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Surface Reactivity as Revealed by Photoelectron Spectroscopy [and Discussion]

C. T. Au, A. F. Carley, M. W. Roberts, J. M. Thomas and F. S. Stone

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Surface reactivity as revealed by photoelectron spectroscopy

By C. T. Au, A. F. Carley and M. W. Roberts
Department of Chemistry, University College, Cardiff CF1 1XL, U.K.

The chemical specificity induced by chemisorbed oxygen at atomically clean surfaces is shown to have diverse implications for the fundamental mechanisms of surface processes. Photoelectron spectroscopy, used in a dynamic mode, has enabled the synergistic chemistry associated with the chemistry of coadsorbed molecules (nitric oxide with water and ammonia) at Zn(0001) and Mg(0001) surfaces to be attributed to the activation of the O–H and N–H bonds. The step-wise reduction of chemisorbed nitrogen to NH(a) and NH_2(a) has been established; with Mg(0001) dehydrogenation of the surface amide rather than complete hydrogenation to NH_3(g) favoured. The reaction pathway is critically dependent on temperature, the concentrations of O^{2-}(a) and OH(a) and the strength of the zinc–nitrogen and magnesium–nitrogen bonds.

At Mg(100) surfaces preadsorbed oxygen, through an electrostatic (ligand) effect, controls the two chemisorption states of acetic acid, one involving sp^3 and the other sp^2 hybridization. Analogous ligand effects are involved in the correlation established between the reactivity of chloride overlayers at pB(110) surfaces and the presence of surface oxygen. In the reaction of halogen hydrides with Pb(110), surface oxygen plays two distinct roles: activation of the halogen hydride and stabilization of the chloride overlayer. The surface oxygen is a prerequisite for both the generation of the overlayer and the reactivity of the overlayer. Two distinct types of oxygen are invoked, one of which is subsurface.

Oxygen interaction with nickel and titanium has been shown through analysis of Ni(2p) and Ti(2p) spectra to involve variable oxidation states. Ti^{2+} and Ti^{3+} are formed preferentially at the titanium–overlayer interface while Ti^{4+} is predominantly at the oxide–gas interface. A localized bonding model for the oxygen overlayer is suggested, which also has analogies with observations made of mixed-halide (chloride and bromide) overlayers at Pb(110) surfaces.

INTRODUCTION

In 1972 the late J. W. Linnett, who reported the first u.v.-induced photoelectron spectrum from a metal surface (Bordass & Linnett 1969), organized a Royal Society Discussion Meeting where some new approaches to the study of solid surfaces were described. During the last decade the understanding of the chemistry of solid surfaces at the atomic level, particularly of metals, has developed rapidly, largely through surface-sensitive spectroscopic methods becoming available and in which photoelectron spectroscopy has played a significant part.

One of the first problems investigated by photoelectron spectroscopy relevant to heterogeneous catalysis was the role of dissociative and molecular chemisorption régimes in the surface chemistry of carbon monoxide (Kishi & Roberts 1975*a*) with obvious implications for the mechanism of the Fischer–Tropsch reaction. The approach was to explore valence by u.v.-induced photoelectron spectroscopy (u.p.s.) and core-electron levels by X-ray-induced photoelectron spectroscopy (X.p.s.) by using a spectrometer capable of working at ultra-high vacuum (Brundle & Roberts 1972). This work was extended to other analogous molecules such as nitric oxide (Johnson *et al.* 1979; Carley & Roberts 1978) and also to adsorbate activation by surface additives (promoters), which in some cases leads to the chemisorptive replacement of the promoter (Kishi & Roberts 1975*b*). Activation of adsorbates by chemisorbed oxygen has since been investigated widely (Au *et al.* 1979, 1982; Au & Roberts 1981; Carley *et al.* 1983; Stuve *et al.* 1981). A disappointing feature, however, has been the lack of information on the nature of the chemisorption bond that has emerged from the core-level spectra of the substrate metal. It has become clear recently that this, in the main, is due to an inability to extract from raw spectra the 'hidden information' diagnostic of changes in the electronic state of the metal. Recent developments have shown that with careful spectral analysis evidence for the presence of variable oxidation states at metal surfaces can be obtained, which throw a new light on the question of surface bonding, defects and their relevance to catalytic activity, particularly of oxides. Through dynamic photoelectron spectroscopic studies surface interactions involving bond cleavage, chemical specificity arising from surface additives and the defect or redox nature of both bulk oxides and oxide overlayers at metal surfaces have been established. In this paper examples are chosen to illustrate the diverse information now possible from photoelectron spectroscopy.

EXPERIMENTAL

The photoelectron spectrometers have been described elsewhere (Brundle & Roberts 1972; Brundle *et al.* 1974; Braithwaite *et al.* 1975). To extract the maximum amount of information from photoelectron spectra, it is essential that the spectrometer is interfaced to a data system; the data systems used in these studies are based on an Apple II+ microcomputer (Carley 1982), the software for which has been produced in-house. Data processing in u.p.s. is restricted to smoothing and primitive spectral subtraction.

X-ray photoelectron spectra frequently consist of two or more overlapping peaks; the decomposition of such profiles allows the quantification of the various surface species, which is crucial for understanding the mechanism of surface reactions. After smoothing and background removal we used a curve-fitting technique, based on a least-squares minimization program, to decompose the X-ray-induced spectra of adsorbates with use of Gaussian profiles for the adsorbate peaks.

The analysis of metal core-level spectra in terms of shifted components, for example during the early stages of oxidation, has been generally neglected. One reason for this, apart from the fact that the raw spectra in such cases often give little indication that anything of interest can be extracted, is that core-level spectra from metals have a complicated theoretical line-shape, which often exhibit a pronounced asymmetry, moderated by instrumental broadening effects. Moreover, the background level is usually much higher than for adsorbate spectra and thus needs to be described more accurately. An alternative to curve fitting in these cases is spectral subtraction. The 'mechanics' of generating difference spectra and the criteria used for assessing the quality of the result are discussed in detail elsewhere (Carley *et al.* 1984; Carley *et al.* 1985*a*). The intensities of the individual spectral components may be used to determine surface concentrations of the species present (Carley & Roberts 1978).

RESULTS AND DISCUSSION

Four different aspects of our recent work are chosen to illustrate the impact that photoelectron spectroscopy is having on the understanding of molecular processes at metal surfaces. They are: complex chemisorption including molecular isomerization; synergistic chemistry of coadsorbed molecules including the hydrogenation of surface nitrogen; oxygen chemisorption and metal oxidation and surface halogenation.

Complex chemisorption

The chemisorption of nitric oxide is complex even at temperatures (80 K) that might have been anticipated to exert significant kinetic control. With both Cu(111) and Cu(100) surfaces, in addition to dissociative chemisorption, there are present two different molecularly adsorbed states assigned as NO(b), bridged or bent species, and NO(l), a linear species, and also $N_2O(a)$ at 80 K (Johnson *et al.* 1979). Comparison with other metals (aluminium, iron, zinc, magnesium and nickel (Carley & Roberts 1978; Kishi & Roberts 1976; Carley *et al.* 1979 and Au & Roberts 1984*a*)), indicates that subsequent to cleavage of the nitrogen–oxygen bond there are three routes that the transient nitrogen adatom N(s) can take:

(*a*) $N(s) \rightarrow N(a)$, chemisorbed nitrogen adatoms;
(*b*) $2N(s) \rightarrow N_2(g)$, dinitrogen desorption,
(*c*) $N(s) + NO(a) \rightarrow N_2O(a)$, ‘addition’ reactions.

Although the oxygen adatom is very efficiently trapped to generate chemisorbed oxygen and surface oxide, in each case the fate of the N(s) species is both highly metal specific and sensitive to temperature. This point is well illustrated by Cu(100) and Cu(111) surfaces, which at 295 K, and in contrast to 80 K, form strong copper–nitrogen bonds (Johnson *et al.* 1979). There is clearly a small but finite activation energy ΔE for chemisorption of N(s) with both Cu(100) and Cu(111) surfaces. However, with aluminium and iron the value of ΔE is significantly smaller since metal–nitrogen bond formation occurs at 80 K, i.e. at the expense of the addition reaction leading to formation of $N_2O(a)$. The precise reason for this is not known although the pattern of *kinetic behaviour* is in line with the relative *thermodynamic* stabilities of the nitrides of the metals. The heats of formation of the bulk nitrides $\Delta H_f^\ominus$ are as follows: Zn_3N_2, -29 kJ mol^{-1}; Mg_3N_2, -462; Al_3N_2, -240; Fe_3N_2, -10.5 and Cu_3N, $+72$. What is also clear is that we are unable to distinguish between the role of d-electrons and sp-electrons in determining the chemical reactivity of metal surfaces to nitric oxide; the sp-metals (Zn, Ma, Al) are at least as active as d-metals (Ni, Fe). For a Mg(0001) surface, a feature that sets it apart from copper is the complete absence of NO(b), one of the two molecularly adsorbed species.

