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Nucleation and Growth of Platinum Clusters in Solution and on Biopolymers

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The molecular mechanisms of platinum cluster nucleation and growth in solution and on biopolymers have been investigated by means of first-principles molecular dynamics. In contrast with the classical picture where clusters nucleate by aggregation of metallic Pt(0) atoms, it was found that Pt-Pt bonds can form between dissolved Pt(II) complexes after only a single reduction step. Furthermore, small clusters were observed to grow by addition of unreduced [PtCl\(_2\)(H\(_2\)O)\(_2\)] complexes, in agreement with an autocatalytic growth mechanism. Moreover, Pt(II) ions covalently bound to biopolymers were found to act as preferential nucleation sites for the formation of clusters. This is a consequence of the presence of heterocyclic donor ligands which both enhance the electron affinity of the metal nuclei and induce the formation of metal-metal bonds that are stronger than those obtained in solution. In fact, in metallisation experiments a clean and purely heterogeneous metallisation of single DNA molecules leading to thin and uniform Pt cluster chains extending over several microns was obtained.

The mechanisms through which metal clusters and colloids form in solution have received a great deal of attention in recent years (1–6). This is due to the importance of achieving accurate control over the processes of cluster nucleation and growth in order to produce clusters of uniform size (7–8) and shape (9). Monodisperse colloidal suspensions present optimal catalytic properties (10), and can be employed for the production of self-assembled particle arrays with peculiar electronic and optical properties (11–13). Moreover, the controlled, selectively heterogeneous metal growth on biomolecular templates allows the fabrication of nanosized metal structures in a perfectly clean surrounding medium (14), which is an important step toward the bottom-up fabrication of nanodevices with metallic functionality. To improve the control on all phases of the cluster formation process, a detailed understanding of the elementary steps of cluster nucleation and growth is desirable. However, very little is known at an atomic level about the agglomeration reactions which take place in solution between reduced metal complexes and eventually lead to the formation of metallic clusters.

In this review we report the results of our studies dealing with the molecular mechanisms of the nucleation and growth of platinum nanoparticles after the reduction of a dissolved platinum salt (1, 2, 14). The [PtCl\(_4\)]\(^{2-}\) ion is chosen as a representative and widely studied example of a square-planar complex capable of producing cluster suspensions upon reduction. Particular attention is paid to defining the minimum reducing conditions necessary to initiate the nucleation of metal clusters and to promoting cluster growth.
We address this problem by means of molecular dynamics techniques taken to the quantum accuracy level (15). Namely, the forces acting on the atoms are computed from first principles, solving the many-body electronic problem within the spin-polarised Density Functional Theory (16). The atoms are then moved according to the classical equation of motion integrated with standard algorithms (17). Both the minimisation of the electronic states and the dynamics of the atoms are performed using the Car-Parrinello (CP) method (18), the gradient-corrected exchange-correlation potential PW91 (19), and separable, norm-conserving atomic pseudopotentials (20). Given the metallic character of small noble metal clusters (21, 22), our CP simulations are performed with the algorithm proposed in References 23 and 24, which is especially suited to treat metallic systems.

Details of the computational techniques and of the simulation parameters can be found in References 1, 2 and 14. All calculations were carried out on the massively parallel computer platforms of the Center for High Performance Computing at the Technical University of Dresden using the LAUTREC code (25). This is a highly optimised parallel code for performing CP molecular dynamics simulations and structure optimisations, originally developed from a serial version by A. De Vita and A. Canning in R. Car's group at EPFL, Lausanne.

**Nucleation of Pt Clusters in Solution**

**Formation of Pt Dimers**

Our investigation begins with a simulation of the reduction of two $\text{[PtCl}_2(\text{H}_2\text{O})_2]$ complexes (Figure 1) surrounded by water molecules randomly placed in a periodically repeated cubic cell.
of edge length 12.0 Å. These complexes are the hydrolysis products of [PtCl₄]²⁻ ions which actively take part in the process of metal cluster formation (3). First the system is annealed for about 0.5 ps in a constant temperature first-principles molecular dynamics (FPMD) simulation at 300 K. A second simulation at 300 K is started after one additional electron is added to the annealed system (Figure 1(a)). The unpaired electron localises immediately on one of the two complexes, causing the detachment of the two water ligands from the central Pt atom and the formation of a linear [PtCl₄]⁻ complex (Figure 1(b)). After that, unexpectedly, a Pt-Pt bond forms between the linear Pt(I) complex and the unreduced Pt(II) complex (Figure 1(c)). The formed dimer remains stable until the end of the simulation, which is stopped after ~ 3.5 ps of simulated time. After quenching the atomic motion, the Pt-Pt distance is 2.87 Å and the calculated bond energy of the obtained dimer is 1.5 eV.

A third FPMD simulation at 300 K is started from this point after adding a second reducing electron to the annealed configuration of the obtained Pt(I)-Pt(II) dimer. In this case a chlorine ligand is immediately lost, and the structure of the dimer gradually changes so that after ~ 1.5 ps the Pt-Pt bond is in the same plane as the other bonds that the Pt atoms have with their ligands. The Pt-Pt equilibrium distance is now 2.6 Å, which is a typical value for Pt(I) dimers (26). Indeed, the final geometry (Figure 1(d)) very closely resembles that of the [Pt₂Cl₄(CO)₂]⁺ ion, which was synthesised via the reduction of K₂PtCl₆ with CO in concentrated HCl solution (27, 28).

Formation of Pt Trimmers

Interestingly, both the Pt(I)-Pt(II) and the Pt(I)-Pt(I) dimers obtained in the previous simulations are able to react further with unreduced Pt(II) complexes. This is observed in two FPMD simulations where a [PtCl₆(H₂O)₂] complex approaches the dimers from the side of the Pt(I) unit, which is expected to be a reactive site for addition reactions (29). In both cases, a further Pt(II)-Pt(I) bond is formed. Bond distances for the trimers are 2.9 Å for Pt(II)-Pt(I)-Pt(II) and 2.8 Å for Pt(II)-Pt(I)-Pt(I). The same reactions were observed to occur in simulation cells filled with water molecules to simulate the solution environment (Figure 2).

We note that the formation of these oxidised complexes (dimers and trimers) is an intermediate step towards the growth of bigger clusters. In particular, during reduction processes at relatively high concentration of Pt(II) complexes and in the presence of mild reducing agents – typical conditions for the formation of monodisperse colloidal suspensions (3) – Pt(II) complexes are likely to react with partially reduced complexes or dimers before reduction. The reduction (possibly involving dechlorination, as shown in Figure 1(d)), is expected to occur via electron transfer from the reducing agent to the formed nucleus, which has higher electron affinity than isolated complexes due to orbital delocalisation on more than one metal atom site. We expect that the growth to bigger particles requires neither the reduction of isolated complexes before addition to the growing nuclei, nor the complete reduction of the nuclei to the zerovalent state. This issue is investigated in a series of FPMD simulations in the next section.

Growth of Pt Clusters via Addition of Pt(II) Complexes

The simulations presented in the previous section revealed that unreduced [PtCl₆(H₂O)₂] complexes easily form Pt-Pt bonds with open-shell platinum complexes and dimers with average oxidation states intermediate between zero and two. This leads to the hypothesis that analogous reactions may occur on the surface of bigger clusters (not necessarily reduced to the zerovalent state) and be an important process for the overall growth mechanism. Therefore, we have performed direct simulations of the addition reactions of [PtCl₆(H₂O)₂] complexes to growing clusters that are in various oxidation states.

In particular, we consider both a metallic, fully reduced Pt₁₂ cluster and a neutral Pt₁₂Cl₄ cluster, where the Pt atoms have, on average, a formal oxidation state of +4/12. The relaxed cluster structures are shown in Figure 3 together with the electronic states that have energy above the Fermi level. It is noteworthy that these empty orbitals protrude widely out of the cluster surface, and are
Thus expected to be highly active acceptor sites in addition reactions. In particular, donation into these orbitals can be expected to occur from the filled $d^2$ orbital of square-planar Pt(II) complexes.

Indeed, the dynamical simulation of the reaction between a [PtCl$_2$(H$_2$O)$_2$] complex and a Pt$_{12}$Cl$_4$ cluster (Figure 4) begins with the adsorption of the Pt(II) complex on the cluster surface (Figure 4(b)). Unexpectedly, the reaction proceeds with the dissociation of the Pt(II) complex soon after the adsorption. While a water ligand detaches from the Pt(II) atom and remains isolated until the end of the simulation, both chlorine ligands adsorb on the cluster surface (Figure 4(c)). The Pt...
atom originally belonging to the Pt(II) complex becomes completely incorporated into the skeleton of the cluster and is indistinguishable from the other Pt atoms at the end of the simulation (Figure 4(d)). The obtained cluster presents a structure consisting of three stacked planes of Pt atoms arranged in a triangular lattice. This geometry ensures a high mean coordination number of the Pt atoms within the clusters and thus a high cohesive energy (21). The same reaction was also observed to occur for the naked Pt12 cluster, both in gas-phase simulations and in a simulation cell filled with water molecules to model the solution environment. Moreover, we observed that a further Pt(II) complex is able to react with the (hydrated) Pt5Cl4 cluster obtained in the simulation shown in Figure 4 (2).

A Novel Mechanism of Cluster Formation

The results of our FPMD simulations strongly suggest that the formation of platinum clusters in solution after reduction of a dissolved platinum salt can be initiated by formation of a Pt(I)-Pt(II) dimer immediately after the first reduction step. This is in contrast with the classical nucleation picture where clusters are supposed to form through aggregation of fully reduced Pt(0) atoms only when they are present in solution in sufficient concentration. We propose that, after the very first step, the formation of clusters does not progress through novel reduction of isolated complexes, but via addition of Pt(II) complexes to already formed nuclei. This mechanism is expected to take place, in particular, under conditions of high concentration of Pt(II) complexes and/or if mild reducing agents are used. We note that under different conditions the full reduction to the zerovalent state prior to cluster nucleation cannot be a priori excluded on the basis of our results.

