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Modelling Reactions at the Active Sites of Chiral Ruthenium Catalysts Using Density Functional Theory

NEW APPROACH TO UNDERSTANDING OF CATALYTIC REACTIONS

By S. A. French

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Selectivity is a key success factor in the chiral catalyst technologies market. Understanding the fundamental processes that occur when a reagent interacts with a homogeneous single site catalyst, both in its approach and at the active site, is therefore critical to the rational design of new catalysts. Ruthenium-based asymmetric hydrogenation catalysts have been considered as part of a collaborative research project. [(S)-XylBINAP-RuH2-(S,S)-DPEN], first developed by Noyori (1–3), is studied as the parent or prototype model of a series of efficient hydrogenation catalysts, among them the catalysts based on the P-Phos, PhanePhos and ParaPhos ligand families (4).

This work addresses homogeneous asymmetric hydrogenation of C=O bonds, from ketones to alcohols, which has applications in the industrial production of pharmaceutical intermediates. The catalyst studied, [(S)-XylBINAP-RuH2-(S,S)-DPEN], is shown in Figure 1.

Each reaction mechanism may be understood in terms of the energies of intermediates and the roles of ligands and additives, as determined by state-of-the-art computational techniques. The knowledge gained will then be exploited for the design and synthesis of ligands for improved catalyst systems. Advances in experimental techniques will allow rapid identification of lead ‘designed’ catalysts by automated parallel screening. With this scheme in mind, a consortium was assembled from leading experts (both industrial and academic) in all areas of the workflow. The partners are the Royal Institution of Great Britain, the University of Liverpool, the University of Southampton, Johnson Matthey, AstraZeneca, GlaxoSmithKline and Pfizer. The aims of the project were to implement an evolutionary improvement in ligand/catalyst design strategies:

COMPUTATION ⇔ SYNTHESIS ⇔ ACCELERATED TESTING

This computation-guided approach for catalyst discovery is expected to be more efficient, faster delivering and more revealing on the molecular aspects of a catalytic cycle than one-at-a-time synthesis or combinatorial methodologies, which usually screen catalysts at random (5); see Scheme I.

Since the project’s conception there has been a step change in the ability of industry to perform high-throughput screening. This acceleration has enormously reduced the time required to identify the right catalyst for any desired transformation from a library of existing catalysts or ligands. The preparation of the library of ligands and catalysts remains, however, the bottleneck in this process.

Fig. 1  The structure of [(S)-XylBINAP-RuH2-(S,S)-DPEN], asymmetric hydrogenation catalyst
For example, the selection of the correct substituents at phosphorus in any family of bidentate phosphine ligands is largely a matter of trial and error, with each component of the family requiring independent and often time-consuming synthesis. The design and synthesis of new ligand backbones is even more time-consuming, and there is no certainty that the new ligands will be effective in the desired transformation. Understanding the factors which govern the relationship between the structure of the ligand and its efficacy in catalysis will accelerate the process of ligand design by evaluation through computer simulation ('in silico') of a large number of structural variations, among which only the most promising structures will actually be synthesised.

The project, supported financially by the U.K. Department of Trade and Industry’s ‘Manufacturing Molecules Initiative’ (6), is focused on two industrially important organic reactions: (a) the production of chiral alcohols via the asymmetric reduction of ketones; and (b) C–C bond forming reactions such as the Heck reaction. Molecular modelling has so far focused on Reaction (a). Computer simulations have been used, at the molecular-mechanical (7) and, as reported here, quantum-mechanical levels, to investigate the structures of proposed catalysts, and to probe the reaction mechanism.

Initially it was proposed to use activation energies calculated by considering transition states (TS) between reactant and products to compare the performance of catalysts. However, difficulties in simulating the reactants and products correctly caused the TS calculations to fail. Therefore an alternative strategy was implemented; a geometric constraint was applied and the reactant brought towards the reactive centre, exploring the pathway of the ketone molecule to the active site. Understanding of the correct relative positions of reactants and products, and further understanding the need to ‘lock’ conformations of ligands, has led to the capability of performing TS calculations on ‘cut down’ (i.e. simplified) model catalysts, as well as exploring the entry of reactants to a real catalyst system.

### Methods

The processes of prime interest to us involve the breaking and creation of bonds, which means that the electronic structure as well as the molecular structure must be modelled. Traditional methods in electronic structure theory, in particular Hartree-Fock theory and its descendants, are based on the complicated many-electron wavefunction. The main objective of density functional theory (DFT) is to replace the many-body electronic wavefunction as the basic quantity by the electronic density. Within this study we have used the DFT code DMol3 (8, 9) for both model TS calculations and constrained optimisations.

All the DFT investigations were performed using the linear combination of atomic orbitals approximation, with a double numerical basis set augmented by polarisation functions (with a 5.5 Å cut-off). The calculations employed the gradient-corrected Perdew-Becker-Ernzerhof (PBE) exchange-correlation functional. The fine accuracy convergence criteria were used throughout for both electronic structure and atomic optimisation calculations. The criteria guarantee that the energy per bond, bond lengths and angles converge to approximately 0.1 eV, 0.01 Å and 1°, respectively.

### Constrained Optimisation Calculations

To understand how the reactant molecule approaches the metal centre and what restrictions are placed on its passage, we have performed a large number of simulations to compile a trajectory of the path followed, and to compare the

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**Scheme I  Roles of research consortium members**

<table>
<thead>
<tr>
<th>Catalyst Modelling (Royal Institution)</th>
<th>Ligand Synthesis (Liverpool, Southampton Universities)</th>
<th>Catalyst Screening (Johnson Matthey)</th>
<th>Commercial Application (Pharmaceutical Companies)</th>
</tr>
</thead>
</table>

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energy barriers that are encountered. At each stage, the geometry of the system is optimised with respect to one constraint, namely the distance between the hydride H on the ruthenium and the C of the carbonyl group in the ketone. (These species eventually become bonded to one another in the alcohol product.) The output from one simulation is used to generate the initial configuration for the next. Initially we used the results to understand the interaction between reactant and catalyst, to identify the most relevant reactants and products for TS calculations, which are described below. The application of the method was then extended to consider four ‘quadrants of attack’ of the ketone to the active site, to probe the potential energy surfaces of the reaction. This will provide vital information concerning the selectivity of the catalysts.

**Transition State Calculations**

The TS calculations have required a workflow applied to a cut down version of the catalyst (Figure 2), to arrive at a final model for the TS. The stages are as follows:

(a) Relaxation of the reactant;
(b) Construction of the product from the reactant using ‘chemical intuition’ to move atoms around;
(c) Constrained relaxation of the product, taking care to avoid conformational changes in the ring;
(d) Full relaxation of the product;
(e) Linear synchronous transit (LST) method to approximate reaction path and provide input to full LST/quadratic synchronous transit (QST) calculation with conjugate gradient (CG) optimisation;
(f) Single-point calculation of TS with frequency analysis;
(g) Animation of negative mode to check which centres are involved;
(h) TS optimisation calculation where mode is followed;
(i) Single-point calculation of TS with frequency analysis;
(j) Animation of negative mode.

**Results and Discussion**

Among the models used to rationalise the structure-activity relationship in asymmetric homogeneous catalysis, the so-called ‘quadrant approach’ is one of the simplest and most effective.

The space around the reactive centre is divided into four volumes, across which the substrate can bind to the metal centre in a number of different conformations. The ligand will prevent access to some quadrants by simple steric interaction, thereby forcing the substrate to bind to the metal in a preferred conformation that, upon transfer of the hydride from the metal to the substrate, becomes the precursor to the favoured enantiomer of the product. Such a model, although very simplistic, allows straightforward rationalisation of the sense of stereoinduction obtainable with a number of well-known hydrogenation catalysts such as Ru-BINAP, Rh-DuPhos and Rh-BisP* (10, 11).

Starting from this simplistic approach (see Figure 3) we have developed a more sophisticated model that takes into account the whole trajectory of the substrate into the ‘reactive pocket’ of the catalyst. It is well known that subtle modifications of the substituents at phosphorus can produce very significant changes in the activity and selectivity of the catalyst (one example of this being the so-called ‘meta-effect’). We suggest that the reason for these effects may reside not only in changes at the transition state, but also in the docking of the substrate into the reactive pocket, well before the bond breaking/bond forming interactions are established.

**Constrained Optimisations: Initial Quadrant**

Initially we have considered the catalyst [(S)-XylBINAP-RuH₂-(S,S)-DPEN] as an exem-
plar of the class of asymmetric materials that we are interested in understanding. As mentioned above, initially we focused on understanding the pathway of the reactant to the active site. With this in mind we chose to model the quadrant and orientation known to lead to the preferred product. Determining the conformational changes forced on the reactant or catalyst during approach would provide a better understanding of where reactants and products should be sited for TS calculations. The Platinum Metals Review website includes an animation showing the final structure from each of the constrained optimisation calculations, starting with a constraint (Ru–H --- C=O) of 8 Å and reducing the separation between the reactant and catalyst in steps of 0.5 Å. It is clear from the animation and subsequent analysis of the potential energy surface for the pathway (Figures 4 and 5) that we can begin to understand the complexity of these systems. There are two distinct energy barriers that the reactant must overcome before arriving at the active site of the catalyst. The reactant must first push into a pocket of the catalyst, before arriving at its final alignment. The C=O of the ketone and the Ru–N bonds lie parallel, thereby maximising orbital overlap with the hydrogen atoms that transfer to form the alcohol. The advantage of computational models is that the changes in geometrical structure as the ketone approaches can be observed ‘frame by frame’. It is then possible to follow the trajectory of approach, analyse the position of the barriers, and view the corresponding changes in atomic structure.

When the reactant enters the pocket of the catalyst, which begins to occur when the constraint (Ru–H --- C=O) is between 5 Å and 4 Å, the ketone-catalyst system stabilises. This is shown by the total energy of the system decreasing, before it has to overcome the largest barrier between 3.5 Å and 2.75 Å. The barrier is due to the interaction of the phenyl ring of the ketone...
with ligands of the catalyst; this interaction increases as the ketone is pulled down onto the active site. At a constraint of 2.75 Å there is a conformational change of the reactant, with the phenyl ring tilting so that all the carbons of the ring are no longer in the plane of the other atomic centres of the ketone. The driving force for this change of conformation is the formation of a hydrogen bond, which holds the ketone as it moves closer to the active site. The hydrogen bond distance reduces further as the reactant is pulled further towards the catalyst, but the position of the oxygen atom does not change greatly; the major movement is that of H(NH) of the catalyst.

For the reactant to leave the pocket there is then another barrier, which requires the alignment of the C=O bond of the ketone to the underlying Ru–N bond of the catalyst. To this end, the carbon moves further down, changing from sp² to sp³ hybridisation, until it is in the same plane as oxygen. This results in the C=O bond lying parallel to the Ru–N bond, maximising overlap with the two hydrogen atoms to be transferred from the catalyst to the reactant. Simultaneously, the Ru–H bond elongates; this would contribute to the barrier at a (Ru–H -- C=O) constraint of 2.25 Å.

**Constrained Optimisations: Other Quadrants**

Having considered the approach of the reactant along the favoured quadrant, we then addressed the question of whether computational calculations contain sufficient detail to predict the selectivity of a specific catalyst. A catalyst that forms products with a high enantiomeric excess (ee) is highly desirable, as these reactions are important in a pharmaceutical context. Here the physiological reaction to one enantiomer may differ greatly from that to another. Using docking calculations, the aim is to investigate the various arrangements, and thereby provide insight into how catalysts may be optimised.

The difference in energy barriers between the different quadrants of approach has the potential to provide such discrimination. From Figures 2 and 6 it is obvious that two of the possible orientations are sterically ‘favourable’ (quadrants Q1 and Q3) and two sterically ‘unfavourable’ (Q2 and Q4) (1). However, this is not sufficient to understand the selectivity, as Q1 and Q3 lead to (R) and (S) products, respectively. In fact what this simple analysis demonstrates is that the channels that would be followed by reactants approaching along Q2 and Q4 should be closed. However, of most importance is to understand why certain catalysts
produce much higher ee than others. To this end we must understand the difference between Q1 and Q3.

Figure 7 shows clearly that for [(S)-XylBINAP-RuH2-(S,S)-DPEN], Q1 possesses a much lower barrier to approach and would therefore be expected to show high ee. This is confirmed experimentally where, depending upon experimental conditions, an ee of around 97% is achieved.
With an understanding of the pathway of the reactant to the catalyst active site and of the stable position of the ketone along this path, we could return to considering the calculations of TS and therefore the activation energies for the hydrogenation processes. We are currently considering other catalysts and reactants to ascertain whether we can correlate the barrier for entry into the catalyst pocket with the selectivity of known systems.

**Transition States**

To make the best use of available computer resources, initial TS calculations were performed on a cut down model of a commercial catalyst (Figure 2). Acetone was initially considered as the reactant molecule. From our understanding of the approach of the ketone to the catalyst, we have been able to determine a stable configuration for the reactant. The constrained optimisation calculations showed that with the ketone hydrogen bonded to the catalyst, \((R_2C=O \cdot \cdot \cdot HNH)\) was at a minimum energy position when the \((Ru–H \cdot \cdot \cdot C=O)\) was held at 2.75 Å, with the hydrogen bond holding the reactant in place. We further optimised this structure to provide the starting point for our TS calculations. The product state has the alcohol physisorbed above the catalyst, and is stabilised by a hydrogen bond between COH \(\cdot \cdot \cdot NH\).

The TS forms a six membered ring (Figure 8). The hydride bond is elongated from 1.7 Å to 1.75 Å. It can be seen from Figure 9 that there is also a change in the hybridisation of carbon, which moves from sp\(^2\) towards sp\(^3\). The TS has a \((O)C \cdot \cdot \cdot H(Ru)\) distance of 1.96 Å and \((C)O \cdot \cdot \cdot H(NH)\) of 1.86 Å. It is possible to visualise the imaginary mode that is associated with the TS, and it is found that the two hydrogen atoms and carbon are the atomic centres that move the most. Figure 10 shows the energy profiles for TS searches using the LST and QST calculation methods.

The activation energy that we have calculated is 3 kcal mol\(^{-1}\), which is in agreement with previous calculations on similar-sized models of the commercial catalyst, while the calculated reaction energy is exothermic by 6 kcal mol\(^{-1}\). The hydrogenation of acetone is therefore extremely facile, proceeding as follows:

- Incipient bond formation is signalled by the shortening of the O \(\cdot \cdot \cdot H\) distance (from 2.11 Å to 1.86 Å) in the N–H \(\cdot \cdot \cdot O\) hydrogen bond, and of the Ru–H \(\cdot \cdot \cdot C\) distance (from 3.02 Å to 1.95 Å);
- Small changes in the same direction are observed in the other bond lengths (< 2%).

