

MOLECULAR EVENTS AT SOLID SURFACES

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Abstract - The application of Photoelectron Spectroscopy to the study of chemisorption on metal surfaces is reviewed with emphasis on the specificity of adsorbate activation.

INTRODUCTION

Surface Chemistry, in spite of intense and sustained effort for over fifty years, still offers an immense challenge to both the experimentalist and theoretician. This is because it is an intrinsically difficult subject to study at the molecular level with special problems unique to surface science. In reflecting on the development of Surface Chemistry over the last fifty years there were important developments in the "thirties" concerning the concept of activated adsorption, and in the "fifties" suggestions were made regarding possible correlations between catalytic reactivity and electronic structure, the role of d-band vacancies, reactivity patterns based on the classification of metals into transition and sp metals, etc. The possibility of rationalising in this way observed molecular behaviour was, however, rather short-lived. It is equally true that the sophisticated kinetic developments in the early sixties which accompanied the use of ultra-high vacuum techniques were shown to have serious shortcomings. These studies led, for example, to the chemisorption of carbon monoxide on tungsten surfaces to be contrasted with that of nitrogen; the former obeying 1st-order desorption kinetics, (and, therefore, molecularly adsorbed), while the latter exhibited 2nd-order desorption kinetics (and, therefore, taken to be indicative of dissociation). We shall see that both these molecules may be dissociatively chemisorbed at room temperature and that they do not represent two essentially different classes of chemisorption behaviour. Also reactivity patterns based on the electronic structure of metals are shown not to be as clear cut as once suggested and in some cases (e.g. NO and H₂O) hitherto unsuspected molecular gymnastics observed. Much of the impetus for current work in Surface Chemistry has come from the development of Photoelectron Spectroscopy, and I will stress this particular aspect.

EXPERIMENTAL DEVELOPMENTS

Since 1970 there have emerged experimental and theoretical techniques (1) which now enable: (a) the chemical composition of a surface to be defined at the molecular level; (b) the electronic structure of both the surface and adsorbed species (including surface bonding) to be studied; (c) the structural dependence of adsorption to be investigated; (d) the role of ordered-defects on surface reactivity to be ascertained; (e) the surface structure of chemisorbed overlayers to be defined; and (f) the location (site symmetry) of surface species to be determined. This is, by any criterion, an impressive list of developments which almost entirely occurred during the period 1970 - 1980, with the majority having been well established by 1975. Most of these have been the consequence of two complementary approaches to surface characterization (a) the use of photons and the study of the induced electron emission, this is referred to as Photoelectron Spectroscopy, and (b) the scattering (elastic and inelastic) of electrons at solid surfaces. Elastic Scattering (Low Energy Electron Diffraction) provides structural information while inelastic processes (e.g. electron energy loss spectroscopy, EELS,) can give information on surface bonding comparable to the use of vibrational spectroscopy to study gaseous molecules.

Simultaneously with the development of experimental techniques that can probe directly the nature of, and bonding at, solid surfaces, there continued to be interest in the kinetics of surface reactions. The most

fashionable approach has been the application of various forms of 'temperature programmed' studies, analogous to the 'flash-desorption' of Becker (2), Ehrlich (3), and Redhead (4); Madix (5), in particular, has used successfully this approach to study heterogeneous reactions involving "simple" molecules, (e.g. CO, H₂, HCOOH).

In this lecture I will lay most emphasis on Photoelectron Spectroscopy (PES) indicating how by combining core-level or x-ray photoelectron spectroscopy (XPS) with ultra-violet photoelectron spectroscopy (UPS) a detailed picture can be obtained of molecular events occurring at solid surfaces. We will see that considerable benefits can accrue from investigating molecular processes occurring at low temperatures (85K - 295K) since under such conditions the dynamic aspects of the molecular events, with frequently inherently unstable surface species being observed, can be studied (6). Such information is valuable to a better understanding of heterogeneous reactions occurring under very different experimental conditions (higher pressures and temperature) where the detection of the unstable surface species would not be easy. With this point in mind recent experimental developments will also be described where spectroscopic (XPS and UPS) data have been obtained with a "high-pressure" photoelectron spectrometer which enables spectra to be determined of both the surface species and gas phase simultaneously with gas pressures of up to ~ 1 torr.

PES depends on the relationship (Equation 1) between photon energy ($h\nu$) and the kinetic energy (E) of the electron emitted when a solid (or gas) is exposed to radiation (x-ray or u.v.). E_B , referred to as the 'binding energy'

$$E = h\nu - E_B \quad (1)$$

of the electron, allows (a) the identification of the atom involved in the ionisation process, and (b) through small changes in E_B , for a given atom,

the environment of that atom to be ascertained. Although XPS usually involves electron ejection from core-levels, the spectra provide valuable information on chemical bonding, this arises from a relationship between 'effective charge on the atom' and the binding energy of an inner-shell electron. Furthermore, the 'charge on the atom' is closely related to the chemical environment (bonding) of that atom. We shall see that 'chemical shifts' reflected in small changes in binding energy of a given core-level electron of a given atom (e.g. O(1s), N(1s), and C(1s)) play a vital role in unravelling the details of molecular events at solid surfaces.