Interestingly, in our FPMD simulations further steps of cluster growth were in fact found to proceed via the addition of unreduced complexes to a growing, partially oxidised nucleus. The reduction to the metallic state may then happen independently of the addition of complexes and is expected to involve the whole cluster, the electron affinity of which is appreciably bigger than that of...
isolated complexes. On the other hand, the electron affinity of the cluster is further increased by the addition of Pt(II) complexes, which have the effect of increasing both the cluster nuclearity and the mean oxidation state of the Pt atoms. In turn, the reduction of the cluster (with possible desorption of Cl\(^-\) atoms, as shown in Figure 1(d)) favours the further addition of unreduced complexes on the cluster surface. Thus, the processes both of reduction and Pt addition become easier and easier with increasing particle size; that is, our model naturally accounts for an autocatalytic cluster growth. This is fully consistent with the auto- accelerating kinetics of metal particle formation observed experimentally during chemical reduction of metal salts (6).

**Nucleation of Pt Clusters on Biopolymer Templates**

According to the mechanism suggested above, each Pt(II) complex that reacts with a reducing electron can be thought of as a 'critical nucleus' for the growth of metallic platinum clusters. Thus, the kinetics of cluster formation can be influenced by selectively acting on the early steps of the nucleation, and in particular on the very first Pt-Pt bond formation reaction. In the following, we show how this property can be exploited to achieve a selectively heterogeneous metal cluster growth on biological templates, such as DNA and proteins.

Pt(II) complexes are known to react with DNA via covalent bonding between the metal ion and nitrogen atoms of the DNA bases (30, 31). The N7 atoms in guanine and adenine bases are very favourable binding sites. Moreover, similar reactions are known to occur with protein amino acids, and in particular with the N3 site of histidine (32).

In a series of FPMD simulations we now investigate how the heterogeneous formation of Pt dimers occurs between free \([\text{PtCl}_2(\text{H}_2\text{O})_2]\) complexes and Pt complexes bound to DNA bases (adenine and guanine) or histidine amino acids, after a single reduction step. We consider two cases: [i] reduction of ions bound to the biomolecular template followed by reaction of the bound Pt(I) ions with free Pt(II) complexes, and [ii] reduction in solution followed by reaction of \([\text{PtCl}_2]^\text{−}\) molecules with unreduced Pt(II) ions covalently bound to heterocyclic ligands.

The calculated HOMO-LUMO (highest occupied molecular orbital-lowest unoccupied molecular orbital) energy gaps of Pt(II) complexes bound to an adenine, a guanine, and two stacked guanines are 2.23, 2.25, and 1.13 eV, respectively. For comparison, the free \([\text{PtCl}_2(\text{H}_2\text{O})_2]\) complex presents a higher energy gap of 2.34 eV. These values indicate that the reduction of Pt(II)-biopolymer complexes should be favoured over the reduction of free complexes in solution. The higher electron affinity of the Pt(II)-biopolymer complexes can be associated with the presence of delocalised orbital states on the heterocyclic ligands (such as guanine, adenine and histidine), which can 'accommodate' the additional electron in a more favourable way. Moreover, as we explain below, the presence of heterocyclic ligands has the effect of stabilising the Pt-Pt bonds formed during the investigated dimerisation reactions. Indeed, in all the simulated heterogeneous dimerisation reactions (14, 33), we observe that immediately after the Pt-Pt bond formation, a water ligand detaches from the Pt(II) complex. Loss of this water ligand considerably strengthens the Pt-Pt bond (Figure 5).

The obtained Pt-Pt equilibrium distances are \(\sim 2.6\ \text{Å}\) in all cases and the bond energies are between 1.8 and 2.5 eV, depending on the hydrolysis states of the formed dimers (14, 33). Therefore, all heterogeneously-formed Pt dimers appear to be more stable than the corresponding homogeneously-formed dimers. The reason for the increased dimer stability lies in the observed water substitution step occurring during the dimer formation reaction which is only possible in the presence of heterocyclic ligands with a strong donor character, such as purine bases or histidine amino acids. In fact, the charge density accumulation on the Pt atoms, induced by the presence of the heterocyclic ligands, leads to a highly repulsive antibonding interaction between the Pt(II) atom and one of its water ligands (Figure 5(b, c)). The water ligand eventually detaches causing a strengthening of the Pt-Pt bond. This in turn has the effect of increasing the electron affinity of the dimer (14), and thus favours further steps of
Fig. 5 Snapshots from a FPMD simulation showing the heterogeneous formation of a Pt dimer covalently bound to a histidine amino acid. The electron density associated with the unpaired reducing electron is depicted as an orange semitransparent isosurface. The black arrow indicates the development of a strong antibonding interaction which causes the detachment of a water ligand. Atom colours: Pt yellow, Cl green, O red, N blue, C grey, H white

reduction and complex addition to the growing nucleus. These results suggest that, going through the autocatalytic growth process described in the previous sections, the first-formed heterogeneous nuclei may quickly develop into larger particles, consuming the metal complex feedstock present in the solution and thus suppressing homogeneous particle formation.

Selectively Heterogeneous Cluster Growth on Biopolymers

To substantiate the results of the simulations reported above we performed metallisation experiments in which an aged solution of K₂PtCl₄ was reduced in the presence of DNA molecules (14). To form Pt(II)-DNA adducts in sufficient concentration, we incubated a 1 mM aged solution of the Pt(II) metal salt with λ-DNA for about 24 hours, keeping the ratio of Pt(II):base at 65:1. This large Pt(II):base ratio is used both to bind as many complexes as possible to the DNA bases (primarily, but not exclusively, to guanine and adenine), and to create a sufficient reservoir of metal atoms for the formation of metallic clusters after the reduction of the whole solution. Indeed, after 24 hours of activation about 3 to 5% of the total complexes are expected to be bound to the DNA. As shown in the previous section, these Pt(II)-DNA complexes are expected to be reduced and to form a nucleus more easily than free complexes in solution.
Therefore, the growth of metallic particles (proceeding through steps of addition of Pt(II) complexes and reduction of the whole cluster) is expected to occur preferentially starting from the complexes bound to the bases.

After the 'activation' step, dimethylaminoborane is added to the solution in excess with respect to the Pt(II) concentration, to induce metal particle formation. TEM imaging of the metallisation products reveals that the chemical reduction of the Pt salt in the presence of activated DNA indeed occurs through a purely heterogeneous reaction channel, and that continuous chains of Pt clusters of size ~ 5 nm aligned along the entire DNA molecule are obtained (Figure 6).

Remarkably, the homogeneous nucleation channel is completely suppressed, as proven by the absence of homogeneously nucleated particles in the background of the sample. An atomic force microscope analysis of the metallisation products revealed that a purely heterogeneous nucleation of clusters is obtained only after long activation times (that is, when a large number of Pt(II) complexes are bound to the DNA bases). When reduction is started immediately after the addition of Pt(II) complexes to a DNA solution, besides a small number of heterogeneously formed clusters, bigger aggregates of homogeneously nucleated particles are found on the sample (14). Moreover, the increasingly heterogeneous reaction channel is linked to an acceleration of the overall metallisation kinetics, with increasing activation times (14).

These results confirm that heterocyclic organic ligands (such as DNA bases) actively promote the heterogeneous nucleation of metal clusters according to the mechanism predicted by theoretical simulations reported in the previous sections. The active effect of the DNA template in promoting the formation of metallic particles enables, in particular, the fabrication of exceptionally thin and regular necklaces of platinum clusters, as shown in Figure 6.

Finally, in very recent work (34), palladium clusters were grown on the surface of cytoskeletal proteins (microtubules) by a two-step procedure similar to the one we used to metallise DNA. It was demonstrated that, after incubation of the microtubules with palladium ions and subsequent reduction, palladium clusters grow on the microtubule surface forming particle arrays which reflect the helical symmetry of the underlying assembly of tubulin monomers. By looking at the correlation between the amino acid positions in tubulin monomers and the distribution of palladium clusters on a microtubule, the authors suggest that the selective arrangement of clusters along the biotemplate is induced by histidine amino acids located on the outer microtubule surface (34). On the basis of our results, we believe that the metal clusters are in fact grown in situ, selectively at the histidine sites to which Pd(II) ions were previously bound after the incubation of the microtubules with a Pd salt solution.

Conclusions

We studied the molecular mechanisms of the nucleation and growth of platinum clusters after the reduction of K₂PtCl₆, both free in solution and
supported on biopolymers. The obtained results are explained by an autocatalytic mechanism of metal cluster formation, where Pt clusters nucleate and grow via the addition of unreduced Pt(II) complexes to partially-reduced Pt complexes or to small clusters.

We note that the observed reactions are fully in agreement with a surface-growth cluster mechanism which was proposed to account for a shape-controlled cluster fabrication (9), based on the competition between the effect of surface stabilisation by capping agents and the addition of new complexes to reactive surface sites. Interestingly, the addition reactions take place with a considerable rearrangement of the cluster structure and involve a redistribution of the ligands on the cluster surface. This suggests that, in general, low-energy structure rearrangements and ligand fluxionality should be taken into account for achieving a controlled growth of noble metal clusters in reduction baths.

