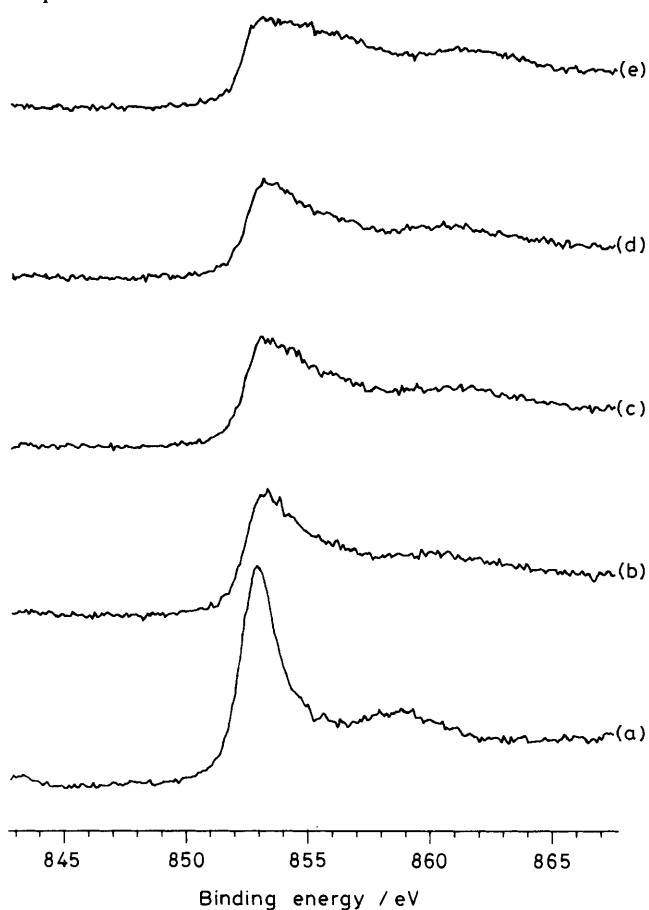# Photoelectron Spectroscopic Evidence for Ni³⁺ Species in Chemisorption at a Ni(100) Surface

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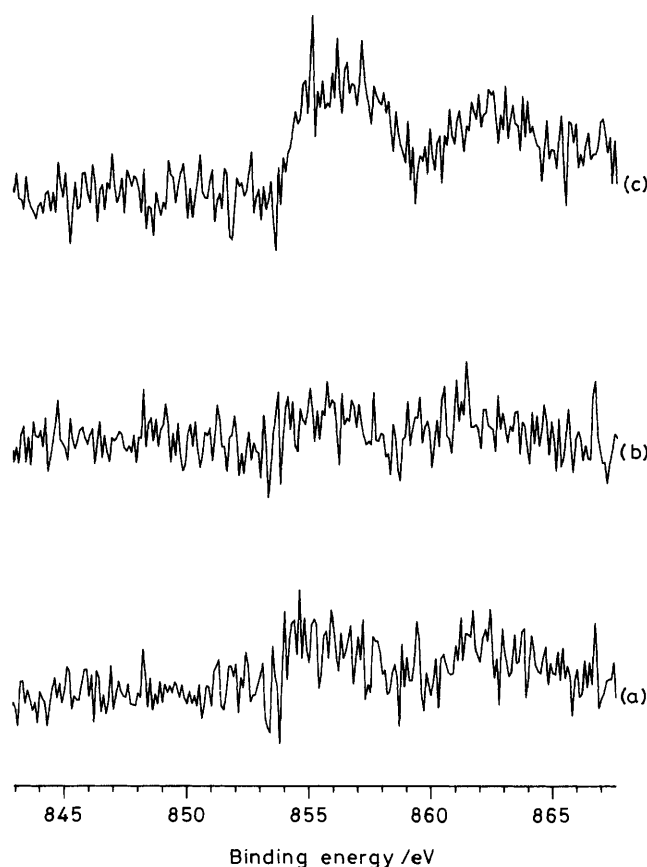*Department of Chemistry, University College, Cardiff, CF1 1XL, U.K.*

It has been shown by $X$-ray photoelectron spectroscopy that $Ni^{3+}$ species are present in the chemisorbed overlayer formed at a Ni(100) surface by the interaction of co-adsorbed water and oxygen; the concentration of $Ni^{3+}$ is estimated to be about $6 \times 10^{14}$ cm$^{-2}$ at 297 K and the species have a characteristic Ni($2p_{3/2}$) binding energy of 856 eV and an associated satellite peak at 862 eV.

We have established[1] that chemisorbed oxygen present at a metal surface at low temperature (80 K), and which we suggest is co-ordinatively unsaturated, exhibits specific reactivity to molecularly adsorbed water. An interesting aspect of this work was that the O(1s) spectra observed with a nickel surface at 295 K, which had been first exposed to oxygen and then water vapour at 80 K, were interpreted as being due to an overlayer of any oxyhydroxide analogous to βNiO(OH). Studies of βNiO(OH) indicated[2] the presence in the Ni(2p) spectral region of peaks which were assigned as Ni³⁺ species. Subsequently we have searched for spectroscopic evidence for the presence of Ni³⁺ species in the surface of a Ni(100) single crystal which are a consequence of the specific reactivity of adsorbed oxygen to molecularly adsorbed water at low temperature.

