Chemisorption and Reaction Pathways at Metal Surfaces: the Role of Surface Oxygen

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1 Introduction

Two previous articles [1,2] in this Journal provide at least personal bench marks as to how some aspects of surface chemistry have developed over the past 30 years or so. The chemisorption of oxygen and the development of oxide overlayers at metal surfaces was in the main being studied in the early sixties by kinetic methods [1] although calorimetry, largely through the work of Brennan, Hayward, and Trapnell,[3] was providing important thermochemical data on the chemisorption process. It is perhaps worth making the observation that little has been achieved in the thermochemical area since then and with the development of the subject, in particular the study of single crystal surfaces, the thermodynamic aspect of surface chemistry has been neglected. Direct experimental methods based on monitoring work function changes during oxygen interaction established [4a] the facile nature of metal surface reconstruction but the interrelationship between charge, bond length, and change in work function mitigated against unambiguous evidence for the nature of the metal–oxygen chemisorbed bond. When surface reconstruction occurs the problem is even more severe since the question as to whether an 'oxide' overlayer had developed needs to be addressed.[4a] It was this that led us into photoemission, first using low energy photon sources [4b] and later by taking advantage of the information emerging from the pioneering photoelectron studies of gaseous molecules (Siegbahn, Turner, and Price) using both X-ray and u.v. sources for studying surfaces under well-defined experimental conditions.[4c]

During the late fifties there emerged some elegant kinetic studies, largely from Ehrlich's group at Schenectady, of the surface chemistry of tungsten surfaces.[5] This followed in the true tradition of Irving Langmuir at the same laboratories who emphasized, with J. K. Roberts at Cambridge, the need for using atomically clean surfaces in fundamental studies of adsorption. The role of both surface structure and precursor adsorption states was established [6] and theories developed

[1] M. W. Roberts, *Q. Rev. Chem. Soc.*, 1962, **16**, 74.
[2] M. W. Roberts, *Chem. Soc. Rev.*, 1977, **6**, 373.
[3] D. Brennan, D. O. Hayward, and B. M. W. Trapnell, *Proc. R. Soc. Lond.*, *A*, 1960, **256**, 81.
[4a] C. M. Quinn and M. W. Roberts, *Trans. Faraday Soc.*, 1964, **60**, 899.
[4b] C. M. Quinn and M. W. Roberts, *Trans. Faraday Soc.*, 1965, **61**, 1775.
[4c] C. R. Brundle and M. W. Roberts, *Proc. R. Soc.* Lond., *A*, 1972, **331**, 383.
[5] G. Ehrlich, *J. Phys. Chem. Solids*, 1956, **1**, 3; *J. Chem. Phys.*, 1961, **34**, 29.
[6] See for example Chapter 8 in 'Chemistry of the Metal–Gas Interface', M. W. Roberts and C. S. McKee,

to account for sticking probability–coverage–temperature relationships.[7] Simultaneously with these developments Eischens[8] and his collaborators at the Texaco Research Laboratories were showing the way ahead for the very significant role that infrared spectroscopy was going to play in surface chemistry and catalysis over the next 30 years. Initially vibrational spectroscopy was confined to finely divided metals supported on high surface area oxide supports and carbon monoxide, with its high extinction coefficient, the adsorbate. During the past decade or so studies of (low area) single crystal surfaces have become possible, largely through the development of high resolution electron energy loss and reflection–absorption infrared spectroscopies.[9,10]

In this article I will confine myself mainly to the approach that we have had most interest in over the past two decades, namely photoelectron spectroscopy (PES). But the influence of the earlier kinetic and more traditional studies in surface chemistry can not be over emphasized since they provided the basis for the general strategy adopted. The advantages of a surface-sensitive spectroscopy (PES) incorporating both core-level (*X*-ray photoelectron spectroscopy XPS) and valence-level (u.v. photoelectron spectroscopy UPS) became clear in the early 1970s with the development of an ultra-high vacuum spectrometer.[4c] Although earlier photoemission work[4b] had shown that the photoelectron escape depth from a metal was no more than about 10 Å, much of the initial effort went into establishing PES as a viable experimental method for studying the surface chemistry of metals.[11] In the case of oxygen species present at a carbon surface, $O(1s)$ spectra indicated that sub-monolayer quantities could be detected.[12] The development of a spectral data base was essential taking advantage of the relationship, already established for gas phase molecules by Siegbahn, between the localized charge on the emitting atom and its measured photoelectron binding energy, E_B. The relationship between molecular and dissociated regimes of chemisorption; the role of surface additives (poisons and promoters); complex chemisorption; redox states at oxide surfaces; intermolecular interactions in the chemisorbed state; and the role of short-lived transients in surface chemistry are some examples of where I believe PES has played a significant role in highlighting questions relevant to a better understanding of heterogeneous catalysis. Some of the early results were discussed[2] in 1977. Much of the present review revolves around the surface chemistry of dioxygen, largely as a result of its wide ramifications and my personal interest; hopefully it is not overemphasized.

Oxford University Press. 1978; G. A. Somorjai, 'Chemistry in Two Dimensions; Surfaces', Cornell University Press, 1981.

[7] P. Kisliuk, *J. Phys. Chem. Solids*, 1957, **3**, 95; 1958, **5**, 78; D. A. King and M. G. Wells, *Proc. R. Soc. Lond., A*, 1974, **339**, 245.

[8] R. P. Eischens, W. A. Pliskin, and S. A. Francis, *J. Chem. Phys.*, 1954, **22**, 1786.

[9] H. Ibach and D. L. Mills, 'Electron Energy Loss Spectroscopy and Surface Vibrations', Academic Press, 1982.

[10] M. A. Chesters, *J. Electron Spectrosc. Rel. Phenom.*, 1986, **38**, 123.

[11] C. R. Brundle and M. W. Roberts, *Chem. Phys. Lett.*, 1973, **18**, 330; *Surf. Sci.*, 1973, **38**, 234; R. W. Joyner and M. W. Roberts, *Chem. Phys. Lett.*, 1974, **29**, 447.

[12] J. M. Thomas, E. L. Evans, M. Barber, and P. Swift, *Trans. Faraday Soc.*, 1971, **67**, 1875.

2 Experimental Developments

Subsequent to the introduction of a laboratory multi-photon source (*X*-ray and u.v.) spectrometer nearly twenty years ago[4c,13] there have been two distinct developments. First in the emergence of synchrotron radiation sources, as at the SERC Daresbury Laboratory, and second in vibrational spectroscopy where both reflection–absorption infrared (RAIRS) and electron energy loss (EEL) spectroscopies are now well established. The rapid development of both RAIRS and EELS for single crystal studies[14,15] has in large part been due to the availability of a very extensive infrared spectra data base for structurally well characterized organic and inorganic compounds. The synchrotron source has the advantage of being both tunable and of high intensity and has led to very significant advances in determining, through studies of *X*-ray absorption fine structure (EXAFS), surface EXAFS and near-edge *X*-ray absorption fine structure (NEXAFS), bond lengths and the structures of chemisorbed species.[16] Although pre-dating PES, Auger electron spectroscopy has not figured as prominently in the studies of surface chemistry largely due to its reputation for perturbing the chemisorbed layer through electron beam damage. It is, however, making significant contribution in surface physics—where perhaps this problem is thought not to be so important—particularly for spatially resolved spectra as obtained in the scanning Auger spectrometer. However, more recently Chesters[17] using very low beam currents has shown that damage can be minimized and useful surface structural information obtained.

3 Experimental Strategy in PES

The usual approach adopted by the chemist to unravel the mechanism of a chemical reaction is to identify the structure and composition of the products and determine the temperature and concentration dependences of the reaction rate. Two dimensional or surface chemistry has not yielded easily to this approach for the obvious reason that, prior to electron spectroscopy, experimental methods that are sufficiently surface sensitive were not available. Not only do we wish to detect but also to discriminate between surface and subsurface atoms and also between the same surface atom in different chemical environments. PES meets all these requirements: The photoelectrons originate from no more than 20 Å below the surface (depending on the electron kinetic energy) with about 30% of the intensity of those from the surface atoms. All chemical elements, other than chemisorbed hydrogen, may be characterized through their core-level spectra

[13] D. Latham, K. Yates, C. R. Brundle, and M. W. Roberts, *J. Electron Spectrosc. Relat. Phenom.*, 1974, **3**, 241.

[14] N. Sheppard, *Ann. Rev. Phys. Chem.*, 1988, **39**, 589; 'Vibrational Spectroscopy of Molecules on Surfaces', ed. J. T. Yates and T. E. Madey, Plenum Press, 1987.

[15] See, for example, 'Modern Techniques of Surface Science', D. P. Woodruff and T. D. Delchar, Cambridge University Press, 1986.

[16] G. Lamble and D. A. King, in 'Studies of the Surfaces of Solids by Electron Spectroscopy: Recent Trends', The Royal Society, London, 1986.

[17] M. A. Chesters and D. R. Linder, in 'Structure and Reactivity of Surfaces', ed. C. Mortera, A. Zechina, and G. Costa, Elsevier, 1989.
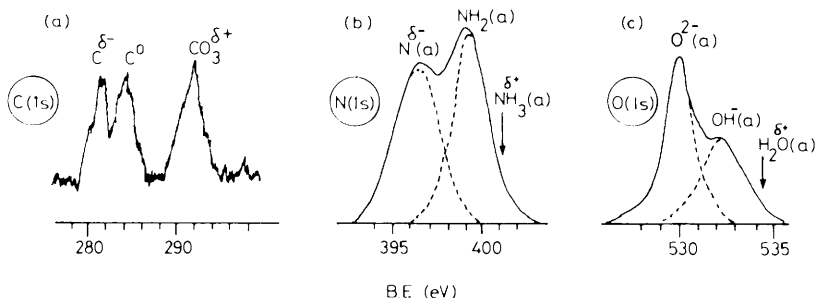
Figure 1 *Chemical shifts and assignments in core-level binding energies for chemisorbed species; (a) reactive chemisorption of* CO_2; *(b) dissociative chemisorption of ammonia; (c) H-abstraction from molecularly adsorbed water by chemisorbed oxygen; molecularly adsorbed ammonia and water would, if present, show* $N(1s)$ *and* $O(1s)$ *peaks at 401 eV and 534.5 eV respectively* ($\downarrow$). *The relative charges on the photoemitting atoms are shown*

and, furthermore, the chemical shift in the measured electron binding energy is sensitive to both charge and chemical environment.

