NOTES

XPS Study of the Interaction of Nickel (II) Ions with Alumina

In the first stage of production of many supported metal catalysts a solution of the metal salt is added to the support. There may be a specific interaction between the metal salt and the surface of the support which influences the subsequent properties of the catalyst, e.g., well-dispersed supported metal catalysts are frequently produced by ion exchange of the metal with the carrier (*1*). Nickel ions are known to adsorb strongly on alumina (*2*). The adsorbed nickel ion is then readily oxidized to a high-valent species, in contrast to the behavior of the parent metal salt (*3*). At ambient temperatures the strongly adsorbed nickel ions probably incorporate surface oxide or hydroxide ions into their hydration spheres (*4*). Under certain conditions, at higher temperatures, a nickel aluminate can be formed (*5*).

Previously (*3*), we have interpreted the ease of oxidation of nickel ions adsorbed on alumina in terms of the basicity of oxide or hydroxide ligands associated with the nickel. We now determine whether X-ray photoelectron spectroscopy (XPS) can provide information on the surface nickel complex. The spectra are processed by computer, which averages several scans. The error bars represent the 67% confidence limit. Approximately 3 hr was required to collect the data for one spectrum.

To correct for charging, particles of gold were mixed with the sample, which was mounted on double-sided Sellotape, and the binding energy, BE, of the gold was assumed to be 83.8 eV. Alternatively, the sample was mounted on a gold mesh and the carbon impurity was taken as reference at BE 285.0 eV. Nickel/aluminas were obtained by equilibrating a solution of the appropriate salt with γ-alumina, rinsing once and then drying the sample at 100°C (unwashed), or washing thoroughly and then drying at 100°C.

The BE of a metal ion is related to the net charge on the ion, which varies according to the ligands involved (*6–8*). A correction must be made, however, for the charging of the insulator sample. Recent studies (*9, 10*) of the reproducibility of BE determinations among several laboratories have shown that standard deviations of approximately ± 0.3 to 0.5 eV may be expected, irrespective of the method of correcting for charging. Relative BEs of several compounds obtained with a single instrument are probably more reliable, though reported energy differences (*9*) (e.g., Al2p–Al2s) are consistent to only approximately ± 0.2 to 0.3 eV. Therefore considerable care must be taken when interpreting BE data from adsorbed species at insulator surfaces.

Table 1 gives the BEs of the compounds examined. The mean BE of the Al2p level in the alumina support is 74.2 ± 0.2 eV. This value may be compared with the average BE, obtained from several laboratories (*9*), of 74.7 ± 0.6 eV. Our absolute value of the Al2p BE falls within the range of the reported values, and our standard deviation is low, as expected from measurements on a single instrument. The gold particle admixture method of charge cor-

TABLE 1

Binding Energies of Nickel Bulk and Supported Compounds

Reference	Sample	Ni2p$_{3/2}$	S2p
Au	NiNO$_3$ (6H$_2$O)	857.1, 857.3[a]	—
Au	Ni(OH)$_2$	856.3	—
Au	NiAl$_2$O$_4$/Al$_2$O$_3$	856.0	—
C	NiSO$_4$(7H$_2$O) 20°C	857.3, 857.1,[b] 857.3[c]	—
C	NiSO$_4$(7H$_2$O) 300°C	857.4	—
C	NiSO$_4$(7H$_2$O) 450°C	857.4	—
Au	NiSO$_4$(7H$_2$O) 20°C	857.7	169.3, 169.6[b]
Au	NiSO$_4$(7H$_2$O) 100°C	857.5	—
Au	NiSO$_4$(7H$_2$O) 280°C	858.0	—
Au	0.1 M[d] NiNO$_3$/Al$_2$O$_3$	856.3	—
Au	0.8 M NiNO$_3$/Al$_2$O$_3$	856.7	—
Au	1.2 M NiNO$_3$/Al$_2$O$_3$	856.2	—
Au	0.025 M NiSO$_4$/Al$_2$O$_3$[e]	856.7	—
Au	0.25 M NiSO$_4$/Al$_2$O$_3$[e]	856.7	168.6
Au	0.5 M NiSO$_4$/Al$_2$O$_3$[e]	856.8	169.1
Au	1.0 M NiSO$_4$/Al$_2$O$_3$[e]	856.9	168.8
Au	0.1 M NiSO$_4$/Al$_2$O$_3$[f]	856.6	169.3
Au	1.0 M NiSO$_4$/Al$_2$O$_3$[f]	856.6	—
Au	Saturated NiSO$_4$/Al$_2$O$_3$[f]	856.5	168.7

[a] Reference (8).
[b] Reference (13).
[c] Reference (9) corrected to Au4f$_{7/2}$ at 83.8 eV.
[d] Molarities quoted are equilibrium solution concentrations after adsorption.
[e] Unwashed.
[f] Washed.

rection is therefore apparently satisfactory, though Johansson et al. (11) report difficulties with a similar graphite mixture on a nonconducting backing. The BE of nickel in nickel nitrate or sulfate adsorbed on alumina is less than the corresponding bulk value (Table 1). This suggests that, after adsorption, nickel is attached to relatively more basic ligands. The BE of adsorbed nickel is close to the value for nickel hydroxide, and slightly higher than the BE of nickel in nickel aluminate. The latter compound has a distinct blue color and is unlikely to be formed by nickel adsorbed at ambient temperature (5). The BE data are therefore consistent with incorporation of surface oxide/hydroxide ligands into the nickel coordination shell. However, the uncertainty in BEs makes further evidence desirable.

