The Electronic Structure of Platinum-Gold Alloy Particles

BETTER CATALYSTS FOR SELECTIVE OXIDATIONS

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Although the platinum-gold (Pt-Au) phase diagram shows a wide miscibility gap due to limited mutual solubility of the components, small particles (< 3 nm) form homogeneous alloys because all atoms retain their atomic electronic structure, and rehybridisation due to band formation does not take place. Supported Pt-Au catalysts are often superior to those containing Pt alone for low-temperature selective oxidations.

Great success has been achieved in a variety of catalytic processes by combining two metallic elements; examples that spring to mind include the platinum-iridium (Pt-Ir) pair for petroleum reforming, the platinum-tin (Pt-Sn) pair for alkane dehydrogenation, and the nickel-gold (Ni-Au) system for steam-reforming of alkanes (1). The recent upsurge of interest in gold as a catalytic element, rather than as an inert component that somehow protects the active one, has led to a series of observations on gold-containing bimetallic combinations (2). In particular, the palladium-gold (Pd-Au) pair has been found more effective than either component by itself in a number of selective oxidations, including those of reducing sugars, alkenes, and hydrogen (to form hydrogen peroxide rather than water). The Pt-Au combination has also proved to be beneficial, performing better than platinum alone in oxygen reduction at the fuel cell cathode (3), in selective oxidation of reducing sugars and other polyols (2), in alkane isomerisation when contained in the cages of the HY zeolite structure (3), and in reactions of environmental importance such as nitric oxide reduction by propene (2).

In the macroscopic state, palladium and gold form a continuous range of solid solutions, so it would not be surprising if chemical methods for preparing nanoscale bimetallic particles were also to lead to microalloy products. Paradoxically, however, detailed structural examination has shown that this is not always the case. Instead a 'cherry' structure often occurs, in which a gold core is surrounded by a palladium shell (4). The beneficial catalytic effect is therefore obtained by the core exerting some kind of modifying influence on the surface atoms. While this has not yet received a theoretical explanation, the Pt-Au system also poses problems of interpretation that have yet to be addressed; these are discussed here.

The Platinum-Gold System

Unlike the Pd-Au system, the Pt-Au phase diagram exhibits a very considerable miscibility gap (5), that is to say, the solubility of each metal in the other is strictly limited (Figure 1). In the region of ambient temperature, the limit of the solubility of
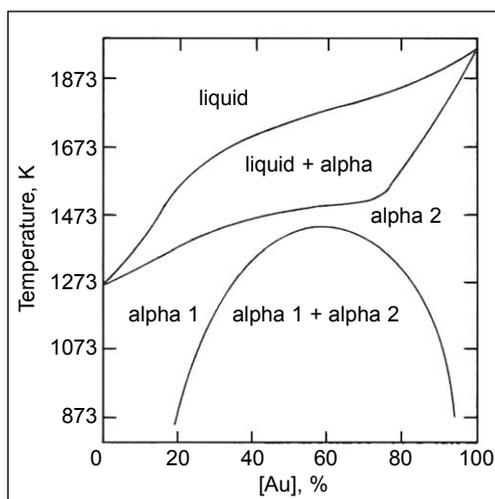

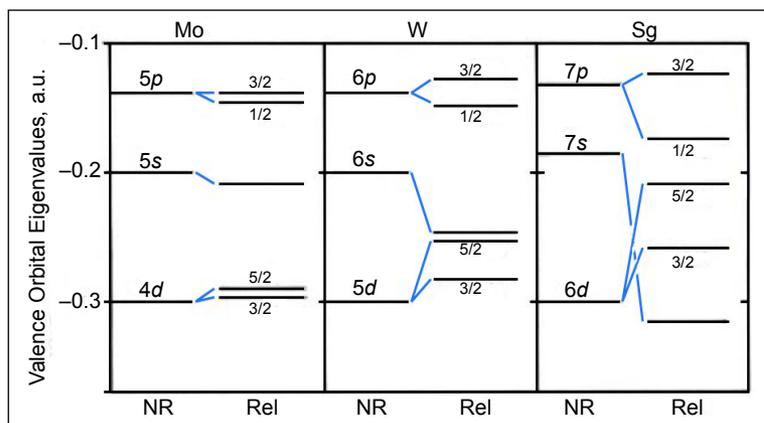*Fig. 1 Phase diagram for the platinum-gold system*