We have discussed elsewhere how through interfacing the photoelectron spectrometer with a microcomputer, photoelectron spectra involving overlapping peaks can be analysed:[18] the usual procedure, after smoothing and background removal, is to curve-fit using a least-squares minimization program and assuming Gaussian profiles for the adsorbate peaks. An alternative procedure, which under some circumstances can be advantageous, is spectral subtraction. The mechanics of generating difference spectra and the criteria used for assessing the quality of the result are discussed elsewhere.[19] Figure 1 shows three examples of photoelectron spectra where the distinction between different but closely related surface species can be made on the basis of chemical shifts in the measured core-level binding energies. These can be supplemented by valence-level spectra, and the variation of peak intensities with electron take-off angle can provide qualitative information on the spatial distribution of the species with respect to the surface normal, *i.e.* whether they are at or just below the surface.

Surface concentrations of species 'a' are calculated[20] from equation 1

$$\sigma_a = \frac{n_s I_a \mu_s \lambda_s \cos\varphi}{I_s \mu_a} \qquad (1)$$

where I_a, and I_s are the normalized intensities from an adsorbate and clean substrate (metal) photoelectron peak, μ_a and μ_s the respective sub-shell photoionization cross-sections, n_s is the number density of the substrate atoms, λ_s the mean free path of the relevant substrate photoelectrons, and φ is the angle of electron collection with respect to the surface normal.

[18] C. T. Au, A. F. Carley, and M. W. Roberts, *Int. Rev. Phys. Chem.*, 1986, **5**, 57.

[19] A. F. Carley, P. R. Chalker, J. C. Riviere, and M. W. Roberts, *J. Chem. Soc., Faraday Trans. 1*, 1987, **83**, 351.

[20] A. F. Carley and M. W. Roberts, *Proc. R. Soc., A*, 1978, **363**, 403.

We emphasize in this article the advantages of quantitative real time photoelectron spectroscopy, particularly at low temperatures, for elucidating the mechanisms of surfaces processes. Spectroscopic evidence for bond cleavage, bond making, and intermediates in surface reactions will be discussed. Although XPS and UPS facilities were available in the prototype ESCA-3 spectrometer,[4c,13] with the use of single crystals structural information through low energy electron diffraction (LEED) became important and this facility was added. More recently at Cardiff XPS, UPS, and LEED have been supplemented by vibrational spectroscopy (EELS) within a single spectrometer. This enables a complete 'chemical' analysis of the surface with core-level peak assignments being complemented by vibrational spectra.

4 Complex Chemisorption

Chemisorption of molecules at metal surfaces was generally considered to be either molecular or dissociative and a broad classification based on the periodic table drew a distinction between transition metals—catalytically active and leading to facile dissociative chemisorption of dihydrogen—and *sp*-metals— catalytically inactive and sluggish in dihydrogen bond cleavage.

Both carbon monoxide and dinitrogen were studied extensively (1955—1965) by kinetic methods and the consensus was that at tungsten surfaces dinitrogen was dissociatively chemisorbed whereas carbon monoxide was molecularly adsorbed.[21] These two molecules therefore were obvious candidates for investigation when photoelectron spectroscopy became available for surface studies in 1970. That carbon–oxygen bond cleavage was facile on some transition metal surfaces (*e.g.* iron)[22] opened the door to speculation[23] on Fischer–Tropsch chemistry. Extensive studies of CO chemisorption have since been reported, with the role of precursor states being emphasized by Rao *et al.*[24] The Bangalore group discovered rather unexpectedly that aluminium was a very effective promoter of CO dissociation at both copper and nickel surfaces. Evidence for the precursor was reflected by an increase in the 5σ—4σ orbital separation and a particularly low C–O stretching frequency in the EEL spectra. The CO is thought to be bonded parallel to the surface by the twin interaction of 5σ-Al and 1π-Cu.

The remarkably facile cleavage of the carbon–oxygen bond led, not unnaturally, to the question as to whether dissociative chemisorption at low temperatures was more ubiquitous than was implied by the reactivity—periodic table classification of Trapnell.[21,25] The structurally similar nitric oxide molecule, but with a somewhat weaker nitrogen–oxygen bond than the carbon–oxygen bond of CO (600 kJ compared with 1 000 kJ), was investigated. Single crystal Cu(111) and

[21] See, for example, 'Chemistry of the Metal–Gas Interface', Chapter 1, M. W. Roberts and C. S. McKee, Oxford University Press, 1978.
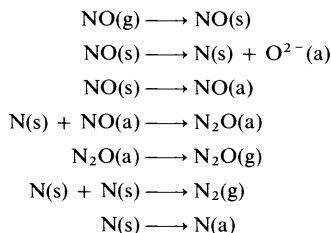
[22] K. Kishi and M. W. Roberts, *J. Chem. Soc., Faraday Trans. 1*, 1975, **71**, 1715.

[23] R. W. Joyner, *J. Catal.*, 1977, **50**, 176; *Vacuum*, 1987, **38**, 309.

[24] C. N. R. Rao, M. K. Rajumon, K. Prabhakaran, M. S. Hegde, and P. V. Kamath, *Chem. Phys. Lett.*, 1986, **129**, 130.
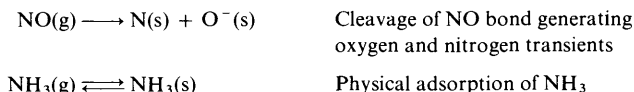
[25] B. M. W. Trapnell, *Proc. R. Soc., A*, 1953, **218**, 566.

Cu(110) surfaces, both known to adsorb CO only weakly ($\Delta H \sim 60 \, kJ \, mole^{-1}$), were however shown to participate in complex chemisorption, *i.e.* involving both bond cleavage and bond making when exposed to nitric oxide at low temperatures.[26] Through a combination of XPS, UPS, and LEED and making use of spectral subtraction methods it was established that the following molecular events occurred:
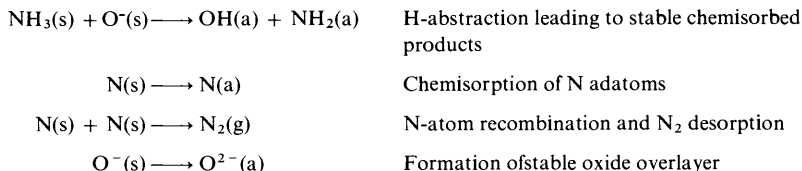
$$NO(g) \longrightarrow NO(s)$$
$$NO(s) \longrightarrow N(s) + O^{2-}(a)$$
$$NO(s) \longrightarrow NO(a)$$
$$N(s) + NO(a) \longrightarrow N_2O(a)$$
$$N_2O(a) \longrightarrow N_2O(g)$$
$$N(s) + N(s) \longrightarrow N_2(g)$$
$$N(s) \longrightarrow N(a)$$

Bond cleavage leading to strongly chemisorbed oxygen $O^{2-}(a)$ and transient nitrogen adatoms N(s) occurred at 80 K. The latter could follow three reaction pathways: recombine and desorb as dinitrogen, be strongly chemisorbed as N(a), or undergo an addition reaction with an undissociated nitric oxide molecule NO(a) to form $N_2O(a)$. Each of these steps could be isolated and spectroscopic evidence (XPS and UPS) obtained for all the surface species; the molecular events occurred at or just above 80 K. We shall see later how the implications of these results were taken up in a more general way through exploring the role of short-lived transients in surface chemistry. The advantages of low temperatures for revealing mechanistic detail are obvious, (s) designates a weakly adsorbed transient species while (a) represents a more strongly adsorbed species. In passing it is worth noting that we have converted a thermodynamically stable molecule, NO, into one of *less stability*, N_2O, the driving force being the formation of the chemisorbed oxygen overlayer, $O^{2-}(a)$. Although two different bonding states NO(linear) and NO(bent) were delineated by XPS, their distinct roles in dissociation are not considered in the context of this discussion (see ref. 26).

Further light was shed on the molecular details of such complex chemisorption from studies of the chemistry of co-adsorbed molecules. We illustrate this with data from the nitric oxide–ammonia Mg(0001) system.[27] Photoelectron spectra observed during the co-adsorption of nitric oxide and ammonia suggested that the chemistry involves two radical-like surface transients, N(s) and $O^-(s)$ and that the stable and spectroscopically identified chemisorbed products, $NH_2(a)$, $O^{2-}(a)$, OH(a), N(a), and $NH_2(a)$ were formed in the following sequence of steps:

$$NO(g) \longrightarrow N(s) + O^-(s)$$ Cleavage of NO bond generating oxygen and nitrogen transients

$$NH_3(g) \rightleftharpoons NH_3(s)$$ Physical adsorption of NH_3

[26] D. W. Johnson, M. H. Matloob, and M. W. Roberts, *J. Chem. Soc., Chem. Commun.*, 1978, 40; *J. Chem. Soc., Faraday Trans. 1*, 1979, **75**, 2143.