Moreover, we found that Pt(II) complexes covalently bound to heterocyclic donor ligands, such as purine DNA bases or histidine amino acids, can act as preferential nucleation sites for the formation of metal particles. In particular, we were able to grow Pt clusters on DNA molecules by a selectively heterogeneous metallisation protocol that avoids any spurious formation of metal clusters in the solution while remaining very simple, and thus is suitable for industrial processes. This approach could open the way to a wide range of applications in nanotechnology, based on the selective metallisation of nanostructured biotemplates formed, for example, by exploiting the properties of self-assembly and molecular recognition of biopolymers (35). The possibility of selectively metallising DNA molecules previously inserted into a lithographically-fabricated circuit structure appears to be particularly interesting for nanoelectronics (36–39). Finally, thin, uniform metal films or arrays of metal particles could be grown onto insulating substrates functionalised with a monolayer of organic molecules terminated with imidazole or similar groups, by electroless in situ metallisation. In this case it should be possible to structure the organic layer previously (for instance via imprinting or analogous techniques (40)) to achieve a complex metallic pattern after selective metallisation.

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Reactivity Imaging of Platinum-Based Fuel Cell Catalysts

The carbon monoxide (CO) poison, present in the hydrogen fuel used in fuel cells, is there either as a byproduct from upstream reforming or as a partial oxidation product formed during the oxidation of liquid fuels. In PEM fuel cells, the CO adsorbs strongly to active catalytic sites in the Pt-based (anode) catalyst and decreases its reactivity. Therefore, anode catalyst materials with higher CO tolerance need to be identified. Combinational methods can identify suitable materials quickly, but new and rapid screening tools for characterising the materials would help towards their successful application in fuel cell catalysis. Now, scientists from the University of Virginia, U.S.A., have demonstrated the use of the scanning electrochemical microscope (SECM) for the quantitative screening of combinatorial samples of PtRu and PtRuMo electrocatalysts in liquid systems (H2SO4), in the absence and presence of CO monolayers, using reactivity imaging (S. Jayaraman and A. C. Hillier, J. Phys. Chem. B, 2003, 107, (22), 5221–5230).

Catalyst activity was characterised as a function of composition and electrode potential by measuring the activity of the catalyst surface toward the hydrogen (H) oxidation reaction, via tip–sample feedback. The SECM was able to decouple the H oxidation activity and poison (CO) tolerance of the catalysts. Both the onset of CO oxidation and the rate of H oxidation could be determined. PtRu electrodes oxidised H in the presence of CO at 0.35 V below that of pure Pt, which shows that Ru can dissociate H2O at lower potentials than Pt. Electrodes with Mo improved the onset potential by an additional 0.2 V.
Fuel Cells at the Hannover Industrial Fair

COMMERCIAL PRODUCTS DEMONSTRATING FUEL CELL AND HYDROGEN TECHNOLOGY

The huge annual Hannover Messe took place as usual in April, profiling many areas of industrial products and developments (1). At this fair, energy systems, in particular fuel cells and hydrogen, were a major theme (2). Despite the difficult economic climate, around one hundred fuel cell exhibitors from some twenty countries displayed the hardware of their latest advances in fuel cell and hydrogen technology. Actual demonstrations of the new technology captured the imagination of the many visitors to the stands.

Among criticisms aimed at the fuel cell industry are the lack of progress towards producing sellable products and towards answering energy questions. Therefore, the positive aspect of this year’s fair was the clear message that units are now being integrated into real products, besides being in their traditional format as power sources. Indeed, perhaps the most impressive examples of a fuel cell in use were shown by the Fraunhofer Institute for Solar Energy Systems (ISE), Germany. ISE displayed a professional video camera and a handheld camcorder, both powered by neat, integrated, multiwatt fuel cells running directly on hydrogen stored as a metal hydride. With a run-time of up to eight hours for the larger video camera, it was easy to imagine a commercial product being developed.

On a larger scale, Proton Motor (Germany) gave details of its upcoming fork-lift truck powered by a proton exchange membrane fuel cell (PEMFC). In common with all PEMFC systems, this system utilises platinum-based electrodes. Lower noise and emissions, together with much faster refuelling/recharging times make this an interesting use for the fuel cell.

Proton Motor is also planning to manufacture a number of fuel cell buses intended for various European projects. These will contribute significantly to demonstrating the suitability of fuel cell vehicles for public transport. Buses from DaimlerChrysler have already been announced for the Clean Urban Transport for Europe (CUTE) project. This public transport programme is one of the first opportunities in Europe for the introduction of fuel cells.

Even though fuel cell products are still not fully competitive due to high costs related to components, manufacturing and materials, it is encouraging to see the industry moving away from pure research and demonstration models towards practical applications. This trend is not only in integrated uses of fuel cells, but also in single primary power sources; and several fuel cell power sources were on display. As a power source, the fuel cell can take the place of an electrical grid connection, a generator or even a battery.

In a typical example, Axane, a subsidiary of the French industrial gas supplier Air Liquide, demonstrated a new prototype PEMFC system: the ‘Roller Pac’. This can generate 2 kW of power for back-up systems for computers, and other uses. New fuel cell systems were also presented by PlugPower (U.S.A.), Roen Est (Italy) and the newly founded direct methanol fuel cell company Bee Power Systems (The Netherlands). Small (educational) fuel cells were on sale at the h-tec (Germany) stand.

The Fuel for Fuel Cells

Many products offered ways of providing the hydrogen fuel for fuel cells. Although there is no clear leading technology in this area, ten or more companies demonstrated solutions to this challenging question. The electrolysis of water was proposed by Norsk Hydro (Norway) and others, while hydrocarbon reforming by fuel processors (very much analogous to the processes going on in commercial oil refining) was demonstrated by, for example, HydrogenSource (U.S.A.) in their sleek 5 kW fuel processor. A third way is to use metal hydrides, and Millennium Cell (U.S.A.) exhibited its metal hydride hydrogen storage system – using it to power a model radio-controlled car.

As expected, the larger transport applications of fuel cells stole the show. No new cars were on display, but visitors engulfed DaimlerChrysler’s A Class-based F-Cell car, and General Motors’
conventionally-styled HydroGen 3 and the quite outrageous AUTOOnomy concept vehicle.

In another hall, politicians scrambled for photo opportunities with a new fuel-cell-powered motor scooter. Jointly developed by Aprilia (Italy) and MES-DEA (Switzerland), the scooter carries a 3 kW PEMFC — effectively supplying its environmental credentials to a young 'fashion' vehicle.

However, perhaps the most creative concept of all came from the British company, Intelligent Energy. Again, using platinum-based PEMFC technology, their compact units could be used for many different power applications. One of them, a 50 kW system composed of two 25 kW stacks, is to be used to power a lightweight single engine Boeing aeroplane (3). Although fuel cells will not be powering the world's airplanes in the foreseeable future, the first flight of this fuel cell plane is planned for December 2003, the one hundredth anniversary of the first powered flight. As a symbol, it allows us to consider where the fuel cell might be in another hundred years, although signs are that we will be using fuel cells in our daily lives much sooner than that.

D. M. JOLLIE

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Polymeric Platinum-Containing Anticancer Drugs

There have been many reviews over the past 30 years on platinum anticancer drugs. Usually, these have described the structure/activity relationships which have been established for platinum complexes. Few, if any, have dealt with polymeric species containing platinum, which is now the subject of the following review of a chapter written by Deborah W. Siegmann-Louda and Charles E. Carraher (Florida Atlantic University) entitled 'Polymeric platinum-containing drugs in the treatment of cancer'. This well informed chapter comes from the future Volume 3 in the book series on polymer science entitled “Macromolecules Containing Metal and Metal-Like Elements”, which will be published by John Wiley & Son (http://www.wiley.com/), in late 2003 or at the beginning of 2004, tentatively priced at U.S. $125.

The polymer-platinum conjugate can act as a drug itself or as a prodrug. For the polymer to act as a prodrug requires a non-toxic polymer backbone containing solubilising entities to make it water-soluble and functional groups capable of reversible binding to the drug species with, ideally, some targeting specificity to enhance accumulation in the tumour. The binding of platinum drugs through oxygen-donor leaving groups, either carboxylate or hydroxyl species, provides a ready means of realising this model. Where the polymer-conjugate acts as a drug itself, the binding of the platinum to the polymer may reduce the elimination of the drug by the kidneys and reduce toxicity by reduction in the amount of hydrolysis products formed. Additionally, the polymer conjugate may circumvent resistance due to reduced cellular influx/enhanced efflux mechanisms that affect small molecules. Finally, the activity may be modified by multiple bonding at a given site. Binding the platinum through nitrogen donors, such as amines, gives materials which exemplify this approach. The active species may be released by chain degradation, where monomeric units are released from the ends of the polymer, or chain scission, where macromolecular units are produced by breaks at random points in the polymer chain.

Examples of each of the above approaches are given in the review. Structural information on the polymer-platinum conjugate is given where this is available along with cytotoxicity data for many samples. Although some materials were found to be more cytotoxic than cisplatin there has been no attempt to date at the commercial introduction of any polymeric platinum drug.

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Understanding Heterogeneous Catalysis

ELECTRON MICROSCOPY IN HETEROGENEOUS CATALYSIS


Catalysis is a truly multidisciplinary subject covering aspects of surface science, materials science, physical/inorganic/organic chemistry, chemical engineering and computer modelling. Catalysts are found in many chemical processes, operating from room temperature to 1100°C (Andrusow process), at pressures from subatmospheric to hundreds of atmospheres, with a whole range of solvents, gas compositions and contact times.