The structure of the TS, therefore, resembles much more that of the reactant complex \([RuH_2–acetone]\) than that of the product complex \([RuH_2–iPrOH]\). This process is therefore a good example of the Hammond principle. This states that the structure of the transition state will resemble that of the product more closely than that of the reactant for endothermic processes, whereas the opposite is true for exothermic reactions. A
previous computational study on a trans-dihydro(diamine)ruthenium(II) Noyori-type model catalyst has evaluated a reaction barrier for the hydrogenation of acetone of 3.6 kcal mol$^{-1}$ at B3LYP/6-31G** level (13). Our results are in apparent agreement with previous calculations on the formaldehyde/methanol transformation by the RuH(NH$_2$CH$_2$CH$_2$NH)(η$_6$-benzene) complex performed at B3LYP (14) and generalised gradient approximation (GGA) (15). This shows that classical reaction barriers computed with GGA functionals are smaller than those obtained with B3LYP by about 2 kcal mol$^{-1}$.

We certainly anticipated that the methodology used would impact on the activation energy ($E_A$), and we are currently evaluating the effect of changing the density functional. Initial results show that increasing electron localisation by moving from GGA via hybrid to meta functionals leads to a slight increase in $E_A$. We are also considering other ketones, and attempting to build up a larger model of the catalyst system, so that we can make direct comparison with experimental data for industrially relevant systems.

Conclusions

The two complementary DFT simulation methodologies of transition state searches and constrained geometry optimisations are now yielding results that are of considerable importance to understanding catalyst behaviour, potentially leading to the prediction and design of new catalysts for the ketone hydrogenation reaction.

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12 http://www.platinummetalsreview.com/images/Q1_new.gif

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The Electronic Structure of Platinum-Gold Alloy Particles

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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
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 4\(d^{10}\), while for platinum it is 5\(d^{9}\) 6\(s^{1}\). 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 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 TiO\(_2\)-SiO\(_2\) by hydrolysis of a solution of the mixed chloro-complexes (9); (c) adsorption of the organometallic complex Pt\(_2\)Au\(_4\)-(C≡C'Bu)\(_4\) from hexane solution onto SiO\(_2\), 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/SiO\(_2\) and PtAu/TiO\(_2\) 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 differs from that of the isolated atom (19); in the free state it is 5d<sup>6</sup>6s<sup>1</sup>, but in the solid state it is approximately 5d<sup>9.46</sup>6s<sup>0.6</sup>. 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 (1):

\[ \delta = E_F/n \]

where \( E_F \) is the Fermi energy level and \( n \) the number of atoms in the particle. When \( \delta \) 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

![Fig. 4  Vegard’s law plot of the lattice parameters of platinum-gold colloids (open points from (11); filled points from (18))](image-url)
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\textsubscript{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\textsuperscript{10}6s\textsuperscript{1+}x (21, 22), and the white line that reveals this weakens as the size of the particle becomes smaller (20).

**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\textsubscript{2}Au\textsubscript{4}(–C≡C\textsubscript{t}Bu)\textsubscript{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.
orbits 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 $6s$, 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.

**References**

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The Author

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”

EDITED BY JIANMIN YU (Kunming University of Science and Technology, China), (in Chinese), Chemical Industry Press, Beijing, China, 2006, 272 pages, ISBN (hardcover) 7-5025-9008-0, Yuan ¥45.00

Combining theory with practice, this introductory book provides detailed data obtained during studies on the refining technologies of the precious metals in China and abroad. The book has 10 chapters, organised by the refining technologies of gold, silver, and the platinum group metals.

The main physical and chemical properties, compounds and complexes of precious metals are introduced in Chapter 1. The separation methods and technologies of the precious metals are reviewed in Chapter 2. The refining technologies, for gold, silver, palladium, platinum, rhodium, iridium, osmium and ruthenium comprise the most important part of the book, and occupy Chapters 3 to 9. The preparation methods of high purity matrices for spectroscopic analysis of the precious metals are specially described in Chapter 10. There are two Appendices which describe the memberships of the Shanghai Gold Exchange and refining product standards in the U.S.A. and Russia, respectively.

The Editor of the Book

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A new scientific event in metathesis chemistry, the NATO Advanced Study Institute (NATO ASI) on New Frontiers in Metathesis Chemistry: From Nanostructure Design to Sustainable Technologies for Synthesis of Advanced Materials (1) was held in Antalya, Turkey, from 4th to 16th September 2006 (co-directors: Y. Imamoglu and V. Dragutan). This event is an appropriate sequel to the memorable Nobel Prize awarded to metathesis scientists Yves Chauvin, Robert H. Grubbs and Richard R. Schrock (Stockholm, November 2005) (2–4), and the XVIth International Symposium on Olefin Metathesis (Poznan, Poland, June 2005) (5).

Prominent scientists and young students from twelve NATO countries (Belgium, Bulgaria, Canada, Czech Republic, France, Hungary, Poland, Romania, Spain, Turkey, U.K. and U.S.A.) and six NATO Partner countries (Armenia, Azerbaijan, Kazakhstan, Moldova, Russia and Ukraine), interested in metathesis chemistry convened in Antalya for two weeks under NATO sponsorship. The purpose was to debate on the newest trends in olefin metathesis and identify future perspectives in this fascinating field of synthetic organic and organometallic chemistry, where platinum group metals (pgms), especially ruthenium, are playing a key role.

Olefin metathesis, one of the most efficient transition metal-mediated C–C bond forming reactions, has emerged during the last few years as a powerful synthetic strategy for obtaining fine chemicals, biologically active compounds, architecturally complex assemblies, new materials and functionalised polymers tailored for specific uses, including sensors, semiconductors and microelectronic devices. Metathesis reactions, such as ring-closing metathesis (RCM), enyne metathesis, cross-metathesis (CM) and ring-opening metathesis polymerisation (ROMP), have moved far beyond their 20th century boundaries. This has resulted in a broad diversification towards sustainable technologies, and in new perspectives for a wide range of industrial applications, from production of smart, nanostructured materials to the manufacture of new pharmaceuticals (6–8).

During the meeting, recent advances in metathesis chemistry were disseminated among a selected audience of distinguished scientists and young researchers. Lectures, discussions and poster presentations, organised by a Scientific Committee (Yavuz Imamoglu (Hacettepe University, Turkey), Valerian Dragutan (Romanian Academy, Romania), Lajos Bencze (University of Veszprém, Hungary), Ezat Khosravi (University of Durham, U.K.) and Kenneth B. Wagener (University of Florida, U.S.A.)) in ten scientific main sessions, dealt primarily with novel metathesis catalysts pertaining to the pgms and several other late transition metals, and their application to key metathesis reactions or tandem metathesis/non-metathesis processes of environmental, industrial and commercial relevance. Such metathesis reactions have profound implications in materials science, nanotechnology, and also in organometallic, organic and polymer chemistry.

**Developments in Ruthenium-Based Catalysts**

As expected, in lectures on catalyst-related topics emphasis was placed on the newest developments concerning ruthenium-based complexes of high activity, selectivity and robustness, popular for their excellent tolerance toward a variety of functional groups. A whole range of alkylidene ruthenium complexes, both neutral and...
ionic, which can be recovered and recycled, were illustrated by Pierre Dixneuf (University of Rennes, France) in his lecture ‘Ruthenium Catalysts for Alkene Metathesis’. He included preparation methods and selected applications. In addition to the broad applications of the classical Schrock molybdenum catalysts and the Grubbs (1st and 2nd generation), Nolan or Hoveyda-type ruthenium catalysts, Dixneuf disclosed in a second seminal lecture: ‘Recent Applications of Alkene Metathesis for Fine Chemical and Supramolecular System Synthesis’, further significant utilisations of other active catalyst precursors, such as the ruthenium allenylidene, 1, and the indenylidene promoter, 2, derived from it. These applications refer specifically to the synthesis of new macrocycles via RCM, to RCM in the synthesis of new ligands, rotaxanes, catenanes and supramolecular systems, and to CM in organic synthesis and supramolecular system formation.

Elaborating on the essential role played by N-heterocyclic carbene (NHC) ligands in creating the most effective ruthenium metathesis catalysts (for example, 4 and 5 vs. 3), Steven P. Nolan (University of Tarragona, Spain) extended the concept of introduction of the valuable NHC moiety to other late transition metal complexes, as outlined in his fascinating talk on ‘The Role of NHC in Late Transition Metal Catalysis’.

As a further topic in this series, the synthesis, catalytic activity and pertinent mechanistic aspects of some recently discovered NHC-endowed late transition metal complexes of palladium, nickel, copper and gold were fully exemplified by Nolan for a set of catalysed transformations other than metathesis (cross-coupling reactions, hydrothiolation of alkynes, ‘click chemistry’ for rapid synthesis of new compounds and combinatorial libraries, and hydrosilylation of carbonyl compounds, as well as cycloisomerisation of polyunsaturated systems) in his comprehensive and original presentation ‘NHC-Metal Complexes of Groups 10 and 11. Recent Developments in Synthesis and Catalysis’.

**New Insights into Catalyst Design**

New insights into catalyst design were provided by Deryn Fogg (University of Ottawa, Canada) and by Natalia Bespalova (United Research & Development Centre, Russian Academy of Sciences).

In her lecture ‘New Insights in Ring-Closing Metathesis: Catalyst Design and MALDI-MS Analysis’, Fogg demonstrated that ruthenium catalysts containing electron-deficient aryloxide (‘pseudohalide’) ligands confer high activity at low
catalyst loadings, while also expanding the structural diversity of the ligand set and the capacity for steric and electronic tuning of activity and selectivity. She pointed out that by using the matrix-assisted laser desorption/ionisation mass spectrometry (MALDI-MS) analysis technique, distinctions in the behaviour of the Grubbs vs. pseudohalide catalysts could be revealed. This provides an in-depth understanding of the RCM mechanism, to be exploited in synthesis of large and medium-sized rings.

In addressing ‘Catalyst Design for Functional Olefins Production via Olefin Metathesis Reactions’, Bespalova dwelt on the modification of well-defined ruthenium carbene catalysts through appropriate changing of the carbenoid moiety and the imidazole ligand, which allows a variation in the catalytic properties. A comparison between performances in CM of the new catalysts with those of the ill-defined catalysts based on tungsten was also presented.

Ligands for Catalysis

Following up on the general notion of NHC utilisation in catalysis, Lionel Delaude (University of Liège, Belgium), in his instructive presentations: ‘Olefin Metathesis with Ruthenium-Arene Catalysts Bearing N-Heterocyclic Carbene’ and ‘Studies on N-Heterocyclic Carbene Ligand Precursors’, dealt mainly with the best methods for obtaining symmetrically N,N-disubstituted NHC ruthenium arene complexes and with ROMP of cycloolefins promoted thereby. Karol Grela (Institute of Organic Chemistry, Polish Academy of Sciences), in an interesting and informative exposition on ‘Catalysts for New Tasks: Preparation and Applications of Tunable Ruthenium Catalysts for Olefin Metathesis’, extended the class of Hoveyda catalysts to related ruthenium systems, showing that the catalyst activity can be enhanced by using adequate electron withdrawing groups (EWGs) as substituents on the isopropoxy-benzylidene ligand. Francis Verpoort (Ghent University, Belgium), in his comprehensive accounts ‘Olefin Metathesis Mediated by Schiff Base Ru-alkylidene Complexes’ and ‘Rational Design and Convenent Synthesis of a Novel Family of Ruthenium Complexes with O,N-Bidentate Ligands’, reported on new strategies in Kharasch addition, enol-ester synthesis and ROMP of dicyclopentadiene (DCPD) using highly efficient Schiff-base ruthenium complexes.

Poster presentations demonstrated additional data in support of the role of NHC ligands in ruthenium-based metathesis precatalysts (Xavier Sauvage, University of Liège, Belgium, and Adriana Tudose, University of Liège and Romanian Academy) and the unexpected activating effect of strong acids on ruthenium complexes incorporating O,N-bidentate ligands (Renate Drozdak and Nele Ledoux, Ghent University, Belgium). Providing interesting information about ruthenium-mediated processes related to metathesis, Chloe Vovard (University of Rennes, France) briefly talked on ‘Ruthenium Catalysed Addition of Diazocompounds to Enynes: Synthesis of Bicyclic Compounds with Vinylcyclopropane Moiety’.

Nanoscience and Materials

In a very attractive lecture, ‘Molecular Nanoscience and Catalysis’, Didier Astruc (University of Bordeaux, France), starting from synthesis of organometallics, catalysts and electron-transfer agents and mechanisms involving electron transfers, dealt eloquently with such hot topics as:
- dendrimers (catalysis, molecular electronics, recognition and transport);
- gold and palladium nanoparticles (sensors and catalysts);
- metathesis reactions with nano-objects;
- ‘click chemistry’.

In another creative subject, ‘Combining Simple Arene Activation with Ru-Catalysed Olefin Metathesis for the Assembly and Functionalization of Nano-Objects’, Astruc revealed convenient routes to desirable supramolecular structures and elaborate synthetic methods. In this extremely broad context, several elegant applications of ruthenium dendritic structures were given (for example, use of 6 in synthesis of polymers, 7).

New trends presently evolving in metathesis chemistry were critically discussed by Hynek
Balcar (J. Heyrovský Institute of Physical Chemistry, Academy of Sciences of the Czech Republic). The new directions cited were:
(a) Eco-friendly protocols for metathesis catalysts;
(b) Supported catalysts and novel techniques for immobilisation;
(c) Applying to metathesis at room temperature the recognised advantages of ionic liquids through the creation of recyclable imidazolium-tagged catalysts;
(d) CM, enyne and RCM as key reaction steps in organic synthesis yielding pharmaceuticals and natural products (sugars, alkaloids, nucleosides, amino acids);
(e) Chiral catalysts enabling enantioselective metathetical pathways in precision synthesis.

In his talk on ‘Molecular Sieves as Supports for Metathesis Catalysts’, Balcar described how siliceous sieves (MCM-41 and -48, SBA-15) and organised mesoporous alumina were successfully used in obtaining new catalysts (principally based on molybdenum and rhenium oxides) and in het-
erogenisation of some well-defined homogeneous catalysts for olefin metathesis and metathesis polymerisation.

The details of extending NHC ligands to osmium, with effect on catalyst activity, chemoselectivity and stereoselectivity, have been widely evidenced by Ricardo Castarlenas (University of Zaragoza, Spain) in his talk on ‘NHC Osmium-arene Catalysts for Olefin Metathesis Reactions’. Pertinent structural and mechanistic aspects regarding this recently introduced class of metathesis catalysts were also addressed.

