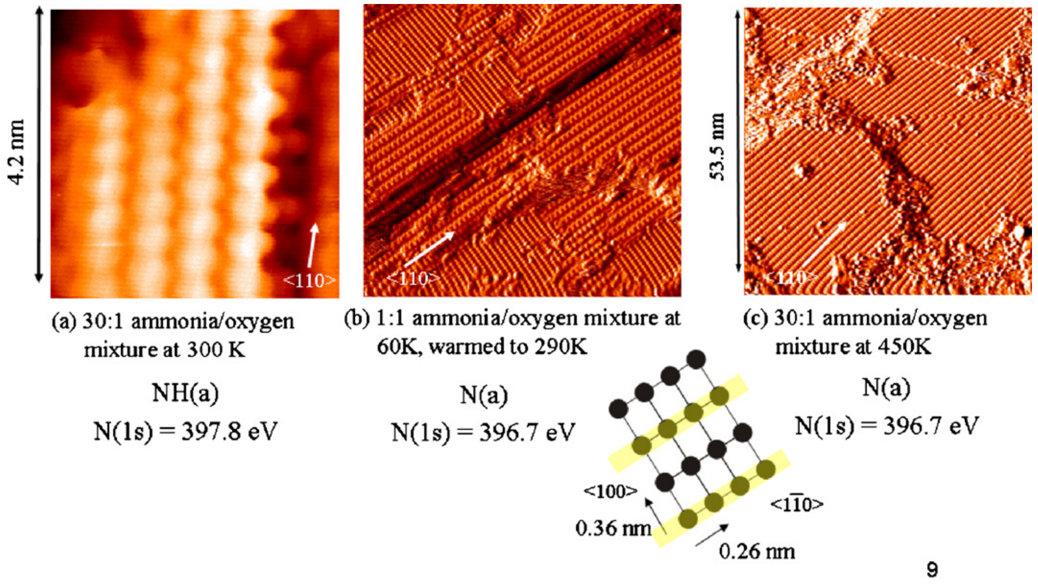
(a) Oxygen chemisorbed at 290K p(2×1) O-Cu(110)

(b) Oxygen chemisorbed at 120K, low coverage. Meta-stable, isolated oxygen adatoms

(c) Oxygen at 110K: high coverage. No ordering of adsorbate

(d) Adsorption at 110K, warmed to 290K.

Fig. 8. STM evidence for oxygen states present at a Cu(1 1 0) surface in the temperature range 100–290 K [23,24].



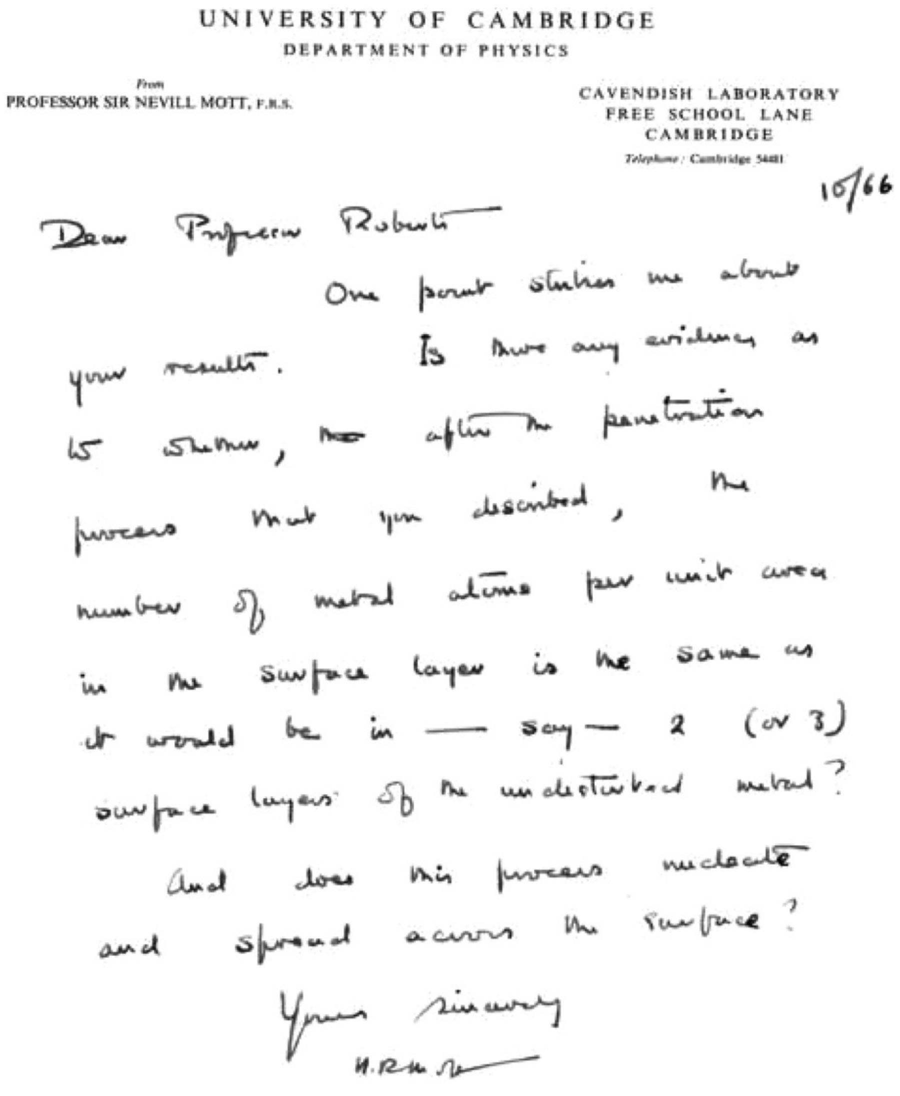
(a) 30:1 ammonia/oxygen mixture at 300 K

