

Surface Characterisation of Heterogeneous Catalysts by XPS: Part I

As it is the surface of a heterogeneous catalyst where the catalysed chemical processes take place, understanding the nature of the outer atomic layers of such surfaces is of great interest to those involved in the creation and improvement of such materials. The surface scientist has various tools to acquire information about a surface but one of the few that directly provides *chemical* information about the outermost atoms is X-ray (excited) photoelectron spectroscopy (XPS) (1).

Background

The XPS technique relies upon the photoelectric effect, first noted by Hertz in 1887 (2). An electron in an atom of a solid may absorb an incident photon and so gain sufficient energy to leave the confines of that atom's potential well. Due to

energy-sapping interactions, these photoelectrons do not travel far in solids – the length-scale is nanometres. So, although photoelectrons are produced wherever X-rays penetrate, only those within a few nanometres of the surface can actually escape the solid completely and they carry information about their origins in their kinetic energy.

Some seventy years after Hertz, exploitation of the photoelectric effect for materials analysis was developed by Siegbahn (3). In a typical analytical instrument, a surface is illuminated by X-rays of a well-defined energy. Given the fixed energies of core energy levels in atoms, the net energy of a photoelectron is also fixed and a binding energy of its origin can be determined. The instrument collects and counts the photoelectrons as a function of their energy.

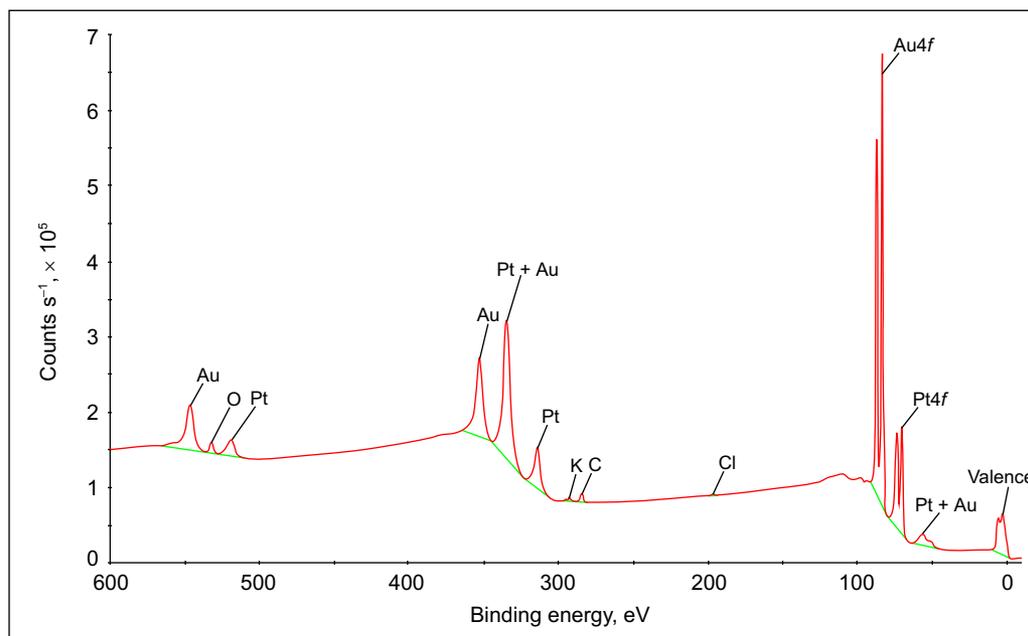


Fig. 1 Part of a survey spectrum from the surface of a platinum-gold fuel cell catalyst material "JMh-11". The green lines define a background; above these lines are the defined photoemission signals, below is a signal from electrons that have undergone energy loss processes. The "valence" peak is from photoelectrons from all elemental bands that are involved in chemical bonding

Identification of Elements

For a given element, the energies of the core levels do not vary a great deal, so each element has a characteristic “fingerprint” spectrum. Figure 1 shows a survey spectrum collected from the surface of a platinum-gold catalyst material, as used in one half of a space shuttle fuel cell system (4). By comparing the various peaks with fingerprint spectra, a trained analyst can determine that the surface of the “as-received” material contains carbon, oxygen, chlorine, potassium, platinum and gold.

Quantification of Elements

Information beyond elemental identification is contained in XPS spectra. The elemental core levels have well-understood chances of X-ray absorption, and therefore the number of photoelectrons from a given core level can be related to the amount of that element in the surface. In our example, the analyst can determine that the mole fractions of emitting atoms are about 55% gold, 18% platinum, 16% carbon, 8% oxygen, 2% potassium and a trace amount of chlorine.

Interpretation

The platinum to gold ratio from the surface layers is 1:3 by XPS, compared with 1:9 by a bulk chemistry method. The surface composition here does not follow that of the bulk, and for catalyst characterisation that kind of information can be very important indeed. The reductive precipitation method used in synthesis could have caused the gold to precipitate first, followed by the platinum; in a sense the surface layers show what happened at the end of the precipitation process, when an excess of platinum seems to have been present.

The presence of impurity elements in our fuel cell catalyst material example is probably related to

the production methods and synthetic precursors used. It is important to note here that surface impurities are sometimes invisible to other analytical methods; even a parts per million (ppm)-level contaminant might well concentrate at a surface and so be clearly visible to XPS. Because of this, the use of XPS to assist in explaining catalyst deactivation and poisoning can be invaluable.

Part II will appear in the next issue of *Platinum Metals Review*, covering the further information that is available from detailed XPS spectra and experimentation to further enhance understanding of a particular surface.

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References

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