New applications of ruthenium-mediated tandem metathesis/non-metathesis processes were fully documented by Deryn Fogg in a presentation on ‘Tandem ROMP-Hydrogenation Catalysis in Tissue Engineering Applications’. This drew attention to a potentially important practical application of polymers obtained in this way (galactose-functionalised polynorbornenes), which have so far proved successful in clinical trials for corneal tissue engineering.

The advantages of another tandem combination, RCM-hydrogenation, were presented by Natalia Bespalova in the lecture ‘Synthesis of Higher Esters Using Tandem Olefin Metathesis-Hydrogenation Reactions’, bringing into prominence the production of valuable highly saturated esters by means of the catalyst pair Bu3SnH/2nd generation Grubbs.

‘Catalytic Cycloisomerisation of Enynes Involving Various Activation Processes’, presented by Christian Bruneau (University of Rennes, France), extended the scope of ruthenium-based metathesis chemistry to a variety of initiating systems of fundamental relevance in catalysis. Skeleton reorganisations, carried out with catalysts based on palladium, cobalt, rhodium, iridium, platinum, gold and ruthenium and involving electrophilic activation, oxidative coupling and metathesis reactions were described, along with applications of metathesis for the transformation of some natural compounds. ‘Cross-metathesis of Vinyl-substituted Organosilicon Derivatives with Olefins in the Presence of Grubbs Catalysts’, presented by Cezary Pietraszuk (Adam Mickiewicz University of Poznan, Poland), evidenced how ruthenium-catalysed metathesis can be fruitfully used in synthesis of novel silicon-containing advanced materials.

**Macromolecular Chemistry**

Ezat Khosravi (University of Durham, U.K.) illustrated the versatility of ROMP in two complementary lectures on ‘Ruthenium Initiators and Oxygen Containing Norbornene Derivatives’ and ‘Synthesis of Novel Polymers via ROMP’. In the first, he highlighted the importance of both the presence and position of the oxygen substituent in norbornene derivatives subjected to ROMP, while also unambiguously establishing the identity of the propagating alkylidene species. In his second lecture, by discussing two examples taken from their ongoing research: (i) polymers with ball-and-chain sequences synthesised by ROMP of dendronised (polycarbonate) monomers, and (ii) synthesis of polymeric bioresorbable materials based on graft copolymers consisting of polyoxanorbornene backbones with poly(hydroxyacid) side-chains, Khosravi demonstrated that ROMP is a powerful tool in macromolecular engineering, allowing synthesis of polymers with novel topologies.

Moreover, Eugene Finkelshtein (Topchiev Institute of Petrochemical Sciences, Russian Academy of Sciences) in his outstanding lecture on ‘ROMP and Other Ring-Opening Processes as an Effective Route to New Carbosilane Membrane Materials’, evidenced ways for producing specialty polymers usable as gas-separating membrane materials when a particular combination of high film-forming, permeability and separation properties is met. Debating on the correlation between the polymer structure and the gas transport parameters, he pointed out the role played by the occurrence, number and location of Me3Si-groups in a variety of copolymers synthesised for this purpose, as further reinforced by Maria Gringolts in a subsequent talk.

The main aspects of the kinetics and mechanism of the carbonyl-olefin exchange reaction, having a formal similarity with olefin metathesis, were elaborated by Christo Jossifov (Institute of Polymers, Bulgarian Academy of Sciences) in his
amply documented presentation ‘Carbonyl-olefin Exchange Reaction and Related Chemistry’. This type of reaction could be successfully performed only when the two functional groups (carbonyl group and olefin double bond) are situated in the same molecule and are conjugated as in α,β-unsaturated carbonyl compounds (substituted propenones). Substituted polyacetylenes having valuable conducting and optical properties could also be obtained by this straightforward methodology.

Presentations from Ken Wagener’s group (University of Florida, U.S.A.) by two of his students, Emine Boz and Giovanni Rojas, on ‘Correlating Precisely Defined Primary Structure with Crystalline Properties in Halogen-Containing Polyolefins’ and ‘Precision Polyolefin Structures’, respectively, showed how acyclic diene metathesis (ADMET) induced by Grubbs ruthenium catalysts can rigorously control the polymer microstructure, and ultimately the product properties.

Special attention was paid to addition polymerisation and copolymerisation of selected monomers (such as silyl-functionalised norbornenes), induced by late transition metal catalysts (nickel and palladium), providing new materials with special properties (high thermal and chemical stability), for applications such as optical components, electrical insulators and photoresists. This was convincingly shown by Eugene Finkelshtein in his lecture on ‘Addition Polymerization of Silyl- and Some Other Functionalized Norbornenes’; by Victor Bykov (Topchiev Institute of Petrochemical Sciences, Russian Academy of Sciences) in his communication on ‘Copolymerization of Ethylene with Norbornene and Their Functional Derivatives on Nickel-ylide Catalysts’; and by Maria Gringolts (Topchiev Institute of Petrochemical Sciences, Russian Academy of Sciences) in her talk on ‘The Influence of Presence, Number and Location of AlkSi Groups in Norbornenes and Norbornadienes on Their Polymerisation and Polymer Properties’.

Nanostructured materials and how they could be used in nanomachines and molecular clockworks were attractively described by Lajos Bencze (University of Veszprém, Hungary), in two complementary lectures: ‘Long Range Transfer of Chiral Information in Rotalicene Type Nanomachines’ and ‘Molecular Clockworks as Potential Models for Biological Chirality’. Going beyond metathesis but in close correlation with this reaction, comprehensive and fascinating lectures on ‘Smart Nanostructured Materials by Atom Transfer Radical Polymerization’ and ‘Environmental and Sensors by Atom Transfer Radical Polymerization’, delivered by Krzysztof Matyjaszewski (Carnegie Mellon University, U.S.A.), illustrated the great potential of precisely controlled macromolecular structures obtained by atom transfer radical polymerisation (ATRP) to be assembled into smart materials, sensors and various molecular devices. A successful combination of ATRP with ROMP to produce new materials with valuable properties was also discussed. In his turn, Osama Musa (National Starch & Chemical Co, U.S.A.) furnished in his attractive lecture ‘Exploration of Novel Thermoset Resins: Faster, Higher and Stronger’, a wide range of applications of advanced materials prepared by different polymerisation procedures.

Concluding Remarks
The social programme was organised in a friendly and warm style, facilitating informal scientific discussion among renowned experts and young researchers, and strengthening contacts and the exchange of information between research groups of different nationalities.

At the end of the event, there was a general discussion on perspectives of future NATO ASI meetings on metathesis chemistry. Comments from a number of participants converged to the idea that, in view of the current upward trend in developments in this field, organising further meetings would be both opportune and highly beneficial, especially for the young generation of scientists involved in metathesis research.

A major conclusion emerging from the lectures, posters and discussions at this Institute is that a principal focus in this highly challenging area of research is the advantages of using new ruthenium catalysts for a multitude of chemical transformations. Further exploration of the metathesis
chemistry of other pgms such as osmium is also of great interest. The application profile of the novel metathesis catalysts is expanding rapidly, particularly in RCM, and CM. These methods may be exploited for the synthesis of therapeutic compounds, as well as in ROMP for the production of specialised and highly functionalised polymers.

Following the useful practice of previous NATO ASI meetings (see, for example, (9)), selected contributions including plenary lectures, short communications and posters will be compiled in a special volume dedicated to this outstanding scientific meeting, and will be published by Springer Verlag in 2007 (10).

References
1 NATO ASI: New Frontiers in Metathesis Chemistry; http://www.nato-asi.tk/

The Reviewers
Ileana Dragutan is a Senior Researcher at the Institute of Organic Chemistry of the Romanian Academy. Her interests are in stable organic free radicals – syntheses and applications as spin probes, olefin metathesis, Ru catalysis, transition metal complexes with free radical ligands and their magnetic and catalytic properties, azasugars and prostaglandin-related drugs.

Valerian Dragutan is a Senior Researcher at the Institute of Organic Chemistry of the Romanian Academy. His research interests are homogeneous catalysis by transition metals and Lewis acids; olefin metathesis and ROMP of cycloolefins; bioactive organometallic compounds; and mechanisms and stereochemistry of reactions in organic and polymer chemistry.
Cascade reactions, also known as domino reactions, are multibond-forming processes in which the first reaction creates the functionality/geometry necessary for the second reaction to proceed, and so on. Volume 19 of the Topics in Organometallic Chemistry series comprises eight chapters written by experts in the relevant areas and is heavily weighted towards palladium(0)-catalysed processes (5 chapters). Additionally, there is an excellent chapter on the Pauson-Khand reaction (mainly cobalt catalysis) and on metathesis (ruthenium).

Chapter 1 (by E. Negishi, G. Wang and G. Zhu) reviews Pd(0)-catalysed cyclisation-carbopalladation and acylpalladation cascades. A logical organisational framework enables systematisation of the sprawling literature, and adequate references to pertinent reviews and early work are provided. The role of proximal alkene and alkyne functionalities in facilitating oxidative insertion of Pd(0) into aryl/vinyl C–halogen bonds is noted. Carbopalladation comprises the major part of this chapter, and the versatility of such processes is amply demonstrated by processes involving polyenes, polyenynes, enylallenes and ynylallenes for the assembly of a bewildering array of fused, bridged and spirocyclic ring systems. The majority of the cascades are one- or two-component processes involving the formation of up to five rings.

The following Chapter 2 (by P. von Zezschwitz and A. de Meijere) covers sequential and cascade combinations of the Heck reaction with 6π-electrocyclisations or Diels-Alder and 1,3-dipolar cycloadditions. The importance of the relative rates of reaction of the substrates and of temperature in cascade design involving three or more components, which in adverse circumstances leads to the sequential one-pot option, is noted. The development of bicyclopropyldiene as a cyclopropyl-1,3-diene source in the three-component Heck-Diels-Alder processes is well reviewed, as is the use of allenes in three-component Heck-Diels-Alder and Heck-1,3-dipolar cycloaddition cascades. The latter provide access to a substantial array of heterocycles. Catalytic cross-coupling with ensuing thermal 6π-electrocyclisations, which results in the annulation of 6-membered carbo- or heterocycles onto various core rings including [2,2]-paracyclophanes, is well exemplified.

A survey of Pd(0)-catalysed cascades involving π-allylpalladium(II) species is given in Chapter 3 (by N. T. Patil and Y. Yamamoto), which is essentially a review of Yamamoto’s contributions to the area. The major focus is on π-allyl generation from allylic systems, including vinyl oxiranes, thiiranes, aziridines and 1,3-dienes. Generation of π-allyl species from allenes is only fleetingly mentioned. The emphasis is on one- and two-component processes and examples of both carbo- and heterocycle formation are given, including Yamamoto’s three-component Pd(0)-Cu(I)-catalysed triazole and tetrazole syntheses from allylic carbonates, trimethylsilyl azide (TMSN₃) and an alkyne or nitrile.

Metal-promoted cyclisative cascade reactions which incorporate Michael addition as a key step are the focus of Chapter 4 (by G. Balme, D. Bouyssi and N. Monteiro). The major emphasis is on Pd-promoted processes but examples of copper(I)-, scandium(III)-, yttrium(III)- and rhodium(I)-promoted processes are included. The review is nicely organised and mainly surveys formation of 5- and 6-membered carbocycles and...
heterocycles, with a strong emphasis on 5-membered oxygen heterocycles in the latter case. Both Michael initiated and terminated sequences are reviewed and exemplified by unimolecular and two- and three-component cascades involving a variety of metal activated intermediates (π-allylpalladium, π-complexed alkynes, alkenes and enolates).

Chapter 5 (by T. J. J. Müller) reviews a series of sequential Pd-catalysed processes initiated by Heck reactions, allylic substitution, amination, Sonogashira coupling, metallation (for example, in situ formation of Stille and Suzuki reagents, Pd migration/insertion into C–H bonds) and cycloisomerisation sequences. Given the huge and buoyant literature, this chapter, of necessity, presents a ‘bird’s-eye’ view of a dynamic field.

The 100% atom economic Pauson-Khand reaction (PKR), a formal [2+2+1]-cycloaddition reaction involving an alkyne, an alkene and carbon monoxide, together with related processes, are covered in Chapter 6 (by J. Pérez-Castells). The concise introduction benefits the non-specialist reader. The current limitations of the catalytic PKR are discussed and the wide range of metal complexes employed are illustrated, as are the various approaches and strategies for chiral induction. The interfacing of the Nicholas reaction (alkylation of Co-stabilised α-carbocationic alkynes) with the PKR and bimetallic Pd-Rh catalysis to generate bridged, fused and spirocyclic ring systems. Other non-carbenoid routes to complex cyclopropanes are also illustrated.

The final Chapter 8 (by C. Bruneau, S. Dérien and P. H. Dixneuf) is concerned with cascade and sequential Ru-catalysed metathesis processes. The cascade processes, which are only briefly reviewed, are enyne metathesis and alkene metathesis, and are largely examples involving Grubbs 2nd generation Ru heterocyclic carbene catalyst and Hoveyda’s catalyst. The metathesis area is so fast moving that reviews have a short ‘shelf life’.

Overall, this would not be considered a volume for personal libraries but is well worth consulting when appropriate. It is to be recommended on that basis.

The Reviewer

Professor Ron Grigg is Director of the Centre for Molecular Innovation, Diversity and Automated Synthesis (MIDAS Centre) at the University of Leeds, U.K. His current interests include cascade reactions catalysed by palladium, iridium, rhodium and ruthenium, and their applications to medicinal chemistry.
Strengthening of Platinum-5 wt.% Copper by Heat Treatment

By Chumani Mshumi and Candy Lang*
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Heat treatment of platinum-5 wt.% copper (Pt-5% Cu) below 500°C is known to result in an ordering transformation which can significantly increase the hardness of the alloy. Microsample tensile testing of Pt-5% Cu shows that low-temperature heat treatment of previously cold-worked specimens results in an increase in yield strength and tensile strength, with a maximum in strength occurring after heat treatment at 300°C; but ductility is unchanged.

The mechanical properties of the widely used jewellery alloy Pt-5% Cu have been investigated by several researchers (see, for example, (1–3)) for the cast, cold worked and annealed conditions. It is however not widely known that platinum containing around 5 wt.% copper undergoes an ordering transformation after low-temperature heat treatment (4, 5). Recent work in the Centre for Materials Engineering (6) showed that the Pt-Cu ordered phase, which can form after heat treatment at temperatures as low as 200°C, can improve the hardness of Pt-5% Cu. If the alloy is cold worked before heat treatment, the increase in hardness after heat treatment is significant. If the alloy is first quenched from high temperatures, an increase in hardness on heat treatment is measurable but not as great.

Given the widespread use of Pt-5% Cu in platinum jewellery, it is surprising that there is little information on this phenomenon in the technical literature. The hardness increase for this alloy has important implications for the manufacture of jewellery, since using low-temperature heat treatment as a final step in the manufacture of a jewellery piece can produce a better finish and improved scratch resistance. Conversely, hardness may be inadvertently increased by heating during manufacture, leading to difficulty in subsequent working of the piece. An understanding of the effect of heating on strength accordingly allows optimal planning of the manufacturing route.