Specificity in the adsorbed state leading to selectivity of reaction products is a central factor in heterogeneous catalysis; for example the reactivity of formic acid at ZnO(0001)–O surfaces can be explained in terms of an intramolecular hydrogen transfer process within the adsorbed molecule (Au & Roberts 1984*b*). In the present paper we provide unambiguous evidence for two states of adsorbed acetic acid at a magnesium surface at 80 K. The C(1s), O(1s) and Mg(1s) spectra are shown (figure 1). There are three significant features.

(*a*) The C(1s) spectrum at 80 K exhibits two components, that at a binding energy of 291.5 eV is assigned to the carboxylate group, while the intensity of the second at 286.7 eV

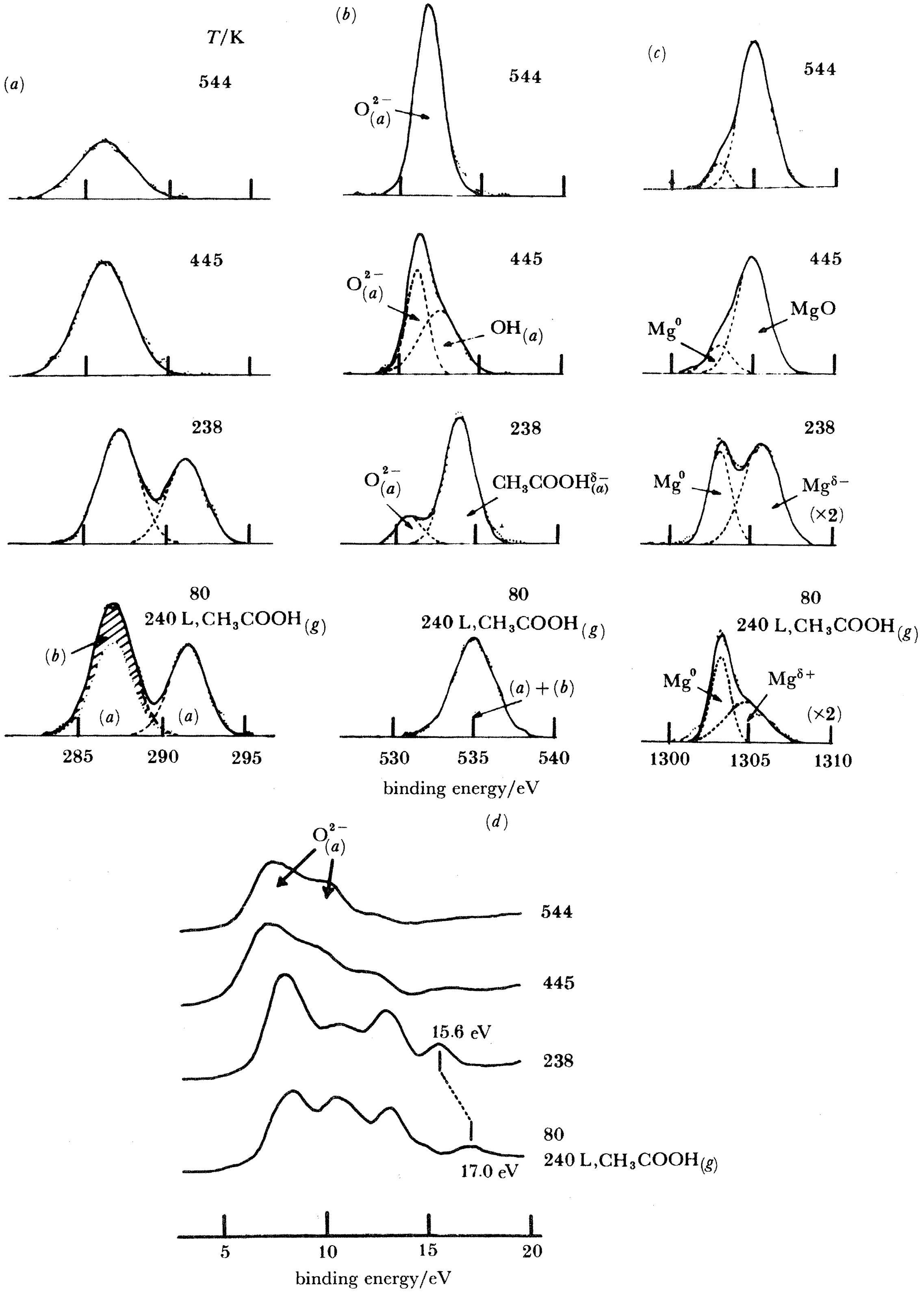


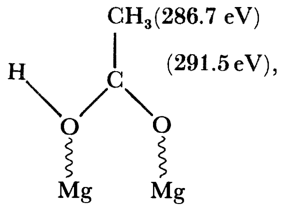
FIGURE 1. (*a*) C(1s), (*b*) O(1s), (*c*) Mg(1s) and (*d*) He(II) spectra for a magnesium surface exposed to CH_3COOH(g) (10^{-6} Torr) at 80 K and warming to 544 K. C(1s) and O(1s) data were obtained with a pass energy of 50 eV and 20 eV, respectively, and an X-ray power (Mg Kα radiation) of 400 W. Mg(1s) data were determined at a pass energy of 10 eV and an X-ray power (Al Kα radiation) of 400 W. 1 Torr = 101 325/760 Pa. 1 L = 1.33×10^{-4} N s m^{-2}.

is substantially greater. In addition to a contribution to the intensity from the methyl group, a second carbon species is obviously present in the adsorbed state, which has associated with it a similar C(1s) binding energy (*ca.* 287 eV). The ratio of the intensities at 286.7 eV and 291.5 eV is about 3:2 at 80 K. At a Zn(0001) surface at 80 K the two C(1s) peaks are of the same intensity, indicating the presence of only one species; the latter is physisorbed. As the temperature increases above 80 K intensity is *transferred* from the 291.5 eV peak to that at 286.2 eV.

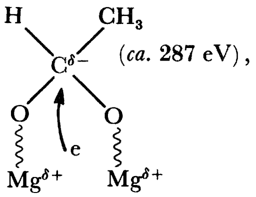
(*b*) The Mg(1s) spectrum at 80 K, and more obviously on warming the adlayer to 238 K and 445 K, exhibits a second high binding energy component at 1305.8 eV, which compares with a Mg(1s) value at 1303 eV for Mg^0. Clearly the surface magnesium atoms have associated with them substantial ionicity ($Mg^{\delta+}$) when the carboxylic acid is adsorbed even at 80 K. The intensity associated with $Mg^{\delta+}$ increases with increasing temperature (figure 1), which correlates with the transfer of intensity from the 291.5 eV peak to the 286.7 eV in the C(1s) spectral region. (*c*) The O(1s) spectra exhibit a single broad peak (535.0 eV) at 80 K with *no evidence* for any intensity at 530.7 eV, which would be expected if carbon–oxygen bond cleavage had occurred. However, at 239 K and above, a second component does emerge at 530.7 eV. The higher binding energy component is assigned to COOH(a); with increasing temperature surface oxide develops.

We suggest that the two structural isomers of acetic acid (*a*) and (*b*),

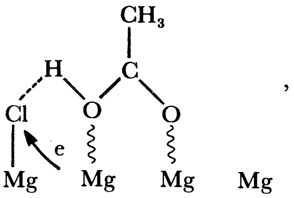
(*a*)



(*b*)



(*c*)



exist in the adsorbed state at a magnesium surface at 80 K, resulting from an intramolecular hydrogen rearrangement, which results in the carbon atom of the carboxylate grouping changing from sp^2 to sp^3 hybridization. The high binding energy of the carbon atom (291.5 eV) associated with the carboxyl group in the absorbed state suggests that it is highly electropositive. It is, therefore, not surprising that electron transfer from the magnesium substrate occurs, which causes the formation of a second species characterized by a C(1s) peak 5 eV lower in binding energy. Surface bonding at 80 K is ionic in character, as indicated by the Mg(1s) peak at a binding energy nearly 2 eV greater than that characteristic of Mg^0. The relative proportions of the two species may be controlled by the preadsorption of either oxygen or dichlorine, which suggests that the H-transfer process is inhibited by electrostatic interaction (*c*). Furthermore, the highly electronegative chlorine adatom inhibits electron transfer to the carboxyl carbon species from the magnesium surface. Thus very little of the second isomer is present at a chlorine pre-treated surface. That electron transfer occurs from the magnesium substrate to the adsorbate is further substantiated by the He(II) induced spectra (figure 1), which show a progressive increase in intensity at 15.6 eV, at the expense of the 17.0 eV peak, in the temperature range 80–323 K and indicative of the involvement of the s-band of CH_3COOH(a). The other peaks in the He(II) spectrum may be assigned to orbitals, associated with CH_3COOH(a) but shifted by about 3 eV to lower energy compared with CH_3COOH(g).