“Electron Microscopy in Heterogeneous Catalysis” is an enjoyable account of the impact of electron microscopy on our understanding of heterogeneous catalysis. The book is the latest installment in the “Series in Microscopy in Materials Science”. Microscopic techniques range from high resolution transmission electron microscopy (HRTEM), which under favourable conditions can image particles less than 1 nm in size, to nanoscale analytical techniques for the determination of elemental compositions of small catalyst particles. Equally important is environmental TEM with reaction cells in which catalysts can be dosed with gases and liquids, making the in situ study of working catalysts possible.

Of particular interest is Chapter 5 entitled ‘Catalysis by supported small metal particles’. Here, an in-depth review of TEM studies in catalysis by supported metals is presented. Catalyst deactivation is examined in some detail, using Pt/Al2O3 and Pd/Al2O3 as two of the examples, with discussions on sintering mechanisms and effects. There is also a review of strong metal-support interaction (SMSI) effects when metal particles become covered by the support under reducing conditions at elevated temperatures. Here, TiO2 as a support is examined in some detail.

Supported bimetallic or even multimetallic catalysts are also used in catalytic processes and the interaction between the components is generally complex. Pd-Cu/C is taken as one example and TEM shows that thermal treatments above 600°C give a f.c.c. continuous Pd-Cu alloy, while below 600°C ordered Cu3Pd and CuPd phases are observed. Further complications arise as the morphology and composition of metal phases in the catalyst are often affected by the nature of the gas stream passing over it. For example, treatment of Cu-Ru/C with CO leads to sheet-like Cu particles and small Ru particles, while H2 treatment gives large spherical Cu particles as well as small Ru particles. However, with Pt-Rh/SiO2, TEM shows that under N2 heat treatments only Pt-Rh alloy particles are formed, while in air rhodium oxide over-layers form around the metal particles. In both these cases the particles are polyhedral or spherical in shape; cubic and twinned particles are generated by high-temperature treatment in H2.

Other chapters cover electron microscopy studies of oxide catalysts, studies of zeolite catalysts, and environmental catalysis and catalyst design – of significant interest to those in these fields.

Because of the broad nature of the subject Gai and Boyes have taken great care to introduce important materials science and chemistry concepts. In fact, the first 80 pages of the book are an introduction. Personally I found the chemistry aspect rather long and starting from too low a point with detail such as ‘a material consisting of atoms of several elements is called a compound’ spoiling the flow of the text. However, the authors have had a difficult task to introduce both chemistry to materials scientists and materials science to chemists and presumably both subjects to physicists and engineers. In spite of this the book is an interesting read and a welcome addition to the existing literature in catalysis science. It is aimed at those working in industry and academia and is suitable for undergraduate level and above.

P. J. COLLIER

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Strengthening Platinum-Palladium-Rhodium Alloys by Ruthenium and Cerium Additions

EFFECTS ON MECHANICAL PROPERTIES AT ROOM AND HIGH TEMPERATURE

By Yuantao Ning* and Xin Hu
Kunming Institute of Precious Metals, Kunming 650221, Yunnan, China; *E-mail: ytning2002@yahoo.com.cn

The effects of cerium and ruthenium additions on the mechanical properties of Pt-15Pd-3.5Rh alloy (wt.%) at ambient and high temperature are examined. The mechanical properties of the alloy were improved by adding cerium (≤0.1 wt.%) or ruthenium (≤0.5 wt.%) solute, with the cerium additions giving a better strengthening effect. Higher concentrations of cerium and ruthenium did not visibly increase the strength properties of the Pt-15Pd-3.5Rh alloy and even reduced some of the mechanical properties at high temperature. Increasing the palladium content in the Pt-Pd-Rh alloy could enhance the alloy strengths at room temperature but damaged the mechanical properties at high temperatures. Observations of the morphologies of fracture sections of alloy samples after creep-rupture tests at high temperature showed ductile fracture for alloys with lower contents of palladium, cerium or ruthenium and brittle fracture for alloys with higher contents of palladium, cerium or ruthenium. The different strengthening mechanisms of palladium, cerium and ruthenium additions to Pt-15Pd-3.5Rh alloy are discussed.

Platinum-palladium-rhodium (Pt-Pd-Rh) alloys are the main catalytic materials used for the preparation of nitric acid by the ammonia oxidation reaction. As early as the 1940s, scientists in the U.S.S.R. had developed an alloy catalyst comprising 92.5 per cent Pt, 4 per cent Pd and 3.5 per cent Rh (Pt-4Pd-3.5Rh). The alloy catalyst was based on a Pt-Rh alloy containing 92.5 per cent Pt and 7.5 per cent Rh with Pd being substituted for part of the Rh. The experience gained using this catalyst over many years in ammonia oxidation reactors, under pressures of 0.1–0.9 MPa and temperatures of 800–900°C, showed that the Pt-4Pd-3.5Rh alloy catalyst was as good as the Pt-Rh alloy catalyst.

This success encouraged the researchers in the U.S.S.R. to continue their investigations and, some 25 years later, another catalyst alloy was developed with lower Pt content, of composition 81 per cent Pt, 15 per cent Pd, 3.5 per cent Rh and 0.5 per cent ruthenium (Pt-15Pd-3.5Rh-0.5Ru). Compared to the Pt-4Pd-3.5Rh alloy, it was reported that the Pt-15Pd-3.5Rh-0.5Ru alloy had 20 to 25 per cent higher mechanical strength and other advantages when used as a catalyst in ammonia oxidation reactors (1). Despite all of this, no data about the effects of the Ru content on the mechanical properties of Pt-Pd-Rh alloy were reported in the literature.

The Pt-4Pd-3.5Rh alloy was introduced into China from the U.S.S.R. in the 1960s to use as the catalyst for the production of nitric acid. Extensive research, undertaken at the Kunming Institute of Precious Metals in China, starting in the 1970s (2), concerning the influence of rare earth metals on the properties and structure of precious metals, indicated that rare earth additions produced a good strengthening effect on platinum (3–5) and palladium (6, 7).

As part of an attempt to develop a new catalyst alloy with higher palladium content, work was undertaken to find a suitable rare earth metal as a fourth component in the Pt-Pd-Rh alloys. In this paper, the strengthening effects of cerium additions on the Pt-15 per cent Pd-3.5 per cent Rh (Pt-15Pd-3.5Rh) alloy are studied. In view of the lack of information about the influence of Ru additives on the mechanical properties of Pt-Pd-Rh alloy, a parallel study was carried out on the...
Table I
The Nominal and Actual Content of Various Components in the Alloys

<table>
<thead>
<tr>
<th>Alloy code</th>
<th>Nominal content, wt.%</th>
<th>Actual content, wt.%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Pd</td>
<td>Rh</td>
</tr>
<tr>
<td>PPR-1</td>
<td>Pt-4Pd-3.5Rh</td>
<td>4.10</td>
</tr>
<tr>
<td>PPR-2</td>
<td>Pt-15Pd-3.5Ru</td>
<td>15.0</td>
</tr>
<tr>
<td>PPR-3</td>
<td>Pt-15Pd-3.5Rh-0.5Ru</td>
<td>15.2</td>
</tr>
<tr>
<td>PPR-4</td>
<td>Pt-15Pd-3.5Rh-1.5Ru</td>
<td>14.82</td>
</tr>
<tr>
<td>PPR-5</td>
<td>Pt-15Pd-3.5Rh-3.0Ru</td>
<td>15.28</td>
</tr>
<tr>
<td>PPR-6</td>
<td>Pt-15Pd-3.5Rh-0.1Ce</td>
<td>14.99</td>
</tr>
<tr>
<td>PPR-7</td>
<td>Pt-15Pd-3.5Rh-0.5Ce</td>
<td>15.20</td>
</tr>
<tr>
<td>PPR-8</td>
<td>Pt-15Pd-3.5Rh-1.0Ce</td>
<td>14.98</td>
</tr>
</tbody>
</table>

mechanical strength of Pt-Pd-Rh-Ru alloys with different Ru additions, and with different Ce additions, to compare the strengthening effects.

Experimental Procedures

Elements Pt, Pd, Rh and Ru having 99.95% purity and Ce with 99.9% purity were used to prepare alloys. The elements, at the nominal contents listed in Table I, were melted and alloyed in a high frequency induction furnace and poured into a water-cooled copper mould under an argon atmosphere. Ingots of the alloys were made into wires of diameter (\(d\)) 0.2 mm by forging, rolling and drawing. The amounts of Pt, Pd, Rh and Ru in the wires were determined by chemical analysis, and the Ce content was determined by quantitative spectral analysis (ICP-AES). The nominal and actual contents of various alloy components are listed in Table I. The large difference between the nominal and actual content for cerium in the cerium-containing alloys was found to be due to the large amount lost in the melting process.

Tensile strengths of the alloys were obtained using a FPZ-100 type electron tensile tester. A creep-rupture apparatus (8) was used to determine creep-rupture values and the lasting strength at high temperatures. Lasting strength is defined here as the stress to produce failure in a particular time at a particular temperature, in this case in 100 hours at 900°C. Alloy microstructures were

![Graph of tensile strength vs temperature](image-url)
observed by transmission electron microscopy (TEM) (JEM-2000EX). The fracture sections of the alloy samples, studied after creep-rupture testing at high temperatures, were observed by scanning electron microscopy (SEM).

**Experimental Results**

**Tensile Strengths at Ambient Temperature for Annealing Alloys**

In Figure 1, the curves (a) showed the dependence of the tensile strength at room temperature on the annealing temperatures for Pt-4Pd-3.5Rh (PPR-1) and Pt-15Pd-3.5Rh (PPR-2) alloys. The strength curves are roughly parallel for both alloys. Over the range of annealing temperatures from 750 to 950°C, PPR-2 has ~ 20 per cent higher tensile strength and ~ 2–5 per cent higher elongation than PPR-1. The curves show that increasing the palladium content in Pt-Pd-Rh alloy does indeed enhance the strength properties at room temperature.

