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# XPS of platinum in Pt/SiO<sub>2</sub> (Europt-1): possibilities and limitations of the method

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Platinum XPS lines of a 6.3% Pt/SiO<sub>2</sub> catalyst in oxidized and reduced states were studied. The observed line shapes can be attributed to line broadening due to electrostatic charging, the extent of which changed during oxidation–reduction cycles. The limits of the method in studying very disperse materials with low metal loading are pointed out.

## 1. Introduction

The common feature of supported metal catalysts is that rather low amounts of metal are dispersed over electrically insulating supports. This amount can be up to 20% with base metals while noble-metal industrial catalysts contain usually a loading below 1% and contain, as a rule, very small metal particles. This causes difficulties in catalyst characterization by electron spectroscopy. Europt-1 has a higher metal loading (6.3% Pt/SiO<sub>2</sub>) partly in order to be able to characterize Pt particles adequately.

In XPS, the metal lines are usually broadened and their BE shifted to higher values due to electrostatic charging of the insulator matrix. A typical method of charge compensation is the use of an electron flood gun [1]: a properly selected gun voltage can shift the peak positions back to their proper position. In the case of inhomogeneous charging, i.e. when various surface sections – insulator islands over another insulator – are charged to a different extent, this method is of little help. Another way to negotiate this hurdle is to *detect*

the presence of electrostatic charging without compensating it: this is the so-called Tubus experiment. The sample and the analyzer tubus are normally connected to a common ground. If an electric potential is applied between the analyzer and its grounding, it creates a homogeneous electrostatic field between the specimen and the entrance slit of the analyzer. This field will influence inhomogeneously charged species in a different way. In other words, with homogeneous charging, a tubus potential has the same effect as the flood gun: causes an energy shift in the peak. With an inhomogeneous charge, in turn, also the peak shape (e.g., FWHM and/or symmetry) will change.

The state of Pt in supported catalyst represents a challenge for surface analysis. In the clean metal, the Pt 4f doublet can respond rather sensitively to the oxidation state of Pt. On the onset of oxidation of a stepped (557) single crystal or a Pt electrode, the asymmetry at the higher BE side of the doublet increased considerably [2,3]. A synthetic spectrum of Pt(0):Pt(II) = 1:1 appears as a broad composite peak between 70 and 77 eV, while the appearance of Pt(IV) brings about a three-peak system with maxima at about 71, 74 and 78 eV, the 4f<sub>7/2</sub> peak of Pt(IV) coinciding roughly with the 4f<sub>5/2</sub> peak of Pt(0) [4].

In spite of support charging, various efforts have been reported to determine peak contribu-

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tions attributed to various oxidation states in supported Pt catalysts, e.g., in Pt/NaY zeolite [5] of a Pt content of 2.4% or 4.8% or in Pt/TiO<sub>2</sub> with even less Pt [6,7].

Europt-1 has been extensively characterized by various surface physical and chemical methods, including XPS [8]. It was reported that Pt 4f “line shape suggests incomplete reduction of platinum” [8]. Indeed, EXAFS data [9] indicated only Pt–O bonds in a Pt catalyst stored in air for a long time. On the other hand, a very careful X-ray diffraction study indicated that oxidation of Pt particles took place in a way that the outer shell of each Pt particle transformed into platinum oxide [10]. The maximum degree of oxidation (at 573 K) affected about 65% of the total amount of Pt present.

One should expect, therefore, XPS lines characteristic of an oxidized Pt. In particular, with prevailing PtO in the oxide phase [10], a broad peak should appear as reported in ref. [4]. The present study discusses the limitations and possibilities of detecting Pt and its chemical state in Europt-1 by XPS.

## 2. Experimental

A Leybold LHS-12 combined equipment for surface analysis was used. This apparatus permitted measurements of disperse samples which could be handled in various gas ambients up to 1 bar at temperatures between 77 and ~700 K, then transferred to the UHV measuring chamber where the electron spectroscopic measurements could also be carried out in this temperature range. Leybold DS-100 software was used for curve smoothing, background subtraction and peak-area integration as well as energy scale shift (actually 2.5 to 4 eV) for postcalibration. The entrance tubus of the analyzer could be either grounded (no electric field) or a voltage between +45 or –45 V could be applied to produce a symmetric and homogeneous electrostatic field at the specimen.

