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The Possible Interpretation of XP Spectra of Supported Pt Catalysts in the Oxidized and Sulfided State

Binding energy (BE) shifts measured by XPS contain information on the chemical state of catalytically active components of supported catalysts. The fact that an active component such as platinum is typically present in low percentages on various supports (SiO_2, Al_2O_3, or others) may raise difficulties in spectrum interpretation. These supports are, as a rule, *electrical insulators;* consequently they acquire an electrostatic charge during XPS measurements which gives rise to three problems.

First, a well-known *charging shift* occurs in BE line position which may reach values of up to 7–10 eV. These may be higher than the BE shifts due to different valence states, which are typically between a few tenths eV and a few eV (*1*). This can be corrected by postcalibrating the spectra to a line with a well-known and stable BE value, as is done regularly in most cases.

Line broadening represents the second problem. It is difficult to determine its extent quantitatively although line broadening has been reported to increase as the BE shift caused by the electrostatic charge increases (*2*). This broadening cannot be easily compensated for, and must not be forgotten when it comes to spectrum interpretation.

The third pitfall arises from *inhomogeneous electrostatic charges*. These mean that a BE difference is still left behind in the minor component(s) after postcalibration of the spectrum of the major component with respect to a line of a well-known binding energy. For example, in the case of a Pt/SiO_2 catalyst, after calibration to the exact BE of the Si line in SiO_2, the Pt 4*f* component can still have an "improper" BE value, its charge being somewhat different from that of the support.

It can be particularly dangerous to confuse the line broadening and/or the false BE maxima due to inhomogeneous charging with lines belonging to different valence states. In the case of Pt catalysts subjected to different treatments, the presence of PtO or PtS entities can be supposed. Their identification is all the more difficult because bulk Pt oxide or Pt sulfide phases are not readily available. Pt(IV) oxide has a BE shift of 2.9 eV toward higher BE, whereas a BE shift of +1.5 eV has been assumed for Pt(II) oxide (*3*). Synthetic spectra constructed on this basis were of great help in identifying various Pt oxide phases on a Pt single crystal subjected to various oxidizing treatments. Studies with highly oxidized dispersed catalysts confirm the problems that result from line broadening; still, the relatively large BE shifts (especially of Pt^{4+} species) made reliable identification still possible (*4*, *5*). We believe, however, that the interpretation of an *in situ* XPS characterization of a sulfided Pt/ZrO_2–SO_4^{2-} catalyst in terms of Pt being present mainly as Pt^{n+}, due to its hindered reduction and also to its partial sulfidation (*6*), was less successful. The XPS evidence was based mainly on the BE position of Pt 4*f* peaks shifted to higher BE values as compared to metallic platinum without considering inhomogeneous charging as a possible contributor to the observed Pt-core-level shifts.

In a previous work (*7*) we pointed out how such a differential electrostatic charge makes it impossible to determine the actual oxidation state of a 6% Pt/SiO_2 catalyst (EUROPT-1). Independent X-ray diffrac-

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tion results (*8*) showed the formation of a thin outer Pt oxide shell as a result of oxygen treatment of the Pt crystallites. The Pt oxide phase disappeared completely and rapidly (within 40 sec) upon the introduction of hydrogen. Repeating an analogous treatment in the preparation chamber of an XPS apparatus resulted only in Pt 4*f* lines of different broadening. Pt 4*f* lines of EUROPT-1 measured after such oxidation and reduction treatments (*7*) are shown in Fig. 1. A third spectrum shows the Pt 4*f* line of a sulfided EUROPT-1 catalyst. The sulfidation involved the contact of the catalyst with a 1 : 10 mixture of H_2S and H_2, at 633 K and a total pressure of 500 Torr for an hour (*9*). The sample was exposed to the surrounding atmosphere during transfer to the XPS instrument. The surface abundance of Pt as determined from line intensities was 0.6%. Sulfur was below the detection limit of XPS. No particular difference is seen between the peak shapes of the three samples.