The effect of the Pt-Cu ordering transformation on mechanical properties other than hardness has not previously been investigated. In this paper we investigate the effect on the strength and ductility of Pt-5% Cu of heat treatments which result in ordering. The tensile mechanical properties of platinum and its alloys have not been studied extensively, owing to the costs associated with tensile specimens of conventional (American Society for Testing and Materials (ASTM)) scale (7). These costs can be considerably reduced by microsample tensile testing, described previously in this Journal (3). Mechanical properties such as yield strength, tensile strength and ductility can be measured using specimens just 8 mm in length. In the present work the mechanical properties of Pt-5% Cu, before and after heat treatments which result in ordering, are fully characterised by microsample tensile testing and hardness testing.

Experimental Procedure
Bars (50 g in mass) of Pt-5% Cu were cold rolled to reduce thickness by 50%, before homogenising at 1000°C for 12 hours in an argon atmosphere. A fully recrystallised grain structure resulted after homogenising. Composition and homogeneity were assessed by scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS). The thickness was then further reduced by 90%, and specimens were cut from the resulting sheet. The 8 mm long specimens for microsample tensile testing were cut with the long axis parallel to the rolling direction. Heat

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treatments were carried out at temperatures between 100°C and 1000°C for 3 hours, followed by furnace cooling.

After heat treatment all specimens were ground, then polished to a 1 μm surface finish. A Zwick microhardness tester with a standard Vickers indenter was used at 100 gf load to measure the hardness of the specimens for each condition. Metallography specimens were etched electrolytically in a solution of 25 g sodium chloride, 20 cm³ hydrochloric acid 32% and 65 cm³ distilled water; an alternating current was used at a potential of 10 V, for an etching time of 40 to 75 seconds, with a stainless steel anode and a graphite cathode used to complete the circuit. Tensile specimens were ground and polished to a 1 μm surface finish on both sides. Measured gauge widths were between 440 μm and 510 μm, and gauge thicknesses were between 125 μm and 350 μm. Tensile tests were carried out using a microsample tensile tester at a strain rate of 10⁻³ s⁻¹.

Results

Figure 1 shows representative engineering stress/engineering strain curves for Pt-5% Cu in the cold worked condition and after heat treatment at several temperatures. Figure 2 is an extract from Figure 1, showing results for the cold worked condition and after heat treatment at

![Fig. 1 Stress-strain curves for Pt-5% Cu (cw = cold worked)](image)

![Fig. 2 Extract from Figure 1: Stress-strain curves for Pt-5% Cu in the 90% cold worked condition and after heat treatment at 300°C (highest increase in strength) and 1000°C (cw = cold worked)](image)
300°C (highest increase in strength) and 1000°C. Relative to the cold worked condition (90% reduction in rolling), yield strength and tensile strength are observed to increase after heat treatment at between 100°C and 500°C. Heat treatment at 600°C and above results in a decrease in strength and an increase in ductility.

Figure 3 shows the yield strength, tensile strength and hardness of Pt-5% Cu as a function of heat treatment temperature. Strength and hardness consistently increase after heat treatment between 100°C and 400°C, as seen in Figure 1. Heat treatment at 500°C results in little change in the properties relative to the cold worked condition; heat treatment at higher temperatures results in a decrease in strength and hardness. Measured values for hardness, yield strength, tensile strength and ductility (percentage elongation after fracture) are given in Table I.

Figure 4 shows the microstructure of the Pt-5% Cu alloy before and after heat treatment. After heat treatment at 300°C (the temperature which resulted in the greatest increase in strength), the heavily deformed and elongated grains from the cold working are unchanged. After heat treatment at 700°C, a recrystallised grain structure is observed, and after heat treatment at 1000°C grain growth has occurred.

**Discussion**

Cold work followed by heat treatment below 500°C results in an increase in the yield strength, tensile strength and hardness of Pt-5% Cu. These results are consistent with a previous report (6) of an increase in the hardness of this alloy due to an ordering transformation. For this alloy the critical
ordering temperature, $T_c$, is around 500ºC (4, 6), which means that a transformation to an ordered state can be expected to occur as a result of heat treatment below 500ºC. This does not result in any change in grain structure relative to the cold worked state, as seen in Figure 4(b); the observed change in properties thus arises entirely from the ordering transformation.

Hardness is expected to be proportional to yield strength (8); this is observed in the results shown in Figure 3. Hardness measurements alone, however, do not provide a complete characterisation of mechanical properties, which requires tensile testing. It is of interest to note that, although heat treatment between 200ºC and 400ºC results in very similar hardness increases, there is a clear maximum in yield strength and tensile strength after heat treatment at 300ºC.

Generally, ductility is expected to decrease as strength increases and vice versa: Figures 1 and 2 and Table I show that when strength decreases as a result of recovery and recrystallisation, ductility increases as expected. Heat treatment of cold worked Pt-5% Cu below 500ºC, however, can result in a significant increase in strength relative to the cold worked value, but ductility remains unchanged. The ordering transformation which occurs below 500ºC accordingly has an unexpected effect on tensile properties, in that an increase in strength is achieved without further loss of ductility.

Heat treatment at temperatures above $T_c$ does not result in an ordering transformation. In this alloy, heat treatment at temperatures above 500ºC leads to recovery and recrystallisation, as shown in Figure 4(c), which results in a decrease in strength. Increasing heat treatment temperature above 700ºC results in grain growth, and a consequent further decrease in strength and increase in ductility are observed.

### Table I

<table>
<thead>
<tr>
<th>Heat treatment temperature, ºC</th>
<th>Vickers hardness, HV</th>
<th>Yield strength, MPa</th>
<th>Ultimate tensile strength, MPa</th>
<th>Ductility, %</th>
</tr>
</thead>
</table>
| No heat treatment; 90% cold worked | 259 ± 11
240 (3)
241 (6) | 896 ± 40
970 ± 100 (3) | 910 ± 53
990 ± 90 (3) | 3 ± 1
2 ± 1 (3) |
| 100 | 292 ± 9 | 932 ± 48 | 972 ± 56 | 3 ± 1 |
| 200 | 320 ± 9
360 (6) | 994 ± 89 | 1056 ± 91 | 2 ± 1 |
| 300 | 322 ± 8 | 1048 ± 55 | 1153 ± 43 | 2 ± 1 |
| 400 | 320 ± 12 | 993 ± 60 | 1055 ± 61 | 2 ± 1 |
| 500 | 282 ± 11 | 887 ± 14 | 952 ± 18 | 3 ± 1 |
| 600 | 251 ± 16 | 711 ± 18 | 805 ± 18 | 4 ± 1 |
| 700 | 222 ± 14 | 652 ± 13 | 749 ± 20 | 10 ± 3 |
| 800 | 172 ± 8
150 (6) | 245 ± 40
280 ± 30 (3) | 477 ± 24
530 ± 40 (3) | 30 ± 7
36 ± 9 (3) |
| 1000 | 158 ± 7 | 228 ± 31 | 469 ± 27 | 31 ± 8 |

Values in italics are from References (3) and (6). Note that in Reference (3) heat treatment time is six hours.
Conclusions

The hardness and strength of cold worked Pt-5% Cu can be significantly enhanced by heat treatment for three hours at temperatures between 200ºC and 400ºC, without reducing ductility. A short, low-temperature heat treatment can thus significantly enhance the mechanical properties of Pt-5% Cu jewellery items which have been produced by cold working.

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Chumani Mshumi is pursuing doctoral research at the Centre for Materials Engineering, University of Cape Town (UCT), South Africa.

Candy Lang is Professor in the Department of Mechanical Engineering, UCT. She is leader of the team developing novel platinum alloys for the jewellery industry.
A one day meeting on the Successful Scale-Up of Catalytic Processes took place on the 5th October 2006. Organised by the Applied Catalysis Group of the Royal Society of Chemistry (1), it was hosted by Davy Process Technology Ltd (2) at Stockton-on-Tees, U.K. In all, almost 60 delegates attended the meeting, with over 80% being from industry. There were a total of six oral presentations, of which three covered work using platinum group metal (pgm) catalysts, especially palladium.

Cost-Effective Palladium-Catalysed Processes

Ian Archer (Ingenza Ltd, U.K.) described the scale-up of a novel process for the synthesis of pure enantiomers of amino acids and amines. The process uses chemo-enzymatic deracemisation to generate a single enantiomer from a racemic mixture (3). A biocatalysed enantioselective oxidation is used to convert one enantiomer of the amino acid or amine to a non-chiral imine, which is then reduced non-selectively back to the amine, see Scheme I.

In order to develop commercially viable processes, Ingenza have needed to develop cost-effective pgm-catalysed reductions. For example, for the stereoinversion of D-2-aminobutyric acid to L-2-aminobutyric acid, over 40 different pgm catalysts were screened for use in the reduction step. Initially, a Pd/C catalyst was identified as the most promising candidate, but the cost proved to be too high, even with reuse of the catalyst and recovery of the Pd metal. Development of a second generation Pd catalyst enabled the costs to be reduced to an economically attractive level.

David Johnson (Lucite International Ltd, U.K.) presented a paper which outlined the development and scale-up of their new route to methyl methacrylate (MMA). This novel process employs two catalytic reaction steps:

(a) carbonylation of ethene in methanol to produce methyl propionate, using a homogeneous palladium-phosphine catalyst;

(b) condensation of methyl propionate with formaldehyde over a basic heterogeneous catalyst (Cs/SiO2).

There were several issues which needed to be addressed during the scale-up of the overall process, including product separation and purification issues, catalyst manufacture, and the demonstration of product quality.

Although the initial research had identified a suitable carbonylation catalyst with a turnover...
number of ~ 50,000 and selectivity in excess of 99.9%, the phosphine ligand was not commercially available at that time and the existing synthesis would have been prohibitively expensive. The company therefore had to develop alternative synthesis routes in conjunction with Professor Peter Edwards at Cardiff University, U.K.

In order to achieve recovery of the methyl propionate, the process was designed to operate on the product-rich side of an azeotrope. This had the unfortunate effect of lowering catalyst activity. Further, it was discovered that carbon monoxide poisoned the catalyst; this necessitated operating the process with a high ethene:CO ratio. However, it was then discovered that addition of polyvinylpyrrolidone was able to stabilise the catalyst activity and also improve the Pd recovery.

**Optimised Palladium Catalyst Performance**

Kevin Treacher (Reaxa Ltd, U.K.) presented an overview of the use of Pd EnCat™ catalysts for organic synthesis. A range of different catalysts are available based on palladium(II) acetate in combination with a variety of phosphine ligands and encapsulated in porous polyurea beads. These catalysts can be used for a variety of synthetic reactions such as Suzuki coupling, Heck reactions and hydrogenations. A catalyst with encapsulated Pd nanoparticles is also available.

A case study of the Suzuki coupling of phenylboronic acid and 4-fluoro-1-bromobenzene to give 4-fluorobiphenyl was presented. Initial screening of different bases in conjunction with a Pd(II) EnCat™ BINAP30 catalyst was carried out in a batch reactor. The best performing system from these tests was then evaluated in three different flow reactor configurations: a continuous stirred tank reactor (CSTR), a tubular reactor and two sequential tubular reactors. With this latter configuration, optimised system productivity in excess of 150 g per g catalyst was achieved; the catalyst still exhibited a stable performance after 250 hours operation.

**Other Approaches**

In addition to these three presentations which included pgm catalysis, the other talks described the approaches to catalytic process scale-up used by different companies. Steven Colley (Davy Process Technology Ltd, U.K.) outlined their approach to process scale-up, with the focus being on the use of mini-plants to generate the data required for process design, and the issues that can be encountered. Simon Froom (BP, U.K.) described the scale-up of BP’s Avada® process (4) for the manufacture of ethyl acetate from acetic acid and ethene. Professor Wolfgang Holderich (RWTH-Aachen University, Germany) described the development of two new processes: the manufacture of caprolactam via the acid-catalysed Beckmann rearrangement of cyclohexanone oxime; and the production of biodegradable lubricants via the esterification of natural oils and glycerides.

**Conclusion**

Overall, the meeting was a resounding success and provided many valuable insights into the varying methodologies which can be used in the scale-up of catalytic processes, whether for more traditional large-scale manufacturing processes or for smaller-scale speciality chemical synthesis. The Applied Catalysis Group of the Royal Society of Chemistry plans to hold a one-day symposium on the Challenges in Catalysis for Pharmaceuticals and Fine Chemicals at the Society of Chemical Industry, London, U.K., on 6th November 2007 (1).

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2 Davy Process Technology Ltd:  
http://www.davyprotech.com/  

**The Reviewer**

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Research into organic light-emitting devices (OLEDs) has been intense over the past 20 years, since the landmark report in 1987 of electrically generated light emission from aluminium tris(8-hydroxyquinoline) (1). Regarded by many as the next generation of display screen technology, OLEDs may eventually rival liquid crystal displays and conventional inorganic LEDs, and commercialisation has indeed recently begun. The key hallmark of research in the field is its interdisciplinarity, embracing synthetic chemists, physicists, physical chemists, and electronic and optical engineers, and elegantly spanning fundamental and applied science.

This new book, edited by two leading German polymer chemists, brings together contributions from a dozen of the leading research groups in the field, representing all of the aforementioned disciplines. The result is a coherent account of the fundamental principles behind the science of OLEDs and of the materials required for their fabrication. The book is not for the novice or the undergraduate student; on the contrary, the majority of the chapters assume familiarity with the underlying physical concepts, and the book is probably aimed primarily at those already working in the field, or intending to enter into it seriously. Perhaps rather disappointingly for the platinum group metal chemist, coverage of iridium- and platinum-based electrophosphorescent dopants is limited to just one chapter that focuses primarily on the triplet energy transfer processes rather than on the chemistry. This is despite the fact that their development as ‘harvesting agents’ for the otherwise non-emissive triplet states has been a buoyant and high-profile area of research in the field over the past six years or so. (Reviews and representative papers in this field include References (2–5)).

The book is logically structured, appropriately beginning with a description of the science behind inorganic LEDs – already very well established – before turning to a sequence of chapters describing the physical processes underlying charge injection and light emission in conjugated polymers. This is followed by more chemistry-oriented chapters describing the synthesis and properties of electroluminescent polymers, charge-transporting/charge-blocking materials and dendrimeric systems, and the use of crosslinking strategies in materials processing. The final three chapters address hybrid inorganic-organic systems, including a useful discussion of nanocrystalline emission (colloidal quantum dots); promotion of triplet emission using phosphorescent dyes, such as cyclometallated iridium complexes and platinum porphyrins (see Figure 1 for representative structures); and organic semiconductor lasers.