Fig. 2 Calculated outer-most atomic energy levels for molybdenum, tungsten and seaborgium (6, 7) (Rel = relativistic; NR = non-relativistic)

platinum in gold is only about 17%, rising to 20% at 973 K, while the solubility of gold in platinum is even less (4% rising to 6%). Between these limits there will be a mixture of the two saturated solutions. The contrast with the Pd-Au system is at first sight surprising, because the palladium and platinum atoms are almost identical in size. The reason for the difference must lie in their different electronic structures; for palladium the outer electron configuration is $4d^{10}$, while for platinum it is $5d^9 6s^1$. The elevation of a *d* electron to the *s* level is a consequence of the relativistic stabilisation of the *s* and *p* levels in relation to the *d* and *f* levels (6, 7). Figure 2 shows calculated energy levels for molybdenum, tungsten and seaborgium, and we may suppose that those for palladium, platinum and eka-platinum (darmstadtium) would be similar. The gap between the *s*- and *d*-levels is much reduced with platinum, and this allows its *d*-electrons to be activated for bonding; this is why the

Fig. 3 Typical high-resolution electron micrograph of Pt₂Au₄/SiO₂ catalyst (10)

Pt(IV) state is readily accessible, but the Pd(IV) state is not (6, 7). It would be an interesting Honours level question for undergraduate students to predict the chemistry of eka-platinum.

Supported Platinum-Gold Catalysts

In view of this knowledge of the Pt-Au phase diagram, it is unexpected to find a number of papers reporting the preparation of supported catalysts containing these elements, the very small particles apparently consisting of homogeneous microalloys of the two components. The word 'apparently' is used advisedly, because very often no evidence for alloy formation is provided, and the conjunction of the two components is only inferred from the catalytic behaviour. It is however of interest to examine the methods that have been claimed to give homogeneous alloy particles. They may be classified as follows (2): (a) simultaneous or sequential exchange of protons of Y zeolite with the ethylenediamine complexes of the two components (8); (b) simultaneous deposition-precipitation onto TiO₂–SiO₂ by hydrolysis of a solution of the mixed chloro-complexes (9); (c) adsorption of the organometallic complex $Pt_2Au_4(–C≡C^tBu)_4$ from hexane solution onto SiO₂, followed by calcination to remove the ligands (10) (this method gives very small particles (2–3 nm, see Figure 3), shown by energy-dispersive analysis to be bimetallic); (d) deposition of Pt-Au colloids onto carbon (11, 12); (e) use of dendrimer-stabilised colloidal particles to make PtAu/SiO₂ and PtAu/TiO₂ catalysts (13). Other proposed

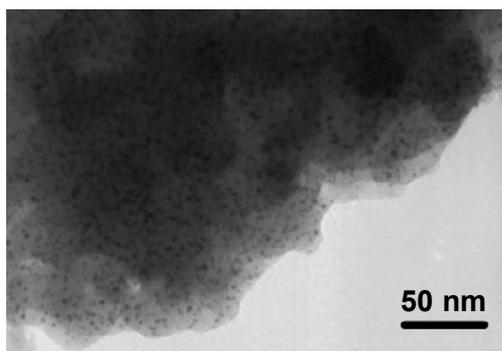methods involve deposition of either platinum onto gold particles or of gold onto platinum particles (14, 15), and are therefore not likely to give homogeneous products in the first instance.

In a number of cases these methods have been shown to form small particles (< 5 nm), but it is significant to observe that the classic method of co-adsorption of chloro-complexes from solution, followed by chemical reduction, gives large particles (> 20 nm) with severe phase separation (16). Co-reduction of solutions of precursors gives first 'frozen' solid solutions that are approximately homogeneous, but which on heating to 700 K equilibrate into a mixture of two phases; this is consequent on the increase in particle size that the heating produces (17). The use of alkanethiol-encapsulated colloids to prepare Pt-Au/C catalysts with various Pt:Au ratios results in particles that are mainly 2 ± 1 nm in size, and their homogeneity has been nicely demonstrated (11) by measuring their lattice parameters using X-ray diffraction. This shows that they exactly obey Vegard's law; that is, the lattice parameters are a linear function of composition (Figure 4). This has also been recently confirmed by Rossi (18), at least for compositions of gold content ≥ 50% (see also Figure 4). We therefore have very clear evidence that sufficiently small particles *can* form true solid solutions, but that with larger particles phase separation is inevitable; they behave as does the macroscopic system. There is no indication in the literature of the critical size at which the change of behaviour takes place; for this information we need to consider other factors.