Complementary valence-level spectra (UPS) do not, however, in general provide a chemical identification of surface species. XPS is unique in this respect enabling all elements (other than hydrogen) to be recognised by their core-level spectra. The general expression for the intensity I of photoelectrons of kinetic energy ϵ_i is given by equation (2), where A is a

spectrometer constant, n_i the concentration of atoms of the i th species, μ_i the photoionisation cross-section, and λ_i the photoelectron escape depth (inelastic mean free path) of electrons of kinetic energy ϵ_i . The parameter

$$I(\epsilon_i) \propto A n_i \mu_i \lambda_i \quad (2)$$

λ_i varies with the kinetic energy of the emitted electrons and is ~ 1 nm (10Å) for O(1s) photoelectrons. With precise knowledge of μ_i and λ_i it is possible to estimate the surface concentrations of surface species. A rough guide to the surface sensitivity of PES is that the "sampling depth" is approximately 3λ and about a third of the photoelectron intensity originates from the surface atoms. The contribution from each underlying atomic layer falls off exponentially with depth below the surface. Having established the wealth of surface information that can be obtained from PES it is natural to explore how quantitative information can be extracted from the raw-spectra. Quantification and analysis is greatly facilitated by using computer techniques. Once the data have been digitised there are a variety of numerical methods which enable the maximum of information to be extracted from the raw spectra. For example, careful quadratic smoothing can improve the signal/noise ratio, while more sophisticated techniques such as deconvolution can enhance the resolution by removing spectrum broadening

due either to the x-ray source of the energy analyser. If there is good evidence for the presence of more than one species in the spectrum (and this can be checked in a number of ways) curve fitting is useful for providing quantitative information on their individual concentrations. This usually involves an iterative refinement of the individual parameters needed to describe the (Gaussian or Lorentzian-shaped) individual peaks until their sum matches accurately the experimental profile.

Although the potential application of Electron Energy Loss Spectroscopy (EELS) was clear in 1967 from studies by Propst and Piper (7), who reported spectra for hydrogen adsorbed on W(100), further developments were comparatively slow. In 1971 Edwards and Propst (8) observed energy-loss spectra for a number of diatomic molecules, (N_2 , O_2 , and CO) adsorbed on tungsten surfaces, but only since 1976 has it been possible to identify the nature of atomic and molecular surface species. This is due to the development of experimental methods with high-resolution energy analysis and largely attributed to three groups: Backx, Willis, Feuerbacher, and Fitton at ESRO, Bertolini et al at Villeurbanne, and Ibach and Lewald at KFA Julich.

DIATOMIC MOLECULES

The first adsorbed molecule to be investigated by UPS was carbon monoxide, it was also the first to be studied by combined *in situ* UPS and XPS (9, 10). It has also been given much attention by the other recently developed experimental methods: LEED, and EELS. Although carbon monoxide had become to be generally accepted in the 'sixties' as typifying that class of adsorbate which retains its molecular integrity on adsorption, it became clear from some of the earliest PES studies of its adsorption on the transition metals molybdenum and tungsten, that there was strong evidence for it being dissociatively chemisorbed at room temperature (and even below). The general strategy adopted in PES was to study O(1s) and C(1s) core-level spectra using Al($K\alpha$) radiation ($h\nu \approx 1486$ eV) and the valence spectra using He(I and II) radiation ($h\nu \approx 21.4$ eV and 40.8 eV respectively).

Although 'shifts' in both O(1s) and C(1s) binding energies were indicative of changes in the bonding of carbon monoxide adsorbed on molybdenum during warming of the adlayer from 85K to 295K, the complementary evidence from UPS, where the molecular orbital structure was probed, was vital to establish dissociative chemisorption (11). The correct assignment of the peaks in the He spectra did, however, turn out to be not straightforward; through analogies with metal carbonyls and also from synchrotron studies the peak at 7 eV was assigned to the degenerate 1π and 5σ orbitals and that at 11 eV to the 4σ orbital.

By studying the chemisorption of CO with a range of metals a pattern of reactivity emerged where a correlation was established between the 'state of adsorption' and 'the heat of adsorption'. This has important implications for the mechanism of the surface bonding (12). At 295K the threshold heat of adsorption above which dissociative chemisorption took place was ~ 250 kJ mole⁻¹. Figure 1 shows the reactivity pattern for the molecular-dissociative regimes of CO chemisorption. Stimulated by the experimental evidence for CO being dissociatively chemisorbed in a facile manner the 'surface-carbide mechanism' for the Fischer-Tropsch synthesis of hydrocarbons has again gained favour (13). Broden et al (14a) suggested that the difference in energy between the 4σ and 1π peaks in the He spectra may serve as an indication of the strength of the carbon-oxygen bond. The larger is the separation, the weaker is the C-O bond. This idea was recently used by Fukuda et al (14b) for the CO-Re studies. An experimental approach that is likely to find more extensive application in the unravelling of the detailed mechanism of CO-bonding is the IR-reflection absorption method. On account of its high resolution it will give detailed information not only on the relationship between ν_{CO} and θ but also on the peak-profile including its FWHM value.

