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Coordination and Activation of Simple Molecules at Metal Surfaces

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A review of our present understanding of molecule–metal surface interactions is provided with emphasis on the activation of carbon monoxide, nitric oxide and dioxygen. Some reference is made to possible analogies with cluster complexes, and some views are offered on the further likely developments which will link with studies directed at an understanding of processes occurring at heterogeneous catalytic surfaces.

Preamble

The quantitative elucidation of structure–reactivity relationships is at the heart of the coordination/organometallic chemistry of metal surfaces, and at the centre of mechanistic studies of heterogeneous catalysis. Developments over the past five years, or so, include:

(i) the definition of the surface crystallography of a number of clean, low Miller-index surfaces and of simple atomic-adlayer arrangements [1, 2]; but the definition of the registry of simple (associated) molecules with respect to the metal surface atoms is still in a very uncertain state [3–5].

(ii) the characterisation of whether adsorption of simple molecules such as carbon monoxide or dinitrogen is associative or dissociative, and the factors (substrate geometry, temperature, *etc.*) which contribute to the facility for dissociation or activation.

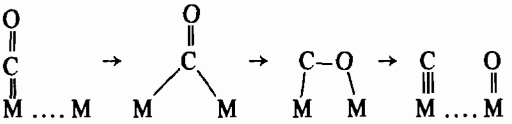
(iii) attempts, of varying rigorousness, to describe the electronic structure of the 'surface molecule' [6, 7]; the theory of reactive scattering of molecules at surfaces is, at best, in a rudimentary stage.

It is a synthesis of results appearing under (ii) that we emphasise here.

Carbon Monoxide Bonding

Photoelectron spectroscopy quite quickly established a general result: dissociative bonding of carbon monoxide at surfaces of early transition metals was a low activation energy process; at low index surfaces of the later transition metals with their relatively high coordinatively saturated sites and 'low free valence', associative binding was commonplace and activation energies for dissociation being *ca.* 100 kJ mol^{-1} rather than the 5–10 kJ mol^{-1} characterising sorption at, say, molybdenum and tungsten surfaces. Activation energies for dissociation change considerably for a high index (step-kink) surface of, say, platinum [8] with its highly coordinatively unsaturated sites accounting quantitatively for dissociation and, therefore, for the (multiply bonded) carbido and oxido-atomic surface species [8] which result from the dissociative chemisorption of carbon monoxide.

Schematically:



A convincing demonstration of the surface sensitivity of the carbonyl dissociation reaction and its relation to the incidence of coordinatively unsaturated

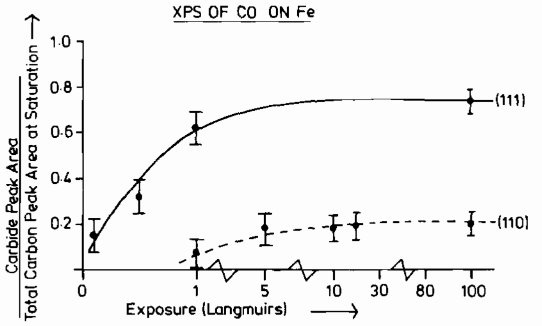


Fig. 1. 'Carbide' peak area as a function of the exposure (Langmuirs, 1L≡10^{-6} torr sec) of Fe(111) and Fe(110) surfaces to CO.

sites on the surfaces is shown in Fig. 1 which, in summary, shows that dissociative sorption of carbon monoxide—measured in high energy photoelectron spectroscopy by the appearance of a 'carbide' peak with a C(1s) binding energy of 282.9 eV (compared with 285.6 eV for a bonded carbonyl group)—is much less at the close-packed (110) surface than at the primitive stepped (111) surface [9]. The difference in activation energy for dissociation at the two surfaces is not dissimilar to that for dinitrogen chemisorption [10] although there are differences which can be imagined, at least in part, to reflect quantitative thermodynamic differences between the varying surface–ligand bonds. But to return briefly to the question of carbon monoxide bonding: all of the studies of chemisorption on iron, except at very low temperature, are indicative of dissociative sorption being the first step in Fischer–Tropsch reactions [11]; however photoelectron spectroscopy has, as yet, not delineated a logical sequence of precursors and intermediates.