Any new book on such an interdisciplinary subject as OLEDs faces the challenge of facilitating mutual understanding of the different disciplines, and aiding scientists from one discipline to gain an appreciation of the issues facing those tackling the subject from a different perspective. The book does achieve this to an admirable extent, although some chapters are, not surprisingly, more successful than others at doing so; the interested chemist may find himself at sea with some of the physics chapters and perhaps vice versa. On the other hand, this is simply inevitable given the depth of coverage: the volume overall is unified in structure and comprehensive in scope.

The book is well produced, with clear diagrams,
many of which are helpfully reproduced in colour. A few chapters, particularly some of those on synthetic aspects such as a key chapter on the synthesis of electroluminescent polymers, were a little disappointing in that they surveyed little post-2000 work. Given the rapid progress of the field, surely it is important to ensure that a volume of this sort is as up-to-date as possible at the time of publication. It was also a little surprising to find that while nine of the twelve chapters employ a common referencing style, three use two other styles. Though a minor peccadillo, one might reasonably have expected a unified style. I was also bemused to read in the publishing and retailing publicity accompanying the book that Ching Tang of Eastman Kodak was one of the contributors, even though there is no contribution from him or anyone else at Eastman Kodak.

Comparison with Other Texts

There are few comprehensive books available on OLEDs. Kalinowski’s recent volume “Organic Light-Emitting Diodes: Principles, Characteristics and Processes” (6) is geared more exclusively to the physics and engineering aspects and, while comprehensive in its treatment of the fundamental physics, is a less tractable work. More closely comparable is Shinar’s edited review “Organic Light-Emitting Devices: A Survey” (7), which covers some material common to the present volume. Nevertheless, Müllen and Scherf’s contribution is an altogether wider ranging survey, bringing in a more diverse range of systems, and has a fresher feel to it. Yet, from the admittedly biased perspective of a platinum group metal chemist, the rather cursory treatment of only a very few iridium and platinum complexes as phosphorescent dopants in Chapter 11 does seem something of a lost opportunity. The inorganic chemist hoping for a survey of the latest developments with respect to this aspect would need to look elsewhere, and in this context, perhaps a forthcoming review volume edited by Balzani and Campagna on the photophysics of metal complexes may help to fill the gap (8).

Conclusion

In summary, “Organic Light-Emitting Devices” provides a comprehensive, wide-ranging and authoritative account of both the science behind OLEDs and of recent developments in the materials used to produce them. It will make a valuable contribution to the research field for chemists, physicists and optical engineers alike.

References

Platinum Group Metal Perovskite Catalysts

PREPARATION AND APPLICATIONS

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Perovskites are a large class of minerals, both naturally occurring and synthetically produced, with important technological applications. In this article, platinum group metal (pgm) perovskites are introduced as a relatively new catalyst material. Due to their high activity, versatile and stable structure and low pgm content, they can offer advantages over conventional catalysts. Some of the typical applications and preparation methods of pgm perovskites are reviewed, with particular focus on their potential use to address current challenges concerning autocatalysts, and in organic chemistry.

The role of the support in heterogeneous pgm catalysis is frequently crucial. The choice of support (usually from carbons, silicas, aluminas, zeolites or other inorganic compounds) can influence the selectivity, activity and longevity of the catalyst. Though catalysts of exceedingly high efficiency are regularly produced, the long-term stability of the pgm system, especially under harsh conditions, can be a problem. In addition, rising pgm demand and costs are incentives towards achieving lower metal loadings and higher activity. Some of these issues can be addressed using pgm-containing perovskites.

The perovskite structure is a highly versatile and widespread mineral form, of great importance in nature and technology (1). They were first described and named by the Russian mineralogist Count Lev Aleksevich von Perovski, who discovered the naturally occurring mineral calcium titanate (CaTiO₃). The common feature of perovskites is the generic structure ABO₃, with A and B drawn from a range of metals, subject to certain size constraints. The range of possible cation substitutions is limited by constraints on thermodynamic stability, as represented in terms of the Goldschmidt factor (1). The ideal perovskite has a cubic structure, with an octahedral configuration of the oxygen atoms at each corner around the B atom (Figure 1) (2). The structure can tolerate significant non-stoichiometry and partial substitution. By varying the types of atoms at the A and B sites, the resulting structure will deviate from the ideal depending on the constituent properties (for example, ionic radius, valence and electronegativity). Fractional incorporation of several different elements at specific sites can be achieved through careful design. With non-stoichiometric substitutions, oxygen ion conductivity may be induced by oxygen vacancies (3). Control of substitution in the perovskite matrix is important for tuning the properties of the material. For instance, catalytic activity is apparently determined primarily by the species at the B site (4).

This review focuses on methods of preparation of pgm-substituted perovskites, on their performance as catalysts, and on their principal current and potential uses. As opposed to perovskites used as a support for a metal catalyst, the main consideration here is of perovskites containing the pgm within the mineral lattice; the latter require initial synthesis.

![Fig. 1 The perovskite structure (2)](image)
Preparation of PGM Perovskites

Synthetic perovskites may be prepared by a range of methods. Routes similar to those for the production of other ceramics include oxide sintering, combustion synthesis and sol-gel methods (5). Oxide sintering entails heating the powders of the constituents together at high temperature. A variant of this is combustion synthesis, where the ignition of a combustible component provides the energy for the formation of the perovskite mineral. Aqueous combustion synthesis has been used to prepare platinum- and ruthenium-containing perovskites, which were subsequently investigated as anode catalysts in direct methanol fuel cells (DMFCs) (6), a promising technology for portable power applications. Perovskite oxides could provide an alternative to more expensive platinum-based catalysts and a solution to problems of CO poisoning. It was found that SrRuO₃ doped with platinum added at the combustion synthesis stage gave performance comparable to that of standard platinum-ruthenium catalysts.

A versatile synthesis of perovskites is by coprecipitation from soluble precursors of the constituent metals in a suitable solvent, followed by solvent removal and heat treatment. S. Petrovic et al. prepared palladium-containing perovskites of the form \( \text{LaTi}_{0.3} \text{Mg}_{0.5-x} \text{Pd}_x \text{O}_3 \) \((0 < x < 0.1)\) by annealing ethanol solutions of the precursors in a nitrogen flow at 1200ºC (7). It was found that at least a proportion of the palladium was not incorporated into the perovskite structure, but existed as a separate metallic phase, which was believed to influence the catalytic activity. The samples were tested in the catalytic combustion of methane, with perovskites with lower palladium loading \((x = 0.05)\) showing higher activity at temperatures over 500ºC, attributed to the finer dispersion of the palladium in the lattice. Other pgm-containing perovskites have been tested for the combustion of light hydrocarbons, which finds important application in volatile organic compound abatement. Perovskites have been suggested as good candidate catalysts (8), for example lanthanum/cobalt perovskites \( \text{La}_{1-x} \text{M}_x \text{CoO}_3 \) \((\text{M} = \text{Ag, Pd, Pt}; 0.08 \leq x \leq 0.2)\) for catalytic methane combustion (9).

Use of PGM Perovskites in Autocatalysts

Reflecting the trend in pgm usage as a whole (10), the major current use of pgm perovskites is in catalytic converters for cars. Catalytic converters have been in use since the 1970s (11) and usually consist of supports of high surface area, coated with pgms. These systems have proved very successful at simultaneously converting CO into CO₂, unreacted hydrocarbons (HCs) into CO₂ and water and reducing nitrogen oxides (NOx) to nitrogen but, at present, the automotive industry faces several challenges.

The conventional means to meet tightening legislative emissions control targets is simply to increase the amount of pgm in the autocatalyst. The need to guarantee catalyst performance over the typical vehicle lifetime of 80,000 km also means that excess metal must be added, since the performance of the catalyst drops off over time. In the harsh conditions experienced in the exhaust stream with temperatures up to 1000ºC, the metal in the catalyst is prone to deactivation by sintering, leading to a reduction in surface area and hence catalytic activity. This issue of ageing performance is expected to become even more important, as the Euro 5 requirements (12) also include an extension of catalyst lifetime to 160,000 km. The robustness of perovskites and the low pgm content typical in pgm-doped perovskites combine to provide a novel solution to these problems.

The palladium-containing perovskite \( \text{LaFe}_{0.77} \text{Co}_{0.17} \text{Pd}_{0.06} \text{O}_3 \) synthesised by coprecipitation of the metal nitrates and perovskite-supported palladium \((\text{LaFe}_{0.3} \text{Co}_{0.2} \text{O}_3 / \text{Pd} \text{ at the same palladium loading})\), were compared for their preparation methods and catalytic behaviour by K. Zhou et al. (13). Both showed excellent three-way catalytic activity, with the supported palladium somewhat better; this is attributed to greater ease of reduction of the surface palladium to generate the active catalyst compared to the palladium in the perovskite, which was shown to be dispersed throughout the lattice by X-ray diffraction (XRD) and transmission electron microscopy (TEM) studies. Platinum-promoted lanthanum manganate type perovskite catalysts, prepared by coprecipitation of the metal hydroxides...
using aqueous ammonia, have also shown potential for automobile applications (14), and ruthenium perovskites La$_{0.7}$Sr$_{1-y}$Ru$_y$Cr$_{1-x}$O$_3$ ($y = 0.7; 0.025 \leq x \leq 0.100$) have been tested as candidates for lean NOx automotive emission control (15).

Work by H. Tanaka and coworkers at Daihatsu Motors has produced a range of palladium perovskites from soluble alkoxide precursors (16). The salts of the constituent metals were combined in toluene in the desired proportions. Hydrolysis of the salts with water gave a precipitate which was isolated and dried in air to obtain the perovskites. For example, palladium-containing perovskite LaFe$_{0.57}$Co$_{0.38}$Pd$_{0.05}$O$_3$ was prepared from lanthanum, cobalt and iron ethoxyethylates with aqueous palladium nitrate solution (16), and LaFe$_{0.95}$Pd$_{0.05}$O$_3$ was synthesised from base metal ethoxyethylates and palladium acetylacetonate (17). Recently, using the same method, platinum- and rhodium-containing perovskites CaTi$_{0.95}$Pt$_{0.05}$O$_3$ and LaFe$_{0.95}$Rh$_{0.05}$O$_3$ respectively, were also prepared (18, 19).

The use of these perovskites in autocatalysts centres around a novel mechanism which exploits the inherent fluctuations between reducing and oxidising atmospheres in the exhaust gases. In a modern three-way catalytic converter, the exhaust stream over the catalyst is controlled to give optimal conditions for the required reactions. This is achieved by control of the air-to-fuel ratio in the engine, using an oxygen sensor which continually monitors the exhaust gas composition and feeds information back to the air intakes. Inevitable time lags between sensing and adjustment lead to alternations between conditions which are oxygen rich and oxygen poor relative to the ideal stoichiometry.

As synthesised, and under oxidising exhaust conditions, the palladium in LaFe$_{0.95}$Pd$_{0.05}$O$_3$ exists as a solid solution dispersed throughout the perovskite lattice. However, under reducing conditions and the high temperatures in the exhaust stream, the palladium segregates to form metallic nanoparticles (1 to 3 nm in size). This process was shown to be reversible, with the palladium redispersing in the lattice on a return to oxidising conditions (Figure 2) (19). This phenomenon accounts for the excellent ageing performance of the perovskite autocatalysts. In conventional autocatalysts using pgm dispersed on a support, sintering over time to ever larger metal particles at the prevailing elevated temperatures leads to a reduction in catalytic activity. In the perovskite catalyst, the oxidising/reducing cycle maintains the catalytic activity by regenerating the palladium metal nanoparticles and preventing metal particle growth. This has led to the catalysts being dubbed ‘intelligent’, due to their capacity to react to their environment, resulting in greater efficiency (16). Recently, the same effect has been shown in platinum and rhodium perovskites, extending the concept to the full range of pgms commonly used.

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**Fig. 2 Schematic of the operation of self-regenerating pgm perovskite autocatalysts (2)**
in autocatalysts (18, 19).

The perovskite-containing catalytic converters are also highly active. A vehicle equipped with such a high activity perovskite autocatalyst achieved the J-ULEV (Japan Ultra Low Emissions Vehicle) emissions standard in 2002, demonstrating that pollutant levels more than 50% below those required by current legislation were measured. Another major advantage of perovskite autocatalysts is the reduced metal content compared with that of conventional autocatalysts of similar activity. Reductions of 70 to 90% have been reported possible (20), translating into potentially significant cost savings.

**PGM Perovskites in Organic Synthesis**

Reactions catalysed by pgms, such as cross-couplings and hydrogenations, are becoming increasingly prevalent in organic synthesis. Where the pgm-catalysed steps are part of the synthesis of active pharmaceutical intermediates (APIs), there are stringent limits on permissible metal contamination, driving a requirement to minimise the release of metals into the process (21). Conventional approaches to achieve this are to move from homogeneous to heterogeneous catalysts, or to ‘heterogenise’ catalysts *via* processes such as immobilisation (22) or microencapsulation (23).

This is another area where the stability, robustness and low pgm content of perovskite catalysts facilitate their application. The perovskite minerals which are air-stable powders are well suited to use in the chemical laboratory. Professor Steven Ley and coworkers at the University of Cambridge, U.K., have tested palladium-containing perovskites in organic transformations which are otherwise carried out with conventional palladium catalysts (24).

Use of perovskite catalysts in a standard Suzuki coupling, between an aryl bromide and aryl boronic acid, showed that the reaction was catalysed with similar rates by a wide range of perovskites containing 5 at.% palladium (25). It also demonstrated that palladium was an essential component for successful conversion, and that the oxidised form of the perovskites worked better under the reaction conditions. Working with the best-performing catalyst, LaFe$_{0.57}$Co$_{0.38}$Pd$_{0.05}$O$_3$, M. D. Smith *et al.* extended the perovskite-catalysed Suzuki reaction to encompass a wide range of different substrates, including aryl iodides and bromides, heteroaryl halides and aryl and alkenyl boronic acids (Scheme I) (26). The application of microwave heating also enabled coupling to aryl chlorides.

The use of a copper-palladium perovskite LaFe$_{0.57}$Cu$_{0.38}$Pd$_{0.05}$O$_3$ allowed the extension of perovskite-catalysed organic chemistry to the Sonogashira coupling reaction of aryl halides and acetylenes (27), again giving good yield across a range of aryl bromide and iodides.