Figure 2 shows the effect of different amounts of Ce and Ru additions on the tensile strengths and elongations of Pt-15Pd-3.5Rh alloy, with Ce and Ru substituted for Pt. All samples were annealed at 900°C for 10 minutes. When the Ru content is increased, the tensile strengths of the PPR-3 to PPR-5 alloys increased almost linearly; the elongation also increased slightly.

For the alloys containing Ce, having codes PPR-6 to PPR-8, the tensile strengths clearly increased when the Ce content was less than 0.1 wt.% Ce; then increased slowly as the Ce content increased beyond 0.1 wt.% Ce. The change in the elongation with increasing Ce content had essentially the same tendency as the tensile strength. From Figure 2 it can be clearly seen that the tensile strengths and elongations of the Ce-containing alloys are much higher than those for the Ru-containing alloys.

**Tensile Strength at High Temperature**

The tensile strengths at high temperatures for all the alloys decreased different amounts as temperature increased. Above ~ 780°C, PPR-2 alloy has lower tensile strength than PPR-1 alloy, see Figure 1(b). Figure 3 shows the dependence of the tensile strengths, at 900°C, of Pt-15Pd-3.5Rh-Ru(Ce) alloys on the amounts of Ru and Ce additions.

The tensile strength of the alloys containing Ru increases linearly with increasing Ru content, however, for the Ce-containing alloys, the tensile strength clearly increases with the increase of Ce when Ce content < 0.1 wt.%, but then did not obviously increase when the Ce content > 0.1

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*Platinum Metals Rev.*, 2003, 47, (3) 113
It was again found that the mechanical properties of Pt-15Pd-3.5Rh-Ce alloys at high temperature are much higher than those of Pt-15Pd-3.5Rh-Ru alloys. For example, the tensile strengths for Pt-15Pd-3.5Rh-0.05Ce and Pt-15Pd-3.5Rh-0.5Ru alloys are 146 and 78 MPa, respectively.

Creep Rupture at High Temperature

The creep-rupture curves of the alloys at 900°C are shown in Figure 4. The curves are broken lines comprised of two straight lines with different slopes. The creep-rupture curves of the PPR-1 and PPR-2 alloys and of Ru-containing PPR-3 to PPR-5 alloys, turned downwards after the turning points, while those of the PPR-6 to PPR-8 alloys, containing Ce, turned upwards after the turning points. Alloy PPR-1 has longer creep-rupture times than PPR-2. This means that increasing the palladium content in the Pt-Pd-Rh alloy shortens the creep-rupture life during the creep process at high temperatures. The Ce and Ru additives greatly enhanced the creep-rupture times and the lasting strengths of the Pt-15Pd-
Table II
Comparison of Mechanical Properties of PPR-1, PPR-2, PPR-3 and PPR-6 Alloys

<table>
<thead>
<tr>
<th>Alloy code</th>
<th>Tensile strength</th>
<th>Creep-rupture time</th>
<th>Lasting strength</th>
<th>Activation energy</th>
<th>Elongation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>σb, MPa</td>
<td>(900°C, 30 MPa), h</td>
<td>σ100h, 900°C, MPa</td>
<td>Q**, kJ mol⁻¹</td>
<td>δ, %</td>
</tr>
<tr>
<td>PPR-1</td>
<td>230</td>
<td>20</td>
<td>18</td>
<td>290</td>
<td>15</td>
</tr>
<tr>
<td>PPR-2</td>
<td>280</td>
<td>10</td>
<td>14</td>
<td>282</td>
<td>9</td>
</tr>
<tr>
<td>PPR-3</td>
<td>320</td>
<td>30</td>
<td>20</td>
<td>312</td>
<td>23</td>
</tr>
<tr>
<td>PPR-6</td>
<td>400</td>
<td>180</td>
<td>35</td>
<td>385</td>
<td>30</td>
</tr>
</tbody>
</table>

*RT is room temperature; **Q is the creep activation energy; δ is the elongation to rupture under tensile testing at 900°C

3.5Rh alloy. Moreover, the creep-rupture times and lasting strengths of the Ce-containing alloys are much higher than those of the Ru-containing alloys, especially at lower load.

The dependence of the creep-rupture time (τ) on the stress (σ) and the temperature (T) can be expressed as follows:

\[ \tau = A_1 \sigma^n \] (i)

\[ \tau = A_2 \exp(Q/RT) \] (ii)

A₁ and A₂ are constants, Q is the creep activation energy, n is a stress-sensitive factor and R is the gas constant.

The effects of the amount of Ce and Ru additions on the creep-rupture time (τ), the creep activation energy (Q), the lasting strength (σ₁₀₀h, 900°C) and the elongation to rupture (δ) are shown in Figures 3, 4, 5 and 6.

Under a load of 29.4 MPa and at a temperature of 800–1000°C, adding Ru in amounts of up to 0.5 wt.% to the Pt-15Pd-3.5Rh alloy obviously increased its creep-rupture time, activation energy, lasting strength and elongation. However, above Ru contents of 0.5 wt.%, although the τ and σ₁₀₀h, 900°C values do not obviously decrease as the Ru content increases, the Q and δ values do decrease. As far as the creep property of the alloy is concerned, Ru additions above 0.5 wt.% are not always favourable to the Pt-Pd-Rh alloy.

With Ce additions up to 0.1 wt.%, the creep-rupture time, lasting strength, activation energy and elongation of Pt-15Pd-3.5Rh alloy greatly increase. However, with Ce contents greater than 0.1 wt.%, the values for σ₁₀₀h, 900°C and δ no longer increase (remain constant), while the value for Q decreases as the Ce content increases. It can be seen from Figure 4 that the Ce-containing alloys possess
higher strength properties and longer creep-rupture times at lower stress than at higher stress. So, low Ce contents (up to 0.1 wt.% Ce) and lower stress loads are very favourable for a longer creep-rupture life and higher lasting strengths in Ce-containing alloys.

Table II compares the mechanical properties of PPR-1, PPR-2, PPR-3 and PPR-6 alloys. It is clear that the PPR-2 alloy has lower mechanical properties at high temperatures, although it has higher tensile strength at room temperatures than PPR-1. Pt-15Pd-3.5Rh-Ce(Ru) alloys containing Ru and Ce additions possess much higher strength properties than PPR-2 alloy (with no Ce or Ru) especially alloys containing Ce. The strength properties of all the Ce-containing alloys are higher than those of the Ru-containing alloys. For example, the creep-rupture time (t) and the lasting strength of the PPR-6 alloy which actually contains 0.05 wt.% Ce are about one order of magnitude and nearly twice as high, respectively, as those of PPR-3 alloy containing 0.45 wt.% Ru (actual content), so a dilute Ce addition to Pt-15Pd-3.5Rh has a much higher strengthening effect than a larger Ru addition.

Microstructures of the Alloys

According to electron diffraction patterns, alloys PPR-1, PPR-2 and PPR-5 are single solid solutions. For the Pt-15Pd-3.5Rh-Ce alloys, PPR-6 alloy is a solid solution, but small amounts of particles of a second phase occurred in PPR-7 and PPR-8 alloys (see Figure 7). The sizes of the second phase particles in the PPR-8 alloy are ~ 50–150 nm in the grains and ~ 300 nm at the grain boundaries. Through energy spectrum analysis, the second phase is found to be a quaternary compound containing Ce; its composition is 81.88 wt.% Pt, 8.57 wt.% Ce, 6.44 wt.% Pd and 3.11 wt.% Rh, which roughly corresponds to the formula Pt(Pd, Rh)$_3$Ce. The compound is clearly a precipitated phase.

**Strengthening Mechanism of Ce and Ru Additions to Pt-Pd-Rh Alloy**

**Strengthening and Brittleness of Pd in Pt-Pd-Rh Alloy**

It can be seen from the above experimental results that increasing the palladium content in the Pt-Pd-Rh alloy increased the strength properties of the alloy at room temperature, but decreased the strength properties and elongation to rupture at high temperatures. SEM observations of the morphology of the fracture sections caused by creep rupture under a load of 29.4 MPa at 900°C for PPR-1 and PPR-2 alloys showed that the fracture of PPR-1 was ductile while that of PPR-2 was brittle (Figure 8). The alloy with the higher palladium content should contain higher oxygen content as oxygen has a higher solid solution in palladium than in platinum. Therefore, the alloy containing the higher oxygen content should contain a higher content of PdO due to the internal oxidation of Pd below 870°C, or should develop fine porosity due to the dissociation of PdO above 870°C (9).

On the other hand, the increase in oxygen content in the Pt-Pd-Rh alloy also led to the formation
of more of the non-volatile oxide Rh$_2$O$_3$ by the diffusion of oxygen along grain boundaries. Analysis of XPS results indicated that the content of Rh$_2$O$_3$ on the surface layer of PPR-2 alloy ($\sim$ 15%) was about 50% higher than the Rh$_2$O$_3$ content on the surface layer of PPR-1 alloy ($\sim$ 10%). The brittleness of the PPR-2 alloy may be due to the higher content of PdO and Rh$_2$O$_3$ distributed along grain boundaries as well as to the formation of strings of fine porosity.

**Strengthening of Pt-15Pd-3.5Rh Alloy by Ru Additions**

A Ru addition brings a good solid-solution strengthening effect to Pt-Pd-Rh alloy, but the strengthening effect weakens with increasing temperature. The affinity of Ru for O$_2$ and the vaporisation rate of the Ru oxide are higher than those of Pt, Pd and Rh. The preferential oxidation and vaporisation of the Ru addition in Pt-Pd-Rh alloy during the creep process at high temperatures could protect and prevent the alloy matrix from oxidation and reduce the amount of Rh$_2$O$_3$ formed along grain boundaries. The content of Rh$_2$O$_3$ in PPR-3 alloy was determined by XPS and is $\sim$ 10%, which is lower than in PPR-2 alloy. When the Ru content is low, for example < 0.5 wt.%, the Ru should give protective and thus strengthening effects to the Pt-15Pd-3.5Rh alloy matrix.