Having noted these broad developments, it is worth registering the position that has been reached in that area of chemistry which seeks to draw analogies, when possible, between heterogeneous transition metal surface chemistry and homogeneous transition metal cluster chemistry, since metal–carbonyl chemistry is at the centre of this attempted correlation.

The synthesis and characterisation of high nuclearity clusters is growing apace [12, 13], and there is an acceptance that their structures may often be rationalised, if not predicted, by the skeletal electron pair model [14]. Structurally, one notes that in complexes such as $[Ni_{12}H_{4-n}(CO)_{21}]^{n-}$, $[Rh_{13}H_{5-n}(CO)_{24}]^{n-}$ and $[Rh_{14}(CO)_{25}]^{4-}$, $[Rh_{17}S_2(CO)_{32}]^{n-}$ the metal clusters have h.c.p. and h.c.c. symmetries respectively; extended Hückel and self consistent field $X\alpha$ calculations are also bearing out the intuitively obvious—as the cluster increases in size, so electronic conditions approximate the bulk metal (band widths, *etc.*). But it also seems clear that interactions between carbonyl ligands are tending to limit cluster sizes and cluster (metal) geometries are modified, therefore, to include more corner and edge atoms so as to minimise ligand–ligand repulsions. We have a fundamental difference from a true metal surface where the carbonyl ligands arrangement reflect a balance between ligand–ligand repulsions on the one hand and preferred binding site energies on the other. Nor in supported, highly dispersed particles is there the possibility for flexibility of the metal framework which would reflect ligand steric demands.

In $Os_{10}C(CO)_{24}^{2-}$ we have a rare example [15] of a completely escapsulated 'carbide' atom in a *ccp* structure, but, more importantly, we see the largest planar surfaces in a carbonyl cluster with carbonyl ligands arranged perpendicular to the face. One of the most important recent features to emerge in transition metal cluster chemistry is, in our judgment, the synthesis of encapsulated species. At once, one has the potential of satisfying electronic requirements of the cluster (rare gas rule) while reducing the number of surface ligands and hence maintaining the possibility of adjacent coordinatively unsaturated sites which are necessary to promote initial reactions such as oxidative addition. Here in concept, we are beginning to approach quantitative analogies with the heterogeneous surface. The pattern of dissociative–associative chemisorption of simple ligands on surfaces can be quantitatively interpreted by the statistical mechanical 'two site hypothesis' [16] entirely analogous to the requirement for *cis*-addition reactions. It is also the case that there remains much speculation on the nature of, say, the 'true' platinum-catalyst surface with Somorjai [17] arguing for the centrality of function of carbido-species at (presumably) sites of otherwise high coordinative unsaturation. Presumably it would be the relatively labile carbidospecies that would be important to catalytic reactions rather than those that are kinetically and thermodynamically stable at sites of low coordination number on early transition metals.

Nitric Oxide as a Ligand and Its Reactions at Surfaces

Interest in the transition metal surface chemistry of nitric oxide arose [18] directly from the characterisation of carbonyl surface chemistry; broadly speaking some similarities in the behaviour of the two ligands can be recognised, but nitric oxide presents a more complex pattern, and one which may find some overlap with metal–nitrosyl chemistry.

A study of the iron–nitric oxide system [18] indicates facile ligand bond cleavage even at 80 K, with nitrogen adatoms forming at low coverage; as with carbon monoxide, higher coverages of the iron surface represented molecularly adsorbed species which dissociates rapidly on warming to 295 K. At the higher temperature the surface had a density of states close to that anticipated for an iron nitride/oxide surface.

Of interest in the context of reactivities of a given ligand and the dependence of reactivity on substrate geometry, have been our studies of the adsorption of nitric oxide on copper surfaces. It was quickly established (Fig. 2) that copper [19] dissociatively chemisorbed nitric oxide at 80 K, the nitrogen adatoms being mobile even at this temperature and reacting according to

$$N(ads) + No(ads) \rightarrow N_2O(ads)$$

No stable Cu–N bond formation is observed, in contrast to the high stability of surface iron–nitride bonds. However, chemisorption of nitric oxide on