The photoelectron spectra of paramag-netic transition metal compounds show a satellite structure associated with the core level peak. These satellites have been assigned to ligand–metal charge transfer transitions (12) but their origin is still controversial (13). However, the satellite position and structure are undoubtedly related to the types of ligands involved.

The 2p$_{3/2}$ spectra of nickel in the bulk nitrate and hydroxide, and in the aluminate, prepared from nickel nitrate adsorbed on alumina (5), are shown in Fig. 1. The satellite structures are symmetrical and are similar for all three samples. The weak intensity of the nickel aluminate spectrum may be the result of incorporation of nickel below the surface. The spectrum of nickel in nickel nitrate adsorbed on alumina is also given in Fig. 1. The satellite structure is similar to that of the above compounds.

The spectra of nickel in bulk nickel

sulphate heptahydrate heated to 100 and 300°C are shown in Fig. 2. The molar ratio (14) of water to nickel is probably 1:1 at 100°C and 0.5 to 1.0:1 at 300°C. The
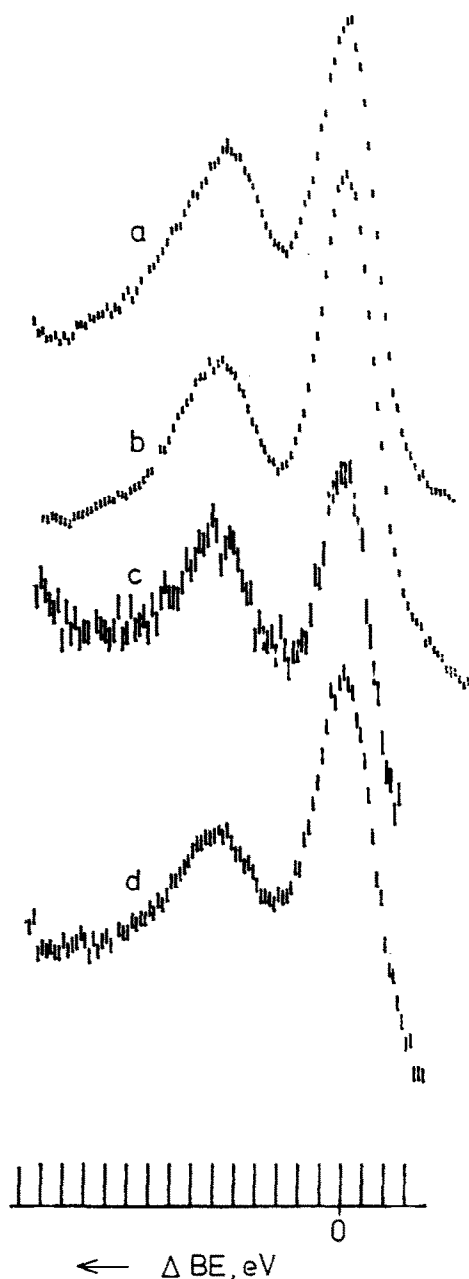

FIG. 1. Nickel $2p_{3/2}$ spectra of nickel nitrate (a), hydroxide (b), aluminate (c), and nickel nitrate adsorbed on alumina (d).
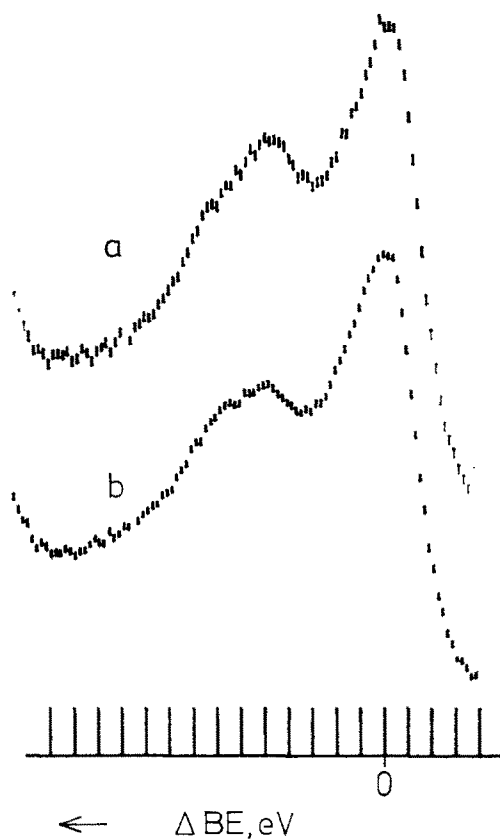

FIG. 2. Nickel $2p_{3/2}$ spectra of nickel sulfate heptahydrate heated to 100°C (a) and 300°C (b).

satellite structures are markedly asymmetric in both samples. Asymmetry in the satellite structure may be associated with a distortion in the crystal structure (15). There is also a slight difference in the satellite structure between the two samples, which is apparent with the computer-processed scans. The number of strong acid surface sites increases considerably when nickel sulfate heptahydrate is heated (14) from 100 to 300°C. It is disappointing that the corresponding change in the spectra is small.