Oxygen chemisorption was an obvious candidate for detailed studies by PES in view of the interest in the inherent instability of the chemisorbed layer, there being considerable thermodynamic driving force for surface rearrangement leading to oxygen incorporation and oxide growth. It was this intriguing question that led us in 1964 to follow-up work function

Dissociation				Molecular			
Ti	V	Cr	Mn	Fe	Co	Ni	Cu
Zr	Nb	Mo	Te	Ru	Rh	Pd	Ag
Hf	Ta	W	Re	Os	Ir	Pt	Au

Fig. 1. Reactivity pattern for carbon monoxide chemisorption on metals at 290K; dissociative chemisorption occurs to the left of the heavy line. With iron dissociation is comparatively slow at 290K, and is, therefore, designated as a border-line case.

studies with a different approach (15) namely the monitoring of the energy distribution of photoelectrons ($h\nu \geq 6.2$ eV). Clearly with the emergence of XPS and UPS the scope for such studies was considerably enhanced. In general three kinds of behaviour have been observed: the most usual is the emergence of a single relatively narrow O(1s) peak (FWHM ≈ 1.8 eV) with a binding energy close to 530 eV (± 0.3 eV), with little or no change in the core-level substrate (metal) peaks, secondly (usually at low temperature, 80K) an O(1s) peak at ~ 530 eV which broadens (FWHM as much as ~ 3.5 eV) with increasing oxygen exposure, but which becomes narrow on warming to 295K. And thirdly a more complex behaviour where there is obviously more than just a single O(1s) peak present, accompanied by changes in the metal-substrate core-levels. Molybdenum or tungsten when exposed to oxygen at 295K are examples of the first category. Copper and silver are examples of the second category while nickel and iron at 295K are examples of the third category. Lead (single crystal and polycrystalline surfaces), shows changes in the Pb(4f) core level, but with a single narrow O(1s) peak. Aluminium exposed to oxygen has a broad O(1s) peak at 295 K accompanied by changes in the Al(2p) level (16). The oxidation of bismuth is a special, and interesting case, to which we will return later (17).

The above observations are understood in terms of the following generalisations. If there is a single narrow O(1s) peak with no observable changes in the substrate core-levels then we have an example of dissociative oxygen chemisorption. On the other hand, (usually only observed at low temperature) if the O(1s) FWHM value is large (~ 3 eV) and narrows on warming to higher temperature (~ 295 K), then this is taken to indicate the presence of both dissociative and molecular chemisorption at the lower temperature. This is observed in the Cu(100) + oxygen system (18). This is also observed in the interplay between dissociative and molecular adsorption of carbon monoxide on some transition metals, and explained in terms of back-bonding of metal electrons into the CO antibonding orbitals leading to weakening of the carbon-oxygen bond and ultimately dissociation. Lead is an interesting example in that the O(1s) peak remains narrow throughout the growth of a surface oxide and this is suggested to arise from the known instability of chemisorbed oxygen on lead surfaces, oxide growth occurring from the initial oxygen exposure. LEED and work-function data support this conclusion (19). There are two interesting features of the oxidation of aluminium, the first is that oxygen uptake is faster at 80K than at 295K and the second is the development (figure 2) of discrete structure in the Al(2p) peak with the onset of oxidation (16). The faster oxygen uptake at lower temperature is indicative of the participation of a weakly adsorbed oxygen state at 80K, a characteristic feature of the kinetics of a number of metal chemisorption systems. The structure in the Al(2p) region of the spectrum is interesting in that although it first develops at 80K, its profile alters during warming to 295K (intensity peaking at a higher binding energy) becoming more typical of Al₂O₃. There is, therefore, evidence for a surface oxide (probably oxygen deficient with more covalent-type bonding) being formed first which is not Al₂O₃. With

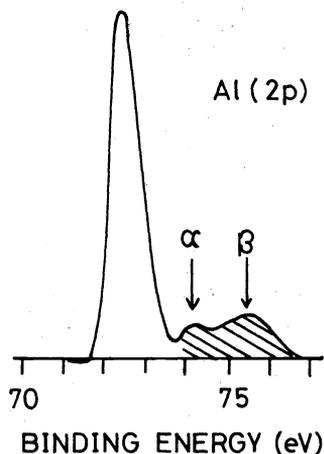


Fig. 2. Discrete structure in the Al(2p) peak during oxygen interaction with aluminium, the α -peak transforms to the β as the temperature is raised from 80K to 295K.

continued oxygen exposure and oxidation the Al(2p) profile moves to higher binding energy compatible with an increase in the ionicity of the Al-O bond. This is consistent with both synchrotron radiation studies of the oxidation of single crystals of aluminium and also work function data (20, 21).