[27] C. T. Au, A. F. Carley, and M. W. Roberts, *Phil. Trans. R. Soc. Lond.*, 1986, **318**, 61.

$$NH_3(s) + O^-(s) \longrightarrow OH(a) + NH_2(a)$$ H-abstraction leading to stable chemisorbed products

$$N(s) \longrightarrow N(a)$$ Chemisorption of N adatoms

$$N(s) + N(s) \longrightarrow N_2(g)$$ N-atom recombination and N_2 desorption

$$O^-(s) \longrightarrow O^{2-}(a)$$ Formation of stable oxide overlayer

This mechanism is a development of that first discussed by Au *et al.*[27] but takes into account the subsequent discovery that the oxide overlayer $O^{2-}(a)$ at a Mg(0001) surface was inactive in H-abstraction from an ammonia molecule undergoing surface diffusive hops at low temperatures and that a more reactive oxygen transient $O^-(s)$ was involved.[28]

5 Activation of Molecules at Metal Surfaces by Oxygen: The Specific Role of Oxygen $O^-(s)$ Transients

Although oxygen is not usually regarded as a promoter for reactions catalysed at metal surfaces, a number of quite distinct promoter-type roles have emerged[29] over the last decade. In general, chemisorbed oxygen can act as a base where it participates in dehydrogenation reactions; the first spectroscopic evidence[30,31] for this was in the activation of hydrogen sulphide and water. With Pb(100) and Pb(110) surfaces chemisorptive replacement of oxygen occurred[30] leading to a sulphide overlayer under conditions (low temperatures) where hydrogen sulphide itself was unreactive. With Cu(100) and Cu(110) surfaces chemisorbed oxygen was hydrogenated[31a] when exposed to water vapour under conditions when the atomically clean surfaces were unreactive to water vapour. Photoelectron spectroscopy established that bond cleavage was facile, and enabled the intermediates to be spectroscopically identified and the mechanisms to be established. The generality of the low temperature activation of molecules by preadsorbed oxygen at metal surfaces is now well recognized and extends to include more complex organic molecules. The trend is that the sequence of events is first H-bonding, and then H-abstraction followed by desorption of water (see also review by Thiel and Madey[31b]). All these events are kinetically facile and can occur well below 200 K. There is a dependence on the fraction of the metal surface θ precovered by chemisorbed oxygen; as θ approaches unity the activity of the oxygen decreases suggesting the need for 'free' metal sites in adsorbate activation.[31a] In at least one system oxygen has been shown to exhibit a *dual role* depending on whether it is at or just below the surface. This was suggested[31c] as a possible explanation for oscillating reactions, *e.g.* H_2 and O_2 over platinum.

[28] C. T. Au and M. W. Roberts, *J. Chem. Soc., Faraday Trans. 1*, 1987, **83**, 2047.

[29] M. W. Roberts, *Adv. Catal.*, 1980, **29**, 55; R. J. Madix, *Adv. Catal.*, 1980, **29**, 1.

[30] K. Kishi and M. W. Roberts, *J. Chem. Soc., Faraday Trans. 1*, 1975, **71**, 1721; K. Kishi, R. W. Joyner, and M. W. Roberts, *Proc. R. Soc.*, *A*, 1977, **358**, 223.

[31a] C. T. Au, J. Breza, and M. W. Roberts, *Chem. Phys. Lett.*, 1979, **66**, 340; C. T. Au and M. W. Roberts, *Chem. Phys. Lett.*, 1980, **74**, 472.

[31b] P. A. Thiel and T. E. Madey, *Surf. Sci. Rep.*, 1987, **7**, 211.

[31c] P. G. Blake, A. F. Carley, and M. W. Roberts, *Surf. Sci.*, 1982, **123**, L733.
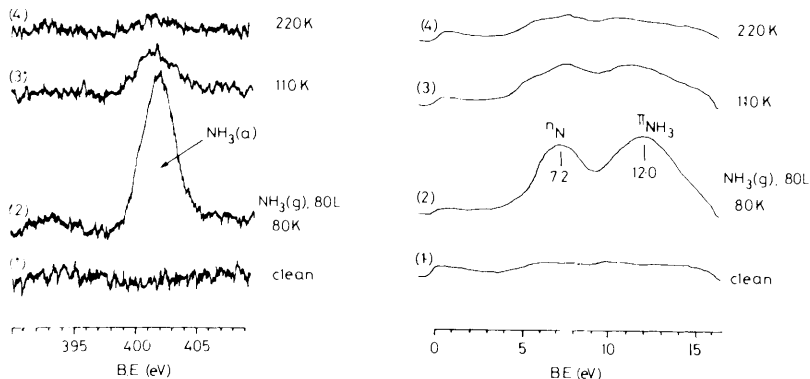
Figure 2 N($1s$) *and* He(I) *spectra* (2) *for ammonia adsorption on* Mg(0001) *surface at* 80 K *and on warming* (3 *and* 4) *the adlayer to* 220 K. *Both core and valence level spectra* (4) *indicate that desorption is complete at* 220 K. *Analogous spectra were observed with the* Mg(0001)–O *overlayer*

Following on from studies of oxygen preadsorbed at Ni(210) surfaces[32] where it was established that the most efficient surfaces for the activation of molecularly adsorbed water were those pre-exposed to dioxygen at 77 K, we explored the proposition that surface oxygen that had not attained its fully coordinated state in the chemisorbed overlayer as O^{2-}(a) was likely to show the highest chemical activity. This led us to investigate the surface reactivity of metal surfaces under dynamic conditions; we concluded that it was important to distinguish between the chemistry associated with stable chemisorbed oxygen at metal and oxide surfaces and that of the oxygen transients which are present only under dynamic oxygen–metal interaction. A good example is the cleavage of the carbon–oxygen bond in carbon monoxide at an aluminium surface in the presence of dioxygen at low temperature.[31d]

Co-adsorption studies[33,34] of dioxygen–ammonia and dioxygen–propene mixtures established the specific role that surface oxygen transients could have in the surface chemistry of atomically clean metals; both the metal Mg(0001) and oxide overlayer surfaces were chemically unreactive to both ammonia (Figure 2) and propene, but when co-adsorbed with dioxygen at 295 K or below H-abstraction was observed at a Mg(0001) surface. Low temperature activation (H-abstraction) was also observed with two other co-adsorbates, nitric oxide and nitrous oxide, both of which are known to be dissociatively chemisorbed at Mg(0001) surfaces thus suggesting that the active oxygen species is atomic rather than molecular dioxygen. A kinetic model was developed[33] on the premise that

[31d] A. F. Carley and M. W. Roberts, *J. Chem. Soc., Chem. Commun.*, 1987, 355.

[32] A. F. Carley, S. Rassias, and M. W. Roberts, *Surf. Sci.*, 1983 **135**, 35.

[33] C. T. Au and M. W. Roberts, *Nature*, 1986, **319**, 206; *J. Chem. Soc., Faraday Trans. 1*, 1987, **83**, 2047.

[34] M. W. Roberts, *University of Wales Science and Technology Review*, 1987, No. 2, 58; C. T. Au and M. W. Roberts, *J. Catal.*, 1987, **106**, 538.
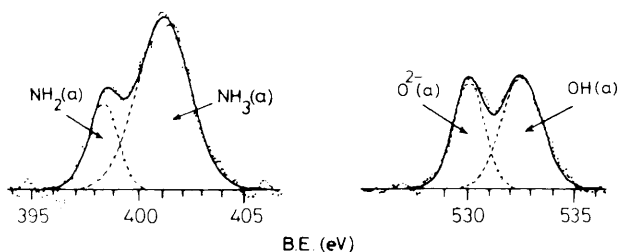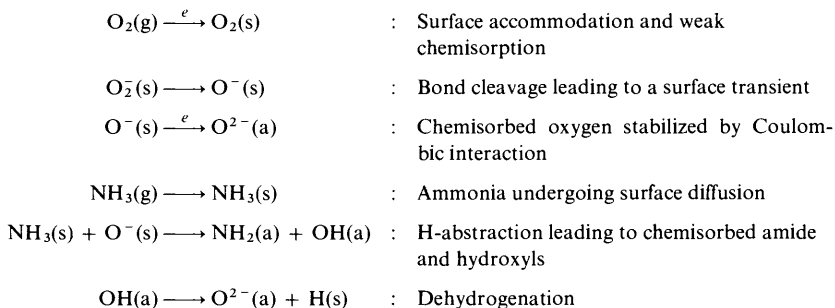
Figure 3 *Co-adsorption of dioxygen and ammonia at* Mg(0001) *at* 110 K; O(1s) *and* N(1s) *spectra showing the presence of* NH₂(a), O²⁻(a), *and* OH(a) *species. Evidence for reactive surface oxygen transients*

the species was $O^-(s)$ since the latter would be expected, by analogy with gaseous O^-, to be highly efficient in H-abstraction. The model was based on the following steps:

$$O_2(g) \xrightarrow{e} O_2(s) \quad : \quad \text{Surface accommodation and weak chemisorption}$$

$$O_2^-(s) \longrightarrow O^-(s) \quad : \quad \text{Bond cleavage leading to a surface transient}$$

$$O^-(s) \xrightarrow{e} O^{2-}(a) \quad : \quad \text{Chemisorbed oxygen stabilized by Coulombic interaction}$$

$$NH_3(g) \longrightarrow NH_3(s) \quad : \quad \text{Ammonia undergoing surface diffusion}$$

$$NH_3(s) + O^-(s) \longrightarrow NH_2(a) + OH(a) \quad : \quad \text{H-abstraction leading to chemisorbed amide and hydroxyls}$$

$$OH(a) \longrightarrow O^{2-}(a) + H(s) \quad : \quad \text{Dehydrogenation}$$

Subsequent to dioxygen bond cleavage, which at Mg(0001) surfaces is very efficient, the transient $O^-(s)$ species may transform to the thermodynamically stable and unreactive $O^{2-}(a)$ species or interact with an ammonia molecule to form the surface amide and hydroxide species (Figure 3). Depending on the relative rates of $O^{2-}(a)$ and OH(a) formation, and therefore their relative concentrations, the hydroxyl species may be unstable and dehydrogenate to O^{2-} (a); this is more likely at small coverages and high temperature (295 K).