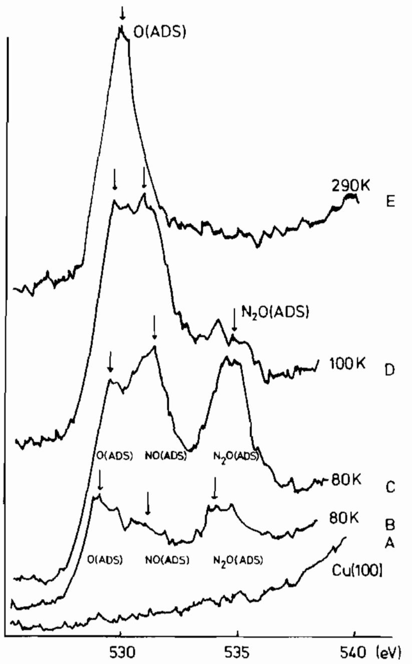


Fig. 2. Assignment of O(1s) spectra for the Cu(111) + NO system; A: clean surface; B: 7L exposure at 80 K; C: 24L exposure at 80 K; D after warming adlayer to 100 K; E after warming adlayer to 290 K.

polycrystalline copper and the Cu(001) [19, 20] surface at room temperature leads to a surface with an appropriate stoichiometry of nitrogen to oxygen of 1:1 and, of course, with complete dissociation. Further, nitric oxide was adsorbed on the stepped-kinked Cu(S)–[4(0001) X 351] surface [21] in which a terrace of (001) symmetry has a width of four atomic rows, the steps have the close-packed (111) orientation and, on average, every fifth atom at step sites is expected to be in a kink position of even lower coordination number. With increasing exposure of nitric oxide to the copper surface, the stoichiometric (O:N) ratio changed from 1.0 (low coverage) to 1.4 (high coverage). The unequal nitrogen and oxygen adatom concentrations at high coverage points once more to oxygen chemisorption accompanied by simultaneous desorption of a nitrogen containing species—presumably N_2O [20]. There may be detailed differences between the low index and high index copper surfaces, but they are small in contrast to the behaviour of the late Group VIII transition metal surfaces. A rationalisation of this trend is couched in terms of a relationship between the reactivity of structural surface discontinuities with the build up of a net positive charge at corner sites which turns out to be proportional to the density of states at the Fermi level—here is a suggestion that may be amenable to confirmation by detailed spectroscopic studies of cluster complexes.

To continue some analogies on metal–ligand bonds in the homogeneous and heterogeneous phases, we note and summarise that for the Cu–NO surface:

(a) nitric oxide was adsorbed in two molecular states at 80 K;
(b) one of these states dissociated slowly at 80 K;
(c) the nitrogen adatoms formed were not chemisorbed by the copper surface;
(d) nitrous oxide was generated within the adlayer at 80 K;
(e) nitric oxide was dissociatively chemisorbed by copper surfaces at 290 K, both the oxygen and nitrogen adatoms being retained by the copper surface.

The two molecular states were suggested to be chemisorbed in the bent (or quasi-bridge bonded) state and linearly bonded. The more strongly (bent) state was shown unequivocally to be the one that gave rise to the dissociated state and this was compatible with the model for CO-bonding on metals where a correlation was shown to exist [22] between O(1s) values, heats of adsorption and 'orbital peaks' in the valence-level spectra. The stronger is the surface bonding, the greater the back-bonding (Chatt–Dewar) contribution and the weaker the intramolecular nitrogen–oxygen bond. On this model the molecule that is more strongly adsorbed is the one that is most likely to dissociate and this is what is observed [20].

We draw particular attention to the role that 'dynamic photoelectron spectroscopy' can play in developing detailed models of molecular events occurring at solid surfaces. The experimental strategy is dependent on investigating the dynamics of complex processes under conditions where the individual molecular events can be observed independently of one another. The details that emerged could only have been unravelled at 80 K, the molecular events at 290 K were, by comparison, uninteresting and decidedly uninformative—a situation paralleled by observations on dioxygen chemisorption (*vide infra*).