There has been considerable work on ascertaining the mechanism by which perovskites function in organic reactions. The lower temperatures involved (typically 80ºC) preclude the type of self-regeneration seen in autocatalysts. Investigation focused on whether the reaction proceeded *via* a homogeneous or heterogeneous mechanism, and evidence has

![Scheme I A selection of reactions catalysed by palladium perovskite](image-url)
been built up by several methods (25). Removal of the bulk catalyst by filtration at partial reaction, followed by returning the filtrate to the reaction conditions, showed that the reaction progressed to significantly higher conversions in the absence of the solid catalyst. This demonstrated that an active solution palladium species was formed, a conclusion supported by solution and solid-phase catalyst poisoning studies. Performance in a three-phase test, employing solution and solid-supported substrates, provides further evidence to support the hypothesis of an active solution species, but also demonstrated that an aryl halide must be present in the solution phase for the reaction to proceed.

Collation of the evidence (25) led to the proposed mechanism shown in Figure 3. The initial step is a reduction of the Pd(III) or other high-valent palladium species in the perovskite, possibly by the solvent, to form a surface-bound Pd(0) species. This is next taken into solution by oxidative addition to the aryl halide. The coupling reaction can now proceed through a fairly conventional solution catalytic cycle, at the end of which the palladium either remains in solution to continue the reaction or is readsorbed onto the perovskite surface.

The release of highly active palladium into solution from the perovskite explains a very efficient catalytic turnover, with loadings of less than 0.05 mol% palladium sufficient. Recapture of the palladium by the perovskite at the end of the reaction cycle accounts for the extremely low residual palladium levels found in the crude reaction products. Palladium contents of less than 2 ppm were found in a Suzuki coupling product (26). The combined benefits of a highly efficient catalyst with low pgm content and very low levels of metal contamination make these attractive catalysts for chemical applications, especially synthesis of pharmaceutical and electronic materials, where exclusion of catalyst residues is essential. Furthermore, the perovskite catalysts have been shown to be recyclable (26), leading to even greater potential cost savings over catalysts which must be disposed of after a single use.

![Fig. 3 Proposed mechanism for catalytic activity of pgm perovskites in organic synthesis (25)](image-url)
Conclusions

The pgm-containing perovskites constitute an active and expanding area of research. The potential and versatility of pgm-containing perovskites as catalysts is shown by the range of applications in which they have been tested – from catalytic combustion to organic synthesis. Their sturdy mineral structure and stability offer advantages wherever high temperatures are involved and in some cases, such as self-regenerating autocatalysts, give distinct benefits where other metal supports are deactivated over time. The high activity often associated with pgm perovskites, combined with the low loadings of pgms required, result in their offering significant potential savings in metal costs.

In the organic chemistry laboratory, where the stable, easily handled pgm perovskites work as highly active and clean catalysts, a whole new application area may open in the near future, reinforcing their significance.

The Author

Thomas Screen was born in London, U.K. He studied Natural Sciences (Chemistry) at the University of Cambridge, U.K., where he was awarded a B.A. in 1996. This was followed by two years working at Johnson Matthey Catalytic Systems Division in Royston before returning to academia and the group of Professor Harry L. Anderson at the University of Oxford. Thomas completed his D.Phil. there on the ‘Synthesis and Properties of Conjugated Porphyrin Polymers’ in 2002 before moving to Germany for a postdoctoral appointment with Professor Klaus Müllen at the Max Planck Institute for Polymer Research in Mainz. On returning to the U.K., Thomas joined Peakdale Molecular Ltd in Chapel-en-le-Frith, Derbyshire, at the end of 2003. Since 2005 he has worked at the new catalyst technologies company Reaxa Ltd in Manchester, U.K.

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“Combinatorial and High-Throughput Discovery and Optimization of Catalysts and Materials”

CRITICAL REVIEWS IN COMBINATORIAL CHEMISTRY, Volume 1

A Selective Review by Dave M. Newman* and M. Lesley Wears**
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Introduction
A new book series begins with this volume, which covers molecular diversity and combinatorial chemistry, high-throughput discovery and associated technologies including characterisation techniques. Given the wide scope of this book, a comprehensive review is not possible. Therefore particular areas of interest having relevance to the platinum group metals (pgms) have been selected for a series of reviews. Here, Dave Newman and Lesley Wears of the University of Exeter, U.K., present a review of two chapters: respectively, Chapter 16, titled ‘Innovation in Magnetic Data Storage Using Physical Deposition and Combinatorial Methods’, by Erik B. Svedberg (Seagate Technologies, U.S.A.); and Chapter 17, ‘High-Throughput Screening of Next Generation Memory Materials’, by Chang Hwa Jung, Eun Jung Sun and Seong Ihl Woo (Korea Advanced Institute of Science and Technology, South Korea). Further chapters will be reviewed in future issues of Platinum Metals Review.

Thin Film Deposition for Data Storage Technology
Chapter 16 focuses closely on the thin film metal deposition techniques that have delivered the complex and task-tailored multilayer thin film structures that underpin the continuing and often spectacular advances in magnetic data storage technology. These are embodied in the hard disk drive now ubiquitous, not just in computer systems, but in reduced-size formats across the full spectrum of consumer electronics. The importance of optimising both material and multilayer performance, not only for the recording medium supporting the stored data, but also for the complex structures that comprise the readout sensor heads is referenced, but unfortunately this section is all too brief, so that the real challenges that have been met and overcome are not readily appreciated in full.

It is the comprehensive, detailed and well written descriptions of the deposition geometries directed to specific ends that provide the real benefit of the work. This section clearly describes the various deposition geometries by which material composition or thickness can be adjusted, to produce series of samples in which specific characteristics are varied in a highly controlled manner. It is supported by clear diagrams and photographs showing the relative dispositions of components in such systems. Concepts such as the movement of substrates and masks in complex patterns over multiply oriented sources are introduced and discussed, with reference to what might be achieved by way of compositional variation and the control of characteristics. A useful and illustrative example is given based on the development of cobalt/platinum (Co/Pt) and cobalt-chromium/platinum (CoCr/Pt) multilayers and, importantly, considerable effort is directed towards introducing the modelling of desirable magnetic-dependent parameters on material composition and thickness.

In summary, the chapter meets its stated aims and what it covers is well referenced. Its narrowness of scope is, however, disappointing. The increasing
importance of pgms to magnetic recording is not fully represented. No mention is made, for example, of the attempts to produce patterned media based on platinum-cobalt (PtCo) or platinum-iron (PtFe) by chemical and biological processes (1–5).

Screening of Thin Film Data Storage Materials

Chapter 17 promotes the use of a thin film deposition/characterisation procedure developed to enable rapid parallel characterisation of data storage materials. The conclusion, however, highlights the limits of this technology when applied to memory materials, due to the unavailability of high-throughput characterisation techniques. The diagrams and text are clear and concise, but the reader would benefit from the figures being close to the text that describes them.

The authors give an overview of current materials and techniques used by the storage industry. However, they fail to address the imminent problems facing the industry, which is surprising as these solutions involve pgms in particular. To increase the areal density of memory materials, the storage industry has committed to perpendicular recording. Although this is alluded to in the final section, where magnetoresistive random access memory (MRAM) and cobalt-chromium-platinum-tantalum (CoCrPtTa) are discussed, the failure to include heat-assisted magnetic recording (HAMR) (6), a technique which involves the deposition of high anisotropic materials which include PtCo and PtFe, may be considered an oversight.

Conclusion

Chapters 16 and 17 together provide a basic introduction to the often complex deposition technologies and operational methodologies now routinely employed in the manipulation and combination of material properties to a specific technological end. In this context they can be recommended; however reference to the importance of pgms is rather limited.

References

ABSTRACTS
of current literature on the platinum metals and their alloys

PROPERTIES

Probing the Interface in Vapor-Deposited Bimetallic Pd-Au and Pt-Au Films by CO Adsorption from the Liquid Phase
PVD was used to prepare Pt, Pd, Au, Pt-Au and Pd-Au films. Their surfaces were characterised by XPS, AFM and CO adsorption from liquid CH3Cl monitored by ATR-IR spectroscopy. The changes observed in the IR frequency and in the shape of the CO signals upon adsorption indicated that morphological changes occur in the Pd films when decreasing the film thickness from 2 to 0.2 nm and when introducing a 1 nm Au film. The Pt-Au surfaces were less sensitive toward CO adsorption.

Electric Field-Induced Modification of Magnetization in Thin-Film Ferromagnets
The magnetocrystalline anisotropy of ordered FePt and FePd intermetallic compounds can be reversibly modified by an applied electric field when immersed in an electrolyte (propylene carbonate and Na+OH–). A voltage change of –0.6 V on 2 nm thick films modified the magnetic parameters is attributed to a change in the number of unpaired d electrons.

Hydrogen-Induced Stress Relaxation in Thin Pd Films: Influence of Carbon Implementation
The influence of C impurities on mechanical properties of thin Pd film/H2 has been investigated in situ by AFM. The systems characterised by C incorporation obtained at the air/HOPG interface upon drop-cast being interdigitated. Similar lamellar arrays were also shown to form lamellar arrays at a 1-phenyloctane/HOPG interface. From STM images, it is concluded that the molecules align with alkyl chains parallel to the substrate. Hydrogen-induced stress relaxation was observed in the Pd/H2 systems.

Hydrogen Sorption Properties of Ternary Intermetallic Mg–(Ir,Rh,Pd)–Si Compounds
Mg–(Ir,Rh,Pd)–Si (1) with the highest Mg content (Mg3IrSi, with channel-like structure) reveals the highest electrochemical H capacity. Generally the capacities of (1) studied are low. Refining the particle size and microstructure of (1) did not result in any significant H-capacity increase.

CHEMICAL COMPOUNDS

Reactivity Studies of Rhodium Porphyrin Radical with Diazo Compounds
Rh(II) tetramethylporphyrin, Rh(tmp), reacted with ethyl diazoacetate and (trimethylsilyl)diazomethane to give Rh(III) porphyrin alkyls. Mechanistic studies showed that Rh(tmp) was coordinated with a diazo compound, which then underwent a rapid H atom abstraction via C–H bond activation to give Rh(tmp)H. This subsequently reacted with a second molecule of the diazo compound in the rate-determining step to give Rh(tmp) alkyl and N2.

Structural and Magnetic Study of N2, NO, NO2, and SO2 Adsorbed within a Flexible Single-Crystal Adsorbent of (Rh3(bza)4(py2))
[Rh3(bza)4(py2)] (1) exhibits gas adsorbency. The structures obtained were characterised as (1)·1.5 N2 (298 K), (1)·2.5 N2 (90 K), and (1)·1.95 NO (90 K) under forcible adsorption conditions and (1)·2 NO2 (90 K) and (1)·3 SO2 (90 K) under ambient pressure. The NO inclusion crystal exhibited antiferromagnetic interaction between the NO molecules and paramagnetism arising from the NO monomer.

Ordered Arrays of Organometallic Iridium Complexes with Long Alkyl Chains on Graphite
fac-[Ir(ppy)3] complexes having long alkyl chains were shown to form lamellar arrays at a 1-phenylcyclohexane/HOPG interface. From STM images, it is concluded that the molecules align with alkyl chains being interdigitated. Similar lamellar arrays were also obtained at the air/HOPG interface upon drop-casting of toluene solutions.

ELECTROCHEMISTRY

Ruthenium–Ligand Complex, an Efficient Inhibitor of Steel Corrosion in H3PO4 Media
The effect of a macrocycle Ru complex (1) on the corrosion of steel in H3PO4 was investigated. Inhibition efficiency (E%) increased with concentration of (1). Electrochemical impedance spectroscopy showed that the dissolution process of the steel occurs under activation control. Polarisation curves indicate that (1) acts as a cathodic inhibitor.
PHOTOCONVERSION
Phosphorescent Dyes for Organic Light-Emitting Diodes
Highly emissive, charge-neutral Pt, Ir, Os and Ru complexes (1) with chelating C-linked 2-pyridylazo-late ligands were synthesised. The photophysical properties of (1) were investigated using spectroscopy, relaxation dynamics, and theoretical approaches, from which the lowest-lying excited states, competitive radiative decay, and radiationless processes were then analysed. The potential use of (1) in OLEDs was evaluated.

Tris(2,2'-bipyridyl)ruthenium(II) Chemiluminescence Enhanced by Silver Nanoparticles
Mixtures of Ag(I) and citrate ions that are used to produce Ag nanoparticles induce intense chemiluminescence with Ru(bpy)32+ and Ce(IV), which can be utilised for the determination of citrate ions and other analytes. Solutions of glycine, proline and tartaric acid (5 × 10⁻⁴ M) that contained AgNO3 (2.5 × 10⁻³ M) gave chemiluminescence with Ru(bpy)32+ and Ce(IV) that was ~ two orders of magnitude more intense than for solutions without AgNO3.

SURFACE COATINGS
Hot Corrosion Behavior of Pt-Ir Modified Aluminide Coatings on the Nickel-Base Single Crystal Superalloy TMS-82+
Pt-Ir films (Ir = 0, 32, 46, 83, 100 at.%) were deposited on TMS-82+ by magnetron sputtering. After annealing and aluminiumising, the Pt-Ir modified aluminide coatings (1) mainly consisted of PtAl2 and β-(Ni,Pt,Ir)Al phases. The hot corrosion resistance of (1) was evaluated by exposure at 1173 K in the presence of 90 wt.% Na2SO4 + 10 wt.% NaCl. The lowest mass gain (0.299 mg cm⁻², after 100 h) was for Pt-46Ir. After annealing and aluminising, the Pt-Ir modified aluminide coatings (1) mainly consisted of PtAl2 and β-(Ni,Pt,Ir)Al phases. The hot corrosion resistance of (1) was evaluated by exposure at 1173 K in the presence of 90 wt.% Na2SO4 + 10 wt.% NaCl. The lowest mass gain (0.299 mg cm⁻², after 100 h) was for Pt-46Ir.

Batch CVD Process for Depositing Pd Activation Layers
CVD was employed for depositing a Pd activation layer for subsequent electroless Cu deposition. The process uses a continuous Pd(hfac)₂ precursor transfer step followed by a batch H₂ reduction step. The resulting layer contains both isolated Pd(0) clusters and dispersed Pd(II) species. Deposited Cu films showed poor adhesion upon drying, which is attributed to weak film attachment at the Pd(II) sites.

APPARATUS AND TECHNIQUE
Platinum Decorated Carbon Nanotubes for Highly Sensitive Amperometric Glucose Sensing
J. Xie, S. Wang, L. Aryasomayajula and V. K. Varadan, Nanotechnology, 2007, 18, (6), 065503
Fine Pt nanoparticles were deposited on functionalised C MWNTs using a decoration technique. An enzymatic Pt/C MWNTs paste-based mediated glucose sensor (1) was fabricated. Improved sensitivity for glucose sensing was shown by (1) without using any picoampere booster or Faraday cage. The calibration curve exhibited a good linearity in the glucose concentration range of 1–28 mM.