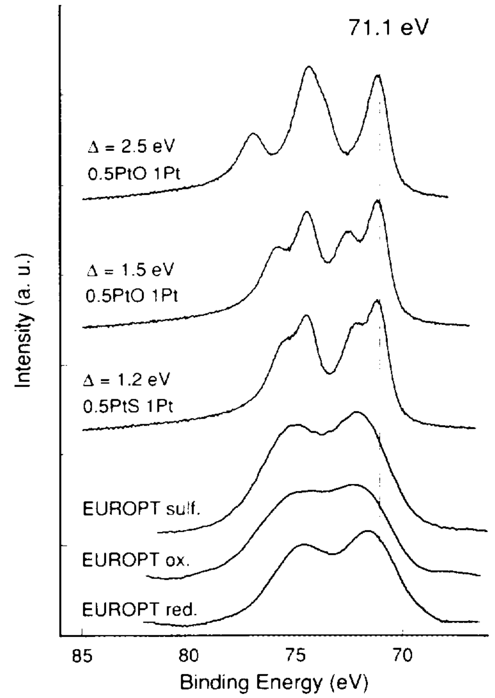

FIG. 1. Actually measured Pt 4*f* spectra of EUROPT-1 (6.3% Pt/SiO_2) in different states (from below): reduced by H_2 *in situ*; oxidized by O_2 *in situ* [both adapted after Ref. (*7*)]; and sulfided *ex situ* with a mixture of H_2 and H_2S at 633 K. The originally higher intensity of this curve has been normalized to the former two spectra. In addition, three synthetic spectra adapted from an actual Pt 4*f* spectrum of Pt black simulating 2 : 1 mixtures of Pt^0 and Pt^{n+} are shown. The BE differences are explained in the text.

It is worth comparing these broadened lines with shifted BE values with spectra of mixtures of PtS and PtO samples that are as free from line broadening as possible. Figure 1 also contains three artificial spectra constructed on the basis of a real Pt 4*f* doublet measured with a chemically purified Pt black called Pt–N in Ref. (*10*). The Pt^{n+} components were produced by multiplying the actual unsmoothed spectrum by 0.5 and shifting them to higher BE values. The BE difference of 2.5 eV is an empirical value for Pt oxide present on Pt black: it was taken from the actual difference between the Pt metal and Pt oxide peaks in the difference spectrum of a purified and oxidized Pt black [Fig. 2 in Ref. (*11*)]. The $D = 1.5$ eV is a value assumed for the difference between Pt and PtO (*3*), while the $D = 1.2$ eV is an empirical value for sulfided Pt taken from an actual difference XP spectrum of unsulfided and sulfided Pt black (*12*). The model does not consider any Pt 4*f* line shape changes due to Pt oxidation, which would possibly involve a different Gaussian-to-Lorentzian mixing ratio (*13*), but has the advantage that it takes the inherent asymmetry of the Pt 4*f* line (*14*) into consideration. The synthetic spectra are similar to those published for Pt after adsorption of sulfur as well as after oxidation of that system whereupon also Pt oxide peaks appear (15).

The figure clearly shows that the spectrum shapes expected in the *absence* of line broadening are markedly different from the actual spectra measured with this Pt/SiO_2 catalyst of high dispersion. *None* of the BE of Pt 4*f* of EUROPT-1 is equal to the expected value of 71.1 eV, and this indicates that the conductivity of the metal particles

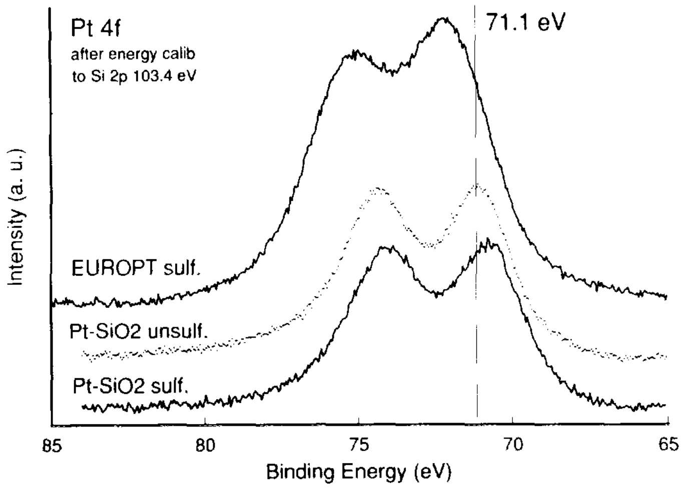

FIG. 2. Actual Pt 4*f* spectra of three Pt/SiO$_2$ samples—as explained in the text—after MgKα satellite subtraction, Shirley background subtraction, and energy calibration to Si 2*p* = 103.4 eV. The spectra have been shifted in the vertical direction, but their height has not been normalized.