The nickel spectra of nickel sulfate adsorbed on alumina are shown in Fig. 3. At low adsorptions the satellite structure becomes symmetric. It is evident, therefore, that an alteration in the ligands has occurred. The similarity of the spectra
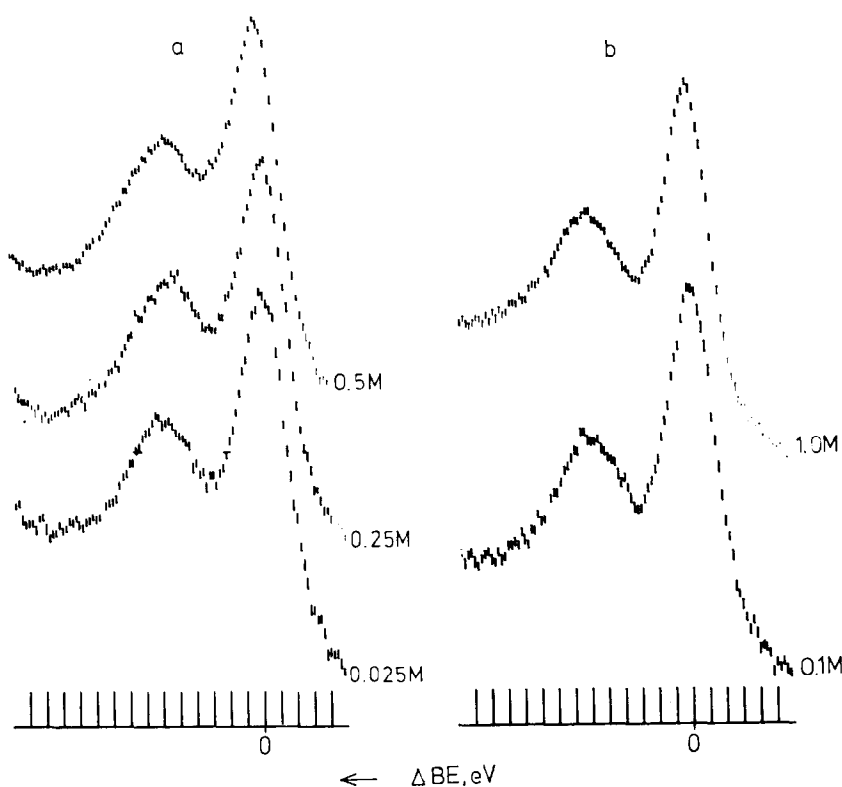
FIG. 3. Nickel $2p_{3/2}$ spectra of nickel sulfate adsorbed on alumina, unwashed (a) and washed (b).

(and BE) of nickel in adsorbed nickel sulfate and bulk nickel hydroxide suggests that the adsorbed nickel is bound to surface oxide/hydroxide groups.

An XPS signal from sulfur in adsorbed sulfate was observed (BE 169.0 eV, cf. 169.3 eV for the bulk compound), commensurate with the adsorbed nickel signal. The sulfate may be bound to an adjacent acidic site.

As the amount of adsorbed nickel sulfate is increased, the nickel and sulfate ions come into closer contact. The spectrum of nickel at high concentrations, on the unwashed samples, is intermediate between the spectra of the bulk sulfate and hydroxide (Fig. 3). If the samples are washed thoroughly after adsorption on the nickel sulfate, the weakly bound material is removed and the spectra then show only a symmetric satellite corresponding to the strongly bound nickel (Fig. 3).

The satellite data therefore give further evidence for the interaction of adsorbed nickel ions with the surface oxide/hydroxide groups.

These results are in agreement with our previous conclusions, from the study of the reaction of ozone with nickel ions on alumina (3), that low adsorptions produce nickel ions bound to basic ligands, and high adsorptions result in, effectively, nickel sulfate being deposited at the surface.

X-ray irradiation causes considerably less damage than electron irradiation (16). Nevertheless, reduction of surface species by the X-ray beam has been observed (6, 7). The black high-valent nickel species, produced from the reaction of ozone with nickel ions on alumina (3), was susceptible to reduction by the X-ray irradiation, and decomposed rapidly to a white material. The high-valent nickel species was not detected therefore by XPS.

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