Above 400 K the four-band structure changes drastically and this is associated with the decomposition of the surface acetate; at 554 K only the O(2p) bands at 7.4 eV and 10.0 eV due to surface oxide are observed.

Adsorbate activation and the synergistic chemistry of coadsorbed molecules

Photoelectron spectroscopy has delineated the molecular details of the specific role that chemisorbed oxygen can have in adsorbate activation at metal surfaces, there now being experimental evidence for oxygen activation of S–H bonds in hydrogen sulphide, N–H bonds in ammonia, O–H bonds in water and alcohols and also C–H bonds in hydrocarbons (Roberts 1980). In each case surface hydroxylation is observed and for H_2S(g) and NH_3(g) replacement of surface oxygen by sulphur and nitrogen. These processes are facile occurring at low temperature (150 K) and with small activation energies (under 80 kJ mol^{-1}). Extended Hückel calculations (Ruckenstein & Halachev 1982) made by using model metal clusters and surface additives provide general support to the conclusion from spectroscopic studies that surface additives can control the electron density at the metal surface atoms and hence the profile of the potential energy curve for the activation (leading to dissociation) of molecules at metal surfaces. It was a natural development of these ideas to explore the molecular details associated with the chemistry of coadsorbed molecules at surfaces. The particular question we set out to answer was whether a molecule such as nitric oxide, known to dissociate in the chemisorbed state, could activate a molecule (either in the adsorbed or gaseous phase) and influence the reaction pathway. Metal substrates were chosen (for example Zn(0001)) so that one of the coadsorbates, water, was inherently unreactive in the absence of the second, nitric oxide. It was established (Au & Roberts 1984*a*) that when coadsorbed, molecularly adsorbed water, unreactive at the atomically clean Zn(0001) surface (Au *et al.* 1982), generated surface hydroxyl species at about 150 K. Furthermore these species participated in the hydrogenation of nitrogen adatoms generated by the dissociative chemisorption of nitric oxide. At 320 K the hydrogenation of N(a) via NH(a) and NH_2(a) to NH_3(g) is complete. In the absence of coadsorbed water the surface nitride species are thermally stable up to at least 450 K.

The mechanism by which surface 'nitrogen' is hydrogenated is relevant not only to the catalytic reduction of nitric oxide and the mechanism of motor exhaust catalysts, but also in understanding the elementary steps in ammonia synthesis and, by analogy, the hydrogeneation of carbon monoxide and its relevance to the mechanism of the Fischer–Tropsch synthesis. The conclusions from the study of the 'zinc' catalysed reduction of nitric oxide led us to investigate a number of different coadsorbed molecules with nitric oxide and including water and ammonia. The aim of the study was to explore whether synergistic effects analogous to those observed in the Zn(0001)–nitric-oxide–water system were of more general significance in surface chemistry and in particular in controlling the elementary steps involved in nitrogen hydrogenation, i.e. N to NH, NH_2 and NH_3. There were good reasons for choosing Mg(0001) surfaces since they were known to be active for the dissociative chemisorption of water vapour (Campbell *et al.* 1985) and were expected to show analogous behaviour to Zn(0001), both being sp metals. There were, however, very distinct differences. When a Mg(0001) surface is exposed to nitric oxide at 80 K the N(1s) spectra indicate the presence of three 'nitrogen' species: N(a), NO(l) and N_2O(a). On warming to 190 K nitrous oxide desorbs while intensity develops at 400.8 eV; the latter is clearly an activated process and is associated with $NO\cdots O^{2-}$(a) interaction. There is also infrared spectroscopic evidence (Pozdnyakov & Filimonov 1973) for coordinated NO species at the surface of bulk MgO. The nitride N(a) species at 396.0 eV is stable up to 450 K with little change in intensity over the whole temperature range. The O(1s) spectra support these assignments (Au *et al.* 1985*a*).

The species formed by the dissociative chemisorption of nitric oxide at Mg(0001) surface at 295 K are readily hydrogenated on exposure to water vapour at the same temperature (figure 2*a*). The N(1s) spectrum indicates that NH_2 species are present, while in the O(1s) spectrum there is evidence for surface hydroxyl species. Water is dissociatively chemisorbed by Mg(0001) and confirmation of the generation of hydroxyl species has been obtained from electron energy loss spectroscopy (Campbell *et al.* 1985). The molecular events that occur when a coadsorbed layer (NO and H_2O) is formed at a Mg(0001) surface at below 130 K and the temperature increased slowly to 480 K are shown in figure 2*b*. Hydrogenation of the chemisorbed nitrogen adatoms occurs up to 300 K, with some desorption of ammonia, but at 400 K dehydrogenation of the NH_2 to a stable nitride, rather than further hydrogenation, is the dominant process. Therefore Mg(0001) appears to differ from Zn(0001), where complete hydrogenation had taken place by 300 K (Au & Roberts 1984*a*). The difference is likely to be due to the hydrogen transfer step from the hydroxyls present at Mg(0001) surfaces (figure 2*a*) being more difficult and also to the greater stability of the magnesium–nitrogen bond.

In view of the relative ease of activation of the O–H bond when water is coadsorbed with nitric oxide at a Zn(0001) surface, we explored whether this is a more general phenomenon. Ammonia was chosen as a coadsorbate since it is not adsorbed to any significant extent at a

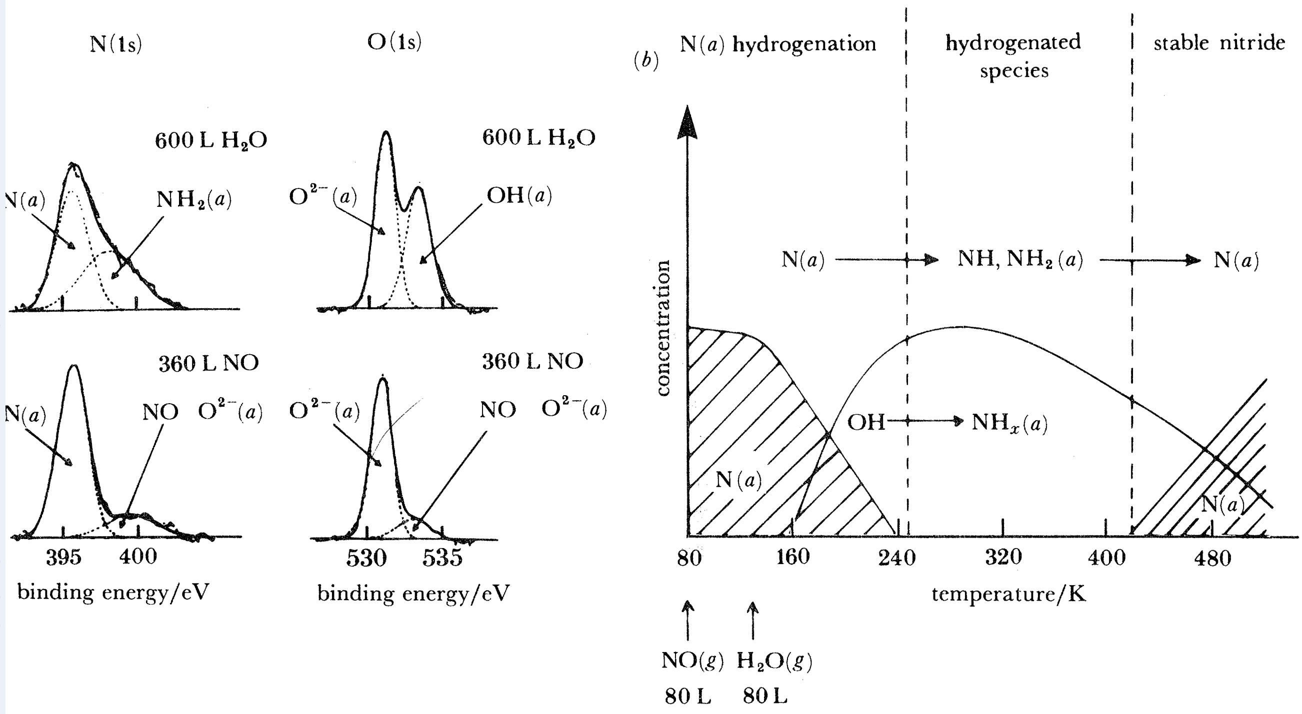


FIGURE 2. (*a*) N(1s) and O(1s) spectra for Mg(0001) surface exposed to NO(g) (10^{-6} Torr) and then H_2O(g) (10^{-6} Torr) at 295 K. N(1s) and O(1s) spectra were obtained with pass energies of 50 eV and 20 eV respectively and an X-ray power (Mg Kα radiation) of 400 W. (*b*) Schematic diagram of hydrogenation and dehydrogenation of surface nitrogen species at a Mg(0001) surface first exposed to NO(g) (10^{-6} Torr) at 80 K and then to H_2O(g) (10^{-6} Torr) at 130 K followed by heating to 540 K.