Before doing so, however, it is worth noting that many scientists express no surprise that their small particles do not behave as the macroscopic alloy does. This lack of curiosity is unfortunate, to say the least, because knowledge of the bonding in homogeneous alloy particles might help in understanding their catalytic behaviour, and hence in further improvement.

Changes in Electronic Structure with Particle Size

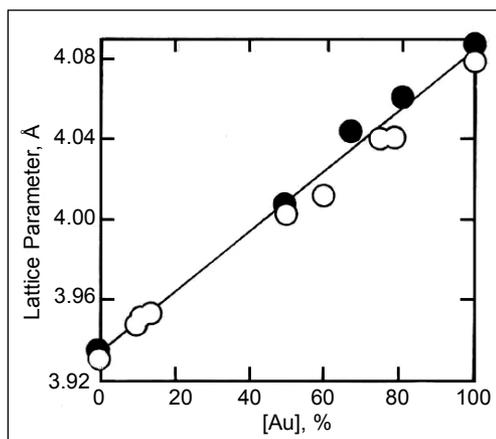It has long been appreciated that the electronic structure of platinum in the macroscopic state

Fig. 4 Vegard's law plot of the lattice parameters of platinum-gold colloids (open points from (11); filled points from (18))

differs from that of the isolated atom (19); in the free state it is $5d^9 6s^1$, but in the solid state it is approximately $5d^{9.4} 6s^{0.6}$. This is because, as the number of atoms forming the particle increases, the electron energy levels of the free atom begin to broaden, then overlap, and finally form a continuous *electron band* in which rehybridisation between the s, p and d valence orbitals can readily occur. The spacing between adjacent energy levels, δ, is given to a first approximation by Equation (i):

$$\delta = E_F/n \qquad (i)$$

where E_F is the Fermi energy level and n the number of atoms in the particle. When δ exceeds the thermal energy $k_B T$ (where k_B is the Boltzmann constant), the levels begin to act independently, and the particle then resembles a giant molecule. For $E_F = 10$ eV, a typical value, the critical number at room temperature is about $n = 400$, but in the transitional region particles become less metallic at low temperature. There is therefore a continuous change from non-metallic to metallic behaviour, without any abrupt transition. Many optoelectronic properties vary with particle size, but the minimum size for showing fully metallic character seems to depend on the technique employed (1). The nature of these changes has been discussed in a recent book (1).

One way of looking at the continuous change from non-metallic to metallic behaviour is to

recognise that atoms on the surface partly resemble free atoms rather than those in the bulk, because they do not form so many bonds to neighbours. The electronic structure of the entire particle is averaged over all the atoms, and therefore depends on the fraction of atoms not having a full complement of neighbours; physical properties can then be correlated with the average number of bonds formed between neighbours. As a rough guide one may say that, moving downward in size, one begins to notice changes at about 3 nm, and they become rapid at about 2 nm. A spherical particle of this size has about 230 atoms of which 140 are on the surface.

In the case of platinum, therefore, one consequence of the rehybridisation of the energy levels is a *decrease* in the number of *d*-band holes per atom as particle size is lowered, and this can be directly sensed by X-ray absorption near-edge spectroscopy (XANES), which exhibits a decrease in the intensity of the white line on the leading edge of the L_{III} X-ray absorption band (20). While it does not appear possible to use this quantitatively, the effect, although small, is quite distinct.

It is less well appreciated that exactly the same phenomenon occurs with gold. Although in the free atom there is a filled *d*-electron level, in the bulk state a small white line is seen, showing again that there has been some rehybridisation, so that the electronic structure of the metal is actually $5d^{10-x}6s^{1+x}$ (21, 22), and the white line that reveals this weakens as the size of the particle becomes smaller (20).

