Kurze Mitteilungen

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Dehydration of Various Aluminium Hydroxides Studied by Photo-electron Spectra *

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Summary

New correlations are found between the chemical shift of the ionization energies of aluminium 2s and 2p, and of oxygen 1s, the width of the corresponding photo-electron signals and the charging effect evaluated from the twin carbon 1s signals of hydrocarbons. The complete dehydration to the various sesquioxide modifications seems to enhance interatomic relaxation and Franck-Condon broadening.

The hydrated or anhydrous forms of aluminium hydroxide, and the sesquioxide, mostly contain octahedral groups $Al(III)O_6$ with protons attached to the bridging oxygen ions. It is not easy by X-ray crystallography to locate such protons, and in the related case [1] grey $Cr(OH)_3(H_2O)_3$ (dissolving in acids as monomeric aqua ions in contrast to the green amorphous polymers) the chromium (III) fill a third of the cavities potentially available for octahedrally coordinated atoms, of which two-thirds are occupied in bayerite $Al(OH)_3$ with resulting pseudo-isomorphism. Among the known hydroxides are bayerite, hydrargillite and the non-stoichiometric nostrandite [2] containing about 0.1 H_2O per $Al(OH)_3$. Boehmite $AlO(OH)$ consists of layers formed by distorted octahedra having oxide anions joined to the lateral OH^- by hydrogen bonds. When losing water, boehmite changes into face-centered cubic γ-Al_2O_3 which seems to be a defective disordered spinel $MM_2^*O_4$ lacking a third of the tetrahedrally coordinated M. The η-Al_2O_3 (with 0.28 H_2O) results from the dehydration of bayerite or nostrandite; it is even more reactive than γ-Al_2O_3 with looser Al-O bonds. The ϑ-Al_2O_3 (with 0.18 H_2O) is obtained from boehmite or the η modification, whereas χ-Al_2O_3 results from the dehydration of hydrargillite. They behaviour of the vacancies left by removal of some water molecules has been discussed by Freund [3, 4]. It is seen in Table 2 that the photo-electron chemical shifts are quite pronounced among these solids. The were previously noted in connection with a study [5] of the reaction of (partly oxidized) aluminium surfaces with gaseous anhydrous HF at various temperatures.

We also used the Varian IEE-15 photo-electron spectrometer with a high-intensity magnesium (1253.6 eV) photon source to compare surfaces of 5N(99.999%) metallic aluminium oxidized under varying conditions. It is only possible to investigate oxygen-free aluminium under very special conditions [6, 7] including ultra-high vacuum. For our purposes, it is more relevant that the amorphous oxide film frequently remains constant in thickness [8, 9, 10] about 20Å (which happens to have the same order of magnitude [11] as

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Table 1: Treatment of samples, identification of crystal structures, and foreign constituents determined from photo-electron and Auger (I'_{eff}) signals.

Compounds	X-ray powder pattern and electron diffraction	∂	Contamination
α-Al_2O_3 (Corundum)	α-Al_2O_3, rhomb.	1.5	–
γ-Al_2O_3	γ-Al_2O_3, cub.	2.4	α-Al_2O_3 (trace)
η-Al_2O_3	η-Al_2O_3, cub.	2.9	–
χ-Al_2O_3	χ-Al_2O_3, hex.	2.6	–
θ-Al_2O_3	θ-Al_2O_3, monocl.	2.0	–
Böhmite AlO(OH)	böhmite, orthor.	2.0	γ-Al_2O_3 (~20%)
Al anodized (H_3BO_3)	amorphous to elect. diff.	–	I'(B1s) ~ 198 eV (trace)
aged natural oxide film on laminated Al-sheet	amorphous to elect. diff.	–	no visible contamination other than O and C
freshly formed oxide film on Al-sheet	–	–	do.
Al-sheet etched with Na_2CO_3 at 100 °C, rinsed with H_2O at 20 °C	amorphous to elect. diff.	–	I'(Na1s) = 1077.2 eV (~11% relative to Al)
Al-sheet etched with Na_2CO_3, 100 °C, rinsed with H_2O, 100 °C	amorphous to elect. diff. (AlOOH)?	1.7	no trace of Na
Al-sheet etched with NaOH at 70 °C rinsed with H_2O, 20 °C and heated 20 min. at 500 °C in vacuum	amorphous to elect. diff.	–	I'_{eff}Na1s2p^2 = 269.4 eV (~2.5% relative to Al)
Al-sheet etched with NaOH at 70 °C, washed H_2O, 20 °C and treated with 8 M HNO_3 3 min. at 80 °C	–	–	I'_{eff}Na1s2p^2 = 269.9 eV (~7%) I'(N1s) = 405.6 eV (~25%)
Al-sheet electropolished in a solution of $HClO_4$ + C_2H_5OH, 30 V	amorphous to elect. diff.	–	I'(Cl2p) = 203.1 eV (~3%)
Hydrargillite α-Al(OH)$_3$	hydrargillite, monocl.	–	bayerite
Bayerite β-Al(OH)$_3$	bayerite, monocl.	–	hydrargillite + nostrandite
Nostrandite γ-Al(OH)$_3$	nostrandite	–	hydrargillite