The protective and strengthening effects in Pt-Rh alloys due to the preferential oxidation and evaporation of small additions of, for example, Mo, W and other elements with higher vapour pressures have been reported (10, 11). When the Ru content is higher, for example > 1.0 wt.% Ru, the rapid vaporisation of the Ru and its oxide should make a large number of fine porosities. The interaction of the porosities with dislocations makes the time taken from forming groups or strings of porosity to rupture shorter, which makes the creep life and the elongation-to-rupture at high temperature decrease. SEM observations of the morphology of the fracture sections showed that PPR-3 alloy was ductile and PPR-5 alloy was brittle in the creep-rupture test (Figure 9). Large cavities were found in the PPR-5 alloy. Thus, large amounts of Ru additions are not desirable for Pt-Pd-Rh alloy.

**Strengthening of Pt-15Pd-3.5Rh Alloy by Ce Additions**

Ce additions have a greater solid solution strengthening effect on Pt-15Pd-3.5Rh alloy than Ru because Ce has a larger atomic radius and a lower solid solubility in the alloy. The larger atomic radius means a larger atomic radii difference between the Ce solute and the matrix of the alloy and larger lattice distortion in the alloy. In fact, a large number of petal-like dislocations were observed in the micro-defects of Pt-15Pd-3.5Rh-Ce alloys, which means that the stacking fault energy had decreased. In theory, solute metals with higher valence and a known solid solubility will make the stacking fault energy of f.c.c. metal
solvent decrease. The Ce additive of higher valance (III) introduced into Pt-15Pd-3.5Rh alloy was found to decrease the stacking fault energy from $115 \times 10^{-7}$ J cm$^{-2}$ for PPR-2 alloy to $65 \times 10^{-7}$ J cm$^{-2}$ for PPR-7 alloy (12). The decrease of the stacking fault energy means the width of the stacking fault increased. It was of great importance to increase the high temperature creep-rupture strength of the alloy because a wider stacking fault made the slip and climb of dislocation more difficult. On the other hand, the lower solid solubility of Ce in the alloy means the precipitate phase separated out even at lower Ce concentrations. This is responsible for the precipitate strengthening that occurs in the Ce-containing alloys.

When the Ce addition is in low concentration, for example $< 0.1$ wt.%, the precipitated phase containing Ce is fine and dispersed, which attached itself to the dislocation lines as shown in Figure 7a. So, it is also a strengthening factor. However, in alloys containing higher Ce contents, the particles of the precipitated phase clearly grew along the grain boundaries. This growth should damage the strength properties of the alloy and especially the ability to resist creep deformation.

The fracture sections of PPR-6 and PPR-7 alloys were ductile but the fracture of PPR-8 alloy was brittle, which was noted in alloy samples by SEM observations of the morphology of the fracture sections after creep-rupture tests. This is the reason why the strength properties of Pt-15Pd-3.5Rh alloys containing high Ce concentrations do not carry on increasing and might even decrease. So, the strengthening mechanisms of the dilute Ce...
additive on Pt-15Pd-3.5Rh alloy should include at least the mechanisms of the solid solution and of the precipitated phase.

On the other hand, the creep rupture for alloys containing Ce was affected by the stress put on the alloy samples. Figure 10 shows the morphologies of fracture sections of PPR-7 alloy under different loads. The fracture was ductile under high stress due to the shorter creep time, and brittle under lower stress due to the longer creep time. During the longer creep process particles of the precipitated phase grow and cerium oxide is also formed by internal oxidation along grain boundaries.

Conclusions
[1] Increasing the Pd content in Pt-Pd-Rh alloys can increase the strength properties of the alloys at room temperature, but reduce them at high temperatures; the tendency to brittleness in the alloys at higher temperatures should also increase.
[2] Adding a small amount of Ru (for example ≤ 0.5 wt.%) has a good strengthening effect on the Pt-15Pd-3.5Rh alloy from solid solution strengthening and a protective effect from the Ru solute in the matrix being preferentially oxidised and vapourised. Higher Ru concentrations could decrease the mechanical properties at high temperature and increase the tendency to brittleness due to the formation of a large number of porosities and porosity groups or strings.
[3] Ce additions to Pt-15Pd-3.5Rh alloy have a much bigger strengthening effect than Ru additions whether at ambient or high temperatures. Adding a small amount of Ce (for example ≤ 0.1 wt.%) can greatly increase the mechanical properties of the alloy by strengthening mechanisms in the solid solution and secondary phases. Ce additions of higher concentrations are not desirable for strengthening Pt-15Pd-3.5Rh alloy because of the growth of secondary phase particles along grain boundaries.

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Videos of Palladium Hydride Phases
The storage of hydrogen in metals is one way to provide the fuel needed for fuel cells. Palladium (Pd) and its alloys are well-known absorbers of large quantities of hydrogen and the mechanisms of this have been reported here frequently, for instance (1). Now scientists in Ukraine, at the Donetsk State Technical University (2), where the Pd-hydride system has been studied for several years, latterly by recording optical microscopy, report video evidence of the mechanism of the generation and growth of the reverse \( \beta \rightarrow \alpha \) hydride phase transformation in subsurface layers of Pd \( \beta \)-hydride at 270–100°C (3).

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Platinum Metals Rev., 2003, 47, (3)
"Ideas do not drive science. Instead, new instruments and techniques are critical to the discovery process, by which progress is measured". That is the view of Professor Sir John Meurig Thomas, which he puts forward at the outset of the book entitled "Surface Chemistry and Catalysis". This book has been published to mark the 70th birthday, in 2001, of Professor M. Wyn Roberts and his continuous years working in the area of surface science. Professor Roberts was appointed to the first Chair of Physical Chemistry at the University of Bradford in 1965, then in 1979 to the Chair of Physical Chemistry at the University of Cardiff. He was awarded the Tilden Medal and Lectureship in 1976, The Royal Society of Chemistry Award in Surface Chemistry in 1987, and the John Yarwood Memorial Medal and Prize of the British Vacuum Council in 1999.

The book is divided into three sections: Surface Science, Model Catalysts, and Catalysis, topics in which he has always been interested. The authors for each chapter were selected from the many eminent scientists who have worked with Professor Roberts in various ways and all are well acknowledged. They are a world-class cast to provide persuasive support for Sir John's point—until Wolfgang Sachtler and an equally impressive team of catalyst scientists draw the reader towards the conclusion that, at least in catalysis, there is a 'virtuous cycle' linking inspired concepts (hypotheses and inventions) with the useful technology that often defines progress.

 Appropriately for a tribute book, each chapter is of a consistently high standard. So, are there highlights? I particularly like the way in which D. C. Meier, X. Lai and D. W. Goodman do not try to skirt around the unavoidable issue of the reality gap between model and real surfaces, nor do they back away from trying to explain the complex electronic relationship between metal particles and a support material. Later, in a very topical chapter on gold catalysis, G. U. Kulkarni, C. P. Vinod and C. N. R. Rao capture the essence of an almost unique area of science, indeed, one in which everyone agrees (or perhaps no-one dares to disagree) that in the case of gold, particles of size 2–4 nm are essential to achieve high catalytic activity.

Then, Jerzy Haber describes the 'living' surfaces of metal oxides, putting a modern twist on the role that reducible oxides play in redox catalysis. This chapter made me think of the classic work of Vol'kenschtein (1), in which he tried to correlate the catalytic activity of metal oxides with their bulk semiconducting properties and which has undoubtedly influenced many catalyst scientists. This work is now rarely cited, except in the field of chemical sensors.

Besides reading like a "Who's Who" of catalysis and surface science, this book covers many of the major categories of surface-active materials. The platinum group metals, favoured for their single crystals as well as for their role in supported catalysts, appear regularly throughout. Two chapters are completely dedicated to the surface activity of gold — currently one of the most active fields of research. Although slightly overshadowed by the precious metals, base metals feature in substantial sections on metal-catalysed hydrogenation, metal oxides, and solid-acid catalysis. Zeolites come off worst in terms of column inches. The chapter by Graham Hutchings redresses the balance, however, by making the point that zeolites and related materials are some of the most useful building blocks in catalyst design. The big theories (such as transition state theory (TST) and strong metal support interaction (SMSI)) are well represented, although most of them are now largely taken for granted.

The editors openly admit that the only obvious failing of this book is that it does not look to the future, even though the authors were asked to do so. However, as a current and retrospective view
of catalysis it achieves a fitting tribute to Wyn Roberts – it makes you think about, and analyse, the route we have taken in catalysis and surface chemistry. Any 'crystal ball' gazing would have made the book seem very dated in a few years time. As for the question of how progress is made – Professor Roberts has already provided us with a few accomplished answers to that during his 50 years' work (2)!

S. E. GOLUNSKI

References


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Johnson Matthey Catalysts Division

In November 2002, Johnson Matthey completed the acquisition from ICI of its Synetix business. Synetix was added to Johnson Matthey's Catalysts & Chemicals Division, which was then renamed Johnson Matthey Catalysts. This division comprises Process Catalysts and Technologies (PCT), Environmental Catalysts and Technologies (ECT) and Fuel Cells. The former Synetix businesses, now part of PCT, bring a complementary range of base metal technologies to Johnson Matthey's traditional precious metals catalysis business.