A Room Temperature Si₃N₄/SiO₂ Membrane-Type Electrical Substitution Radiometer Using Thin Film Platinum Thermometers
The temperature control of the thin film thermometer, using two control loops and a chopping procedure, was investigated. Sensing and heating elements were patterned in a Pt thin film, deposited on a 150 μm × 1560 μm membrane made of a 280 nm thick Si₃N₄/SiO₂ bilayer. The sample was fabricated in a 500 μm thick Si substrate by chemical anisotropic micromachining and then passivated with a 1 μm thick SiO₂ layer. The device was operated in a primary vacuum chamber, with no coolant or large heat sink other than the sample holder itself.

Measurement and Modeling of Hydrogen Transport through High-Flux Pd Membranes
H₂-selective Pd membranes (1) were fabricated with microsystem technology. Permeation experiments were carried out over 623–873 K at H₂ feed partial pressures of 0.2–1.0 bar. At 823 K, a permeance of 18 mol H₂/m² s bar⁻¹ was measured for (1) (thickness 0.5 μm). (1) was stable for a rather long period; however, SEM analysis showed the formation of a grain-structured surface. At 873 K the H₂/He selectivity of (1) decreases rapidly, caused by the formation of holes.

Quartz Crystal Microbalance Sensor Based on Nanostructured IrO₂
Nanostructured IrO₂ crystals (1) were grown on an Au-coated quartz substrate by MOCVD, and their gas sensing properties studied by the quartz crystal microbalance (QCM) technique. Propionic acid adsorbed and desorbed reversibly on the IrO₂ surface at room temperature. (1) with nanoblade and layered-column morphologies showed higher sensitivities than (1) with incomplete-nanotube and square-nanorod morphologies. An IrO₂ QCM sensor was sensitive to ppm-level propionic acid vapour.
Characterization of a Glucose Sensor Prepared by Electropolymerization of Pyrroles Containing a Tris-bipyridine Osmium Complex


A glucose sensor (1) was obtained by electropolymerization using pyrroles containing a tris-bipyridine (bpy) Os complex, pyrrrole (py), pyrrole propanoic acid (PPA) and glucose oxidase (GOx). Tris-bipyridine Os pyrrrole complexes (Os-py) with different methylene moieties were evaluated. The electrocatalytic response of glucose was observed at electrodes modified with Os-py, except for the one immobilised with Os-py containing the shortest methylene moiety. The electrocatalytic response to glucose of (1) with [Os(bpy)2(py(6)-bpy)]2+/3+ was stable for > 100 days.

**HETEROGENEOUS CATALYSIS**

Comparison of Two Palladium Catalysts on Different Supports during Hydrogenation


Soybean oil was hydrogenated using 5% Pd/C and 10% Pd/Al2O3, at various ratios in a reactor (at 165ºC, 2 bar H2 and 500 rpm stirring rate). Reaction rate, trans isomer formation, selectivity ratios and melting behaviours were monitored. The activity of Pd/C was ~ 10 times higher than that of Pd/Al2O3.

Molecular Level Dispersed Pd Clusters in the Carbon Walls of Ordered Mesoporous Carbon as a Highly Selective Alcohol Oxidation Catalyst


Pd/ordered mesoporous C (1), where temperature stable Pd clusters (< 1 nm) are uniformly embedded in the C walls, can be synthesised by a nanocasting route. The activity of (1) was tested in the oxidation of alcohols (benzyl alcohol, 1-phenylethanol, cinnamyl alcohol) using sc-CO2 as the reaction medium. The selectivity to the corresponding aldehyde was > 99%. (1) are are stable and reusable.

The Fabrication of Reactive Hollow Polysiloxane Capsules and Their Application as a Recyclable Heterogeneous Catalyst for the Heck Reaction


4(Triethoxysilyl)butyrotrile and dimethylmethoxysilane monomers were consecutively cocondensed onto a microemulsion of preformed polysiloxane. The templated polydimethylsiloxane was removed by exposure to solvents. The above product is then reacted with Pd(OAc)2 in anhydrous toluene and reduced with KBH4 in EtOH to produce the hollow polysiloxane capsule-supported Pd complex (1). (1) is highly active and stereoselective for the Heck arylation of alkenes. (1) can be retrieved and reused.

FT-IR Study on CO Hydrogenation to C2-Oxygenates over Rh-Based Catalyst


Evolved species from Rh-Mn-Li/Ti/SiO2 (1) during CO hydrogenation were investigated using in situ FT-IR spectroscopy. High pressure favoured the adsorption and activation of CO; high temperature favoured the dissociation of adsorbed CO. High pressure and high temperature promoted CO adsorption on (1) and allowed CO dissociation. Enhanced CO insertion activity produced good performance for C2-oxygenate formation.

Effect of Ru Nanoparticle Size on Hydrogenation of Soybean Oil


Ru nanoparticles were used as catalysts (1) for the selective hydrogenation of soybean oil at 353 K and initial pressure of 1.5 MPa. PVP-Ru-MeOH with mean size of 3.10 nm, which had the highest activity, produced the lowest cis isomer content, only 30.6% cis isomers remained. (1) with larger mean sizes of 9.06 and 17.22 nm, which have lower activity, produced less trans isomer: 49 and 46%, respectively. However, (1) with the smallest size but the lowest hydrogenation activity, Ru-MeOH with mean size of 1.13 nm, was more active for the isomerisation.

**HOMOGENEOUS CATALYSIS**

Promoting Role of [PtI2(CO)]2 in the Iridium-Catalyzed Methanol Carbonylation to Acetic Acid and Its Interaction with Involved Iridium Species


The catalytic activity of the Ir complexes involved in MeOH carbonylation is enhanced when [PtI2(CO)]2 (1) is added. Under CO (1) readily gives [PtI2(CO)5]. The turnover frequency value, which is 1450 h⁻¹ for Ir alone, reaches 2400 h⁻¹ for a Pt/Ir = 3/7 molar ratio.

Catalysis by Ir(III), Rh(III) and Pd(II) Metal Ions in the Oxidation of Organic Compounds with H2O2


PdCl2, RhCl3 and IrCl3 were used in the oxidation of benzaldehydes (unsubstituted, p-chloro, p-nitro, m-nitro, p-methoxy) and cinnamaldehyde; anthracene and phenanthrene; cyclohexanol and benzyl alcohol by 50% H2O2. Traces of the chlorides catalyse these oxidations, resulting in good to excellent yields. PdCl2 is the most efficient catalyst. Oxidation in aromatic aldehydes is selective at the aldehyde group only.
Asymmetric Transfer Hydrogenation of Ketones and Imines with Novel Water-Soluble Chiral Diamine as Ligand in Neat Water


A H₂O-soluble Rh(III) catalyst (1) was prepared from o-(N-tosyl)-1,2-diphenylethylenediamine and [Cp*RhCl₂]. (1) was efficient for the catalytic asymmetric transfer hydrogenation (ATH) of ketones and imines with sodium formate as H donor in neat H₂O. (1) can catalyse the ATH of α-bromomethylketones and imines besides simple ketones. High yields and enantioselectivities can be achieved within a few hours at 28°C.

Stability of the First-Generation Grubbs Metathesis Catalyst in a Continuous Flow Reactor


Ethylene pretreatment of (PCy₃)₂Cl₂Ru=CHPh (1) prior to cross-metathesis of ethylene and α-2-butenes to form propylene in a continuous flow reactor (CFR) produced a direct effect on catalyst deactivation. Similar pretreatment of (1) with α-2-butenes caused far less change in the catalytic activity. Continuous removal of products in the CFR was important for separating the effects of catalyst decay and catalyst deactivation caused by the terminal olefin, propylene.

**FUEL CELLS**

Deposited RuO₂–IrO₂/Pt Electro catalyst for the Regenerative Fuel Cell


RuO₂–IrO₂/Pt (1) was prepared by even deposition of Ir hydroxide hydrate and Ru hydroxide hydrate on Pt black and calcination in air. The RuO₂–IrO₂ was well dispersed and deposited on the surface of Pt black. URFC with deposited (1) showed better performance than that of URFC with mixed (1) catalyst. Cyclic performance of the URFC with deposited (1) was very stable during 10 cyclic tests.

Pt–Ir–IrO₂NT Thin-Wall Electro catalysts Derived from IrO₂ Nanotubes and Their Catalytic Activities in Methanol Oxidation


Lattice O of IrO₂ nanotubes (IrO₂NT) was removed under high-vacuum thermal annealing to facilitate nucleation of 3–5 nm Ir grains and subsequent synthesis of PtIr catalyst on the tube walls. The amount of Ir being reduced, the Ir grain size, and the deposited Pt size influence the surface area and the catalytic activity. Pt–Ir–IrO₂NT reduced at 500°C exhibited higher activity than Pt–IrO₂NT and Pt–IrNT in MeOH oxidation, and also a higher current density than that of PrRu in the high potential region.

Fast Preparation of PtRu Catalysts Supported on Carbon Nanofibers by the Microwave-Polyol Method and Their Application to Fuel Cells


PtRu alloy nanoparticles (24 ± 1 wt.%, Ru/Pt atomic ratios = 0.91–0.97) supported on C nanofibres (CNFs) were prepared by a microwave-polyol method. The DMFC activities of PtRu/CNFs measured at 60°C were higher than for standard PtRu (29 wt.%, Ru/Pt atomic ratio = 0.92) catalyst loaded on C black (Vulcan XC72R).

The Effect of Heat Treatment on Nanoparticle Size and ORR Activity for Carbon-Supported Pd–Co Alloy Electro catalysts


An impregnation method was used for the synthesis of Pd-Co/C (1), in which NaBH₄ was the reducing agent. (1) heat-treated at 300°C had average particle size of 8.9 nm, and the highest ORR catalytic activity. Electrocatalytic ORR activity was also examined in an acidic solution containing MeOH. (1) has MeOH tolerant capabilities.

**ELECTRICAL AND ELECTRONIC ENGINEERING**

Heterostructured Magnetic Nanoparticles: Their Versatility and High Performance Capabilities


The recent advances in the development of magnetic nanoparticles (such as FePt, CoPt₃) are reviewed, with a focus on multicomponent heterostructured nanoparticles including alloys, core–shells, and binary superlattices synthesised via nonhydrolytic methods. Their multifunctionality and high performance capabilities are demonstrated for applications in high density magnetic storage, catalysis, and biomedical separation and diagnostics. (94 Refs.)

Lithography-Free In Situ Pd Contacts to Templated Single-Walled Carbon Nanotubes


C SWNTs were synthesised from an embedded Fe catalyst in a modified porous anodic alumina (PAA) template (1). Pd is electrodeposited into (1) to form nanowires. Individual vertical channels of C SWNTs are created, each with a vertical Pd nanowire back contact. Further Pd deposition resulted in annular Pd nanoclusters that form on portions of C SWNTs extending onto the PAA surface. Two-terminal electrical characteristics produce linear I–V relationships, indicating ohmic contact in the devices.
NEW PATENTS

METALS AND ALLOYS

Reflective Alloy
TANAKA KIKINZOKU KOGYO KK

A Ag alloy with excellent reflectance maintenance can be used as a sputtering target. A first dopant element is chosen from Pt, Pd, Rh, Ru, Ir and Au. A second dopant is selected from Cu, Mn, Si, Cr, Ni, Co, Fe, Sc, Zr, Nb, Mo, Ta, W, In, Sn, Pb, Al, Ca, Ge, Ga, Bi, Sb, Sr, Hf, Gd, Sm, Nd, La, Ce, Yb and Eu. The total concentration of the two dopants is 0.01–5.0 at.

CHEMICAL COMPOUNDS

Nitrogen-Containing Metal Hydroxide Complexes
JOHNSON MATTHEY PLC

A substantially halide-free amine-metal hydroxide complex can be made by partitioning an aqueous solution of a HCl or NaCl salt of one or more metal halides, in the presence of a base, with an organic solvent system containing an amine. The metal is selected from Pt, Pd, Au, Ag, Cu and Ni. A reducing step may further be carried out at ≤ 5°C, to afford substantially halide-free metal nanoparticles.

PHOTOCONVERSION

Organic Electroluminescent Element
KONICA MINOLTA HOLDINGS INC

An organic electroluminescent element (1) includes a light emitting layer containing an Ir or Pt guest complex with a metal, M, selected from Ir, Pt, Pd, Ru, Os, Re or Pb. Ligands include a 3–60 C straight or branched alkyl or alkenyl, alkynyl, cycloalkyl, aromatic, aromatic heterocyclic or heterocyclic group. (1) can be made to emit blue or white light and can be used as an illuminator in a device with a liquid crystal display.

Organometallic Electroluminescent Device
SAMSUNG SDI CO LTD

The title device can be made to emit light ranging from blue to red and contains an organometallic complex with a metal, M, selected from Ir, Pt, Pd, Ru, Os, Re or Pb. Ligands include a 3–60 C heterocyclic group bonded to M via N and bonded to a 3–60 C aryl group which is bonded to M via C; plus a heterocycle containing at least 2 N atoms and bonded to M via N.

Cyanophenylpyridine Iridium Complex
CHEMIPROKASEI KAISHA LTD

A phenylpyridine Ir complex for use in an organic electroluminescent device contains 0–4 electron withdrawing groups on the pyridine ring, plus 1–4 CN groups and 0–2 F atoms on the phenyl ring. Light is claimed to be emitted with shorter wavelength than other phenylpyridine Ir complexes.

ELECTRODEPOSITION AND SURFACE COATINGS

Bright Rhodium Electrodeposition
R. J. MORRISSEY

An electroplating solution for obtaining bright white Rh electrodeposits contains a soluble sulfate or phosphate compound of Rh with excess H2SO4, H3PO4 or a mixture. One or more N-containing heterocyclic compounds with at least one N atom in a 6-membered aromatic ring, such as pyridine, picoline, pyrimidine, pyridazine or pyrazine or derivatives thereof, is added as a brightening agent.

Platinum-Cobalt Alloy Plating Solution
TANAKA KIKINZOKU KOGYO KK

PtCo alloy films can be formed by using the claimed plating solution, containing a bivalent Pt salt selected from Na2[Pt(C2O4)2], K2[Pt(C2O4)2], [Pt(NH3)4]Cl2, [Pt(NH3)2]SO4, [Pt(NH3)2(NO3)2, [Pt(NO3)2(NH3)2] and K2PtCl6, at [Pt] = 1–30 g dm–3 and a bivalent Co salt at [Co] = 1–60 g dm–3. An inorganic or carboxylic acid or a salt thereof, or a polyaminocarboxylic acid, at 1–200 g dm–3 is included as a buffer.

APPARATUS AND TECHNIQUE

Chromatographic Method of Separating Ruthenium
ANGLO AMERICAN PLATINUM CORP LTD

A chromatographic method separates Ru from a feed solution containing chlorocomplexes of other Pt group metals including Ir and Rh, by converting Ru to a nitrosyl complex, which is temporarily retained on the column. Subsequently Ru is eluted using an oxidising or reducing eluent.