and the likely semimetallic character of surface Pt sulfides do not preclude the accumulation of inhomogeneous charge, since the very small Pt particles (ca. 1.7 nm) are spatially separated from each other. Nevertheless, the lower conductivity of oxidized and sulfided Pt enhances their BE shifts. The BE difference (PtO) − (Pt) should be higher, but the oxidized and sulfided Pt still exhibit nearly the same Pt 4*f* spectrum, the shape of which is determined predominantly by line broadening rather than by the appearance of components of Pt^{n+}.

A specially designed TUBUS experiment (*7*) confirmed the conclusion that electrostatic charge can cause uncertainties in the BE maxima higher than the changes which could have been attributed to the appearance of a possible Pt oxide phase. This treatment applies a potential to the lens entrance element which is usually at ground potential. It does not eliminate electrostatic charging as, e.g., a flood gun does; instead, it adds additional positive or negative charge to the existing charge, causing additional BE shift and line shape changes. Changing line shapes under the influence of different TUBUS potential point to an inhomogeneous electrostatic charge; this was the actual situation observed with Pt/SiO$_2$ (*7*).

Since the maxima of the oxidized and sulfided broad Pt 4*f* lines lie at higher BE values in Fig. 1 than those of reduced Pt, it can still be argued that the shift is eventually due to the presence of a high fraction of Pt^{n+} after these treatments. We believe that Fig. 2 offers good arguments against this assumption. Three spectra are shown here. The first is that of the sulfided EUROPT-1 identical to that seen in Fig. 1 and exhibits, indeed, a BE shift of about 1 eV toward higher energies. The other two spectra belong to a Pt/SiO$_2$ catalyst of much lower dispersion (crystallite size about 20–40 nm). The lower dispersion of this sample gives rise to a better separation of the Pt 4*f* doublet due to less line broadening. The BE maximum of the unsulfided sample agrees well with the value of 71.1 eV expected for Pt metal (*3*, *10*), while the BE maximum of its sulfided counterpart is at a lower BE value. Hence, the figure shows XP spectra of two sulfided Pt catalysts, one of them showing a *positive* and the other a *negative* BE shift. Obviously, no negative BE shift can arise from a Pt sulfide component. Both shifts can be attributed to inhomogeneous charging which depends also on sample morphology and dispersion but the extent of which is unpredictable. The "correct" BE value (71.1 eV) of this unsulfided sample shows the absence of inhomogeneous charging. The larger Pt particles—being predominantly in the metallic state—are in good electric contact with the support, as opposed to the very dispersed EUROPT-1.

Since the spectrum shapes in Ref. (*6*) resemble those observed with EUROPT-1 rather than those of the simulated spectra, the interpretation of the ESCA results by the authors of Ref. (*6*) appears incorrect and warrants further discussion. It seems to be more likely that the observed Pt 4*f* line shapes arise due to line broadening and BE shifts used by inhomogeneous charging. Such a phenomenon could easily explain different peak positions with different supports (ZrO_2 and SO_4^{2-}–ZrO_2). The relative areas of Pt^{n+}/Pt^0 between 4.5 and 6.1 obtained by a fitting procedure using literature BE values and disregarding inhomogeneous charging would, therefore, be an evaluation artifact. Sulfided Pt catalysts may, indeed, expose a rather low fraction of the metallic Pt surface. However, the loss of metallic character by Pt can be due to the presence of large *surface* PtS islands, as indicated by the appearance of the XPS line of S^{2-} species (*6*). This sulfur is sufficient to produce a surface insulating or semiconducting layer which gives rise to an inhomogeneous electrostatic charge, producing the spectral changes observed. On the other hand, it can suppress CO chemisorption, as shown also by IR measurements (*6*), and eliminate the catalytic activity almost entirely (*16*).

The relatively low amount of PtS in the sulfided Pt catalyst samples described in the present work is confirmed also by difference spectra (*12*). Further experiments are in progress to determine also the *catalytic* properties of the samples.

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