A phenomenological illustration of the molecular events involved is shown in Figure 4. A detailed kinetic analysis is given elsewhere[33] but the essential point in the mechanism is the distinction made between two 'residence times'. First the surface residence time $\tau = \tau_O \exp (\Delta E_{des}/RT)$ where ΔE_{des} is the activation energy of desorption and secondly the site residence time defined by $\tau_s = \tau_O \exp (\Delta E_{diff}/RT)$ where ΔE_{diff} is the activation energy for surface hopping or diffusion. The number of molecular hops N_τ made by ammonia during the surface residence time τ is $R_s\tau$ where R_s is the hopping rate given by τ_s^{-1}; N_τ may be very large even though θ_{NH_3} is negligible. In the Mg(0001)–ammonia system at 295 K the value of τ is 3×10^{-6} s and N_τ about 400 so that several hundred surface sites
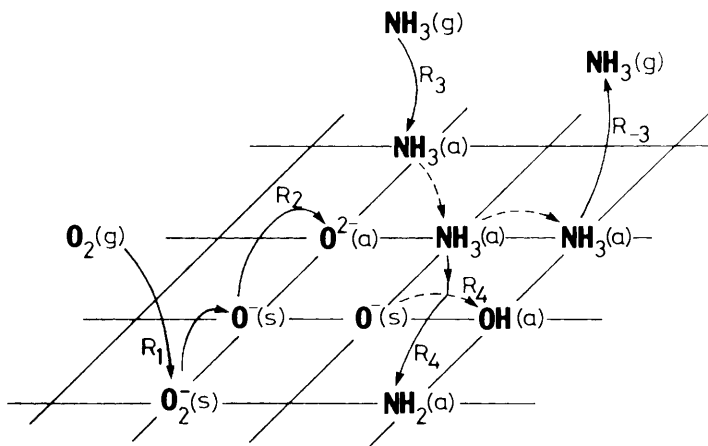
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Figure 4 *Molecular events in the co-adsorption of dioxygen and ammonia at* Mg(0001): *dioxygen dissociation* via *transients* $O_2^-(s)$ *and* $O^-(s)$: *ammonia undergoing surface diffusion, desorption and H-abstraction by* $O^-(s)$ *to generate* OH(a) *and* NH₂(a)

are visited by the hopping ammonia molecule during its residence time (τ) at the surface. Very approximately the 'site residence time' τ_s is about 10^{-8} s for a non-activated hopping ammonia molecule. During this time ammonia undergoes an efficient H-abstraction reaction with the transient $O^-(s)$ species before the latter 'picks up' a second electron to form the unreactive oxide $O^{2-}(a)$ species. Clearly experimental methods need to be developed to test the model. However computer simulation studies[35] support the steady state model *assumed* by Au and Roberts;[33,34] the approach adopted is to solve the following relevant differential equations:

$$\frac{-dS}{dt} = 0.2S + 10^{-2} \exp\frac{(-E_{\text{diff}})}{RT} \sigma_O - \sigma_{NH_3}$$

$$\frac{d\sigma_O}{dt} = 0.2S - \frac{\sigma_{O^-}}{\tau_{O^-}} - 10^{-2} \exp\frac{(-E_{\text{diff}})}{RT} \sigma_O \cdot \sigma_{NH_3}$$

$$\frac{d\sigma_O^{2-}}{dt} = \frac{\sigma_{O^\cdot}}{\tau_{O^\cdot}} + k_5 \sigma_{OH} S$$

$$\frac{d\sigma_{NH_3}}{dt} = 5 \times 10^{14} - 10^{13} \exp\frac{(-E_{\text{des}})}{RT} \sigma_{NH_3} - 10^{-2} \exp\frac{(-E_{\text{diff}})}{RT} \sigma_O - \sigma_{NH_3}$$

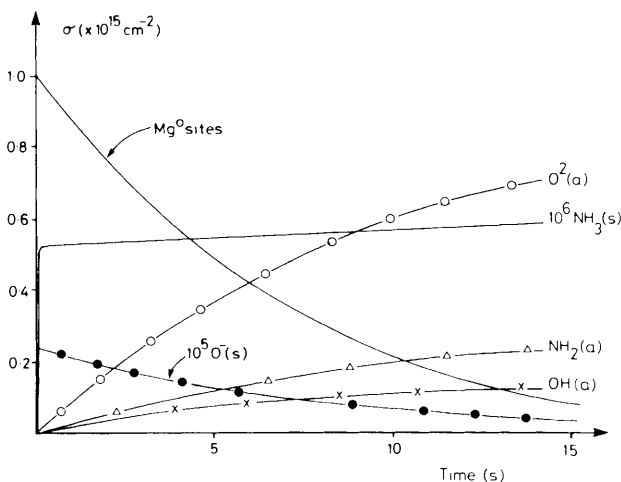[35] P. G. Blake and M. W. Roberts, *Catal. Lett.*, 1989 (in press).

Figure 5 *Computer modelling of the kinetics of the co-adsorption of a dioxygen–ammonia mixture* (5:1) *at a* Mg(0001) *surface:* $O^-(s) + NH_3(s) \longrightarrow O^{2-}(a) + NH_2(a) + OH(a)$

$$\frac{d\sigma_{NH_2}}{dt} = 10^{-2} \exp\left(-E_{diff}\right)/RT\,\sigma_O^-\sigma_{NH_3}$$

$$\frac{d\sigma_{NH}}{dt} = 10^{-2} \exp\left(-E_{diff}\right)/RT\,\sigma_O^-\sigma_{NH_3} - k_5\sigma_{OH}S$$

where S is the number of Mg^0 surface atoms, the σ terms are concentrations of the relevent species, E_{diff} and E_{des} are activation energies for surface diffusion and desorption of NH_3, and τ_{O^-} is the surface residence time of the transient $O^-(s)$. For each of the kinetic steps in the model, the concentration of $NH_3(s)$ remained invariant throughout the reaction at 5×10^8 molecules cm^{-2} (Figure 5) and $O^-(s)$ was initially about 2×10^9 cm^{-2} but decreased *slowly* during the reaction. Taking values of ΔE_{diff} of 14 kJ mole^{-1} and the experimentally determined (by XPS) surface concentration values for $NH_2(a)$ and $O^{2-}(a)$ the value of $\tau_{O\,(s)}$ was about 10^{-5} s; for a ΔE_{diff} value of zero $\tau_{O^-(s)}$ is about 10^{-8} s. It should be noted that the experimental conditions were chosen ($NH_3:O_2$ ratio 5:1 or greater) such that the probability of a hopping ammonia molecule intercepting the active surface transient was high at 295 K. In this way the amide reaction pathway was favoured over oxide overlayer formation (Figure 4).

A significant point that also emerged from this analysis[35] is that an Eley–Rideal mechanism involving the direct reaction of $NH_3(g)$ with $O^-(s)$, could not account for the observed rate since it predicted a rate that is a factor of about 10^6 smaller than that observed experimentally.
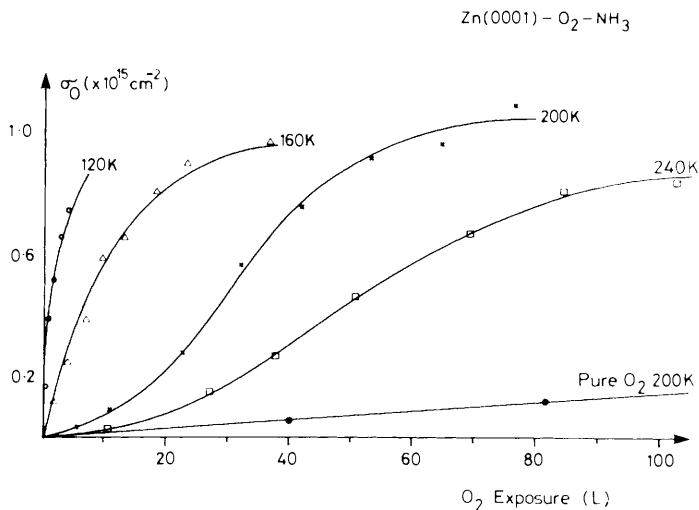
$Zn(0001) - O_2 - NH_3$

Figure 6 *Chemisorption of dioxygen and dioxygen–ammonia mixture* (1:5) *as a function of temperature and oxygen exposure at a* Zn(0001) *surface: note the inverse dependence of the rate of dioxygen bond cleavage on temperature, characteristic of a surface precursor complex* $O_2^- --- NH_3$. *At 120 K the rate of dioxygen bond cleavage is increased in the presence of* NH_3 *by a factor of about* 10^3

6 Activation of Dioxygen Bond Cleavage and the Chemical Reactivity of Surface Dioxygen

The dissociative chemisorption of dioxygen at Zn(0001) surfaces is, in contrast to that at Mg(0001), highly inefficient,[36] the reactive sticking probability being close to 10^{-4} at 80 K and 10^{-3} at 300 K. Zn(0001) is, therefore, an ideal surface for exploring a number of issues relevant to dioxygen–metal interaction:

(a) Can metal-induced dioxygen bond cleavage be catalysed through inter-molecular interactions involving dioxygen complexes, *i.e.* at a stage in the dynamics (Figure 4) prior to bond cleavage?

(b) What evidence can be adduced regarding the existence of discrete dioxygen species with characteristic surface life-times?

(c) If the presence of such species can be established, do they exhibit discrete chemical reactivity?

(d) More general aspects of oxygen dissociation, the mode of development of the oxide overlayer at a metal surface and its relation to bulk oxide surfaces.