One of the interesting features that has emerged out of such studies is the close similarity that exists between nitric oxide bonding/reaction with metals of inherently different electronic structures. Aluminium, nickel, iron and copper all show very similar behaviour [23, 24] and where differences were observed they were more in degree than in kind. In the case of nickel [23] a clue to a site sensitive mechanism was obtained from controlled pre-exposure of a clean nickel surface to oxygen over a range of temperature. The various adsorption states proposed for nitric oxide could be delineated, dissociation could be inhibited and N_2O formation controlled. Recent EELS studies [25] of adsorption on Ni(III) surfaces at and above 150 K indicated molecular adsorption in twofold bridging sites, at low coverage in a bent configuration but in a linear configuration at higher coverage. Dissociation occurs on warming the adlayer to 250 K. Clearly the model proposed is very similar to that which emerged from 'dynamic photoelectron spectroscopy'. A general and recurrent theme in studies of the surface chemistry of nitric oxide is, in summary, the recourse that is made to analogies with metal–nitrosyl chemistry.

Dioxygen and Its Reactions

The surface chemistry of oxygen is potentially one of the most profitable areas of investigation. On the one hand it is relevant to the creation of a new surface phase (as in metal oxidation) or on the other it impinges directly on a better understanding of selective oxidation in heterogeneous catalysis. It is also true that the recent observation (*vide infra*) of some very labile surface dioxygen species brings aspects of surface and coordination chemistry closer together.

The Ag(110) + oxygen system [26], where particular advantage accrued from the application of 'High Pressure Dynamic Photoelectron Spectroscopy', is particularly illustrative of these propositions. The initial interaction at ~200 °C is dissociative chemisorption, but this is followed by oxygen incorporation into the lattice, oxide formation and lastly the development of a *surface species* which we have, on the basis of the He(II) and O(1s) spectra, assigned to the superoxide or peroxide species. We have, therefore, observed in one particular system the sequential development of four stages of silver 'oxidation' and in particular in the last stage the species that is considered to be the 'active ingredient' in selective oxidation.

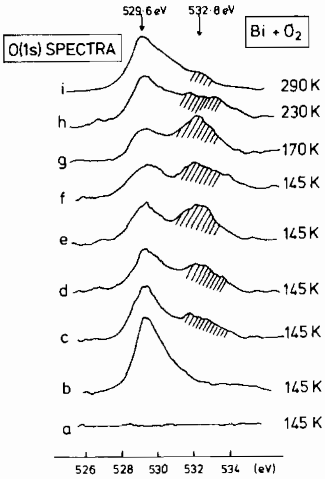


Fig. 3. Photon-induced conversion of O^{2-}(a) to a surface peroxide (or superoxide) species at 145 K and the thermally induced reconversion.

Following these studies the bismuth–oxygen system was examined [27], bismuth being a catalyst with potentially interesting selective oxidation characteristics. Some interesting observations were made (Fig. 3) on the interconversion of two distinct states of chemisorbed oxygen: the adsorption of oxygen on a Bi(0001) crystal surface at 145 K was characterised by an O(1s) peak at a binding energy of 529.6 eV. However, on continued exposure to the photons (hν = 1487 eV) at the same temperature a second adsorption state emerges with an O(1s) peak at a binding energy of ~532.8 eV. The second species develops at the expense of the first species, *i.e.* we are observing a photon-induced conversion of one 'chemisorbed oxygen state' into another. Furthermore on warming to 295 K (in the absence of photons) there occurs a reconversion into the initial chemisorbed state. Clearly the second state (O(1s) ≃ 532.8 eV) is thermally unstable and reverts easily to the 'initial chemisorbed state'. At 295 K only one chemisorbed state exists, there being no observable photon induced state presumably because its stability (life-time) at 295 K is small. We suggest that

$$O^{2-}(a) \underset{\text{thermal}}{\overset{h\nu}{\rightleftharpoons}} O_2^-$$

describes the molecular processes involved (we cannot exclude the peroxide ion) and therefore two electron photoredox reactions. Clearly to observe high catalytic selectivity stabilisation of the superoxide or peroxide species would be necessary, a view which carries over to discussions of oxidation or oxygen transfer processes in homogeneous and biological systems.

Although chemisorbed oxygen is usually regarded in mixed-adsorbate systems as a 'surface poison' (*e.g.* it prevents CO dissociation on a stepped platinum surface) there is now very clear evidence that it can induce reactivity in adsorbate bonds which would not occur in its absence. This evidence has been accumulating over the last five years with observations of how chemisorbed oxygen present on lead [28] (single crystal and polycrystalline) surfaces could effect dissociation of H_2S, with the removal of chemisorbed oxygen by desorption of water vapour and the subsequent sulphidation of the surface. The clean lead surfaces do not sulphide under identical experimental conditions.