Recent high resolution electron energy loss spectra for oxygen interaction with Ag(110) surfaces at low temperature have been interpreted (22) in terms of molecular dioxygen adsorption with the onset of dissociation as the temperature of the surface is raised to 295K. The low vibrational frequency of the O-O stretch vibration is explained in terms of charge transfer from the metal into the π^* antibonding orbital, i.e. analogous to the model proposed for CO dissociation on metals. Furthermore the O(1s) FWHM at 80K supports the presence of a range of "different" molecular oxygen species, "different" in the sense that the extent of back-bonding varies with coverage, and this is reflected in increasing O(1s) values (i.e. FWHM increases with θ). Similarly a large FWHM O(1s) peak (which narrowed on warming to 295K) was observed with CO adsorption at 80K, largely molecular at this temperature, but dissociated at 295K (10, 11).

COMPLEX CHEMISORPTION

Carbon monoxide is an example where during chemisorption a strong bond (~ 800 kJ mole⁻¹) is broken at low temperature, i.e. with close to zero activation energy. Both fragments C(a) and O(a) are retained by the surface, and this is understandable since with transition metals such as W, Mo, Ti, and Fe, there is a strong thermodynamic driving force for 'carbide' and 'oxide' formation. This, however, need not always be the case. For example, the fragments of dissociation may participate as active intermediates to build up other stable molecules. Such an example is the chemisorption of nitric oxide on both single crystal and polycrystalline copper surfaces (23a). In this case N₂O is generated within the adlayer at 80K following N-O cleavage with the oxygen fragment retained at the surface. At no stage is there any evidence for N(a) being formed, this would be recognised easily through an N(1s) peak at about 397 eV well away from the N(1s) peaks characteristic of NO(a) and N₂O(a). With iron, N-O bond cleavage occurs at 80K and an N(1s) peak emerges at ~ 397 eV. It follows that although N-O cleavage is facile

with copper the nitrogen adatom generated is not chemisorbed at 80K, but is available for further reaction to form $N_2O(a)$, presumably by addition to $NO(a)$ which is known to be present from the $N(1s)$ spectra. An interesting point concerning the generation of N_2O is that it is thermodynamically less stable than NO , the driving force for its formation being the 'oxidation' of copper, for which the $O(1s)$ spectrum provides conclusive evidence.

Detailed analysis of the $N(1s)$ spectra indicate the initial formation of two molecularly adsorbed NO species (figure 3). One of these is characterised

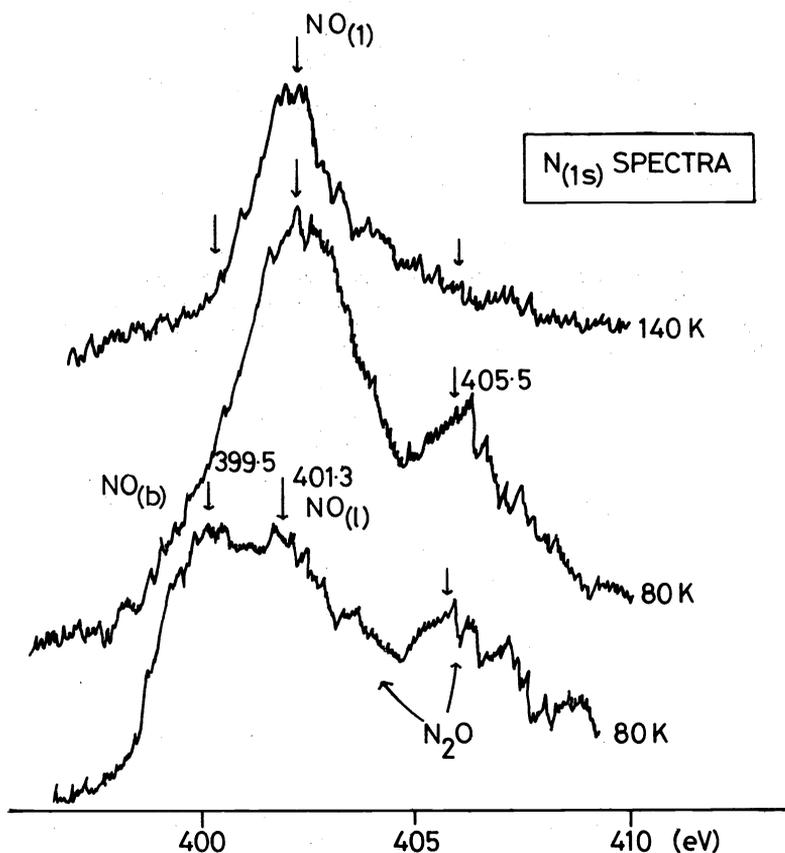


Fig. 3. $N(1s)$ spectra for NO interaction with a $Cu(100)$ surface at 80K and on warming the adlayer to 140K. Peak assignments are given. Corresponding $O(1s)$ peaks are not shown (see reference 23(a)).