The dissociative chemisorption of dioxygen at an atomically clean Zn(0001) surface as a function of oxygen exposure at 200 K is shown in Figure 6; it is highly inefficient. However, in the presence of ammonia (7:1 NH_3/O_2 mixture), which itself is only weakly adsorbed ($\Delta H \sim 40$ kJ mole^{-1}), the rate of oxygen

[36] A. F. Carley, M. W. Roberts, and Song Yan, *J. Chem. Soc., Chem. Commun.*, 1988, 267; *Catal. Lett.*, 1988, **1**, 265.
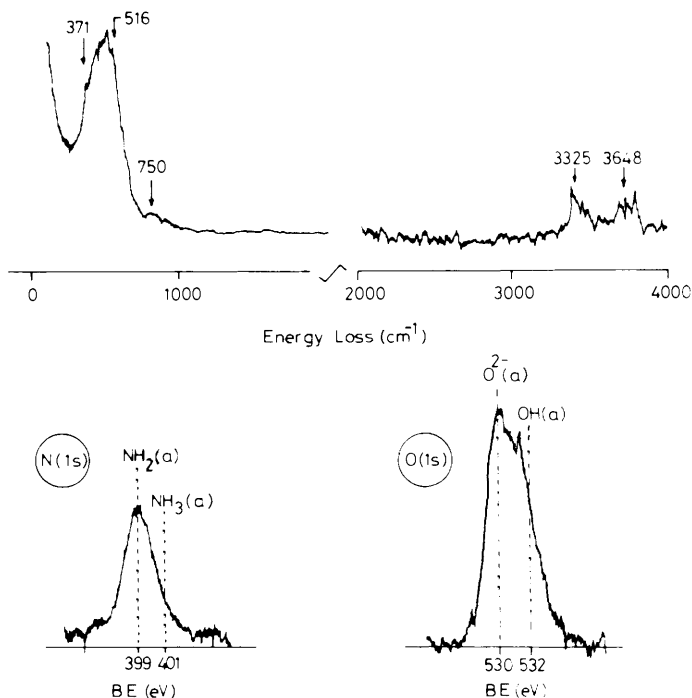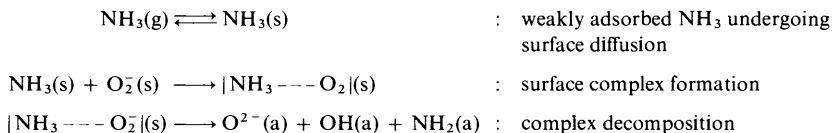
Figure 7 EEL *and* XPS *spectra for chemisorbed species formed by co-adsorption of* NH_3 *and* O_2 *at* Zn(0001); 750 cm^{-1} δ_{OH}; 3 325 cm^{-1} ν_{NH}; 3 648 cm^{-1} ν_{OH}; 520 cm^{-1} ν_{Zn-OH}; 370 cm^{-1} ν_{Zn-O}

dissociation is enhanced by a factor of nearly 10^3 indicating the role of a dioxygen surface transient and the N(1s) spectra provide clear evidence for chemisorbed amide, NH_2(a), species. The inverse dependence of the rate of dioxygen dissociation on temperature is shown in Figure 6; this is characteristic of the participation of a 'weakly' adsorbed precursor state. Furthermore the stoicheiometry of the reaction established through analysis of the O(1s) and N(1s) spectra suggests that the following steps are involved:

$$NH_3(g) \rightleftharpoons NH_3(s) \qquad : \quad \text{weakly adsorbed } NH_3 \text{ undergoing surface diffusion}$$

$$NH_3(s) + O_2^-(s) \longrightarrow |NH_3---O_2|(s) \qquad : \quad \text{surface complex formation}$$

$$|NH_3---O_2|(s) \longrightarrow O^{2-}(a) + OH(a) + NH_2(a) \quad : \quad \text{complex decomposition}$$

The nature of the stable chemisorbed species was established by a combination of core-level and vibrational spectroscopies (Figure 7) using a specially designed
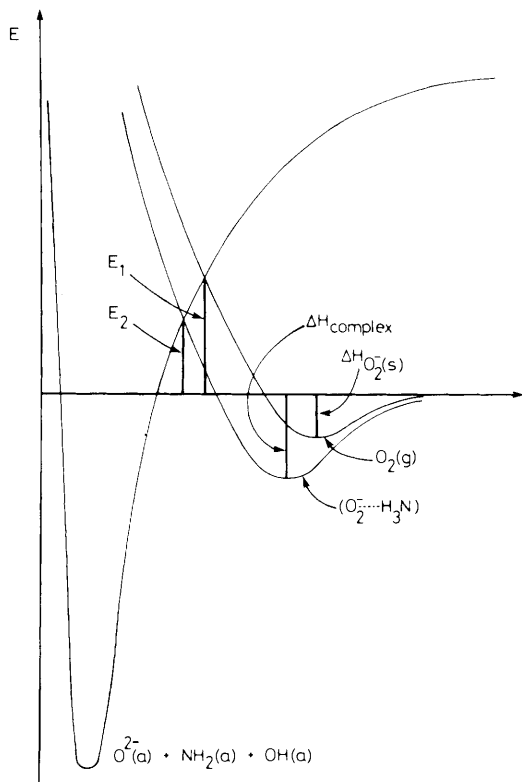
Figure 8 *Energy profile in one dimension for dioxygen–ammonia interaction with* $Zn(0001)$ *surface; the precursor surface complex* O_2^- $---NH_3$ *provides both a low energy pathway* (E_2) *and enhanced surface trapping of the peroxo-transient* $O_2^-(s)$. *See also Figure 4*

spectrometer incorporating XPS, UPS, LEED, and EELS.[36] The crucial intermediate in this reaction scheme involves the inherently unstable dioxygen–ammonia molecular-ion complex which is the precursor state responsible for the inverse temperature dependence of the reaction kinetics (Figure 6).

If we consider the ammonia molecule as a probe—recalling that it is chemically unreactive at both the atomically clean $Zn(0001)$ and the oxide overlayer $ZnO(0001)$ surfaces—then the observed chemistry establishes that the metal-catalysed dioxygen dissociation involves the following steps:

1. $O_2(g) \longrightarrow O_2(s)$ surface accommodation

2. $O_2(s) \longrightarrow O_2^-(s)$ 1st step of chemisorption; dioxygen bond weakening leading to a superoxo dioxygen surface transient

3. $O_2^-(s) \longrightarrow O^-(s)$ bond cleavage leading to an oxygen atom transient

4. $O^-(s) \longrightarrow O^{2-}(a)$ chemisorbed oxygen—the oxide overlayer

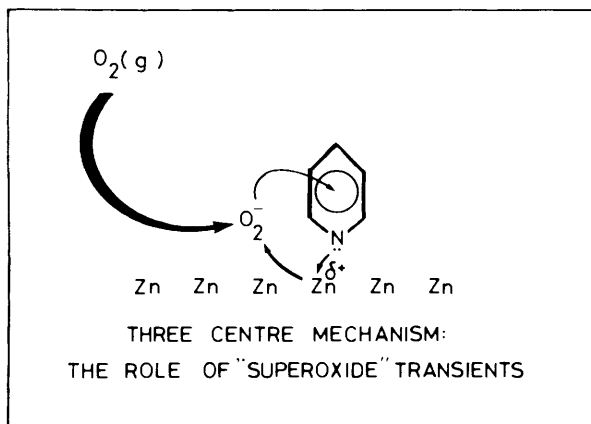464

O$_2$(g)

O$_2^-$

N

δ^+

Zn   Zn   Zn   Zn   Zn   Zn

THREE CENTRE MECHANISM:

THE ROLE OF "SUPEROXIDE" TRANSIENTS

Figure 9 *Three-centre mechanism involving* $Zn^{\delta+}$, *pyridine, and* O_2^-(s) *in the 'catalytic' cleavage of the dioxygen bond; the role of the superoxide surface transient*

If we think of steps 1 and 2 as a single event and responsible for the highly inefficient cleavage of the dioxygen bond, then the role of the ammonia molecule is to improve accommodation through complex formation; in other words the ammonia provides a highly efficient low energy pathway (Figure 8) for oxygen bond cleavage. For the Zn(0001)–dioxygen–ammonia system accommodation of dioxygen leading to complex formation at low temperatures is close to unity (Figure 6). Other molecules (*e.g.* pyridine) when co-adsorbed with dioxygen can also 'catalyse' oxygen bond cleavage[36] and a three-centre type mechanism is suggested (Figure 9).

What is equally important is that these experiments establish that the dissociative chemisorption of oxygen at a metal surface involves a sequence of discrete steps and that the chemical reactivity of the oxygen species generated at each stage must be taken into account. The obvious and rather trivial corollary to this is that we must distinguish between oxygen activation when oxygen is pre-adsorbed at a surface and that generated as a transient under dynamic conditions. Furthermore the relative surface life-times of O_2^-(s) and O^-(s), which we anticipate will vary both from metal to metal and for different crystal planes of the same metal, will determine which species is more significant in catalysis at metal surfaces. This is an issue relevant to the selective oxidation of hydrocarbons and discussed extensively for bulk oxide surfaces by Haber,[37] but not hitherto considered in the chemistry of clean metal surfaces. The point emphasized is that when a molecule (dioxygen) collides with a metal surface it will exchange energy and momentum with the surface atoms, after which it may become trapped. The latter may return to the gas phase either more or less immediately or after being

[37] J. Haber, *Proc. Indian Nat. Sci. Acad.*, 1985, **51**, 76.

accommodated; alternatively the dioxygen may after various degrees of accommo-dation interact chemically with the surface. It is the intermediate trapping states that we know so little about and which we suggest are relevant to the co-adsorption experiments described here.

