

Faraday Discussion 138: Nanoalloys – From Theory to Applications

PRE-EMINENT ROLE OF THE PLATINUM GROUP METALS

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A Faraday Discussion on “Nanoalloys”, organised by the Royal Society of Chemistry, and sponsored by Johnson Matthey and the Collaborative Research Network for Nanotechnology (CRNNT) of the University of Birmingham, was held in the Department of Chemistry, University of Birmingham, U.K., on 3rd to 5th September 2007 (1). It was attended by about sixty participants from the U.K., Europe and the U.S.A., mainly from academia. As usual with Faraday Discussions, preprints were available in advance, and authors had only five minutes to present the highlights of their work. There was therefore ample time for discussion, which never flagged and was at times vigorous and forthright.

The term ‘nanoalloy’ has been coined to describe the assembly of a small number of atoms of metallic elements of two (or sometimes more) kinds. Although there is no consensus, the term ‘cluster’ is used for an assembly formed in the gas phase, where the number of atoms is small (e.g. < 100) and countable by mass spectrometry, whereas the term ‘nanoparticle’ describes larger assemblies usually made by chemical routes (e.g. as colloids) and ranging in size from about 1 to 10 nm. Both clusters and nanoparticles can be deposited on supports, and their physical and catalytic properties examined in that state. Such small assemblies are of great current interest because their properties often differ significantly from those of the corresponding bulk materials, and nanoalloys are formed between pairs of elements that do not form homogenous bulk alloys.

Theory and Simulation

Of the twenty-five papers presented, seventeen concerned one or more of the platinum

group metals (pgms), the palladium-gold combination being the most popular. Many of the papers involved collaborations between several institutions; the details of these are given in (2). The Discussion was divided into four parts: the first part dealt with ‘Theory and simulation of nanoalloy structures and dynamics’, and need not detain us, as in the main the work presented appeared to be somewhat remote from practical reality, and failed to produce insights into observable properties. In some of the papers, imaginative structures were invented and studied, irrespective of whether they had been or could be prepared. Thus F. Calvo (Université Claude Bernard Lyon 1, France) studied the interchange of palladium and platinum atoms in icosahedral particles containing alternating layers of the two kinds of atoms, and E. P. M. Leiva (Universidad Nacional de Córdoba, Argentina) *et al.* examined by computer simulation how bimetallic nanoparticles could arise by collision of two clusters, one of each kind. There were no computations of the number of angels that could dance on the point of a nanoalloy particle, but it would not have been surprising if there had been.

Optoelectronic and Catalytic Properties

The Discussion returned to earth for the section on ‘Electronic, optical and magnetic properties of nanoalloys’; the term ‘optoelectronic’ covers all three. Condensation controlled by laser vaporisation, reported by M. S. El-Shall (Virginia Commonwealth University, U.S.A.) *et al.* enabled nanoalloy particles to be made of a number of binary combinations (PdAu, PtAu, PdFe, PtFe, PdNi and PtNi), those involving iron and nickel being superparamagnetic. The magnetism of CoRh nanoparticles was reported

by G. M. Pastor (Universität Kassel, Germany) and colleagues. The average spin moment per atom is larger than for macroscopic materials, and the likely structures have a rhodium core and a cobalt-rich outer layer. The structure of CoPt particles was investigated theoretically by C. Mottet (Centre de Recherche en Matière Condensée et Nanosciences (CRMC-N), Marseille, France) *et al.*

The six papers in 'Nanoalloys in Catalysis' on catalytic properties of nanoalloys having one of the pgms as a component stimulated a lively discussion. G. J. Hutchings (Cardiff University, U.K.) *et al.* reported their latest results on hydrogen peroxide synthesis by oxidation of hydrogen using catalysts containing palladium and/or gold. With carbon as support, high activities were obtained, and binary compositions contained homogeneous alloy particles, but with titania and alumina supports core-shell structures occurred. P. A. Sermon (University of Surrey, U.K.) *et al.* advocated using alkane conversions (hydrogenolysis, isomerisation) as a means of characterising the surface of PtAu and PtSn nanoparticles, illustrating their catalytic capability by reference to the reactions of *n*-hexane and methylcyclopentane. P. Wells (University of Southampton, U.K.) and colleagues showed that the oxygen reduction activity of the Pt₃Cr nanoalloy phase was better than that of platinum alone in model fuel cells; this work had input from D. Thompsett of the Johnson Matthey Technology Centre, U.K.

Structure-performance relationships in PdRh/ γ -Al₂O₃ catalysts for the NO-CO reaction were described by M. Tromp (University of Southampton, U.K.) and coworkers. Inclusion of palladium prevented dissociative oxidation of rhodium by NO, but did not stop its extensive disruptive oxidation by CO. Sir John Meurig Thomas (University of Cambridge, U.K.) and associates showed that organometallic cluster compounds comprising ruthenium and tin atoms could be decomposed on a silica support to give effective catalysts for the selective hydrogenation of cyclododecatriene to cyclododecene and for other reactions.

Structural Studies

The fourth section of the Discussion concentrated on 'Structural studies of nanoalloys', the palladium-gold combination proving the most popular. The use of energy dispersive X-ray spectroscopy for investigating the structure of supported PdAu catalysts used for hydrogen peroxide synthesis was explained by C. J. Kiely (Lehigh University, Bethlehem, Pennsylvania, U.S.A.) and colleagues. The principal conclusions of this work were mentioned in connection with the Cardiff University work (see above). Strongly size-controlled synthesis of icosahedral palladium-gold nanoparticles has been accomplished in inert-gas condensation in a sputtering reactor by E. Pérez-Tijerina (Universidad Autónoma de Nuevo León, Monterrey, Mexico) and colleagues; particles were homogeneous and did not show core-shell structures. This combination was also studied by C. R. Henry (CRMC-N, Marseille, France) and his associates; they prepared bimetallic particles uniformly dispersed on nanostructured alumina film by sequential condensation of the two kinds of atoms.

Concluding Remarks

In conclusion, this Discussion clearly demonstrated the potential for practical applications of small bimetallic particles. What is of particular interest and importance is the fact that small homogeneous alloy particles can be formed from pairs of elements for which the bulk phase diagram shows a miscibility gap. This point did not receive emphasis in this Discussion, and it is unfortunate that theoreticians have not addressed the problem, the nature of which has recently been considered in the context of the platinum-gold pair (3).

Discussion on the papers relating to catalysis focused on the utility of physical characterisation of catalysts before (or occasionally after) use in understanding their catalytic performance. It was noted that in many papers much more time and effort appeared to have been spent on the characterising than on the catalytic reaction, the

investigation of which was often brief and simple. Failure to consider *why* a particular structure or composition behaved as it did betrays a lamentable lack of curiosity, and retards the development of basic theory. The discussions, together with the texts of the papers, will be published in full by the Royal Society of Chemistry in 2008 (2); they should make interesting reading.

References

- 1 Faraday Discussion 138: Nanoalloys – From Theory to Applications, 3rd–5th September, 2007, University of Birmingham, U.K.: <http://www.rsc.org/FD138>
- 2 “Nanoalloys from Theory to Applications”, Faraday Discussions No 138, RSC Publishing, Cambridge, U.K., 2008: <http://www.rsc.org/shop/books/2008/9780854041190.asp>
- 3 G. C. Bond, *Platinum Metals Rev.*, 2007, 51, (2), 63

The Author



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