(b) 1:1 ammonia/oxygen mixture at 60K, warmed to 290K

(c) 30:1 ammonia/oxygen mixture at 450K

Fig. 9. Reaction pathways in the oxidation of ammonia at Cu(1 1 0) observed by STM with in situ XPS for chemical identification: (a) NH formation at 300 K; (b) N(a) formation associated with active oxygen states present during the disorder–order transition at low temperature; and (c) N(a) formation at 450 K [24].

the mobility of both the substrate metal and oxygen adatoms at copper, magnesium and aluminium surfaces [24] prior to nucleation, is the general issue which Mott had raised with us in 1966 (see below). That catalytic activity is now seen to be correlated with disordered surface structures is also becoming more widely accepted through the STM studies of both the Wintterlin and Somorjai groups. Time-resolved images have highlighted the complex, random and Brownian-like behaviour of adsorbates at low temperatures and coverages, for example oxygen chemisorption on Pt(1 1 1) at 105 K [25], drawing attention to the limitations of extracting mechanistic information of even inherently simple catalytic oxidation reactions from kinetic studies alone.



UNIVERSITY OF CAMBRIDGE
DEPARTMENT OF PHYSICS

From
PROFESSOR SIR NEVILL MOTT, F.R.S.

CAVENDISH LABORATORY
FREE SCHOOL LANE
CAMBRIDGE
Telephone: Cambridge 54481

10/66

Dear Professor Roberts

One point strikes me about your results. Is there any evidence as to whether, after the penetration process that you described, the number of metal atoms per unit area in the surface layer is the same as it would be in — say — 2 (or 3) surface layers of the undisturbed metal?

And does this process nucleate and spread across the surface?

Yours sincerely
N.F. Mott

6. Summary

It was in the mid-1960s that Surface Science emerged as a distinct discipline within surface chemistry and catalysis. The breakthrough came with the development of surface sensitive spectroscopies, Auger and photoelectron spectroscopies, but mainly applied in post-reaction analysis of surfaces. However, as significant as this approach still is, clear limitations are exposed when surface reactions at surfaces are monitored under real-time dynamic conditions. This is an aspect that coadsorption spectroscopic studies highlighted, with STM providing the conclusive atom-resolved evidence, for the participation of transient states and the mobility of both adsorbates and substrates. Models developed for the chemisorption of oxygen at metal surfaces based on work function and photoemission studies in the early 1960s were further clarified through STM with in situ XPS for chemical identification of the observed images, oxygen states at nickel, copper, aluminium and magnesium are examples.

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