Analogies can also be made with matrix isolation studies[38] of metal–dioxygen complexes generated photolytically; in all cases the initial step is the formation of the peroxo complex $M(\eta^2\text{-}O_2)(CO)_4$ where dioxygen is bonded to the metal thus:

$$
\begin{array}{c}
O\!\!-\!\!-\!\!O \\
\diagdown\ \diagup \\
M
\end{array}
$$

The peroxo complex then cleaves to give the more stable binary oxide MO_2. It is the peroxo (or superoxo?) species—the precursor to oxide formation—that we suggest is significant in the low temperature chemistry of dioxygen at Zn(0001) surfaces. Recently Capote *et al.*[39] using EELS have drawn attention to the chemical reactivity of molecular oxygen at Ag(110) surfaces at 95 K; under such conditions losses are observed at 280 and 660 cm^{-1} and are assigned to $\nu(Ag\text{–}O_2)$ and $\nu(O\text{–}O)$ respectively. Both carbon monoxide and sulphur dioxide undergo facile oxidation; with CO, adsorbed carbon dioxide and carbonate are formed, while with SO_2 a surface sulphite. The mechanism of CO oxidation by molecular surface oxygen is not clear but one possibility is that the role of carbon monoxide is analogous to the role of ammonia in catalysing dioxygen bond cleavage at Zn(0001) surfaces (Figure 6). That CO is only weakly adsorbed does not mitigate against this mechanism; it is the surface residence time of a hopping CO molecule that is more significant, as was shown in co-adsorption studies of CO and O_2 at aluminium surfaces.[40a] That a peroxo-type species is the oxidant present at an Ag(110) surface at 95 K there is no doubt; with this substrate dioxygen interaction at low temperatures is predominantly non-dissociative. The same appears to be the case for dioxygen at a Pt(111) surface at 87 K where Yates and his colleagues,[40b] relying on earlier EELS evidence of Gland *et al.*[41] and Lewhald *et al.*,[42] studied by kinetic methods the reactivity of what they believed were peroxo species in the oxidation of HCN. The peroxo (low temperature) species is highly reactive compared with chemisorbed oxygen atoms at the Pt(111) surface.

Recent work[43] in this laboratory has confirmed the low sticking probability of dioxygen at Ag(111) surfaces at low temperatures and pressures reported by Campbell,[44] after an exposure of 10^3 L at 80 K there being no evidence for any

[38] M. J. Almond, J. A. Crayston, A. J. Downs, M. Poliakoff, and J. J. Turner, *Inorg. Chem.*, 1986, **25**, 19.

[39] A. J. Capote, J. T. Roberts, and R. J. Madix, *Surf. Sci.*, 1989, **209**, L151.

[40a] A. F. Carley and M. W. Roberts, *J. Chem. Soc., Chem. Commun.*, 1987, 355.

[40b] X. Guo, A. Winkler, P. L. Hagans, and J. T. Yates, *Surf. Sci.*, 1988, **203**, 33.

[41] J. L. Gland, B. A. Sexton, and G. B. Fisher, *Surf. Sci.*, 1980, **95**, 587.

[42] S. Lewhald, H. Ibach, and H. Steininger, *Surf. Sci.*, 1982, **117**, 342.

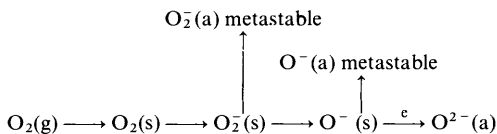[43] Song Yan and M. W. Roberts (to be published).

[44] C. T. Campbell, *Surf. Sci.*, 1986, **173**, L641.

oxygen-containing species in the O(1s) spectral region. However, when dioxygen is co-adsorbed with ammonia at 120 K—even for exposures as small as 30 L—full coverage of oxygen ($\theta = 1$) is observed as reflected by the intensity of the O(1s) spectrum. There is also a peak in the N(1s) spectrum at a binding energy of about 400 eV. Thus the efficiency of dioxygen accommodation and chemisorption at an Ag(111) surface is increased (through co-adsorption) by a factor of about 10^3 under conditions where ammonia itself is only weakly adsorbed and present (in the absence of dioxygen) at only low surface coverage ($\theta < 0.1$).

The close analogy between our observations of dioxygen chemistry with Zn(0001) and Ag(111) surfaces is striking; in both cases there is enhanced efficiency in the surface 'trapping' of dioxygen leading to complex formation which in the case of Zn(0001) decomposes to give spectroscopically identifiable products; we are unsure as to the fate of the complex on Ag(111) other than it is thermally unstable.

Evidence for the discrete O$_2$(s) step (see above scheme) has been reported recently by Ranke[45] who showed that with Pt(111) at 20 K the O(1s) binding energy was about 536 eV—not far from the gas phase value—whereas at 100 K the value is close to 531 eV and he assigned this to the peroxo-like species, O_2^{2-}. It is, as Ranke indicates, difficult however to distinguish between peroxo and superoxo species O_2^-, although Outka *et al.*[46] in a NEXAFS study determined the O–O distance to be 1.37 $\pm$ 0.05 Å compared to 1.21 Å in the free molecule. This value falls between that of superoxo and peroxo complexes. Above 150 K the molecule dissociates at Pt(111).

The development of overlayers at metal surfaces, particularly at low temperatures, where either bond cleavage or the second electron-transfer step become rate determining would favour the formation of oxygen defects. In the gas phase only the first two of the following three steps are exothermic and it is the coulombic or Madelung energy that is responsible for the stability of O^{2-}(a), and O_2^{2-}(a) at oxide surfaces: $O_2(g) + e \longrightarrow O_2^-(g)$ $\Delta H = -20$ kJ mole^{-1}; $O(g) + e \longrightarrow O^-(g)$ $\Delta H = -136$ kJ mole^{-1}; $O^-(g) + e \longrightarrow O^{2-}(g)$ $\Delta H = 820$ kJ mole^{-1}; $O_2^-(g) + e \longrightarrow O_2^{2-}(g)$ $\Delta H = +670$ kJ mole^{-1}. It is therefore perhaps not surprising that under low temperature, non-equilibrium conditions, the species at the surfaces of metal oxide overlayers often exhibit substantial concentrations of metastable O_2^-(a) and O^-(a) species. Both have been characterized at overlayers—no more than a few atom layers thick—by photoelectron spectroscopy.

$$O_2^-(a) \text{ metastable}$$
$$\uparrow$$
$$\qquad O^-(a) \text{ metastable}$$
$$\Big| \qquad \qquad \uparrow$$
$$O_2(g) \longrightarrow O_2(s) \longrightarrow O_2^-(s) \longrightarrow O^- (s) \xrightarrow{\ e\ } O^{2-}(a)$$

[45] W. Ranke, *Surf. Sci.*, 1989, **209**, 57.
[46] D. A. Outka, J. Stohr, W. Jark, P. Stevens, J. Solomon, and R. J. Madix, 1987, *Phys. Rev.*, **B35**, 4119.

7 Precursor States in Adsorption

Although it is widely accepted that precursor states play an important role in surface processes, there are two distinct and very different aspects. First, whether there is indeed direct experimental evidence (*e.g.* spectroscopic) for the presence of a precursor state, and secondly whether such states play a significant kinetic or dynamical role. For example, in the case of dinitrogen chemisorption on iron the spectroscopic evidence is reasonably clear in that it was shown[47a] that a low temperature molecular dinitrogen state was a precursor to dissociative chemisorption; furthermore this can account for the low ($\sim 10^{-6}$) sticking probability.[47a,b] On warming to above 80 K the molecular state(s) with N($1s$) peaks at 400 eV and 406 eV is replaced by nitrogen adatoms with an N($1s$) value of 397 eV. Similarly Prince *et al.*[47c] identified physisorbed oxygen present at 40 K as an intrinsic precursor to chemisorbed dioxygen at an Ag(110) surface. The notion of the dynamical role of precursors is nevertheless based largely on the characteristic plateau relationship between sticking probability and surface coverage,[6,7] the latter being considered to be diagnostic of the participation of adsorption precursors. In a recent article Auerbach and Rettner[48] draw attention to the inadequacy of this approach for developing unique models and discussed the advantages of molecular beam techniques. In the case of dioxygen interaction with a W(110) surface, the mechanism for sticking apparently undergoes a transition from 'precursor-mediated' to 'direct behaviour' with the energy of the dioxygen molecule. For a Boltzmann distribution around 300 K both channels operate. They conclude that 'many more detailed experiments are required to provide a firm physical basis for understanding the dissociative chemisorption process'.

An approach suggested by co-adsorption studies is to use a carefully chosen probe molecule—itself unreactive at the surface—to search for precursor states *suspected* to be present from kinetic studies. Under favourable circumstances, and some are described in this review, surface transients may be trapped forming complexes which dissociate to generate stable surface species which are then characterized spectroscopically (Figure 7). The probe molecule provides therefore an alternative and very efficient reaction pathway (Figure 8) for the precursor state, and by so doing establishes the latter's existence. The 'site' residence time τ_s would be only one factor (see earlier discussion) in determining the efficacy of the probe molecule in revealing precursor states, a more stringent requirement being 'chemical specificity' (see also ref. 33).

8 Mixed-valence States at Metal Oxide Overlayer Surfaces

It was interest in the nature of thin oxide overlayers at metal surfaces that led us into photoemission[4] as a means of exploring the proposition[49] put forward in

[47a] D. W. Johnson and M. W. Roberts, *Surf. Sci.*, 1975, **87**, L255.
[47b] G. Ertl, M. Huber, and N. Thiele, *Z. Naturforsch.*, 1979, **34**, 30.
[47c] K. C. Prince, G. Paolucci, and A. M. Bradshaw, *Surf. Sci.*, 1986, **175**, 101.
[48] D. J. Auerbach and C. T. Rettner, in 'Kinetics of Interface Reactions', ed. M. Grunze and H. J. Kreuzer, Springer Verlag, 1987.
[49] C. M. Quinn and M. W. Roberts, *Nature*, 1963, **200**, 648.