the mean depth of escape without inelastic collisions of photo-electrons with a kinetic energy of about 1000 eV) in a reasonably dry atmosphere without corrosive ingredients, whereas immersion of aluminum in boiling water gives a product similar to boehmite containing between 18 and 45 weight percent water [12, 13]. As previously noted [14] the metallic phase is «shining through» the thin oxide films, producing (somewhat weaker) Al2s and Al2p signals at ionization energies I some 2.5 to 3 eV below the oxygen-containing materials.

The X-ray diffraction patterns were obtained with a Guinier camera (Nonius) and the electron diffraction patterns with a Philips EM300 electron microscope. The various aluminium compounds were prepared in the Neuhausen laboratories. The cleaning and other treatments of 5N aluminium sheet are indicated in Table 1, summarizing the same 17 kinds of samples as Table 2 giving the photo-electron signals $I'(\mathrm{M}nl)$ corrected for charging effects (when needed) according to the technique [14, 15] of evaluating the quantity C'_{st} as the difference between 290 eV and the highest $I^*(C1s)$ due to hydrocarbon films, and adding C'_{st} to the I^* recorded by the instrument for all the other signals. The quasi-stationary positive potential maintained on non-conducting samples can be identified with the distance ∂ between the two $I^*(C1s)$. If the sample is sufficiently conducting (at least under the influence of the X-rays) only one C1s signal is observed. Thus, sample no. 7 was anodized at 30 V in 1 M boric acid to give a 400 Å thick oxide layer. However, the relatively low value 4.0 eV of C_{st} may suggest a beginning tendency toward quasi-stationary charging. It is difficult to perform a univocal deconvolution in more components of such C1s signals with ∂ below 1 eV, and of the frequent, broad and rather symmetric O1s signals (in part due to adsorbed water). One reason is that adjacent Gaussian curves [14] with comparable heights and the same one-sided half-width $\delta(-)$ combine to a slightly broader signal looking like a Gaussian to a good approximation.

Fig. 1 shows the rather unexpected phenomenon that I'(O1s) increases roughly to the same extent in the various samples as their I'(Al2s) and I'(Al2p). As also seen from Table 2, the difference between the two latter ionization energies remains 44.8 eV within a-tenth eV, as found also for other compounds [5, 14]. We would like to correct the error that I'(Al2p) = 80.7 eV was reported [5] for α-Al_2O_3 rather than 79.5 eV. For comparison, the gaseous Al^{+4} has ^2S representing

Table 2: Recorded I^*(C1s) of hydrocarbons with concomitant parameter of charge compensation C'_{st} and ionization energies of aluminium 2s and 2p and oxygen 1s with one-sided half-widths $\delta(-)$ of the signals. Atomic ratios obtained by semi-quantitative analysis from signal heights.

Compounds	I^*(C1s) eV	C'_{st} eV	I'(Al2s) eV	$\delta(-)$ eV	I'(Al2p) eV	$\delta(-)$ eV	Al	I'(O1s) eV	$\delta(-)$ eV	O/Al
α-Al_2O_3	285.7 287.2	2.8	124.2	1.3	79.5	1.0	1	536.3	1.1	3
γ-Al_2O_3	285.3 287.7	2.3	124.3	1.6	79.5	1.2	1	536.4	1.5	3
η-Al_2O_3	285.1 288.0	2.0	124.4	1.5	79.6	1.2	1	536.5	1.4	3
χ-Al_2O_3	285.3 287.9	2.1	124.1	1.5	79.3	1.3	1	536.3	1.6	3
θ-Al_2O_3	285.7 287.7	2.3	124.0	1.4	79.4	1.2	1	536.0	1.3	3
AlO(OH)	285.6 287.6	2.4	124.2	1.4	79.4	1.1	1	536.6	1.5	3
Al_{anod}	286.0	4.0	125.2	1.2	80.5	0.9	1	537.8	1.2	3
aged	285.5	4.5	124.4 121.8	1.5 1.0	79.6 76.9	1.2 0.8	1 0.6	536.5	1.3	2
fresh	285.5	4.5	124.0 121.9	1.4 0.8	79.2 76.7	1.2 0.9	1 1.2	536.5	1.3	1.5
Na_2CO_3/20 °C	285.0	5.0	125.3 122.4	1.2 1.0	80.5 77	1.1 1.1	1 0.15	537.2 538.5	1.1 1.0	2.5 2.3
Na_2CO_3/100 °C	284.5 286.2	3.8	124.1	1.4	79.2	1.4	1	536.7	1.4	3
NaOH/500 °C	285.5	4.5	125.7 123.1	1.2 1.1	80.8 77.5	1.0 0.9	1 0.23	537.8 535.9	1.1 1.0	4 2
NaOH/HNO_3	285.7	4.3	125.2 122.8	1.2 0.9	80.3 77.6	0.9 0.6	1 0.6	537.5 535.2	1.1 0.9	5 2 .
electrop.	285 6	4.4	125.3 123.0	1.3 1.0	80.4 77.8	1.0 0.7	1 0.4	537.2 536.2	1.1 1.0	3 1.2
α-$Al(OH)_3$	286.0	4.0	124.6	1.2	79.8	1.1	1	537.4	1.1	5
β-$Al(OH)_3$	286.0	4.0	125.1	1.3	80.3	1.0	1	537.8	1.3	4.5
γ-$Al(OH)_3$	286.1	3.9	124.7	1.3	80.0	1.1	1	537.5	1.1	5