Mg(0001) surface at 295 K. At 80 K physical adsorption occurs, but desorption is complete at 200 K which, making use of the Frenkel equation, suggests a heat of adsorption of no more than 35 kJ mol^{-1}. The N(1s) binding energy of NH_3(a) at 80 K is at 401.8 eV. Figure 3 shows N(1s) spectra observed at 295 K; there are two distinct components one at 396.0 eV and the other at 399 eV. The former is obviously due to chemisorbed nitrogen adatoms, N(a), generated in the dissociative chemisorption of nitric oxide, while that at 399 eV is what would be expected from an NH_2(a) species (Matloob & Roberts 1977). In view of the relative inactivity of magnesium surfaces to NH_3(g) at 295 K it is clear that activation of the nitrogen–hydrogen bonds is induced by nitric oxide. Since the dissociative chemisorption of NO is facile it is reasonable to suggest the formation of the stable O^{2-}(a) at a Mg(0001) surface is rapid. However, since the OH(a) component of the O(1s) spectrum is very small at this stage (figure 3), we suggest that the reaction pathway for the reduction of nitric oxide by ammonia is:

$NO(g) \rightarrow N(a) + O^{2-}(a)$, dissociative chemisorption;
$O^{2-}(a) + NH_3(g) \rightarrow OH^-(a) + NH_2(a)$, N–H bond activation†;
$N(a) + OH^-(a) \rightarrow NH(a) + O^-(a)$, hydrogen transfer;
$O^-(a) \rightarrow O^{2-}(a)$, metal oxidation;

$$\left.\begin{array}{l} H(a)+NH \rightarrow NH_2(a) \text{ and} \\ NH_2(a)+H(a) \rightarrow NH_3(g), \end{array}\right\} \begin{array}{l}\text{stepwise reduction} \\ \text{of chemisorbed nitrogen.}\end{array}$$

At low surface coverages the surface hydroxyl species are unstable and result in metal oxidation with hydrogen transfer leading to hydrogenation of the nitrogen adatoms. There are, therefore, two possible routes for surface-amide formation. Quantitative analysis of the N(1s) and O(1s) spectra indicate that in the final state at 295 K the concentration of nitric oxide dissociated is 0.45×10^{15} cm^{-2} (estimated from the total O(1s) intensity) and the quantity of amide formed is also 0.45×10^{15} cm^{-2}. The concentration of chemisorbed nitrogen is 0.33×10^{15} cm^{-2}, so that the loss of nitrogen adatoms is 0.12×10^{15} cm^{-2}. This may be due to dinitrogen desorption, although a more likely possibility is that it has occurred through step-wise reduction to ammonia, which then desorbs. The concentration of surface hydroxyls that have dissociated is 0.38×10^{15} cm^{-2}, which is sufficient to supply the necessary hydrogen atoms for nitride reduction.

The N(a) and NH_2(a) species (figure 3) on exposure to water vapour (30 L‡, 295 K) hydrogenate to NH(a) and NH_3(g), the total surface 'nitrogen' concentrations before and after exposure to water vapour being 0.78×10^{15} cm^{-2} and 0.38×10^{15} cm^{-2}, respectively. It is obvious from the corresponding O(1s) spectra (figure 3) that dissociative chemisorption of H_2O(g) has occurred, resulting in increased intensity at 531 eV, O^{2-}(a), and 533 eV, OH(a). We estimate that 1.2×10^{15} hydrogen atoms per square centimetre are generated by this process, which is more than sufficient to hydrogenate the N(a) and NH_2(a) species. Further hydrogenation can occur only by increasing the temperature that effects hydroxyl dissociation accompanied by surface oxidation, i.e.

$$OH^-(a) \rightarrow O^-(a) + H(a),$$

$$O^-(a) \xrightarrow{e} O^{2-}(a).$$

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† See note added in proof.
‡ 1 L = 10^{-6} Torr s.

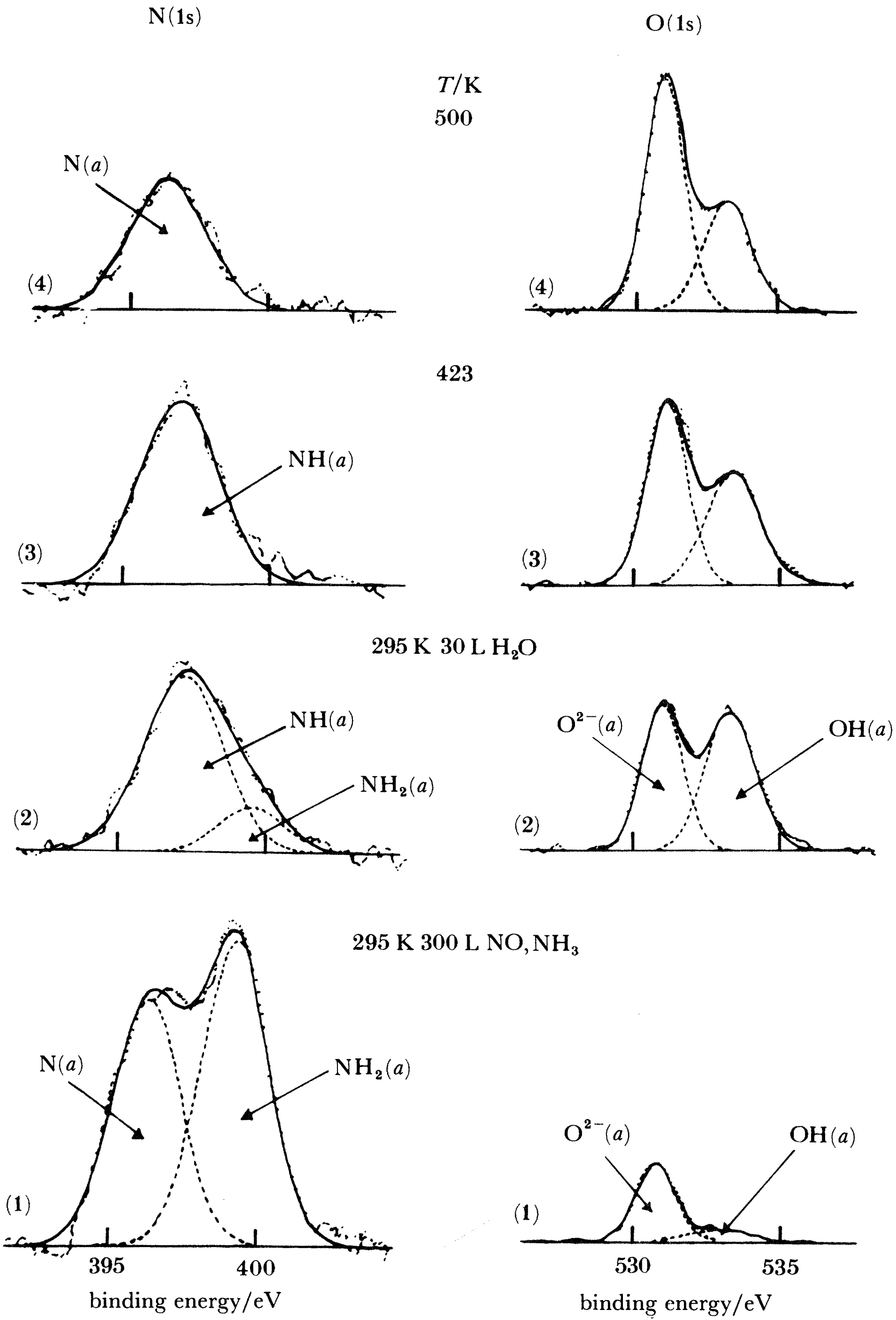

FIGURE 3. N(1s) and O(1s) spectra for a Mg(0001) surface: (1) exposed to a mixture of NO(g) and NH_3(g) (10^{-6} Torr; NO:$NH_3 \approx 1:5$) at 295 K; (2) exposed to H_2O(g) (10^{-6} Torr); (3) and (4) followed by warming to 423 K and 500 K, respectively. Analyser conditions as in figure 2.

Chemisorption of oxygen, oxygen overlayers and mixed-valence states

Photoelectron spectroscopy, mainly X-ray-induced, has recently provided detailed information on the defect nature of nickel oxides (Roberts & Smart 1984) and also on the chemisorption of oxygen at both nickel single-crystal surfaces (Carley *et al.* 1984, 1985*a*) and also polycrystalline nickel (Srinivasan *et al.* 1979 and references therein). The particular aspects discussed relevant to the present work may be summarized as follows: the nature of, and bonding involved in, oxygen chemisorption; the stability of the chemisorbed oxygen adatoms with respect to surface rearrangement and oxide formation; whether there is evidence for defect or mixed-valence states and the relevance of the experimental data to contemporary theory. Although there have been extensive studies of oxygen interaction with nickel surfaces by a variety of experimental techniques, work function and photoemission (Quinn & Roberts 1963, 1965), kinetic and photoelectron spectroscopy (reviewed by Wandelt 1982), questions relating to the defect nature of thin oxide overlayers, i.e. explicit evidence for Ni^{3+} states, have largely remained unanswered. Of general significance is also the relation (if any) between the surface and bulk defect (equilibrium) concentrations, not only for bulk oxides but also during the growth of oxide overlayers at single-crystal metal surfaces.