by an $N(1s)$ value of ~ 399.5 eV and is the species that undergoes dissociation, while the second ($N(1s) \approx 401.5$ eV) is more weakly chemisorbed and desorbs at ~ 180 K. They have been assigned to 'bent' (or 'bridge-bonded') and linearly bonded NO respectively. Hannoeh and Folman (23b) have recently reported infrared studies of NO interaction with silicon at 77K which they have also interpreted in terms of N_2O formation. Although it was not possible to delineate in such detail the surface species formed on aluminium surfaces (16), similar chemistry was involved, although in this case N(a) was formed initially, and only subsequently did $N_2O(a)$ form. This is in line with the known relative thermodynamic stabilities of copper and aluminium nitrides, although it is kinetic factors that account for the difference in behaviour. There is apparently a small activation energy for N chemisorption on copper reflected by its absence at 80K. This agrees with the experimental observation that with copper at 295K, nitric oxide dissociates to give N(a) and O(a), both fragments being retained at the surface.

CHEMISORPTIVE - REPLACEMENT REACTIONS

An important class of chemisorption reactions has been recognised recently, namely, those that are specifically induced by chemisorbed oxygen. A clear-cut example of this is the dissociative chemisorption of hydrogen sulphide by lead (single crystal and polycrystalline) surface (24, 19). A 'clean' lead surface is inactive to hydrogen sulphide at 295K, on the other hand pre-exposing the lead to oxygen results in dissociative chemisorption of hydrogen sulphide, hydroxylation, followed by dehydroxylation with the replacement of the chemisorbed oxygen by surface sulphide. Each stage in the surface process can be followed by XPS and is complete at ~ 180 K. Similar molecular processes have been observed with Cu(111)-O interactions with both HCl and H_2S (25). Figure 4 shows the curve fitted O(1s) spectra for the Cu(111)-O +

O(1s) AFTER 16L HCl AT 80K

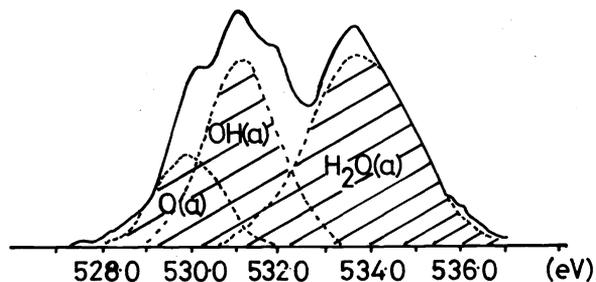


Fig. 4. Curve-fitted O(1s) spectra for the Cu(111)-O + HCl system at 80K (HCl exposure 16L).

HCl system at 80K. Clearly we now have the possibility of studying in detail how the concentrations of all the surface species participating in

the chemisorption-replacement reaction vary with time. We conclude that chemisorbed oxygen activates the S-H and Cl-H bonds resulting in hydrogen abstraction in each case, the driving force for the surface sulphidation (chloridation) coming from the dehydroxylation process, i.e. the formation of H_2O which then desorbs. In the case of lead it is interesting to note that sulphidation of the clean metal by H_2S does not occur readily until above $\sim 400K$ and the sulphide formed does not have the same structure (by LEED) as that resulting from the replacement reaction. We have, therefore, the possibility of controlling the sulphide structure formed, possibly as a meta-stable phase, with characteristic surface properties. These observations have important implications to surface technology ranging from the physics of devices to corrosion.

SURFACE HYDROXYLATION

Having established that chemisorbed oxygen could activate such adsorbates as H_2S it was natural to explore whether chemisorbed oxygen had any specific interaction with a molecular adlayer of water (26). A Cu(111) surface was chosen since it was known that it adsorbed water weakly, desorption being complete at $160K$ ($\Delta H \approx 40 \text{ kJ mole}^{-1}$). Figure 5 summarises the $O(1s)$