Europt-1 is granular, the majority of grains being between 0.25 and 0.5 mm [8]. It was introduced either in the form of prefabricated self-supporting wafers pressed with 45 MPa or as loose granular material in the stainless steel sample

holder. Alternatively, this loose material was pressed into the sample holder by a pressure of 10 MPa. The latter method could result in a reliable full coverage of the sample holder by the material, otherwise signals were obtained from the sample holder, too, through the holes in the wafer or between the individual catalyst grains.

## 3. Results and discussion

Pt 4f spectra of a Europt-1 as received and after 32 h oxidation at 573 K are shown in fig. 1. Both spectra appear as broad peaks with no proper separation of the 5/2 and 7/2 contributions. The peak maxima do not correspond to literature values after postcalibration to the Si line (in SiO<sub>2</sub> BE = 103.4 eV [10]). In the case of no pretreatment (curve 1), the separation between the 4f<sub>7/2</sub> and 4f<sub>5/2</sub> lines is rather poor and a small peak corresponding to oxidized Pt (likely Pt<sup>4+</sup>) appears at the high energy end. The BE values of all contributions are higher than the literature values [3,4]. After a short oxidation at 573 K, essentially the same curve shape was measured at 573 K (curve 2). After a lengthy oxidation, however, even the poor separation disappeared between the 5/2 and 7/2 components. An artefact due to the loss of surface oxide during sample transfer into the UHV system is not likely since curve 3 was measured after cooling the sample after oxidation to 78 K. XRD experiments also indicate that about 36% of the oxide was still present after evacuation of the sample in UHV [11]. After reduction in 500 mbar static H<sub>2</sub> at 573 K (curve 4), the separation improved slightly and the BE values were shifted closer to the literature values but were still not satisfactory. Again, measurements at 80 K gave the same peak shapes as curve 4 determined at 573 K.

This phenomenon indicates that calibration to the Si line did not remove the effect of charging entirely: an inhomogeneous (“differential”) charging can be suspected, i.e. the electrostatic charging of the support and Pt islands – whether they are in oxide or metallic form – is not uniform. Therefore, potentials of +45 and –45 V, respectively, were applied to the analyzer tubus. Fig. 2 shows

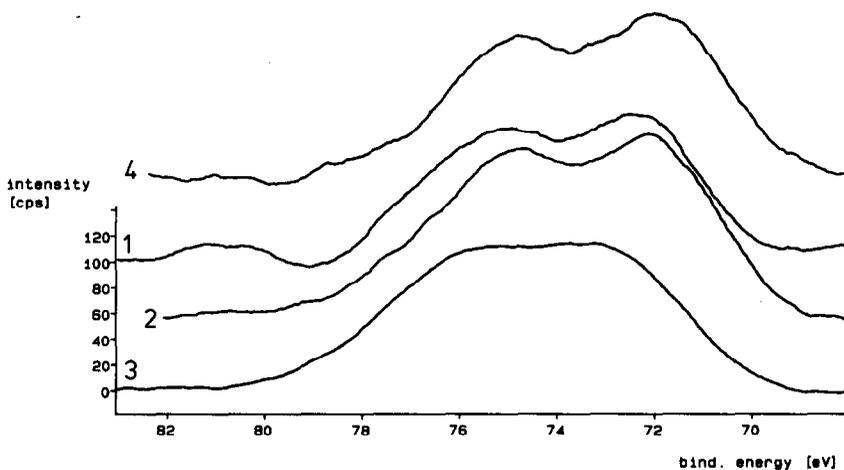


Fig. 1. Pt 4f XPS spectrum of Europt-1 in "as-received" state (1); after oxidation in 500 mbar O<sub>2</sub> at 573 K for 3 h (2) and for 32 h (3) and after reduction in 500 mbar H<sub>2</sub> at 573 K for 0.5 h (4). Curve 1 was measured at 300, curve 3 at 80, curves 2 and 4 (new sample) at 573 K. Energy scale postcalibrated to BE = 103.4 eV of the Si line in SiO<sub>2</sub>.

that under these conditions, the spectral shift of the Pt peak was not symmetrical: the negative tubus brought about a broadening, the positive one a contraction of the peak. Hence the positions of the two peak maxima were also shifted asymmetrically. On the oxygen and silicon peaks, however, the positive and negative shifts were much closer to the expected symmetric shift of uncharged line shapes.