Although core-level spectra from metal substrate peaks have rarely provided any quantitative data on the participation of variable oxidation states in metal–oxygen interaction, there have been some examples where features present in core-level spectra after extensive oxidation, usually at high temperature, have been interpreted as being due to mixed oxidation states, for example Fe^{2+}, or Fe^{3+} and Ni^{2+} and Ni^{3+} (Srinivasan *et al.* 1979; and the review by Wandelt 1982). The strategy adopted to extract information on oxidation states from core-level spectra was described in the experimental section. To provide confidence in the assignment, for example, Ni(2p) difference spectra, data were obtained for various model defect nickel oxides, i.e. those which, on the basis of well established chemistry of the solid state, would be expected to exhibit mainly Ni^{2+} or Ni^{3+} states. The assignments were confirmed by obtaining spectra during the thermal transformation of one to the other, the extend of transformation being conveniently (for nickel oxides) accompanied by a well characterized colour change (green to black), reflecting the conversion of Ni^{2+} to Ni^{3+} (figure 4). The following points emerge.

(*a*) During oxygen chemisorption at 295 K with both Ni(100) and Ni(210) surfaces, there is no evidence in the Ni(2p) difference spectra for $Ni^{2+,3+}$ species even though, for example, with Ni(100) the surface oxygen concentration is 1×10^{15} cm^{-2} and with Ni(210) about 1.6×10^{15} cm^{-2}.

(*b*) As the oxygen adatom concentration increases above these values evidence for both Ni^{2+} and Ni^{3+} states emerge and for the Ni(210) surface the respective concentrations have been determined. The quantitative separation of the individual concentrations of Ni^{2+} and Ni^{3+} was not feasible with Ni(100). However, the ratio of adsorbed oxygen to $Ni^{2+,3+}$ was always greater than 1.5.

(*c*) The theoretical studies of Heine and his group (V. Heine, personal communication 1984; Gallagher *et al.* 1979; Godby *et al.* 1984) suggest that oxygen chemisorption at Ni(100) surfaces involves (in band terms) a 'local orbital' being formed between the O(2p) orbital and the Ni(4s4p) band, the local orbital being spread over the neighbouring nickel atoms. This model is used to rationalize low-energy electron diffraction (l.e.e.d.) and other features (such as the dipole moment) of oxygen chemisorption. Only when oxidation sets in do the Ni(3d) electrons participate in bonding and only then does experimental evidence for Ni^{2+} and Ni^{3+} states appear in the Ni(2p) difference spectra.

(*d*) The observation of these features in the Ni(2p) spectra supports the theoretical prediction that only when oxidation of the metal occurs are the 3d electrons involved. During oxidation nickel–nickel bonds are broken and we suggest that when this occurs the symmetry of the Ni(3d) electrons is perturbed so that their ability to screen the Ni(2p) electrons is diminished. Charge transfer occurs from the Ni(3d) band during oxide formation and chemically shifted features

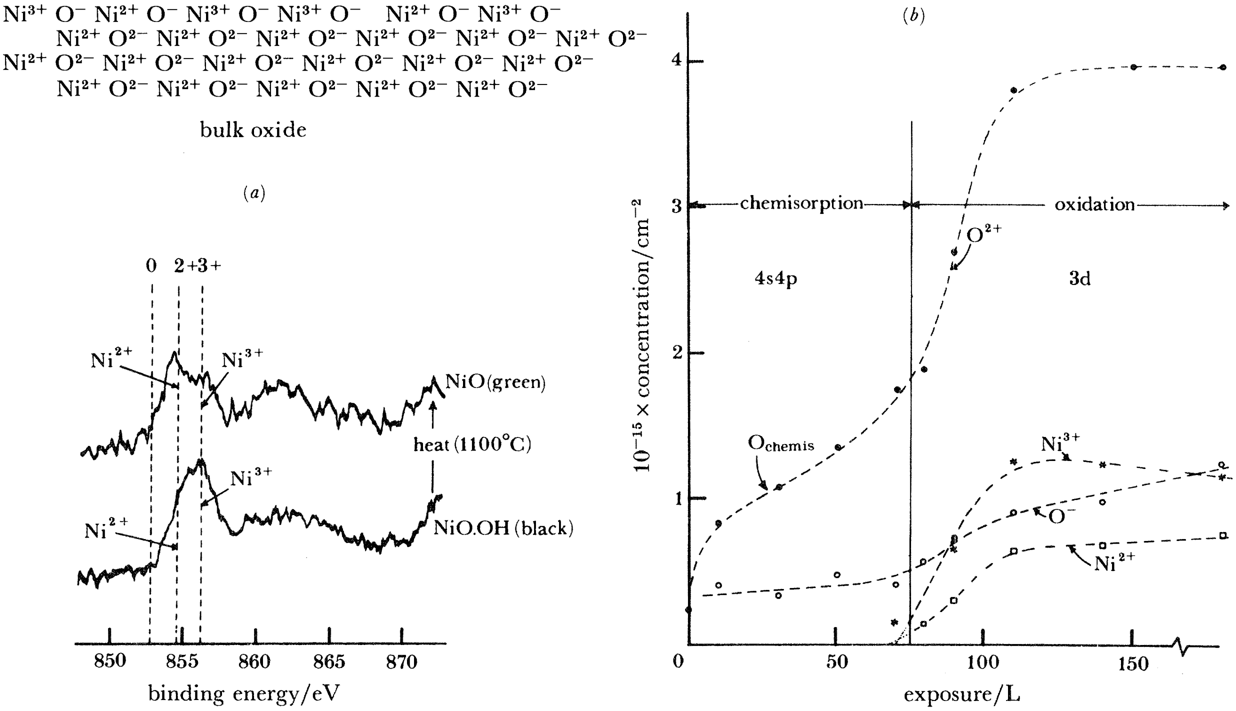

FIGURE 4. (a) Ni(2p) spectra for NiOOH before and after heating to 1100 °C in air. Also shown is a schematic of a 'NiO' surface. (b) Surface species observed during the exposure of a Ni(210) single crystal to oxygen at 295 K.

in the Ni(2p) difference spectra develop. We shall also see that in nickel halogenation only when nickel–nickel bonds are broken in halide overlayer formation are peaks observed in the Ni(2p) spectral region that can be assigned to Ni^{2+} states.

(*e*) The concentration of Ni^{3+} states that are at (or close to) the surface is, by comparison with what might be expected from bulk defect equilibrium values, very high. The *bulk stoichiometry* of a typical oxygen excess (black) nickel oxide conforms to $NiO_{1.02}$ compared with $NiO_{1.0002}$ for the stoichiometric (green) oxide. Quantitative analysis of the stoichiometry of the surface region of the bulk oxides using the O(1s) and Ni(2p) spectra always indicate an oxygen excess, the ratio usually being about 2:1 (Roberts & Smart 1984). With NiO(100) after extensive heat treatment *in vacuo*, the ratio was close (1.16) to that expected of stoichiometric nickel oxide. The concentration of Ni^{3+} species in the present studies, whether of oxide overlayers at single-crystal surfaces or defective bulk oxides, correspond to substantial fractions (for example 50%) of the total nickel within the photoelectron sampling depth (*ca.* 15 Å†). Furthermore, angular-dependent studies suggest that they are at the surface by comparison with Ni^{2+}, and have associated with them O^- species. A redox-type surface reaction,

$$Ni^{2+}(s) + \tfrac{1}{2}O_2(g) \rightarrow Ni^{3+}(s) + O^-(s), \qquad (1)$$

is suggested to account for this correlation, which is entirely compatible with the classical studies of both Kuchynka & Klier (1963) and Gravelle & Teichner (1969). Furthermore the photoelectron spectroscopic data support the concept of localization of charge at specific sites, since the timescale of a photoelectron process is of the order of 10^{-16} s. This is about a factor

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† 1 Å = 10^{-10} m = 10^{-1} nm.

of 10^7 smaller than that in electron spin resonance (e.s.r.), which explains the lack of e.s.r. evidence for O^- and Ni^{3+} species in defective nickel oxides, where dipolar interactions of the kind O^-–Ni^{3+} and O^-–O^- will be important.