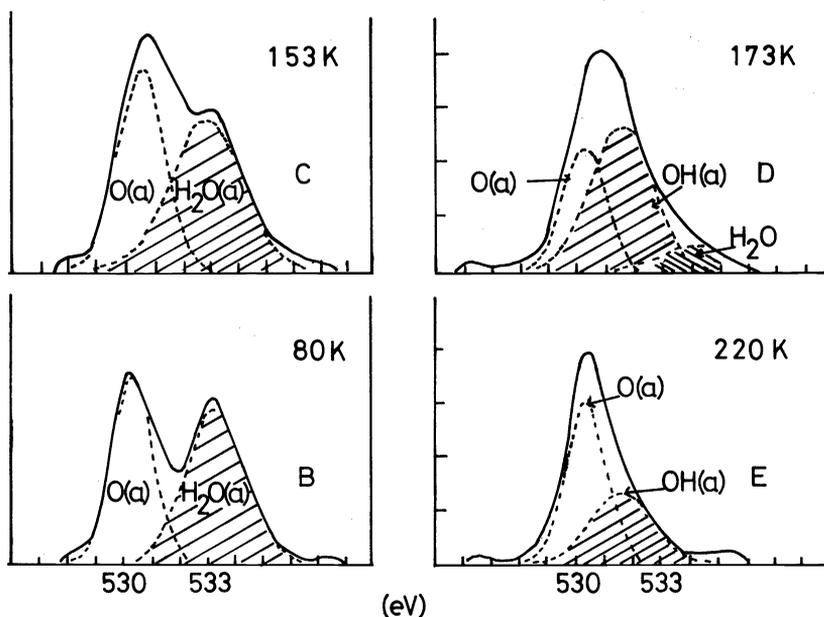


Fig. 5. $O(1s)$ curve-fitted spectra for Cu(111)-O interaction with water vapour in the temperature range 80K to 220K. Note onset of surface hydroxyl formation at $\sim 170K$.

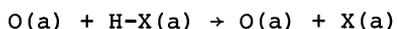
spectra for a Cu(111)-O surface ($\theta_{\text{oxygen}} \approx 0.4$) after exposure to water vapour at 80K and during thermal activation of the adlayer to 295K. The evidence is unequivocal that activation of the adsorbate occurs in the temperature range 160 - 200K when with the clean Cu(111) surface desorption

of the molecular water adlayer would have been complete at 160K. Sexton and Fisher (27) have also reported very similar surface activation effects in the Pt(111)-O + H₂O system. The behaviour of zinc (28) was similar to that of copper and platinum in that surface hydroxyls were generated from water interaction. The hydroxyl species are, however, appreciably more stable and distinct peaks in the valence level (as well as core-level) spectra were assigned to OH(a) and hydrogen bonded, O(a)...H-O-H(a) species. The hydrogen-bonded species are unstable above ~ 170K.

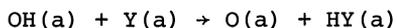
Further studies have established that chemisorbed oxygen can participate in hydrogen-abstraction reactions from a wide range of adsorbates, (NH₃, HCOOH, C₂H₄, CH₃COOH) with direct spectroscopic (mainly XPS) evidence for the formation of surface hydroxyl species (29). Again we see the possibility that chemisorbed oxygen can have a specific activating role in that, for example with Cu(111)-O surface imide (NH) species are formed at room temperature on exposure to ammonia. Kishi and Ikeda (30) have described the chemisorbed oxygen as having strong basic characteristics (so also have Madix et al (31) while Moroney, Rassias, and Roberts (25) have suggested the participation of 'strong hydrogen bonding' as the kinetic driving force for oxygen-induced chemisorption with the thermodynamic driving force a consequence of the formation of water.

When we turn to "bulk oxides" and their reaction with water vapour we find strong analogies with our observations of activation by chemisorbed oxygen on single crystal surfaces. A "completely" oxidized Cu(111) surface ($\theta > 1$) shows no activating effect on H₂O(a), in contrast to the observations with a partially covered ($\theta \approx 0.4$) surface. With bulk Cu₂O or CuO there is also no evidence (32) of hydroxylation by water vapour (at pressures up to 0.5 torr) even up to ~ 450°C. However, if Cu₂O is exposed to oxygen containing traces of water vapour, then surface hydroxylation occurs, the evidence for which is the development of a high binding energy contribution (~ 531.5 eV) to the O(1s) profile. We suggest that the role of oxygen is to provide at the surface, chemisorbed oxygen which then abstracts the 'hydrogen' from water.

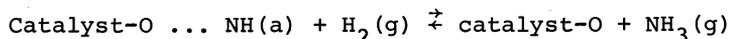
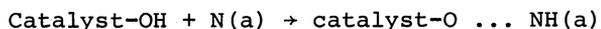
The exact role of water in heterogeneous reactions (corrosion and catalysis) has been a subject of speculation for over fifty years. In 1922 Boswell hypothesised (33) that "adsorbed water plays a vital part in the hydrogenation process". In 1935, Otto Beeck (34) wrote "The great difficulties of proving this (Boswell's hypothesis) ... seems to have led it to receiving little attention". In 1981 we are not much wiser! but the relevance of water vapour is still very much of scientific interest, its significance recently having been recognised by a group at Bell Laboratories in studies of the corrosivity of carbonyl sulphide. In the absence of water vapour COS is essentially inert (Science, 212, 663 (1981)). Although the central role suggested above for activation by chemisorbed oxygen is hydrogen abstraction there is also the possibility that a 'more basic' surface



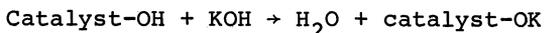
species Y may participate in hydrogen abstraction from the surface hydroxyl. We, therefore, have the presence of water vapour providing a kinetically



favourable route for hydrogenation. Altenburg, Bosch, Van Ommen, and Gellings (35) have made recently some interesting comments relevant to the general role of surface hydroxides in catalytic reactions. They suggest that in ammonia synthesis a possible sequence is



If the surface is loaded with potassium so that the K-OH groups interact with the surface hydroxyls present on the unpromoted iron oxide supported on Al₂O₃ catalyst, i.e.



then the possibility of forming $\text{NH}_{(a)}$ species is eliminated and the predominant surface species is $\text{N}_{(a)}$.