The carbon spectra represent a special case (fig.

3). One of its contributions was apparently insensitive to the tubus potential, i.e., it was not charged. Its BE value corresponds to the carbon peak measured on an empty sample holder, therefore we identify it as a C contribution from the latter. Carbon on the sample holder is unavoidable in the spectra because the physical coverage of the sample holder by the granular material is very difficult but not impossible to achieve. An example where the sample holder was almost perfectly covered by

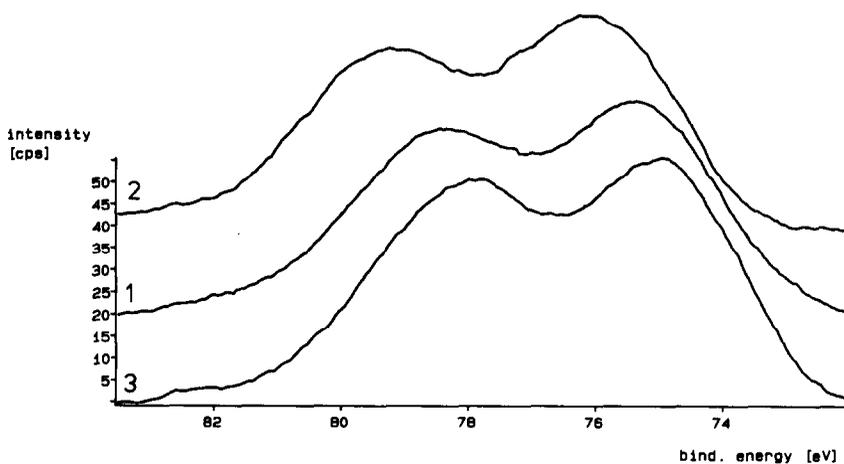


Fig. 2. Pt 4f spectrum of Europt-1 (treatment 1 h 13 mbar H<sub>2</sub> at 673 K); curve 1: as is; curve 2; Tubus +45 V; curve 3: Tubus -45 V. BE values are given as measured (no postcalibration).

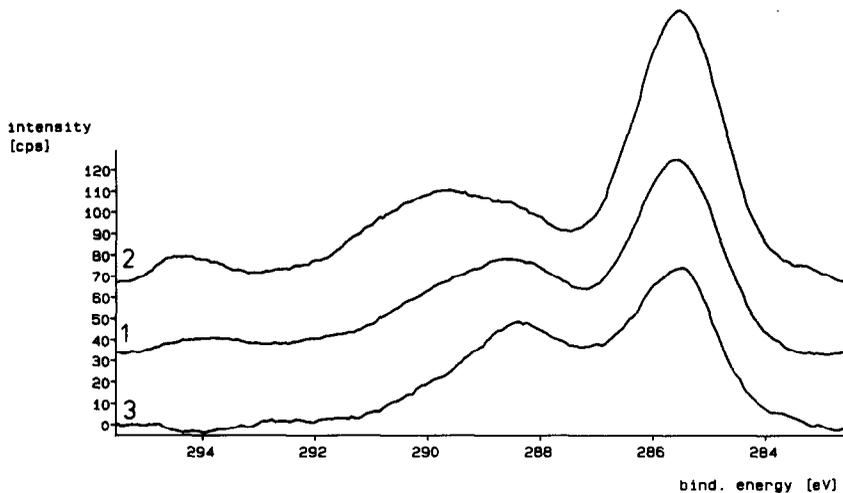


Fig. 3. C 1s spectra of Europt-1 (treatment and curves as in fig. 2). The right-hand side contribution insensitive to Tubus is due to the sample holder, that on the left-hand side is the carbon impurity of the catalyst. BE values are given as measured.

Europt-1 (the loose material being pressed in situ into the sample holder cavity) is reported in ref. [14].

After postcalibration to Si, the peak due to sample holder C impurity shifted to unrealistic values but the other contribution (on the left-hand side) acquired now values of about 284.6 eV which corresponds to a true BE of partly hydrogenated not quite graphitized carbonaceous polymer on the catalyst [12]. The charged C 1s contribution

has a much larger line width which is a direct indication of the inhomogeneity of the charging field. Note the change of symmetry of this latter carbon peak with and without external potential. A similar phenomenon indicating the coexistence of charged carbonate and uncharged C-deposit contribution was reported for Pd/CaCO<sub>3</sub> catalyst [13]. The separation of charged and uncharged species permitted us to determine the real carbon content of Europt-1 after various treatments [14].