The Ti(2p) spectra observed during the interaction of oxygen with polycrystalline titanium surfaces at low temperature (Carley *et al.* 1985*b*) have been analysed by using the spectral-difference approach (figure 5). It is clear that initially, at 295 K, i.e. for oxygen adatom concentration up to 9×10^{14} cm^{-2}, there is only a relatively small concentration of Ti^{4+} present and the predominant oxidation states are Ti^{2+} and Ti^{3+} (figure 5, curve 1). However, as the oxygen surface concentration increases, and the oxide overlayer develops, the Ti^{4+} contribution becomes more significant until, at an estimated oxide thickness of *ca.* 10 Å (figure 5, curve 3) it is the dominant oxidation state. Angular-dependent studies of the Ti(2p) spectral region (figure 5) confirm that the Ti^{4+} state is predominantly at the oxide–gas interface and the Ti^{2+} and Ti^{3+} species at the titanium–oxide interface. When oxygen interaction was studied at 80 K and the adlayer warmed to 295 K, intensity was transferred from the Ti^{4+} region of the Ti(2p) spectrum to lower binding energy ($Ti^{2+,3+}$). This reflects the high mobility (activation energy of no more than 20 kJ mole^{-1}) of Ti^0 with consequent reduction of Ti^{4+} to $Ti^{2+,3+}$ states at the metal–oxide interface. We suggest this is strong experimental evidence that cluster-like oxide species develop and that Pauling's rule for local electrical neutrality is maintained with a distribution of oxidation states existing across the oxide overlayer, the lower oxidation states being predominantly at the metal interface.

Surface halogenation

Although some sp metals, such as lead, are unreactive to the halogen hydrides, surface halogenation may be induced (Carley *et al.* 1982) by preoxidation, when chemisorptive replacement of the oxygen by the halogen occurs; the process is kinetically facile being driven thermodynamically by the formation of water. By monitoring O(1s), Cl(2p), Br(3d) and Pb(4f) spectral regions the kinetics and hence mechanism of the chemisorptive replacement of oxygen by both HCl(g) and HBr(g) were studied (Blake *et al.* 1982, 1985). Of particular interest was the observation that a metastable chloride overlayer is formed during replacement, its stability being dependent on the presence of surface oxygen at a coverage of greater than about 0.1. Below this value the chloride is removed through interaction with HCl(g). The analogous bromide overlayer is unreactive to both HCl(g) and HBr(g); however, the chloride overlayer interacts and is removed by HBr(g). Although the primary objective of this work was to look for evidence for adsorbate–gas interaction as might occur in the Cl^-(s)–HCl(g) system, taking a lead from the strong hydrogen bonding known to occur in the HCl_2^- and HF_2^- species and our studies of the activation of water (Roberts 1980), we confine our discussion to observations of the formation and reactivity of mixed halide (Cl and Br) overlayers formed by chemisorptive replacement of oxygen in the Pb(110)–O system. The concentrations of O^{2-}(a), Cl(a) and Br(a) (figure 6) during chemisorptive replacement indicate that the chloride and bromide develop simultaneously, but exhibit quite distinct reactivities, the chloride component of the overlayer being metastable and removed while the bromide overlayer is stable and unreactive. It should be noted that the chloride is removed only when the surface oxygen concentration falls to less than 0.1×10^{15} cm^{-2}. The chemical reactivity of each halogen is qualitatively and quantitatively independent of the presence of the other. Furthermore the mechanism by which a chloride species is formed can determine its subsequent chemical reactivity; the chloride overlayer

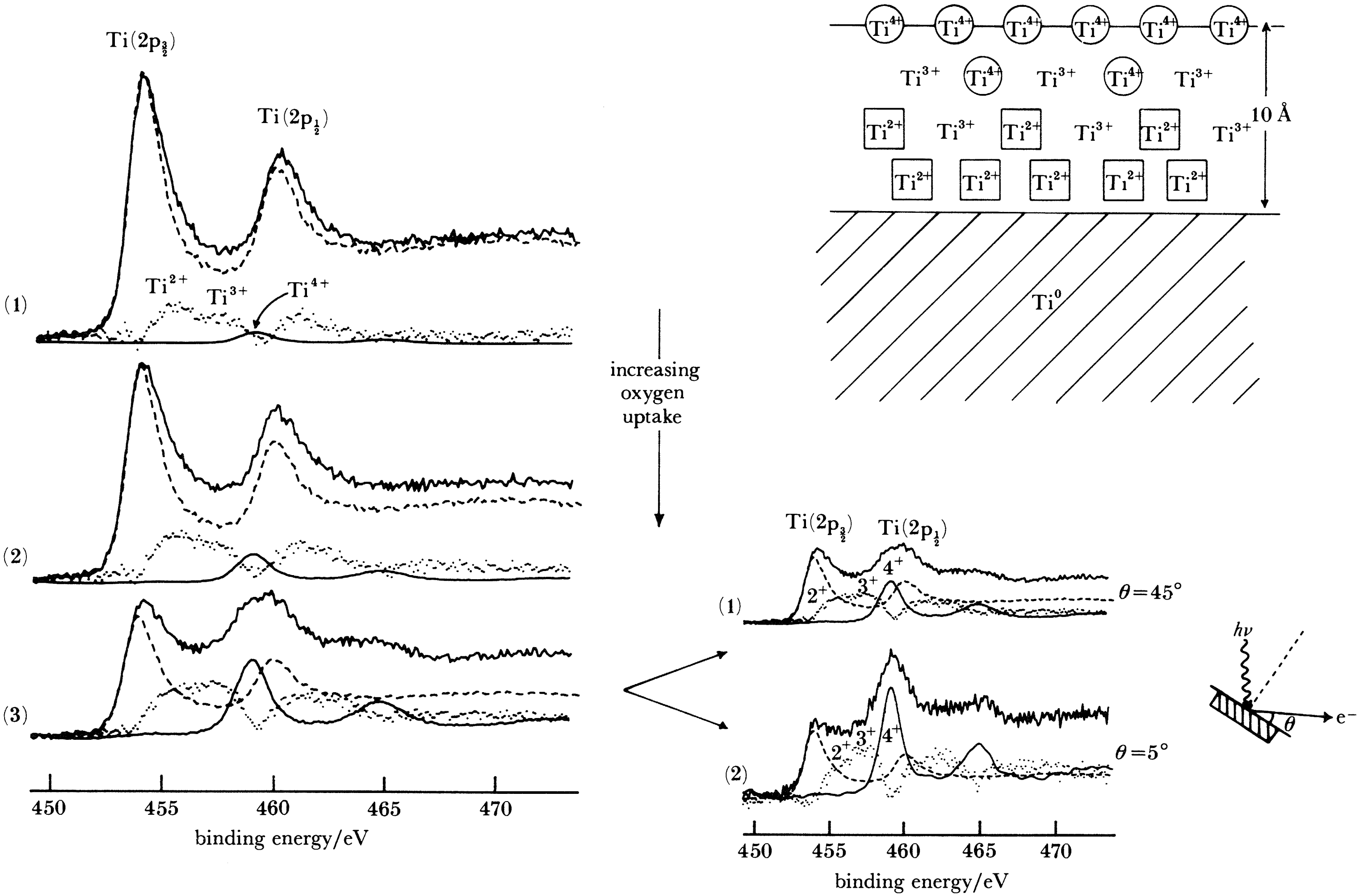

FIGURE 5. Ti(2p) spectra observed during oxygen interaction with polycrystalline titanium at 295 K together with difference spectra (see text) highlighting the Ti^{2+}, Ti^{3+} and Ti^{4+} species and their behaviour with oxygen uptake. For curve (3), spectra taken at two different take-off angles θ, are shown. The 'standard' take-off angle was 45°. Also shown is a schematic model of the oxide overlayer corresponding to curve (3), deduced from the Ti(2p) difference spectra and their variation with take-off angle. The spectra were recorded at 20 eV pass energy with Al Kα radiation (400 W).

generated by dissociative chemisorption of dichlorine is unreactive to HCl(g). Reactivity is, therefore, very localized and dependent on individual molecular interactions rather than dependent on structural or cooperative long-range effects. For a single-component chloride overlayer, l.e.e.d. has established (Au *et al.* 1985*b*) that after removal to generate the clean surface according to X.p.s., the symmetry of the diffraction pattern is what would be expected of a Pb(110) surface.

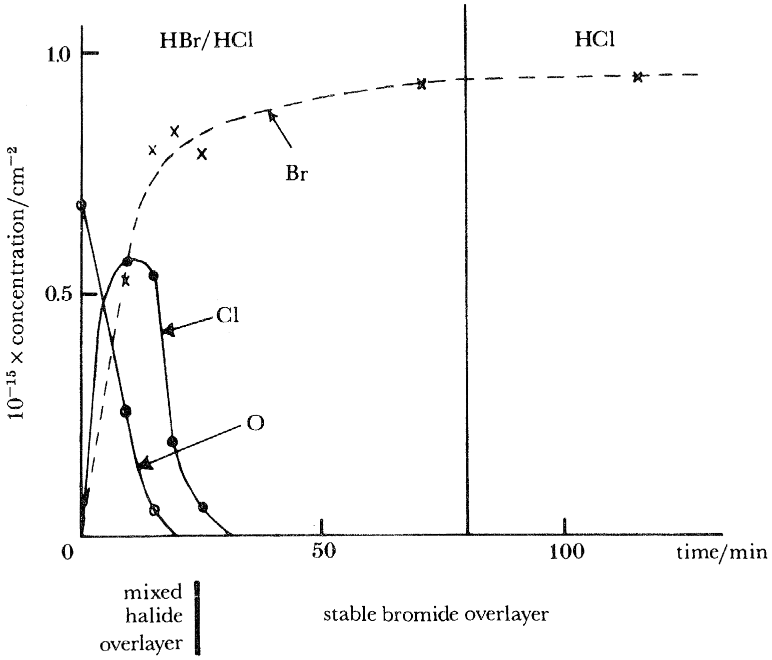

FIGURE 6. The variation of surface concentrations of Br, Cl and O with time for the exposure of a Pb(110) crystal to a HBr/HCl (*ca.* 4:1) mixture ($p = 10^{-6}$ Torr) followed by exposure to HCl ($p = 10^{-5}$ Torr). All exposures were at 295 K.