1963 that 'the chemisorbed oxygen overlayer at nickel surfaces was metastable, non-stoicheiometric and likely to exhibit both Ni^{2+} and acceptor (Ni^{3+}) states'. The question at issue was whether or not the oxide overlayer conformed to the accepted stoicheiometry, NiO, when it was no more than two or three atom layers thick. As emphasized by Day[50] the perception of the whereabouts of the valence electrons, and so the definition of a metal oxidation state, depends on the time-scale of the experimental method used to study for example bond lengths or electronic states. One advantage that XPS has is its inherently very fast time-scale ($\sim 10^{-16}$ s). Electron spin resonance spectroscopy was used by Che and Tench[51] to study bulk nickel oxides but no evidence for either Ni^{3+} or O^- species was obtained; this the authors attributed to the comparatively long time scale of ESR (10^{-9} s). Early experiments of oxide overlayers at nickel surfaces with XPS were also disappointing in the sense that raw $Ni(2p)$ spectra, although modified after oxygen chemisorption, did not reveal either Ni^{2+} or Ni^{3+} species. We returned to this problem some years later,[52a] however, encouraged by XPS studies of model bulk oxides[52b] of nickel and the development of spectra analysis facilities based on microprocessors. Two conclusions are emphasized: (a) the non-stoicheiometric nature (oxygen-excess) of bulk oxide surfaces, (b) evidence in the $Ni(2p)$ spectra for two valence states, Ni^{2+} and Ni^{3+}; furthermore various treatments (thermal, exposure to water vapour, hydrogen, or nitrogen dioxide) can influence the ratio of Ni^{2+} and Ni^{3+}, at the surface of an oxide overlayer no more than two or three atom layers thick.

In some recent elegant studies Cimino and his colleagues[53] have, through a combination of XPS and EPR, established that for high surface area NiO–MgO solid solutions the lack of EPR evidence for Ni^{3+} species is (as was suspected) due to magnetic interactions. That Ni^{3+} species are present is established by XPS but Cimino *et al.* show that only when these are 'isolated' can they be observed by ESR. A quantitative comparison between ESR and XPS estimations of Ni^{3+} is therefore feasible provided the limitations of detection by ESR to magnetically non-interacting ions is taken into account.

During the formation of the chemisorbed oxygen overlayer at the open-face Ni(210) surface, evidence for both Ni^{2+} and Ni^{3+} is present[52] in the $Ni(2p)$ spectra but only when the total oxygen uptake increases beyond about 1.5×10^{15} atoms cm^{-2}. The significance of such redox states has become of much interest recently in that one of the most efficient catalysts for the partial oxidation of methane is based on Li-doped nickel oxide. Certainly the $Ni(2p)$ spectra of such active catalysts exhibit features[54] which can be assigned to Ni^{3+} species.

[50] P. Day, *Sci. Prog.*, 1982, **68**, 83.

[51] M. Che and A. J. Tench, *Adv. Catal.*, 1982, **31**, 77.

[52a] A. F. Carley, P. R. Chalker, and M. W. Roberts, *Proc. R. Soc. Lond., A*, 1985, **399**, 167.

[52b] M. W. Roberts and R. St. C. Smart, *J. Chem. Soc., Faraday Trans. 1*, 1984, **80**, 2957.

[53] A. Cimino, D. Gazzoli, V. Indovina, M. Inversi, G. Moretti, and M. Occhiuzzi, in, 'Structure and Reactivity of Surfaces', ed. C. Morterra, A. Zechina, and G. Costa, Elsevier, 1989.

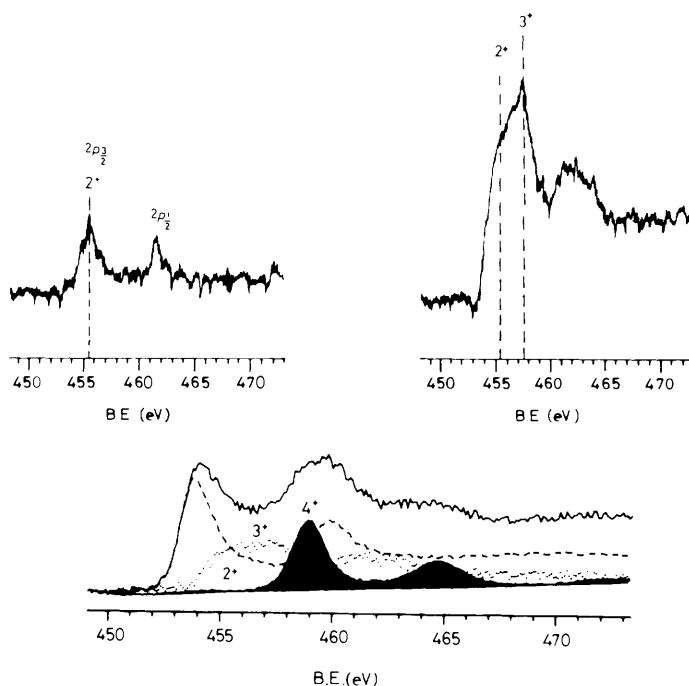[54] K. Otsuka, M. Hatano, and T. Komatsu, *Catal. Today*, 1989, **4**, 409.

Figure 10 *Variable oxidation states of* Ti *within the chemisorbed overlayer: with dioxygen evidence for* Ti^{2+}, Ti^{3+}, *and* Ti^{4+} *is present in the* Ti(2p) *difference spectra; for* CO *dissociative chemisorption only* Ti^{2+} *is present whereas with nitric oxide both* Ti^{2+} *and* Ti^{3+} *develop*

A system that has similarly revealed variable metal oxygen states within the chemisorbed overlayer is titanium [55]—whether as a result of the dissociative chemisorption of dioxygen, carbon monoxide, or nitric oxide. The intriguing observation with titanium is that although evidence for the sequential development of Ti^{2+}, Ti^{3+}, and Ti^{4+} is seen in the Ti(2p) spectra on exposure to dioxygen, with carbon monoxide the Ti^{2+} state develops uniquely (Figure 10). With nitric oxide both Ti^{2+} and Ti^{3+} are present in the 'nitride-oxide' overlayer but there is no evidence for the highest oxidation state Ti^{4+}. The formation of variable metal oxidation states in a molecule-specific way at metal surfaces, and so far reported only for titanium,[56] can be rationalized in terms of the contribution of the Madelung energy to the stability of the higher oxidation states. The latter becomes more significant as the oxide overlayer develops beyond the chemisorbed layer thus enabling (as with dioxygen) the development

[55] A. F. Carley, P. R. Chalker, M. W. Roberts, and J. C. Riviere, *J. Chem. Soc., Faraday Trans. 1*, 1987, **83**, 351.
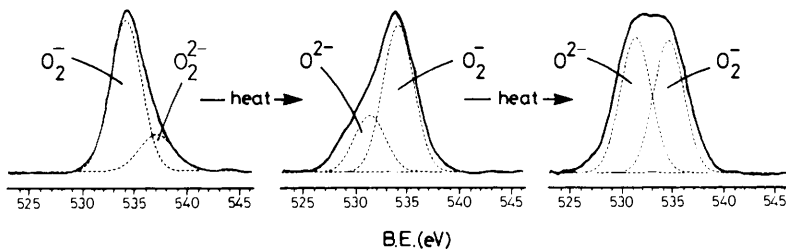[56] A. F. Carley, J. C. Roberts, and M. W. Roberts, *Surf. Sci.*, 1989 (in press).

Figure 11 O(1*s*) *spectra during thermally induced transformation of surface peroxo species* O_2^-(a) *to stable oxide* O^{2-}(a) *species at an oxidized magnesium surface*

of Ti^{4+} states. Kinetic reasons dictate that the development of the overlayer is most facile with dioxygen and least with carbon monoxide.

In addition to variable metal oxidation states (Ni^{2+}, Ni^{3+}) associated with, for example, the nickel oxide overlayer[52] the O(1*s*) spectral region reveals evidence for both O^{2-} and O^- species, although care must be taken to distinguish between O^- and OH species. As a matter of routine the C(1*s*) spectral region should also be scanned since there is a danger of mistaking surface oxygen and CO_3 species at oxide surfaces, particularly since the photoionization cross-section of the C(1*s*) orbital is small and about one third of the O(1*s*). Interest in oxide overlayers at Mg(0001) surfaces led us to explore[57] its interaction with H_2O_2; problems of handling the vapour in a stainless steel system prompted us to investigate whether it was feasible to inject directly on to the clean metal or metal oxide surface in a pure helium atmosphere—*via* a glass capillary—liquid H_2O_2. The O(1*s*) spectrum is shown in Figure 11, the assignment of the O(1*s*) peak at 532.3 eV to O_2^- species is supported strongly by the high chemical reactivity of this species to other molecules—making the distinction with the unreactive O^{2-} species conclusive. Also Ganguly and Hegde (personal communication) in studies of valence fluctuations in oxides of lead reported recently an O(1*s*) peak at 532.7 eV for PbO_2 and assigned it to O_2^{2-}. This compares with 529.7 eV for PbO. Further confirmation of the assignment of the 532.3 eV peak to O_2^- is provided by its thermal decomposition to give the more stable O^{2-} oxide species (characteristic of MgO) with an O(1*s*) binding energy of 531 eV (Figure 11). A similar strategy was used to assign Ni^{3+}, Ni^{2+}, O^{2-}, and O^- species in the nickel–oxygen system.[52]

Of particular relevance to the chemistry of MgO surfaces are the extensive ESR studies of Tench at Harwell and the Turin group, and in a recent paper Giamello *et al.*[58a] (see also references therein) emphasize that superoxide ions (O_2^-) can not be formed at *pure* MgO *surfaces* from dioxygen alone. Either prior irradiation to generate surface defects or *presorption* of some specific molecules is essential; in the latter case electron transfer from the *adsorbed anions* is the mechanism of O_2^- formation. This has similarities to the three-centre mechanism

[57] G. Hawkins and M. W. Roberts (unpublished work).
[58a] E. Giamello, P. Ugliengo, and E. Garrone, *J. Chem. Soc., Faraday Trans. 1*, 1989, **85**, 1373.

proposed to account for oxygen bond cleavage at metal surfaces (Figure 9) but also differs in that in the activation of dioxygen through co-adsorption, the co-adsorbate is on its own unreactive.