Extending our studies to water [29] it was shown that the Cu(III)–O surface adsorbs water more strongly than the clean Cu(III) surface. Furthermore the X-ray induced spectra (Fig. 4) indicated the formation of 'surface hydroxyl' species at low temperature (~170 K). Clearly the hydrogen of the molecular water adlayer was interacting strongly with the chemisorbed oxygen, and the adlayer had characteristics more akin to an 'OH' adlayer than molecularly adsorbed water. This 'OH-like' adlayer was clearly unstable and reverted rapidly to H_2O(ads) which desorbed above about 200 K. With the clean Cu(III)

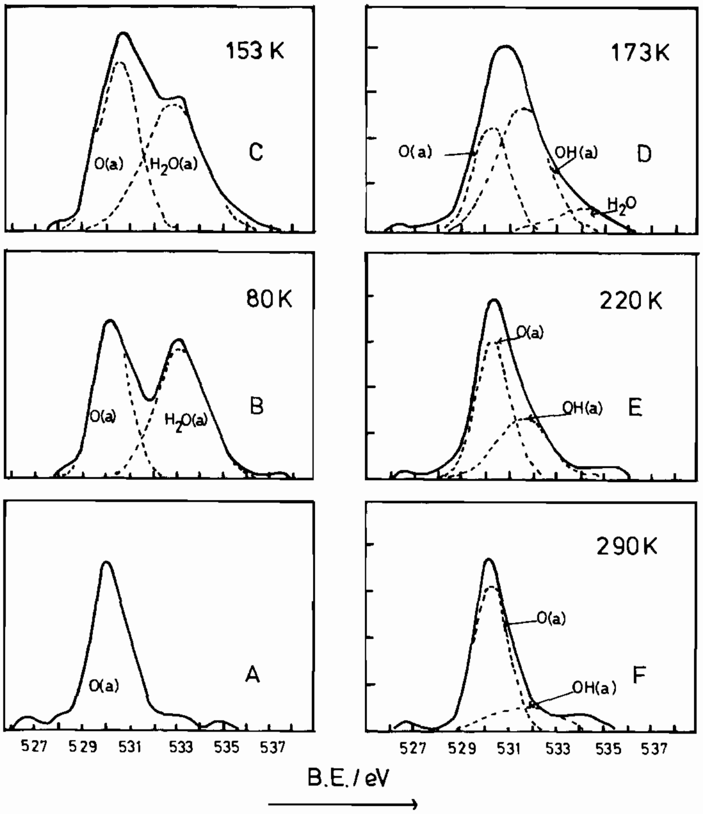


Fig. 4. O(1s) spectra and assignments for exposure of Cu(111)–O surface to water vapour at 80 K and during warming adlayer to 290 K.

surface the molecularly adsorbed water desorbed at appreciably lower temperature (~150 K). It should be noted that desorption (with the clean surface) occurs at about the same temperature as hydroxylation occurs with the Cu(III)–O surface. It is now firmly established that our spectroscopic observations of oxygen induced reactivity with such adsorbates as H_2O and H_2S can be extended to a very wide range of reactants ranging from HCOOH [30] and CH_3-COOH to C_2H_4. Clearly the chemisorbed oxgygen is acting as a strong base extracting, through strong O–H interaction, the otherwise unreactive 'hydrogen'.

What do all of these very recent insights into the surface chemistry of metal dioxygen imply? Firstly, the need to characterise highly labile species and precursors on a wide spectrum of metals, particularly transition metals; for the 'd' block elements, we have limits of understanding of the nature of dioxygen binding in mononuclear complexes; we have no clearly defined and understood cluster complexes; and we have not systematicised the sequence of events which leads to what is known about the oxidation of transition metal surfaces—here dynamic photoelectron spectroscopy promises early results.

Secondly, the results on the bismuth–oxygen species open up the whole issue of photoredox reactions of coordinated species which may or may not be 'stabilised' by interactions with water or other hydrogen atom or proton donors. There is clearly a need to investigate the precursor and labile species in 'd' block metal surfaces; there may emerge indications which are relevant to an understanding of the photoredox reactions of well characterised (bridged) complexes such as those of ruthenium.

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