By studying the Pb(110)-Cl plus HCl(g) interaction over a range of temperatures the rate of chloride removal (in atoms per square centimetre per second) was shown to conform to the kinetic expression

$$\frac{\mathrm{d}[\mathrm{Cl(a)}]}{\mathrm{d}t} \propto [\mathrm{Cl(a)}]\,P_{\mathrm{HCl}}\exp\left(\frac{-10{,}800}{RT}\right). \qquad (2)$$

If the value of the activation energy (10800 J mol^{-1}) is substituted into the simple collision theory expression $PZ\exp(-E/RT)$, then the value of P is 0.43, which implies that nearly every collision of hydrogen chloride with the chloride overlayer that has sufficient energy (10800 J mol^{-1}) leads to reaction and chloride removal. We assume that since no dichlorine is observed mass spectrometrically, a 'volatile' lead hydrogen dichloride is formed.

Chloride overlayers at Pb(110) surfaces, whether formed from HCl(g) by chemisorptive replacement of oxygen or by the dissociative chemisorption of dichlorine, exhibit very distinct Pb(4f) components, which are shifted substantially (*ca.* 2 eV) from the metal peak. Magnesium surfaces similarly exhibit a Mg(1s) shifted peak (figure 7) during the formation of a surface dichloride overlayer (Au & Roberts 1985). Time-dependent spectra indicate that at 295 K the chloride is formed by a nucleation mechanism, while angular-dependent photoelectron spectra suggest that discrete units of $MgCl_2$ form with one chlorine at, and the other below, the surface magnesium atoms. In contrast, Ni(100) surfaces interact extensively with dichlorine at 295 K (figure 7), but exhibit no shifted Ni(2p) component, as might be expected from the development of Ni^{2+} species. The Ni(2p) intensity decreased gradually to about one tenth of its initial value

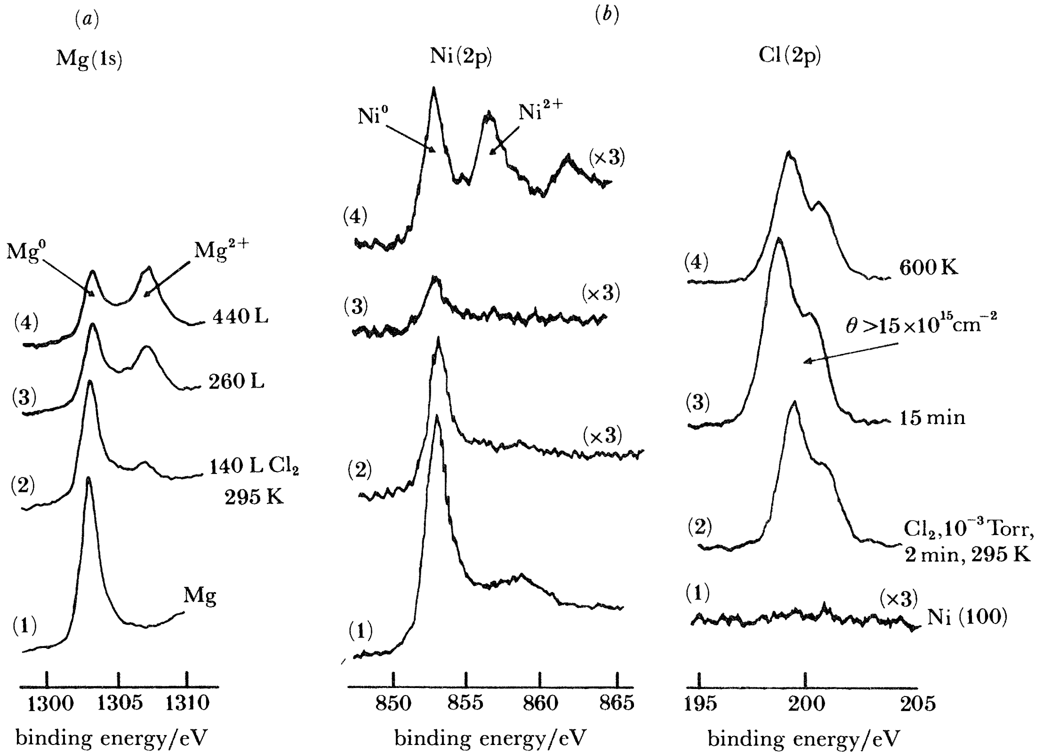

FIGURE 7. (*a*) Mg(1s) spectra for a magnesium surface exposed to dichlorine (10^{-6} Torr) at 295 K. Analyser conditions were as in figure 1. (*b*) Ni(2p) and Cl(2p) spectra for a Ni(100) surface exposed to dichlorine at 298 K followed by heating to 600 K. Spectra were recorded at 20 eV pass energy with Al Kα radiation (400 W).

during exposure to dichlorine, which, if the usual exponential relation (figure 8) between intensity and overlayer thickness is obeyed, indicates *a priori* the formation of an overlayer of substantial thickness, at least 15 Å. Analysis of the Cl(2p) intensity confirms this in that the chlorine surface concentration is equivalent to at least 15×10^{15} cm^{-2}. Figure 8 indicates that a value of the inelastic mean free path (λ) of 14 Å is a good fit to the experimental I_d/I_0 relation derived from a model of the overlayer. Thus, following dissociative chemisorption of dichlorine, a molecular chlorine overlayer is formed, which is about 20 Å thick and does not involve nickel directly in its bonding. This 'molecular overlayer' is surprisingly stable, although above 350 K intensity increases in the Ni(2p) spectral region, indicative of the presence of both Ni^0 and Ni^{2+} species (figure 7). Iodine interaction with Ni(100) shows some similarities in that a molecular physisorbed layer has been observed (Jones *et al.* 1983), which has an unusually high heat of adsorption (*ca.* 60 kJ mol^{-1}). The Cl(2p) intensity decreases after heating by about 25% (figure 7) due to partial desorption of the molecular chloride overlayer. X-ray-induced valence spectra (figure 8) indicate that as the Ni d-band intensity decreases with chloride interaction