If, therefore, we reflect on the step-wise mechanism proposed for oxygen dissociation at metal surfaces and leading to oxide growth (see scheme) then we have direct experimental evidence for the superoxo species either present during the early stages of interaction as a transient—as for example established in the Zn(0001)–ammonia system—or present as a surface-stabilized but chemically very reactive species as at a Mg(0001) oxide surface.

9 Activation of CO_2 at Metal Surfaces

Interest in the use of carbon dioxide as a raw material in the synthetic chemical industry has increased over the last decade with it being suggested as the main source of methanol from CO–CO_2–hydrogen mixtures and that surface oxygen was a promoter of synthesis.[58b] As for the chemisorption of carbon dioxide at 'clean' metal surfaces, the early work of Collins and Trapnell[59] suggested little reactivity with copper, rhodium, and palladium but some evidence for dissociative chemisorption with aluminium. Nickel and zirconium were also reported[60] to react dissociatively while Eischens,[61] in one of the earliest surface infrared studies, reported carboxylate-type species with nickel. Electron spectroscopic data have been reported by Madix[62] and Bradshaw[63] with silver, controversy reigns over whether or not CO_2 chemisorption is dissociative at rhodium surfaces,[64] and a combined theoretical/experimental approach has been reported by Freund *et al.*[65] for nickel.

At Cardiff interest has been confined mainly to the adsorption of CO_2 at copper and the *sp*-metals aluminium and magnesium.[66,67] Both aluminium and magnesium surfaces are (except with oxygen) relatively unreactive and for this reason offer some advantage over transition metals (such as nickel or iron) which are particularly prone to contamination by carbon monoxide present as trace quantities in ultra high vacuum systems. This can lead to ambiguity in the interpretation of $C(1s)$ spectra and therefore in the supposed reactivity of CO_2.

The observed temperature and pressure dependences of CO_2 chemisorption at

[58b] G. C. Chinchen, M. S. Spencer, K. C. Waugh, and D. A. Whan, *J. Chem. Soc., Faraday Trans. 1,* 1987, **83**, 2193.

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aluminium surfaces provide clues as to the mechanism. At 295 K poly-crystalline aluminium is unreactive to CO_2 at low pressures (10^{-6} mbar) however at much higher pressures (1 mbar) XPS provides evidence for dissociative chemisorption leading to surface carbide, oxide, and carbonate. These surface species are however, also formed if high cover-ages of physically adsorbed CO_2 at 80 K are warmed to 295 K. The prerequisite for CO_2 reactivity is therefore a high value of θ_{CO_2}; this can be achieved at 10^{-6} mbar at 80 K but has to be increased substantially (1 mbar) at 295 K. The theoretical model proposed by Freund and Messmer[65] coincided with the experimental data reported for aluminium;[66] the significance of high surface coverages—CO_2 clusters—and the bent adsorbed CO_2^- anion in disproportionation reactions was emphasized[66,67] with the metastable 'carbonate' species being 'reduced' to surface oxide and carbide by the metal. Support also comes from electron attachment studies[68] to gaseous

$$|CO_2^- \text{---} CO_2|(a) \longrightarrow CO_3(a) + CO(g)$$

CO_2 clusters formed by adiabatic expansion; the electron affinity of the $(CO_2)_n$ cluster being shown to be dependent on the value of n. As n increases the attachment of low energy electrons becomes increasingly more efficient and for $n > 2$, $(CO_2)_n^-$ ions are formed at close to zero electron energy. On the other hand the isolated 'monomer' molecule has a negative electron affinity of about 0.6 eV. We see therefore in the adsorption of CO_2 at metal surfaces a strong relationship between the experimental evidence for the role of high surface coverages—or cluster-type surface chemistry—with both theoretical[65] and super-sonic beam gas-phase studies.[68]

Although there is experimental evidence for CO_2 interaction with copper surfaces,[67] probably to form CO_2^-(a), what is as yet not clear is the separate roles played by surface structure and the photoelectrons. The latter is certainly not significant in CO_2 interaction with Au(100) surfaces[69] but has some influence with copper and nickel;[65] the effect is therefore metal-specific. There is *a priori* evidence for electron capture by CO_2—either when adsorbed at low work function surfaces such as sodium- and caesium-doped Cu(100),[70,71] with lithium, when $Li^+CO_2^-$ is formed, or in the presence of photoelectrons at clean Cu(100) surfaces at 80 K. There is an obvious analogy with gas phase cluster chemistry where the electron affinity of the cluster can change from positive to negative as a function of cluster size so that high surface coverages of CO_2 may therefore favour dimer formation. What is also clear is that the surface chemistry of CO_2 at aluminium[66,67] or magnesium surfaces involving carbonate formation (see above) can be mimicked at Cu(100) surfaces when the latter is doped with

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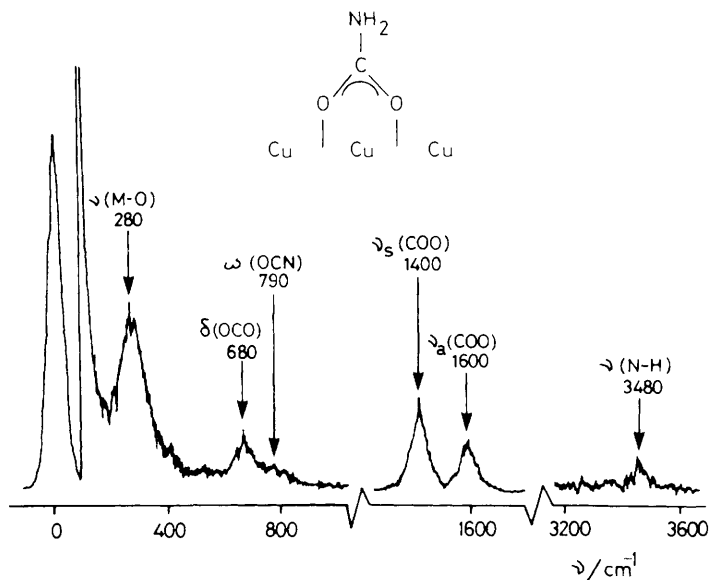[70] V. M. Browne and M. W. Roberts (unpublished work).

Figure 12 *Vibrational spectra (EELS) at 295 K for chemisorbed carbamate species formed at a Cu(100) surface at low temperature (~ 180 K) through the co-adsorption of CO_2 and NH_3; the individual molecules are only physically adsorbed at the Cu(100) surface*

caesium.[71] This is the kind of information that is vital to understanding the role of alkali metal promoters in catalysis.

We probed CO_2-copper chemistry further[72] by exploring the proposition that at low temperatures a weakly adsorbed CO_2 transient (CO_2^-?) could form which might be chemically trapped by a second molecule (ammonia), which itself was chemically unreactive at the copper surface. Although mixtures of CO_2 and NH_3 were unreactive when exposed at 10^{-6} mbar to a Cu(100) surface at 295 K, when co-adsorbed at 80 K and the mixed-adlayer warmed to 295 K, a strongly chemisorbed carbamate species was formed. This was established by a combination of XPS and EELS (Figure 12) and suggests that reaction occurs *via* a precursor van der Waal's complex $NH_3:CO_2$. Such interactions have been established[72] in supersonic expansions of a mixture of NH_3 and CO_2 in argon and are thought to involve the lowest unoccupied π^* orbital of the CO_2 interacting with the lone pair electrons of the ammonia, the latter acting as a Lewis base. The structure of the NH_3–CO_2 complex is thought to be T-shaped from molecular beam electric resonance methods[73] with the N-atom pointing towards the carbon, the C–N bond length being about 3 Å. The analogy with the

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(CO_2^-–CO_2) T-shaped dimer, suggested to be the important intermediate in the CO_2 surface chemistry of magnesium and aluminium,[66,67] is obvious. It also provides support for the proposition that although the difficult step with copper surfaces is to stabilize CO_2^-(a) it can be achieved by quite different routes: high CO_2 pressures or low temperatures (*cf.* cluster chemistry); alkali metal promotion (low work function surfaces), or intermolecular interactions (*cf.* copper–NH_2CO_2 formation).

10 Conclusions

Emphasis has been given in this Review to the part played by photoelectron spectroscopy (and to some extent EELS) in establishing the facile nature of bond breaking, bond making, and also in providing evidence for intermolecular interactions involving co-adsorbed molecules at metal surfaces. The role of weakly adsorbed molecules—unreactive at the clean surface—in determining reaction pathways when co-adsorbed is a facet of the chemistry of metal surfaces that has previously received little attention. Yet such co-operative effects within the adlayer must be a central issue in the context of the exchange of energy of molecules with surfaces and the mechanism of metal-catalysed reactions; the discovery that the rate of dioxygen bond cleavage can be enhanced by a factor of nearly 10^3 at say, 100 K, illustrates the kind of information that is emerging.

The chemistry of dioxygen when co-adsorbed at metal surfaces is shown to be dominated by surface oxygen transients, in the case of Zn(0001) they are superoxo-type species O_2^-(s) but with Mg(0001) they are O^-(s). By comparison the thermodynamically stable oxide overlayer is relatively unreactive. These observations also provide direct experimental evidence for the discrete stepwise nature of dioxygen dynamics at atomically clean metal surfaces including the existence of species with surface lifetimes which are long compared with the vibrational frequency. The chemical trapping of such oxygen intermediates by probe molecules undergoing surface diffusion leads to spectroscopically identifiable species and thus experimental evidence for precursor surface states.