Synetix was formed in 1998 from three ICI businesses: Katalco, Vertec (adhesion promoters) and Tracerco, and from businesses from Unilever: Unichema catalysts and the HTC catalysts business from Crosfield. It also included the former BASF syngas catalysts, linked to the ammonia and methanol markets.

Subsequently, units such as J & J Dyson's 'Dycat' business related to the hydrogen industry and to refineries and the oil and gas areas, and the former catalyst units of Celanese: 'Hoecat' for edible oils and 'CelActiv' linked to the alcohol sector, were acquired. In India, the catalyst business of Hindustan Lever – linked with oleochemicals and the Taloja facility for catalysts for oleochemicals and edible oils, were also acquired.

Synetix also brings expertise in chiral catalysis.

‘Platinum Today’ Website – New Informative Features

The ‘Platinum Today’ website (www.platinum.matthey.com), which along with the Ingenta Select site (www.ingentaselect.com), gives access to the electronic version of Platinum Metals Review, has been redesigned. ‘Platinum Today’ contains new features and services designed to maintain its position as the premier source of information on the platinum group metals and the platinum industry.

‘Platinum Today’ carries the Johnson Matthey publication ‘Platinum 2003’, the annual review of the platinum metals markets, as well as a library of earlier issues. The site also includes data on prices, metals supply and demand, applications and mining resources. It has an up-to-the-minute news service and a full news archive, a list of upcoming platinum industry conferences and events, and a photo library containing high quality digital images.

Five home pages cater for specific interests: Market Analyst; Press/Media; PGM Producer/Trader; Technical Research; and PGM User. These can be selected from a drop down menu. There are links to other Johnson Matthey sites which give access to technical data and to Johnson Matthey's platinum group metals products and services.

‘Platinum Today’ has all the facilities and services expected of a well-run site, such as a 'search' function which enables a word search to be conducted on any item on the site; a 'Register for Email' facility, enabling alerts for new issues of Platinum Metals Review, price reports and updates to be received; 'FAQ's'; and a 'Contact us' link.

Platinum Metals Review can be accessed via the Technical Research homepage or the 'Publications' button. The features: 'Back Issues, Instructions to Authors, Request Back Issues and Existing Reader Address Change' – are retained. The address of Platinum Metals Review on ‘Platinum Today’ is: www.platinum.matthey.com/publications/prm.html.
"Platinum 2003", Johnson Matthey's market report on the supply and demand for the platinum group metals (pgms) during 2002, was published in May. The annual report describes the worldwide utilisation of pgms by the pgms industry and includes forecasts for the next 6 months.

In 2002, total demand for platinum grew by 5 per cent to a new high of 6.54 million oz, driven by strong sales to the Chinese jewellery market and greater use of platinum in autocatalysts.

Demand from the jewellery industry accounted for 2.83 million oz, with 1.48 million oz being sold to the Chinese jewellery industry. The use of platinum in autocatalysts grew to 2.61 million oz, helped by tighter emissions regulations and by growth in diesel car sales: for instance in Europe, diesel cars accounted for 40% of new car sales.

Industrial demand for platinum increased to 1.59 million oz mainly due to demand for platinum-based catalysts from the chemical and petroleum refining industries. Purchases from the electrical industry, for example for use in computer hard disks, were marginally down, while demand from the glass industry was affected by less investment in new manufacturing capacity.

While supplies of platinum increased to 5.97 million oz, they failed to keep pace with demand. Platinum output in South Africa increased sharply to a record high of 4.45 million oz, an increase of 8.5 per cent, but this was offset by a sharp fall in Russian sales. As a result, the deficit in the platinum market widened to 570,000 oz. The deficit was covered from market stocks in Switzerland, and by sales from the U.S. Defense National Stockpile Center. The platinum price responded by rising from $481, at the start of 2002, to a peak of $607 in December. Since the beginning of 2003 the platinum price has remained firm and Johnson Matthey forecasts a trading range of $590 to $690 through to November 2003.

The demand for palladium slumped by almost 30 per cent to 4.78 million oz, the lowest level in nine years. Purchases of palladium for use in autocatalysts fell to 3.08 million oz in 2002, almost a 40 per cent drop, due to the substantial use of stocks by some auto makers. Purchase of palladium for the electronics industry recovered somewhat in 2002, increasing to 710,000 oz, but remained below consumption as manufacturers drew on their stocks. Demand for palladium in dental alloys recovered due to the fall in metal price throughout 2002. Other demand grew, led by an increase in jewellery alloy manufacture.

Palladium supplies dropped to 5.25 million oz as Russian sales were cut to levels not seen since 1990. Despite this the market remained in surplus, with a price fall from $440 in January to under $230 in December.

Johnson Matthey forecast that palladium will trade between $120 and $180 over the next few months.

Rhodium demand increased to 596,000 oz, driven by higher loadings in autocatalysts, but the demand from the chemical catalyst and glass manufacturing industries weakened slightly.

The survey includes substantial data augmenting the commentary and two special reports, one describing mining development entitled "The expansion of platinum mining in South Africa", and the other on 'Autocatalyst development and the use of pgm'.

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Recovery of Value Fission Platinoids from Spent Nuclear Fuel

PART II: SEPARATION PROCESSES

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Several processes are reviewed for recovering fission platinoids from radioactive liquids and solid material that typically originate during the reprocessing of spent nuclear fuel by the Purex process. The liquids are radioactive high-level liquid waste and the solution obtained on dissolving the spent nuclear fuel in nitric acid (dissolver solution). The solid is the undissolved fuel residue (dissolver residue). The processes described here have been particularly developed to recover platinoids or, if aimed at the separation of actinides, platinoid recovery is included. Hydrometallurgical processes are predominantly based on solvent extraction, electrodeposition and ion exchange, and less frequently on precipitation and extraction chromatography. Pyrochemical processes are based on extraction or distillation.

In Part I of this paper, general aspects of the recovery of fission platinoids from wastes resulting from reprocessing spent nuclear fuels by the Purex process were described (1). The main platinoid fractions are released from the Purex process in the radioactive high-level liquid waste (HLLW) and in the undissolved residue of the fuel. The platinoids of main interest: palladium (Pd) and rhodium (Rh), exist in aqueous nitrate solutions typically as Pd(II) and Rh(III). The behaviour of the platinoids in basic separation operations was also reviewed in Part I, and solvent extraction and electrolytic deposition were shown to be the most effective methods for use in separation processes to recover fission platinoids.

In this paper, separation processes for the recovery of platinoids from HLLW and undissolved residues are reviewed, from hydrometallurgical processes (ion exchange, solvent extraction and electrochemical procedures) to pyrometallurgical processes. With one exception, the processes are all described in periodical, patent and report literature. Before the various processes are discussed, some important criteria have to be noted when planning and developing separation processes. The most important are:

- no significant amounts of additional waste should be produced, and
- no reagents should be added which would interfere with vitrification of the final waste.

Thus, for example, solvent extraction supported by salting-out with large amounts of inert salts, or ion exchange comprising elution with concentrated salt solution, are not acceptable. In addition, gas evolution or the use of highly combustible chemicals must be avoided. Chemicals having unsatisfactory radiation and chemical stability must not be used; however, in certain cases, the lack of stability can be compensated for by extraordinary efficiency or selectivity. Finally, the only separation procedures of interest are those which can be started with acid solutions, as even moderate denitrification or neutralisation of the HLLW (say to < 2 M HNO₃) inevitably causes precipitation of hydroxides or other solids.

As already mentioned, there are two principal aspects to separating fission platinoids:

- The whole group (Pd, Rh, ruthenium (Ru)) is
Platinoids and Tc Recovered by Elutions in the Hanford Ion Exchange Process

<table>
<thead>
<tr>
<th>Order of elution</th>
<th>Eluant (38 l each)</th>
<th>Amounts of metals eluted, g</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Pd</td>
<td>Rh</td>
</tr>
<tr>
<td>1</td>
<td>1 M HNO₃</td>
<td>0.1</td>
</tr>
<tr>
<td>2</td>
<td>3 M HNO₃</td>
<td>0.5</td>
</tr>
<tr>
<td>3</td>
<td>6 M HNO₃</td>
<td>0.6</td>
</tr>
<tr>
<td>4</td>
<td>6 M HNO₃</td>
<td>trace</td>
</tr>
<tr>
<td>Total metals eluted by HNO₃ solutions</td>
<td>1.2</td>
<td>2.3</td>
</tr>
<tr>
<td>5</td>
<td>10 M NH₄OH</td>
<td>8</td>
</tr>
<tr>
<td>6</td>
<td>10 M NH₄OH</td>
<td>2</td>
</tr>
<tr>
<td>Total metals eluted by NH₄OH solutions</td>
<td>10</td>
<td>nil</td>
</tr>
<tr>
<td>Overall metals eluted</td>
<td>11.2</td>
<td>2.3</td>
</tr>
<tr>
<td>Overall metals adsorbed</td>
<td>12</td>
<td>3</td>
</tr>
</tbody>
</table>

Valuable platinoids — primarily Pd and secondly Rh — are selectively separated.

Processes with different principal objectives have been developed or conceived. Although the recovery of fission platinoids is the primary objective in some cases, in others the main objective is to separate actinides or long-lived fission products from HLLW, and platinoid recovery is only achieved if additional process steps are included. Not all the processes aim to obtain individual platinoids in a more or less pure state. Some processes merely result in a mixture of two or three fission platinoids as products.

In only a few cases has process development included all the necessary steps, namely laboratory batch and continuous-flow experiments and subsequent continuous-flow tests with real HLLW. Typically, development has not gone beyond the laboratory scale, and few processes were tested with real HLLW.