It has recently been shown (36) that β -nickel hydroxide (NiO.OH) exhibits reactivity quite distinct from, and different to, the behaviour of nickel oxides.

HYDROCARBONS

The study of chemisorbed hydrocarbons is important in view of the widespread use of the catalytic conversion of hydrocarbons into valuable chemical intermediates, and in particular their partial oxidation. Central to the mechanism of their oxidation is a proper understanding of the surface bonding and in this context PES has been singularly successful. Spicer et al (37) reported He(I) spectra for C_2H_4 , C_2H_2 and C_6H_6 chemisorption on a nickel, copper and iron surfaces, comparing their data with the earlier spectra of Eastman et al (38). The main conclusions from these studies were that (a) the orbitals of the molecules in the adsorbed state could be recognised and a direct comparison made with the corresponding gas-phase spectrum, (b) that selective shifts in orbital energy occur when a molecule transfers from a weakly adsorbed (physical) state to chemisorption, and (c) a catalytic reaction, for example, the self-dehydrogenation of C_2H_4 on nickel, could be observed spectroscopically. Similarly Mason and his colleagues (39) have shown that with Pt(111) surfaces (in contrast, for example, to nickel) both propene and ethylene are adsorbed molecularly at 290K.

Following observations by PES that O(a) can exhibit specific activation of such adsorbates as H_2S , H_2O , and NH_3 the possibility of Cu(111)-O surfaces activating C-H bonds in C_2H_4 was explored (29). The generation of O(1s) peaks diagnostic of surface hydroxyl species was observed when a Cu(111)-O ($\theta \approx 0.4$) surface was exposed to ethylene at $\sim 370\text{K}$ (figure 6).

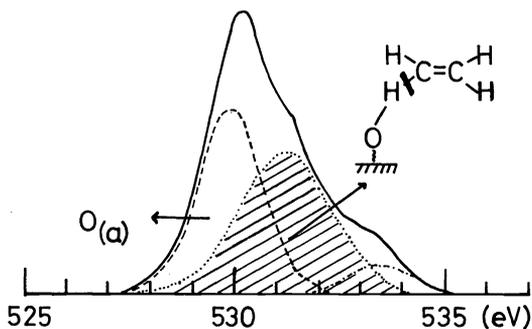


Fig. 6. Curve-fitted O(1s) spectra of Cu(111)-O surface after exposure to $\text{C}_2\text{H}_4(\text{g})$ at 373K. Note evidence for oxygen-induced hydrogen abstraction. C(1s) spectra not shown.

Accompanying the change in the O(1s) profile due to hydroxylation was a C(1s) peak at ~ 285 eV. Similar experiments with atomically clean Cu(111) surfaces generated neither detectable O(1s) nor C(1s) peaks confirming the specific activating influence of O(a). Also for θ (oxygen) ≈ 1.0 there was little evidence for C_2H_4 activation, there is, therefore, a significant role played by the copper (as well as O(a)). The hydrogen-abstraction process

from $C_2H_4(a)$ is clearly an activated process, and much less facile than from $H_2S(a)$, $HCl(a)$, and $NH_3(a)$. Independent evidence for the activating influence of chemisorbed oxygen has also emerged recently from kinetic studies by Somorjai and his colleagues (40). Small amounts (10 - 30% of a monolayer) of oxygen present on platinum surfaces were shown to increase the rate of dehydrogenation of cyclohexene by an order of magnitude, but complete 'oxidation' of the platinum surface renders the surface totally inactive in keeping with the generally accepted 'poisoning' characteristics of oxygen.