Figure 1 shows the Ni($2p_{3/2}$) spectra for the clean Ni(100) surface and after exposure of the surface to oxygen and water vapour under various conditions which are described in the legend. The clean surface which exhibited a sharp LEED (low energy electron diffraction) pattern with (100) symmetry has a Ni($2p_{3/2}$) peak at a binding energy of 853 eV [Figure 1(a)]. After exposure to oxygen at 80 K the LEED pattern is diffuse while the photoelectron peak is attenuated and becomes assymetric on the high binding energy side [Figure 1(b)]. There is little change evident in the photoelectron peak after warming the adlayer to 295 K [Figure 1(c)], and this is confirmed by the Ni($2p_{3/2}$) difference spectrum shown in Figure 2(a) which indicates only a small increase in intensity at about 856 eV and 861 eV. This difference spectrum was generated by subtracting a suitably scaled spectrum (b) from spectrum (c) (Figure 1). The scaling factor used was that which gave the best correspondence between the leading edges (*i.e.* to low binding energy) of the two spectra. The optimum match could be judged visually or according to a least squares fitting procedure. The profile of the difference



**Figure 1.** Ni($2p_{3/2}$) spectra from a Ni(100) surface. (a) Clean sample at 80 K; (b) after exposure of the clean surface to oxygen (160 l at 1 × 10⁻⁶ Torr) at 80 K; (c) after warming (b) to 295 K; (d) after exposure of the clean surface to oxygen (160 l at 1 × 10⁻⁶ Torr) at 80 K followed by water vapour (15 l) at 80 K; (e) after warming (d) to 295 K. Pass energy = 20 eV; 10 scans × 20 s.



**Figure 2.** Ni($2p_{3/2}$) difference spectra (see text) between: (a) spectra 1(c) and 1(b); (b) spectra 1(d) and 1(b); (c) spectra 1(e) and 1(d).

spectrum provided a further sensitive check on the quality of the subtraction process, the presence of negative intensity or residual signal at 853 eV being indicative of either over estimation or under estimation of the scaling factor respectively. Exposure of the Ni(100)–O (80 K) surface to water vapour at 80 K did not influence the Ni($2p_{3/2}$) spectrum [Figure 1(d)] and this is confirmed by the difference spectrum shown in Figure 2(b). On warming the Ni(100)–O + $H_2O$ (80 K) to 295 K there is an increase in the intensity of the Ni($2p_{3/2}$) region at high binding energy, Figure 1(e), and the difference spectrum Figure 2(c) establishes that a new feature has emerged at a binding energy of 856 eV. Associated with this photoelectron peak is a satellite at about 6 eV higher binding energy than the parent photoelectron peak at 856.0 eV. We assign the new feature to $Ni^{3+}$. The chemical shift between $Ni^{2+}$ and $Ni^{3+}$ observed in this work, 1.4 ± 0.2 eV, agrees well with that observed[2] during the thermal decomposition of *bulk* $\beta$NiO(OH) (*ca.* 1.2 eV) where it was not feasible to resolve completely the two species *via* spectral subtraction. A detailed study of a number of nickel oxide preparations exhibiting a range of defect concentrations[3] has also provided good evidence that $Ni^{3+}$ species present at the *surface* of high area semiconducting bulk oxides have a Ni($2p_{3/2}$) binding energy of about 856.1 eV. When a Ni(100)–O (295 K) surface was exposed to water vapour at 80 K, and then warmed to 295 K, no new features were generated in the Ni(2p) difference spectrum providing further justification for the analytical procedure used in processing the spectra.

The spectrum shown in Figure 2(c) corresponds to a surface $Ni^{3+}$ concentration, estimated from our modified[4] form of the Madey–Yates–Erickson equation, of $6 \times 10^{14}$ cm$^{-2}$. This may be compared with a concentration of $3 \times 10^{14}$ cm$^{-2}$ of 'water molecules' remaining in the adlayer at 295 K. The spectrum shown in Figure 1(e) may thus be envisaged as being due to an incomplete oxyhydroxide overlayer.[2] Previous oxidation studies of Ni(100) surfaces were reviewed recently by Wandelt.[5]

We have, therefore, established that it is feasible to generate defect sites ($Ni^{3+}$) in the surface of a Ni(100) single

crystal by utilising the inherent high chemical reactivity of chemisorbed oxygen present at low temperature to molecularly adsorbed water. The overlayer has spectral features which are analogous to those of bulk $\beta$NiO(OH) but whether the detailed structure of the overlayer (equivalent to about two atomic layers) present at the single crystal Ni(100) surface can be considered in terms of an overlayer with nickel vacancies or a brucite type overlayer with alternative $Ni^{3+}$ ions and (OHO)$^{3+}$ groupings, the latter being stabilised by the presence of hydrogen bonded intercalated water molecules,[2] is not known. It is proposed to investigate this by means of synchrotron radiation. What is, however, clear is that the localized bonding or Friedel model[6] is applicable to this system, discrete $Ni^{3+}$ species being present with a well defined electron binding energy. It is the interplay between $Ni^{2+}$ and $Ni^{3+}$ species that is responsible for the observed catalytic reactivity of doped high surface area nickel oxides, as shown in the classical work of Hauffe, Verwey, and Schwab where correlations between catalytic activity, electrical conductivity, and defect character were established.[7]

## References

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