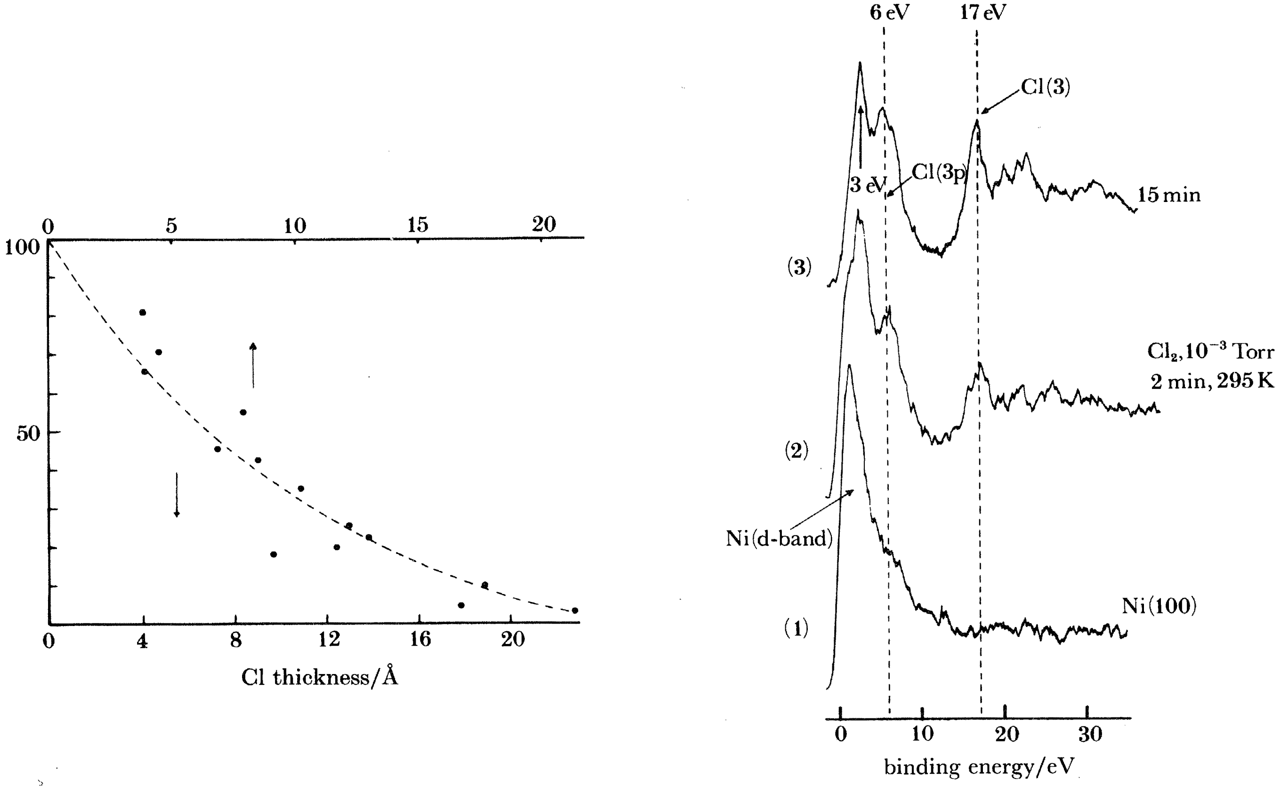

FIGURE 8. (*a*) A comparison of the experimental values (circular points) of I_d/I_0 as a function of surface chlorine concentration with the theoretical values (broken line) ($\lambda = 14$ Å). (*b*) X-ray-induced valence spectra corresponding to figure 7*b*. The spectra were recorded at 50 eV pass energy with Al Kα radiation (400 W).

a distinct and sharp resonance peak emerges about 3 eV below the Fermi level. This we attribute to the development of a discrete molecular orbital associated with the molecule dichlorine overlayer. The unusual thermal stability of this overlayer must be associated with the Ni(100)–Cl chemisorbed layer, but its precise role is not clear; presumably there is a strong electron back-bonding component from the *c*(2 × 2) adlayer that contributes to overlayer stability.

GENERAL COMMENTS

By studying the role of surface oxygen in the surface activation of otherwise unreactive molecules, a detailed picture has emerged of the molecular events involved in the synergistic chemistry of coadsorbed molecules. Dissociative chemisorption of nitric oxide is followed by the step-wise hydrogenation of the chemisorbed nitrogen in which oxygen activation of O–H and N–H bonds in the coadsorbate is important. This is not only relevant to ammonia synthesis but also, by analogy, to the catalytic chemistry (methanol synthesis and Fischer–Tropsch reaction) associated with the reduction of carbon monoxide, where the latter's dissociation at iron surfaces was established by photoelectron spectroscopy (Kishi & Roberts 1975*a*).

In parallel with these catalytic studies investigations of the interaction of oxygen with metal surfaces, in particular nickel and titanium, revealed significant information on bonding and the emergence of higher oxidation states of the metal. Evidence for the latter was obtained by analysis of the metal substrate's core-level photoelectron peaks, and for nickel the experimental data find strong support from recent theoretical studies of Heine and his groups for the separate roles of Ni(4s4p) and 3d electrons. They also throw light on earlier work-function and photoemission studies, where the question of the presence of defect states (Ni^{3+}) in chemisorbed oxygen overlayers formed at low temperatures was first raised (Quinn & Roberts 1963, 1965). The conclusions also have implications for the relation between surface and bulk defects in oxides (Blaisdell & Kunz 1984).

Oxygen chemisorption at titanium involves mixed-valence states Ti^{2+} and Ti^{3+} predominantly at the metal–oxide interface, and Ti^{4+} at the oxide–gas interface. Such information is important since variable oxidation states are considered to be essential for determining the reaction pathway in many catalytic reactions (Somorjai 1984). Clearly the evidence with titanium (and nickel) is that we have all the ingredients of a redox system during the early stages of oxygen interaction; furthermore facile titanium diffusion can lead to reduction of Ti^{4+} to $Ti^{2+,3+}$. That non-stoichiometry or mixed-valence states exist at the metal–oxide interface, the evidence with titanium being that the sub-oxide forms first, also raises questions related to whether the overlayer can be considered as being made up of 'ion clusters' linked together by 'metal' bridges. Metal sub-oxide structures of this kind have been discussed (Simon 1979).

The surface chemistry of the halogens and the role of surface oxygen both in the activation of the halogen hydrides and in controlling the reactivity of the chloride overlayer further illustrates the specific influence of adsorbed oxygen. Although much of this work was at low pressures, the importance of extending to the higher pressure régime is well illustrated by the stable molecular dichlorine overlayer, which is formed at a $c(2\times 2)$ Ni(1000)–Cl surface. Clearly the chemisorbed layer acts as a template for the molecular overlayer. Associated with this overlayer is a sharp resonance 3 eV below the Fermi level, which we suggest reflects bonding analogous to the localized bonding that is observed in the interhalogen compounds (Popov 1967).

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Note added in proof (12 *December* 1985). Since this work was completed we have established that the active oxygen species is a transient O^-(s). (Au, C. T., Carley, A. F. & Roberts, M. W. *Nature, Lond.* (In preparation).)

Discussion

J. M. THOMAS (*Department of Physical Chemistry, University of Cambridge, U.K.*). It is remarkable that Professor Roberts finds Ni^{3+} ions in such relative abundance in the surface regions of his nickel oxide. Bearing in mind the efforts that were made in the past to increase the concentration of Ni^{3+} ions in NiO (by cation substitution for example), one wonders whether, armed with the information that he has now uncovered, we could proceed now to undertake some definitive, systematic attempts to correlate catalytic activity of non-stoichiometric nickel oxide surfaces with their concentration of ions of variable valency.

M. W. ROBERTS. Although the primary objective of our work was to obtain spectroscopic evidence, for variable oxidation states at oxide surfaces, the ultimate aim was to investigate how these states might vary under catalytic reaction conditions. In this connection it is also important to emphasize that earlier estimates of the concentration of Ni^{3+} in doped nickel oxide depended on *bulk analysis* by classical methods, the present data provide for the first time estimates for the concentrations of Ni^{3+} in the *surface region*. Our data suggest that the majority of the Ni^{3+} species are in fact concentrated in the surface region. We are currently extending our work to lithium-doped nickel oxide.

F. S. STONE (*School of Chemistry, University of Bath, U.K.*). It is very interesting that NO should dissociate at as low a temperature as 80 K on both Zn(0001) and Mg (0001). I would like to ask if Professor Roberts has information on the proportion of the adsorption that is dissociative. May I also enquire how Professor Roberts would rank the four metals Zn, Mg, Cu and Fe with regard to their propensity for dissociatively adsorbing NO, and whether the products of onward reactions with H_2O and NH_3 are similar.

M. W. Roberts. The rather surprising feature of studies of nitric oxide chemisorption by a range of metals (Cu, Zn, Mg, Ni, Fe, Al) is that no obvious distinction could be made between the relative activities of sp and transition metals. If we use as a criterion the extent of dissociative chemisorption at 80 K then Zn and Mg are more reactive than Fe. We can begin to understand the high activity of Zn, Al and Mg, now that the role of sp-electrons in chemisorption has been emphasized by theoretical studies. Although, and in addition to dissociative chemisorption, two molecular states of nitric oxide, NO (bent or bridged) and NO (linear) are observed, the most significant difference between the metals is to be seen in the fate of the nitrogen adatom, N(s), generated by the dissociation of nitric oxide at 80 K. The following molecular events were observed, their relative importance depending on the metal:

$$\mathrm{N(s)} \xrightarrow{1} \mathrm{N(a)}, \quad \text{chemisorption;}$$

$$\mathrm{N(s)+N(s)} \xrightarrow{2} \mathrm{N_2(g)}, \quad \text{desorption;}$$

$$\mathrm{N(s)+NO(a)} \xrightarrow{3} \mathrm{N_2O(a)} \quad \text{addition reaction.}$$

With Cu(100) step 1 is not observed at 80 K while step 3 is very significant; with aluminium step 1 is dominant at low coverages, while step 3 occurs only at higher coverage.

Which molecular event dominates is, therefore, very much dependent on the relative rates of the above. At 80 K with Cu(III) there is a significant, but small energy barrier to the formation of N(a), so that during the surface lifetime of N(s) there is a high probability of steps 3 and 2 occurring. With Cu(III) at 295 K, the dominant step is the formation of N(a). With completion of the monolayer involving both O^{2-}(a) and N(a), the concentration of NO(a) present is very dependent on the metal, with Cu(III) it is not observed while with Mg(0001) a small coverage is present; MgO is known to chemisorb nitric oxide.

Therefore to understand the detailed mechanism of nitric oxide chemisorption the kinetics of all these *individual steps* must be established. In parallel with these surface oxidation also occurs, which is part of the thermodynamic driving force. There does, however, appear to be a correlation between the strength of the metal–nitrogen bond and its ease of hydrogenation by coadsorbed water.