Although aluminium is generally regarded as low down in the hierarchy of metal-chemisorption activity, which is compatible with it being an sp metal, observations with nitric oxide (16) indicated that there was no real fundamental distinction between it and such transition metals as copper, nickel and iron (6). It was for this reason that its reactivity to the hydrocarbons, ethylene and acetylene was explored. Figure 7 shows $C(1s)$

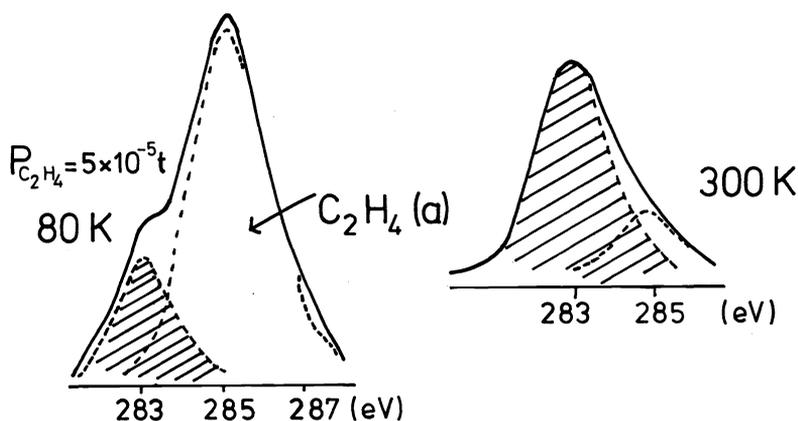


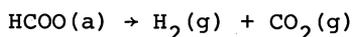
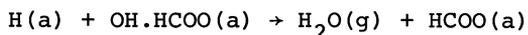
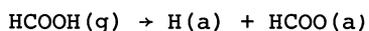
Fig. 7. $C(1s)$ spectra for C_2H_4 interaction with aluminium surface at 80K and after warming the adlayer to 300K.

spectra for the adsorption of ethylene (41) on a polycrystalline surface at 80K and after warming of the adlayer to 300K. It is clear that although adsorption is initially mainly molecular at 80K, the He spectra indicating clearly the M.O structure of the ethylene molecule, there is a slow transition (dissociation) reflected in the $C(1s)$ profile moving to lower binding energy and the gradual erosion of the 'peaks' in the He-spectra. Both these are accelerated on warming the adlayer to 300K. The experimental evidence is interpreted as indicating facile C-C bond cleavage confirming the high 'bond-breaking' ability of aluminium, both N-O and C-C cleavage occurring with close to zero activation energy. The high reactivity of aluminium to other organic molecules (CH_3OH) was also reported recently by Rodgers et al (42). By using PES they showed that methanol adsorption at 130K was molecular but above 170K a surface methoxide formed. This methoxide was stable up to 500K, but then decomposed to give CH_4 .

LIGAND EFFECTS IN CATALYSIS

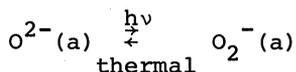
A feature of recent PES studies has been the experimental evidence for the role of mixed-ligands in heterogeneous reactions. In particular the involvement of surface hydroxyls has been shown to have an important stabilising influence on chemisorbed formate species (43). For example atomically clean lead surfaces are comparatively inert to formic acid vapour at room temperature, on the other hand, the surface hydroxy-formate, formed by exposing 'oxidised' lead surfaces to formic acid vapour, is stable in vacuo at 295K. However, further exposure of this surface to $HCOOH(g)$ leads to the hydroxy-formate adlayer decomposing to give essentially an atomically

clean lead surface. Presumably the hydroxyl ligand stabilises the adlayer, a vacant ligand-site being a pre-requisite for the formate to decompose (6). When the surface hydroxyl is removed (as water) on exposure to HCOOH(g) the formate decomposes:-



This observation resembles the manner in which, for example, a chloride ligand stabilises the hydroxypalladation adduct against "ordinary" decomposition thus allowing it to interact with the CuCl_2 (essential) in the transition state to give the observed products.

PES studies (17) of the bismuth + oxygen system have revealed the photo-induced conversion of adsorbed oxygen at 140K to an inherently unstable second oxygen species. The latter is reconverted thermally to the initial state on warming the adlayer (in the absence of photons) to 295K. We have tentatively suggested that there is interconversion between O^{2-} (a) and O_2^- (a) which has analogies with photoredox reactions in the homogeneous phase.



Clearly to observe high catalytic selectivity stabilisation of the superoxide (or peroxide) species would be necessary a view which carries over to discussions of oxygen or oxygen transfer processes in homogeneous and biological systems. This may also be the central issue in heterogeneously catalysed selective oxidation reactions.

GENERAL COMMENTS

The subject of Surface Chemistry is at an important "cross roads" in its development. Whether we see it develop at a rate commensurate with the advances made over the last decade will depend on whether or not sufficient impetus is generated at both the fundamental and technological frontiers. It is for the first time possible to obtain detailed information at the atomic level regarding solid surfaces, and this is relevant to a wide range of technological areas. There is, I believe, at present no comparable situation in the Physical Sciences. A proper understanding of interfacial science in all its various ramifications is long overdue. It would undoubtedly lead to possible improvements in existing catalysts and the development of new ones, the understanding of metallic corrosion (including the role of water vapour), and a better knowledge of the factors that influence adhesion, lubrication, and electrode reactions. Some of the examples I have chosen to discuss in my lecture have a direct bearing on these topics, others reflect mere academic curiosity!

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