

## Surface Characterisation of Heterogeneous Catalysts by XPS: Part II

In Part I of this Final Analysis series (1), the identification and quantification of elements by X-ray (excited) photoelectron spectroscopy (XPS) was discussed. A statement was made that the core energy levels do not vary a great deal – but there is usually some variation for a given element in different chemical forms. This can be thought of as being caused by variations in the oxidation state and the local chemical or structural environment resulting in a variation in the net electrical charge on a given atom. The change in the electrical charge affects the energy of the photoelectron and so manifests as a slight shift in the measured core level binding energy. Such chemical shifts can be resolved in XPS spectra and this is a key aspect of the technique for catalyst characterisation.

### Qualification of Elements

In our earlier example, a platinum-gold fuel cell catalyst material was studied in an “as-received” form (1). Basic chemistry teaches us that only gold

is likely to have no surface oxide at all, and that even platinum is not as inert (see for example, (2)). So an interesting exercise might be to compare signals from the surface of the catalyst material before and after reduction using hydrogen gas. This can be achieved in a suitably-equipped spectrometer. Although the system is evacuated, a reaction cell isolated from the vacuum system can be used to create a reactive surface for study without the oxidation that would be expected on exposure to air. In the case of our catalyst material, a flow of hydrogen over the material while heating to 100°C was performed before re-evacuation and re-analysis.

Figure 1 shows the region of the platinum and gold 4f signals, their most useful photoemission lines, in much more detail than the survey spectrum shown in the previous Final Analysis article (1). The signals before and after the reduction of the material are shown. The platinum 4f signal is from 70 eV to 76 eV and that of gold is from

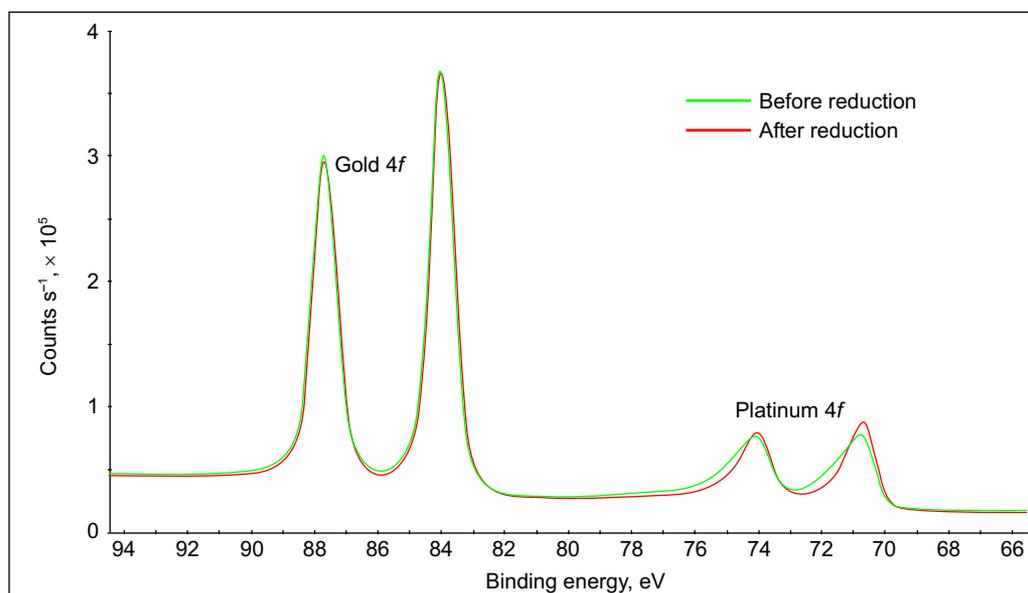


Fig. 1 Higher-resolution spectra of the surface of a platinum-gold fuel cell catalyst material “JMH-11”, showing the platinum 4f and gold 4f regions before and after reduction using hydrogen

82 eV to 90 eV. In both cases the level is split into two peaks due to electron spin and angular momentum considerations in the core level (this is termed spin-orbit coupling or *jj*-coupling), but in general the stronger line is considered.

The principal gold line at 84 eV is typical of the metal as a bulk material in both spectra. The lack of a significant change in the line shape after reduction implies that the element was not changed by this process.

The same is not true of the platinum line, at about 71 eV. There is a distinct tail on the high-binding-energy side of the doublet peaks before reduction. This is characteristic of an oxidised surface layer, perhaps a platinum(II) hydroxide or similar species. There are few other ways of determining this type of chemical information from the near-surface region selectively. Therefore XPS is a valuable analytical tool for heterogeneous catalysts, since the surface chemistry determines catalytic activity. Detailed quantification is possible: the application of numerical methods can afford an estimate of the relative contribution from the oxidised material compared with the metal. In this case, it is perhaps one-third as intense as the signal from the metal. The intensity of the signals, when averaged over the whole system, is directly related to the relative amount of the form considered. The results are usually best considered in conjunction with other analytical techniques, such as electron microscopy, which can give a good idea of structure. This information can then help in interpreting the XPS data.

Still more spectral interpretation is possible. The post-reduction platinum signal is asymmetric and very similar to that of the bulk metal, but the maximum of the signal is at 70.7 eV, compared with reference data for bulk platinum at 71.1 eV. As a result, we can also say that the surface layers might be something like an alloy rather than discrete particles of pure elements, as a change in binding energy from the pure element is the result of a degree of electron transfer between the elements in an alloy. In this case, X-ray diffraction (XRD) measurements determined that the material is indeed an alloy of Pt and Au.

## Summary

The results presented in this two-part series show several aspects of the use of XPS for the surface characterisation of heterogeneous catalyst materials. The major point of note is that a material's surface is not necessarily the same as the bulk in terms of its chemical composition. Analysis of the bulk catalyst material here revealed pure metals, while the surface has a very large amount of carbon present, together with impurities deposited during or after synthesis. Furthermore, the surface has some degree of oxidation.

In any field where the surface is important, in particular catalysis, understanding its chemical nature is vital. XPS is best seen as a (semi)-quantitative tool for comparative studies to obtain chemical information from the outer few atomic layers of a surface. Indeed, Nobel Laureate Kai Siegbahn (3), who developed the technique, originally termed it "electron spectroscopy for chemical analysis" (ESCA) (4).

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## References

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