$1s^22s2p^6$ at 44.48 eV above the groundstate $^2P_{3/2}$ belonging to $1s^22s^22p^5$. This invariance with chemical surroundings of the $I(M2s) - I(M2p)$ is also found in the adjacent elements M. The difference 45.2 eV in Table 2 for the weak signals of the metallic phase is within the experimental error.

It is not trivial that all the I values on Fig. 1 decrease by progressive loss of water from hydroxides. Similar effects have been observed [16] by dehydration of serpentine and chrysotile, in particular on I(O1s). Nefedov *et al.* [17] pointed out that the latter quantity is (to a good approximation) a linear function of the reciprocal value of the distance from the oxygen nucleus to the closest neighbour atom. This situation might suggest a purely electrostatic Madelung potential of the size corresponding to a charge close to +1.2 on the neighbour atom. However, there is little doubt that a major part of the interatomic contribution to the I variation is the relaxation effect [18, 19] corresponding to the electronic density adapting to the absence of an electron from an inner shell. There is plenty of evidence [20,21] from the molar polarizabilities (derived from measurements of the refractive index) that oxide changes tremendously from (the easily oxidizable) Cs_2O and BaO to the much less polarizable Al_2O_3, SiO_2 and ClO_4^- (corresponding to what Fajans called "tightening" due to the small, highly charged cations), and in particular, protons forming (bridged or unidentate) hydroxo ligands have a strong effect.

Fig. 2 shows the relation between the one-sided half-width $\delta(-)$ and the I'values. The low I' values caracterizing the oxides with lowest proton content tend to correspond to broader signals. Besides the instrumental contribution to $\delta(-)$, the main origin [14] of the width is vibronic co-excitation according to Franck and Condon. It can be excluded that a predominant contribution originates from shortened life-time (say, due to Auger transitions [22]) as already seen from the fact that the signals discussed here have Gaussian and not Lorentzian shape. It is more difficult to exclude