Effects of Particle Size Variation on Catalytic Activity

Much has been written on this subject (1), and only a very brief note is appropriate here. There is a major conceptual difficulty in that, in the size range where the *electronic* structure of metal particles is changing, there are also major changes in the *geometric* arrangement of atoms on the surface, if structural models are to be believed. It is therefore impossible to assign the catalytic effects of particles of size less than about 5 nm unambiguously to either a geometric or an electronic factor. It is not possible to have one without the other. If,

however, an effect persists above 5 nm, it is more likely due to there being a need for an active centre of specific geometry, as electronic variations will have petered out by this stage. Of course, where the rate of a catalysed reaction is independent of particle size (as for example with alkene hydrogenation), there is no problem; where there is a progressive change, there have been many attempts to connect this with a requirement for surface atoms of specific coordination number (1), but simultaneous changes in electronic structure are often overlooked.

Electronic Structure of Platinum-Gold Alloys

The theoretical interpretation of bonding in macroscopic alloys is a somewhat complicated matter, and various models have been used to explain what is observed (5). In this short article we can only sketch what are likely to be the main relevant factors in the Pt-Au system. Experimentally it is found that each component retains its individual band structure, although the energies and the widths of the bands may alter. For example, for a low concentration of one component, its band widths will be narrower than for the bulk, because of limited overlap with the levels of other like atoms. This means that there is no actual transfer of electrons from filled to partially vacant bands, as was originally thought, and a more realistic model involves electron pairing, i.e. covalent bond formation, between unpaired electrons on the two types of atom.

Perhaps the easiest situation to understand is the small alloy particle (of diameter < 2 nm) in which all the atoms remain atom-like, and therefore retain their atomic electron structures. Pairing of the *s* electrons on each atom will allow Au–Au, Pt–Pt, and Pt–Au covalent bonds to be formed (as in the complex $Pt_2Au_4(-C\equiv C^tBu)_4$) (10). This process can occur at all Pt:Au ratios, and complete mutual solubility is possible.

The situation with larger particles (diameter > 2 nm) or macroscopic forms is somewhat different. Gold then loses its strong electronegative character that determines much of its chemistry, because of the rehybridisation of its valence

orbitals through electron band formation. The number of *unpaired* 6s electrons on the gold atoms is lowered, the capacity for bond formation with the 6s electron of platinum is decreased, and the solubility of platinum in gold is therefore limited. A similar effect operates at the other end of the phase diagram; there are only 0.4 unpaired s electrons on the platinum atoms available for bonding with the gold's $6s^1$, and solubility is therefore very limited.

The presence of a support to stabilise very small particles is an inevitable complication when considering their structure and catalytic activity (1). Electron transfer across the metal-support interface is now largely discounted as a factor, because its occurrence would immediately create an opposing image potential; with reducible supports, however, there may be some effect of limited extent at the interface, and this has been suggested as one of the causes of the Strong Metal-Support Interaction (1). Geometric distortion of the metal structure close to the interface is probably more common, as the particle 'struggles' to adapt to the structure of the support with which it is in contact.

No doubt the true explanation (if indeed there is one) will turn out to be far more complicated, and perhaps less easily understood. However, there does not appear to have been any theoretical analysis of Pt-Au bonding in small particles, so perhaps this article will alert theoreticians to the existence of the problem, and attract them to work on it.

Conclusion

The many examples of superior catalytic properties shown by bimetallic catalysts containing palladium or platinum with gold (2, 3, 5) at present lack a theoretical foundation. An important step in understanding how they work is the realisation that the Pt-Au pair are able to form homogeneous alloy particles, provided their size is not greater than about 3 nm, in spite of the fact that in the bulk state there is a wide miscibility gap. The problem is compounded by the recent observation that *trimetallic* catalysts (for instance PtNiFe, PtVFe) show interesting behaviour in electrocatalytic oxidations, relevant to the operation of fuel cells (23, 24). Theoretical work is urgently needed to underpin these new developments in catalysis using platinum or palladium with gold.

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Geoffrey Bond held academic posts at Leeds and Hull Universities before joining Johnson Matthey PLC in 1962 as Head of Catalysis Research. In 1970 he was appointed Professor in Brunel University's Chemistry Department, and is now an Emeritus Professor at that University.

"The Separation and Refining Technologies of Precious Metals"

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The Editor of the Book

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