Manufacture of Iridium Crucible
TANAKA KIKINZOKU KOGYO KK

A crucible made of Ir or Ir alloy is manufactured by joining a cylindrical trunk portion to a circular base by welding. A second step involves remelting and solidifying the welded portion at the inside bottom corner using a welding current of 150–180 A, lower than that used for joining. The crucible resists leaks during use.

Analytical Reagent for Amino Acids
NAT. INST. ADV. IND. SCI. TECHNOL.

An analytical reagent to detect amino acids, in particular histidine, methionine or cysteine, or peptides and proteins containing these, by a colouring reaction, is based on a cyclopentadienyl Rh complex (1), plus a pigment such as an azo dye. Substituents on (1) may include 1–10 C straight or branched alkyl or alkoxy chains; phenyl, amino, nitro, thiol or hydroxyl groups; carboxylic or sulfonic acids, salts, esters or amides; or ketones, halogens or sugar residues.
HETEROGEOUS CATALYSIS
Platinum Catalysts with Nanonetwork Structures
INST. NUC ENERGY RES. European Appl. 1,728,618
A method for preparing Pt and Pt alloy catalysts (1) on supports with nanonetwork structures includes first dispersing nanospheres of a structure-directing material (2), which may be an organic polymer or SiO2, of diameter 50–2000 nm, onto a support material to obtain a compact structure of 1–10 layers. (1) is then formed in the void spaces by chemical reduction from aqueous solution or vacuum ion-sputtering. Finally, (2) is removed by thermal decomposition (polymer) or by chemical dissolution (SiO2). Uses may include fuel cells or catalytic converters.

Perovskite-Type Composite Oxide
DAIHATSU MOTOR CO LTD European Appl. 1,728,766
A perovskite-type composite oxide (1) containing a solid solution of Pd has the formula $A_xB_{2-y}PdO_{3+y}\delta$ where $A = $ a rare earth or alkaline earth element; $B = $ a transition element (excluding rare earth elements and Pd), Al or Si; $x > 1$; $0 < y \leq 0.5$; and $\delta$ represents an O excess. (1) can be used in a catalyst composition for exhaust gas purification or as a coupling reaction catalyst for organic synthesis.

Catalyst and Process for its Manufacture
JOHNSON MATTHEY PLC World Appl. 2006/134,403
A catalyst, of average particle size 1–150 μm, contains at least one skeletal porous sponge metal selected from Ni, Co, Fe and Cu, with two promoter metals: a first selected from Pd, Pt, Ru, Rh, Os and Ir (0.01–5 wt.%); and a second from Fe, Ni, Co, Zn, V, Ce, Cu, W, Mo, Ti, Nb, Mg, Ag, Cd, Pr and Nd (0.01–5 wt.%). Processes for manufacture include impregnation or precipitation of promoter metals from a solution onto the sponge metal. The catalysts may be used for hydrogenation of an organic nitro compound or nitrite to the corresponding amine.

Improvements in H2O2 Formation Catalysts
UNIV. COLL. CARDIFF CONSULT. LTD World Appl. 2007/007,075
Catalysts for direct reaction of H2 and O2 to form H2O2 consist of particles of Au or Pd, or preferably, Au and Pd, deposited on an acid-washed support such as SiO2, TiO2, Al2O3, Fe2O3, a stable zeolite or activated C. Weight ratio of Au:Pd may be ~ 5.25:1. Reaction is carried out in H2O-MeOH at 2–40ºC. High selectivity to and production of H2O2 is observed, with low decomposition. The catalysts have extended life.

Manufacture of Diesel Range Hydrocarbons
NESTE OIL OYJ. U.S. Appl. 2007/0,006,523
A process for converting vegetable oils to middle distillate hydrocarbons which can be used in diesel fuels is claimed. A feed containing > 20% triglyceride $C_{17}$-$C_{20}$ fatty acids, or fatty acid esters is hydrotreated in the presence of a Pd, Pt, Ni, NiMo or CoMo catalyst on an Al2O3 and/or SiO2 support, to give n-paraffins. These are isomerised to branched-chain paraffins in the presence of a supported catalyst which contains one of Pt, Pd or Ni.

Recyclable Ruthenium Metathesis Catalysts
Z.-Y. J. ZHAN U.S. Appl. 2007/0,043,180
A Ru catalyst (1) includes a substituted benzylidene ligand having an electron withdrawing group; plus an electron donating ligand such as a heterocyclic carbene or a phosphine. Additionally, one of the ligands in (1) may be chemically bound to the surface of a polymer, resin, PEG or silica gel support to give a supported Ru catalyst composition (2). Either (1) or (2) may be used for olefin metathesis reactions such as RCM, CM, ROMP or for polymerisation reactions. (2) is recyclable.

Polymer Immobilised Platinum Catalyst
JAPAN SCI. TECHNOL. AGENCY Japanese Appl. 2006-198,491
A crosslinked polymer formed from monomers containing an aromatic side chain, a hydrophilic side chain and a bridge formation radical is used to immobilise a Pt catalyst (1). Formation of (1) is carried out by forming ultrafine particles of Pt on the crosslinkable polymer in a solution containing a polar solvent to form a micelle, followed by a crosslinking reaction, for example, by heating. (1) can be used for hydroisolation, hydrogenation or boration reactions.

Catalyst for Removing NOx from Exhaust Gas
ASAHI CHEMICAL CORP Japanese Appl. 2006-218,352
A catalyst for efficient removal of NOx from diesel exhaust gas in a lean-burn atmosphere (≥ 5% O2) at 150–300ºC is claimed. Particles of Pt and/or Ir of mean diameter 0.4–20 nm are coated with a layer of refractory material with a melting point ≥ 1000ºC, such as Mo, W, V, Fe or their oxides, to thickness 0.1–1 nm, and supported on a hardly-soluble carrier such as mesoporous SiO2, Al2O3, ZrO2 or CeO2-ZrO2 with specific surface area 100–1400 m2 g−1. A high catalytic activity is claimed to be maintained even after catalyst regeneration.

Fuel Reforming Catalyst
NISSAN MOTOR CO LTD Japanese Appl. 2006-231,132
H2-rich gas is produced by reforming fuel in the presence of a Rh-containing catalyst. Rh is carried on an inorganic monolith support in an upstream part of the system, with Co on a second inorganic carrier in the downstream portion. Rh is present in 0.1–10 wt.% and Co in 0.5–20 wt.% of their respective catalyst powders, and the mole ratio of Co:Rh is between 0.2–9.0.

HOMOGENEOUS CATALYSIS
Preparation of a Siloxane
SHIN ETSU CHEM. CO LTD U.S. Appl. 2007/0,037,997
A 1-(alkoxysilylethyl)1,1,3,3-tetramethyldisiloxane is prepared by adding a vinyl-containing alkoxy silane in portions to 1,1,3,3-tetramethyldisiloxane in the presence of a Rh compound, which is free of P-containing ligands and may include a halide or a 1,5-cyclooctadiene ligand. Reaction is carried out at a temperature between 0–60ºC.
Isolating Rhodium Catalysts

A distillation process is used to separate a compound (1) having at least 2 functional groups selected from nitrile, carboxylic acid, carboxylic ester and carboxamide groups, from a mixture containing a Rh catalyst compound. (1) may be a monooolefinically unsaturated compound obtained by dimerising two terminal olefins in the presence of a catalyst containing Rh, Ru, Pd or Ni, preferably Rh, and may further be hydrogenated in the presence of the same catalyst to give (1) as a saturated compound. Distillation may be carried out with an average mean residence time of 1–45 min, at 50–200°C and 0.05–50 kPa.

FUEL CELLS

Voltage Cycling Durable Platinum Catalysts

An electrocatalyst layer (1) with increased voltage cycling durability is claimed. Pt or Pt alloy particles are annealed at 800–1400°C to reduce their surface area to < 80% of their pre-annealed state, have average particle diameter 3–15 nm, and are deposited on a support structure such as C, activated C, graphite, C nanotubes, ionomers, conductive oxides, conductive polymers or a mixture. The electrocatalytically active surface area of (1) is > 50% of its original extent after ~ 15,000 voltage cycles at 0.6–1.0 V.

Exhaust Gas Purification Method for Fuel Cell Vehicle

A CH₄ removal catalyst for accelerating the oxidation of CH₄ in fuel cell vehicle exhaust to H₂ and CO includes 1–10 wt.% of at least one of Rh, Pt and Pd, preferably Pd, on a porous carrier. A second catalyst downstream of the first, for conversion of H₂ and CO into H₂O and CO₂, contains 0.1–3 wt.% of at least one of Rh, Pt and Pd, preferably Pt. The system can be used with fuel cell, compressed natural gas or hybrid vehicles.

Platinum-Palladium-Titanium Catalyst

A composition for use as a fuel cell catalyst is made from Pt, Pd and Ti or their oxides, carbides and/or salts. The sum of the concentrations of Pt, Pd and Ti is > 90 at.%, and preferably > 94 at.%. Concentrations of each element are in the ranges (in at.%): 5–60 Pt, 5–50 Pd and 15–75 Ti.

Manufacturing Method for an Electrode

A catalyst ink (1) contains particles of Pt on C support, dispersed in a solution which includes a liquid proton conductive material such as Nafton. A catalyst electrode is manufactured by applying (1) in droplet form onto a conductive material such as a C material, resulting in formation of a ternary phase interface between the C/Pt/proton conductive material, then carrying out thermal compression bonding.

Carbon Monoxide Oxidation Catalyst

A catalyst composition (1) for electrochemical oxidation of CO includes a Rh porphyrin compound having up to eight substituents, selected from alkyl groups, H or halides, which may be supported on a conductive support such as C black. (1) can be used in a CO sensor or for an anode in a SPFC.

ELECTRICAL AND ELECTRONIC ENGINEERING

Magnetic Film for a Magnetic Device

A multilayer magnetic film for a high-density magnetic recording device includes alternately laminated ferromagnetic and Pd or Rh metal or alloy films, which are formed by a dry processing method such as sputtering, vacuum deposition or chemical vapour deposition. A Pd film layer has thickness ≥ 0.05 nm, or a Rh film layer, 0.1–0.4 nm. The ferromagnetic film layer may be composed of an FeCo containing alloy which may also include one of Pd, Rh or Pt.

Magnetic Recording Medium

A high-density magnetic recording medium is claimed which includes a magnetic layer of PtFe alloy film (1) having high magnetic anisotropy and fine crystal grains with small size distribution. An amorphous inorganic compound such as an oxide of Si, Al, Ti, Ta, Zr or Zn is used as a substrate, to which a layer of Fe oxide is applied. Onto this, a layer of Fe and then a layer of Pt are formed, each layer having thickness 1–4 nm. These layers are heated to induce counter diffusion between layers and produce (1).

MEDICAL USES

Textured Iridium for Vascular Devices

Vascular devices such as stents can be made from textured polycrystalline Ir. The method of texturing includes cold/warm working Ir at 700–1100°C to break up the polycrystalline structure and promote the desired orientation. Ir is then recrystallised to give a majority of grains aligned in <110> direction. Lattice matched second phase particles inhibit recrystallisation in undesired orientation and may include Ir₅Th, Ir₅Ru, Ir₅Ta, Ir₅V, Ir₅Th, Ir₅Zr or Ir₅W.

Platinum Complexes for Targeted Drug Delivery

Biotin-containing Pt complexes for the treatment of oncological or inflammatory disorders can also be used for the treatment or prevention of infections, and may include a further molecule such as an antibody, a ligand or a receptor bound to the biotin moiety. Synthesis consists of mixing cisplatin or transplatin in H₂O and an organic solvent such as dichloroethane or hexane, adding a biotin-containing ligand, then treating the mixture with NO₂⁻.
Although rapid advances have been made in equipment and materials used in the process, casting platinum for jewellery is still a challenge. At around 2000°C, getting the melt temperature absolutely right for the size, type and number of pieces being cast is a fine balancing act, as is judging the correct mould temperature. Too low and the result could be an incomplete fill; too high and shrinkage porosity may occur.

It is often the caster who is blamed for porosity, but it should be remembered that a casting does not have the same structure as wrought material. All castings are porous to some extent, and it is unfair to compare any casting with a piece made from sheet or wire. Even poured ingots start out porous, but have the porosity ‘squeezed’ out of them during forging, rolling or drawing to sheet and wire.

Polishing platinum is very different from polishing gold. The surface of gold ‘smears’ and can be buffed to a high polish. Platinum, however, must be polished with abrasives, and since the whole of a casting is porous it is impossible to achieve the same surface finish on an untreated cast platinum product as could be obtained on a handmade or stamped and machined platinum piece.

An ‘as-cast’ structure is also softer and more brittle than a worked structure, and untreated platinum castings can be more prone to denting and deforming than pieces made from wrought platinum. Platinum-cobalt or platinum-ruthenium alloy systems are commonly used because they provide relatively hard castings (see Table I). So jewellers should ensure that they use one of these, or an alloy of equivalent hardness.

Getting the alloy right is essential, but there are other measures that manufacturers and designers can take to improve their cast platinum pieces and reduce the time and effort spent finishing them.

The first is to help reduce the amount of porosity in a piece, both through its design and by paying attention to how it is sprued. Rapid changes in cross-section and sprueing into fine sections can cause flow problems and result in poor castings. New designs should be discussed with the caster, seeking their input in the model making process.

The second measure is further processing of the casting after delivery. Much can be done to improve the ‘as-cast’ structure on the surface of the casting by using a burnishing process (1, 2).

Burnishing a platinum casting squeezes out porosity near to the surface, and puts some work into the piece. The hardened surface makes it more resistant to denting and deformation. Although this is an extra process, it actually saves on finishing time by smoothing out the rough cast surface and reducing polishing time.

This is an abridged version of an article originally published as Reference (3).

### Table I

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Hardness, Hv</th>
</tr>
</thead>
<tbody>
<tr>
<td>95% Pt-5% Co</td>
<td>135</td>
</tr>
<tr>
<td>95% Pt-5% Ru</td>
<td>130</td>
</tr>
<tr>
<td>95% Pt-5% Cu</td>
<td>108</td>
</tr>
<tr>
<td>95% Pt-5% Ir</td>
<td>80</td>
</tr>
<tr>
<td>95% Pt-5% Pd</td>
<td>68</td>
</tr>
</tbody>
</table>

**References**

3. N. Swan, Jewellery in Britain, 2004, (19), 5

**The Author**

Neill Swan is Sales and Marketing Manager with Johnson Matthey Precious Metals Marketing, and has worked for the company for 27 years. His responsibilities now include managing the company’s platinum and palladium jewellery market development activities in the U.S.A., Switzerland, China and the U.K.