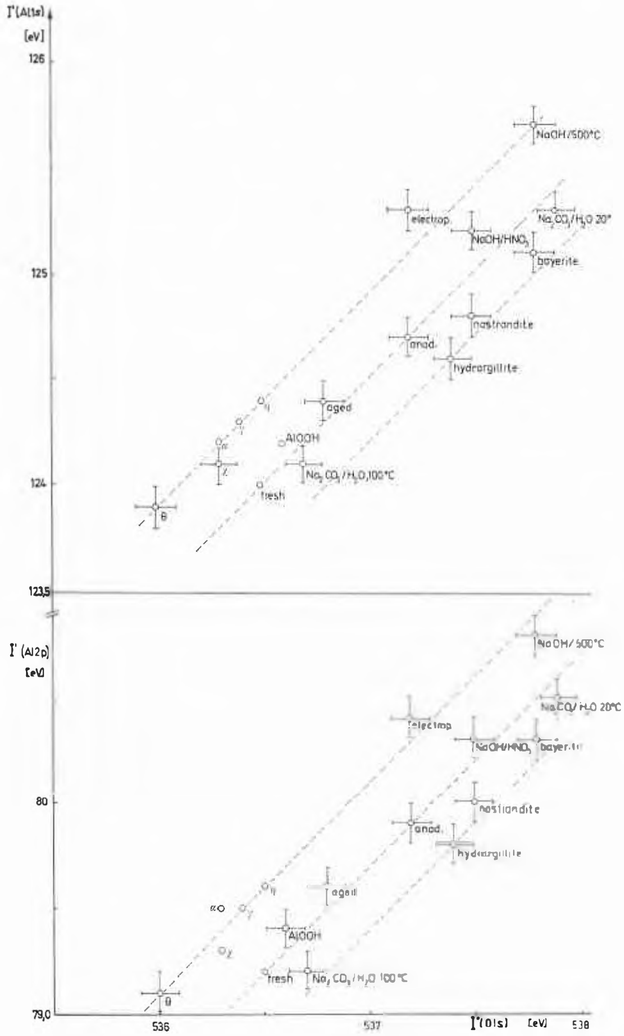

Fig. 1: Correlation between ionization energies of oxygen 1s and of aluminium 2s and 2p. It may be noted that the oxides (classified with Greek letters according to their crystalline modification) fall close to a straight line with unit slope. An exclusively electrostatic Madelung potential would produce the opposite slope.

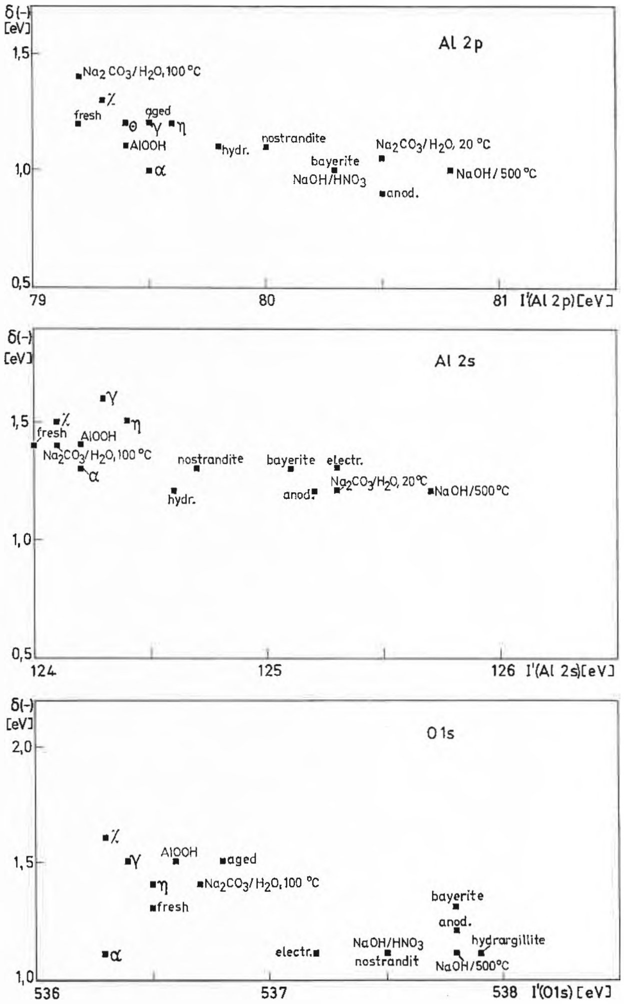

Fig. 2: Correlation between one-sided half-width $\delta(-)$ of the photo-electron signal and the corresponding I' (corrected for charging effects as described in the text).

the presence of moderately non-equivalent atoms of the same element, in view of the mathematical properties of Gaussian error-curves discussed above [14]. As seen from Fig. 2, Al2s signals are only marginally broader than Al2p signals and hence, they are less influenced by Coster-Kronig transitions than S2s which gives a markedly broader signal than S2p [23]. It has previously been noted [14, 24] that anions such as F^- give broader photo-electron signals of inner shells than isoelectronic cations such as Na^+ and Mg^{+2}. This can be rationalized on the basis of the *Franck-Condon* principle, the equilibrium internuclear distances changing more by removal of the negative charge of an anion than by increasing the positive charge of a cation. In analogy to molecular spectra, it may also be argued that short internuclear distances (as found in anhydrous oxides) favour vibronic broadening, and at the same time, interatomic relaxation effects decrease I in disagreement with Nefedov [17]. As mentioned above, marginal evidence exists that Al2s is more influenced by interatomic effects than Al2p.

One of the undoubted advantages of photo-electron spectrometry is that amorphous surfaces, like glasses [23, 25], can be treated equally well as crystalline solids. The kinetics of the reaction of aluminium with gaseous hydrogen fluoride has been investigated at length [5, 26] and the reactivity shown to vary a great deal between water-containing, anodized surfaces as one extreme, and corundum, the opposite extreme of inertness. Further on, the new photo-electron results have allowed confirmation of the presence of oxide films 20 Å or thicker and their semi-quantitative evaluation [26].

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