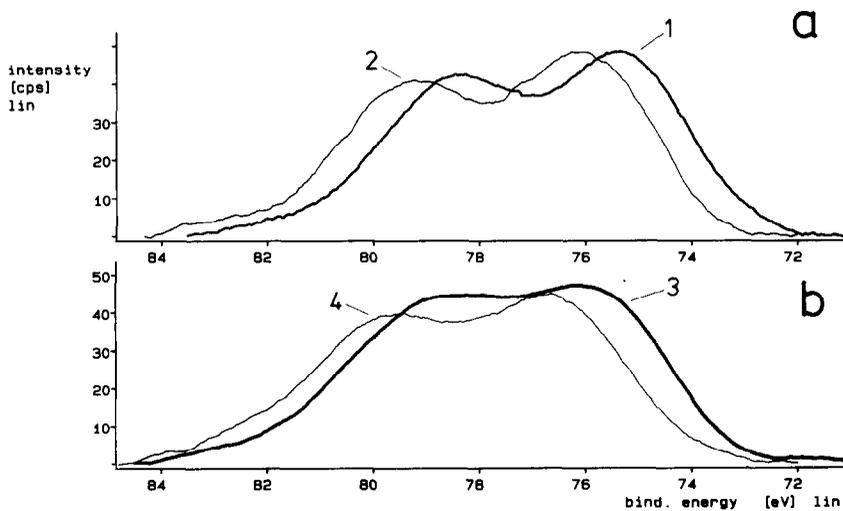


Fig. 4. Pt 4f spectra of a reduced (a) and oxidized (b) Europt-1. Reducing treatment as in fig. 2; oxidation, 1 h 13 mbar O<sub>2</sub> at 723 K. Thick lines (1 and 3): without Tubus; thin lines (2 and 4), Tubus at +45 V. BE values are given as measured.

Fig. 4 shows that the application of the same tubus voltage to an oxidized and reduced Pt brings about not only a shift in the same direction and of the same extent but changes also the peak shape: applying a tubus to an oxidized Europt creates exactly the same peak shape as observed in the case of reduced Pt. We conclude, therefore, that the effect (line broadening and a slight shift of the two maxima) is due entirely or at least predominantly to an inhomogeneous electrostatic charging of Pt particles and the support. Oxidized Pt particles have an insulator oxide envelope, therefore they are charged to a higher extent and, consequently, the line broadening becomes more pronounced. This charge can be decreased either by applying an external tubus voltage or by reducing Pt chemically. However, even metallic Pt has no electrical conductance to the apparatus, hence, they are also charged and all the phenomena connected to it (line broadening and uncertain peak positions) appear.

Although the components of the Pt4f peak doublet reported for Pt/TiO<sub>2</sub> exhibited a better separation, similar line width values and BE shifts were observed also there [7]. In that case the metal was vacuum sputtered on to the outer surface of the support. The actual Pt content in Europt-1 as determined by XPS [14] was about 1/3 of the nominal value of 6.3% indicating that a considerable fraction of Pt particles must be situated in pores, cracks, etc. This becomes obvious when one compares the electron micrographs of Pt/TiO<sub>2</sub> [7] and Europt-1 [15] and is supported also by the adsorption kinetics of oxygen on Europt-1 [16]. All these mean that Pt in Europt-1 is less accessible than in the Pt/TiO<sub>2</sub> sample described in ref. [7]. This geometry of Europt-1 renders the evaluation of the XPS results even more difficult. We believe that the line broadening and peak maxima shifts described here reflect the inherent physics of XP spectroscopy rather than the chemistry of the small metal particles. These results agree with those of Altman and Gorte [17] who studied small Pt particles on alumina film and concluded – in agreement with theoretical predictions [18] – that most of the core-level shifts were due to potential differences between the cluster and substrate which are charged to a different extent. Extreme care is

recommended, therefore, when measuring and interpreting electron spectroscopy of small metal particles on an insulator support, especially with any sorbed overlayer over them. It may be an inherent limitation of electron spectroscopy to reliably detect oxidic or other monolayers over disperse particles.

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