Some of the early process designs are hardly applicable now because they do not fulfil the criteria specified above. However, they are reviewed in order to show the increasing tendency to respect the criteria. Purely conceptual process flowsheets based on compiled information are not reviewed here. Such designs may be published before the start of experimental work as a basis for planning process development, or they may be only mere considerations. The only flowsheets to be critically reviewed here will be those that are at least partly based on original experimental data.

Hydrometallurgical Separation from HLLW

Hanford (U.S.A.) Ion Exchange Process

This process (2, 3) aims to separate platinoids from the supernatant of the Hanford alkaline wastes originated in the production of plutonium for nuclear weapons. The process was developed as long ago as the 1960s, using anion exchange as the principal separation method, and tested on an expanded laboratory scale but not extended to large-scale production operation.

In a typical test, around 12 g Pd, 3 g Rh and 11 g technetium (Tc) were adsorbed from about 4000–6000 l of supernatant on a 6 l column of Amberlite IRA-401 (20–50 mesh) at a flow rate of 4–12 l min⁻¹. (A 7 l column of Amberlite XE-238 became plugged under similar conditions after 200 l throughput.) Successive elutions with 38 l portions of HNO₃ and NH₄OH solutions removed Rh from the column together with part of the Pd and the major part of the Tc. The Table gives the amounts of eluted metals and compares the over-

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all metal amounts gained with metal amounts adsorbed.

Using the reversed phase chromatographic technique (extraction chromatography) Pd could be sorbed from the supernatant on a column of a trifluorochloroethylene polymer (Plaskon) carrying methylicacrylammonium chloride as an extractant. The capacity of the sorbent at 30% extractant content was 31 mg Pd g⁻¹ of sorbent. A > 90% fraction of Pd was eluted with 10 bed volumes of 10 M NH₄OH. Rh together with Tc was sorbed, in the next step of the process, from the Pd-free supernatant on a column of Amberlite XE-238. To prevent gassing and heat evolution in the succeeding elution with diluted HNO₃, any nitrite, carbonate and hydroxyl ions were first removed from the column by successive washings with water, 0.1 M HNO₃ and 0.25 M HNO₃ (2 bed volumes of each). The elution of Rh was advised to be subsequently accomplished with 2 bed volumes of 1 M HNO₃, 3 bed volumes of 3 M HNO₃ and 5 bed volumes of 6 M HNO₃ (2).

Thus, in the former route, sorption from the supernatant with subsequent elution steps yielded two fractions. One fraction, obtained by elution with HNO₃ solutions, contained all the Rh, all the Tc and eventually ~ 10% of the Pd inventory. The other fraction, obtained by elution with NH₄OH solution, contained the major part of the Pd contaminated by ~ 1% of the Tc inventory. This incomplete separation was attained after a number of time consuming operations — taking far too long for today's requirements. Moreover, if Pd and Rh were sorbed from typical waste — acidic HLLW — the Rh sorption would not be efficient enough.

Also hardly applicable in a modern process would be the subsequent, rather laborious, separation and purification of the platinoids in the two fractions. To purify the raw Pd product in the NH₄OH eluate of ¹⁰⁶Ru, ¹³⁷Cs and ⁶⁰Co, the ammonia eluate was evaporated by a factor of 20. Rh(III) precipitated quantitatively, presumably as a hydroxide, accompanied by ~ 2% Tc and all of the ¹⁰⁶Ru, ¹³⁷Cs and ⁶⁰Co. The Rh solid was then roasted at 500°C for 8 hours followed by leaching with aqua regia; this removed part of the ¹³⁷Cs and ⁶⁰Co. The remaining solid was then fused with NaHSO₄ at 500°C for 8 hours and dissolved in water. Filtration of the obtained solution removed part of the ¹⁰⁶Ru. Precipitation as hydroxide separated Rh from ¹³⁷Cs. Dissolving the Rh(III) hydroxide in 6 M HCl, evaporating to dryness, and redissolving in water, followed by repeated precipitation of ammonium hexanitrilotrophodate (NH₄)₃Rh(NO₃)₆ (3 times) removed the remaining parts of ¹⁰⁶Ru and ⁶⁰Co (3).

Indian Solvent Extraction Process

In this process (4), Pd(II) is extracted from simulated HLLW in two successive contacts with barren (not loaded with the metal to be extracted) 0.01 M triisobutylphosphine sulfide (TIPS) in Solvesso 100. The two combined portions of the loaded solvent are scrubbed with 2 M HNO₃ and Pd(II) is stripped by 0.01 M thiourea. Diocetyl sulfide and α-benzoin oxime can also extract Pd(II) effectively but, compared to TIPS, the sulfide has lower loading capacity for Pd(II), and the oxime exhibits lower radiation stability.

Only laboratory data have been obtained for this process, which could indeed be a reasonable starting point for further process development, provided that Rh recovery is not required.

Japanese Solvent Extraction Process

This is a partitioning process (5, 6) that has been in development at the Japan Atomic Energy Research Institute (JAERI, Tokai-mura) since the 1970s. Initially it was aimed at separating actinides from partially denitrated HLLW by extraction into diisodecylphosphoric acid in an alkane mixture, leaving most fission products in the raffinate. More recently, the process has been extended to include a separation step, in which platinoids are separated together with Tc. In one option the separation step involves further denitration of the raffinate by formic acid, in which, at pH > 2, the platinoids are precipitated as metals together with
hydrated TcO$_2$. Tc is then selectively leached under the oxidation to Tc(VII) using oxygen, ozone or hydrogen peroxide, while the platinoids remain in the precipitate.

Alternatively, a column of active carbon adsorbs all the Pd(II) and all the Tc(VII), as well as 16% Rh(III) and 49% Ru(III)NO. Tc(VII) is eluted with 2 M KSCN + 4 M NaOH, accompanied by 41% Ru(III)NO, 2% Rh(III) and 18% Pd(II). The major part of the Pd(II) (82%) and small fractions of Ru(III)NO (8%) and Rh(III) (14%) are retained on the column.

The process, although excellent for separating actinides from HLLW, is little suited to recover platinoids. Obtaining a precipitate that contains all three platinoids is hardly satisfactory even as an intermediate step, and the chromatographic procedure yields incompletely separated platinoids.

**Swedish Solvent Extraction Process**

This process (7) is primarily aimed at separating actinides from HLLW. Pu, Np, Tc and I are expected to be extracted in a first step by 0.2 M *Aliquat 336* in diisopropylbenzene at 3.4 M HNO$_3$. Then, according to a mathematical simulation, 80% Ru and 100% Pd are predicted to be extracted at 3 M HNO$_3$ by 50% *tributyl phosphate* in aliphatic kerosene. Full stripping is to be accomplished by 9 M HNO$_3$.

Irrespective of the complexity of the process (three various extractants are being used in three process cycles) it only assumes that a Pd/Ru mixture will be obtained. No data on the behaviour of Rh are given and no experimental tests of the platinoid recovery have been reported.

**Russian Solvent Extraction Process**

This process (8) is the most recent development in the field, utilising the extractability of Pd(II) by trialkyl amine and quaternary ammonium extractants in aromatic diluents from 3 M HNO$_3$ saturated with NO + NO$_2$. To develop the process, Pd(II) was shown to be moderately extracted by *tributyl, methylidioctyl, trioctyl, triisoctyl, tridecyl and tridecyl amines*, and efficiently extracted by *trialkylethyl* and *trialkylmethyl ammonium nitrates* and by *Aliquat 336* (9). The efficiency of the Pd(II) extraction by *tributylamine* and *Aliquat 336* in diethylbenzene is suppressed when the contacted phases are irradiated by gamma rays, but is still high enough even at a dose of 100 W h$^{-1}$ (10).

To extract > 99% Pd(II) at 3 M HNO$_3$ and room temperature, seven phase contacts with 0.5 M *Aliquat 336* or 14 phase contacts with 1 M *tributylamine* in benzene are needed at a phase volume ratio of organic/aqueous (org/aq) = 1/5. The loaded organic phase is then scrubbed, again at room temperature, with 1 M HNO$_3$ at org/aq = 10. Pd(II) is stripped into 6 M HNO$_3$ at 52.5°C and org/aq = 5. The overall Pd(II) yield is 97–98%. Ag(I), Sb(III), Ru(III)NO, Zr(IV), Am(III), Np(V), Ce(III), Sr(II) and Cs(I) are weakly extracted and are satisfactorily, or even very efficiently, separated from Pd(II). Pu(IV) and U(VI), although extracted together with Pd(II), are separated because they are essentially not stripped. Tc(VII) is not separated, being extracted and partially stripped simultaneously with Pd(II).

The process is promising for Pd recovery. It concentrates Pd(II) by a factor of 25 and separates it from the bulk of important fission products and minor actinides. Nevertheless, addition to the process of a final purification step, in which Tc would be efficiently separated from Pd, is necessary. The process is still in development and tests with real HLLW as well as scale up are planned.

**American Extraction Chromatographic Process**

This process (11) was developed for the U.S. Atomic Energy Commission in the early 1970s. It is suggested in this process that the HILW should be successively contacted with three separate beds of impregnated carbon. The first bed which carries *dimethylglyoxime* adsorbs only Pd, the second bed, carrying *diacetyl disulfide*, adsorbs only Tc, and the third bed carrying *N-phenylbisourea* adsorbs Ru together with Rh. The three loaded beds are then separately calcined, and Pd and Tc are leached from the ash of the first and second beds, respectively. The ash of the third bed is stored to allow the radioactivity to decay.

In addition to the disadvantages of extraction chromatography, in this case mainly losses of the
complexants from the carbon support, the impossibility of regenerating the extractants and the necessity of incinerating large amounts of carbon represent a serious drawback. We are not aware of any reports of further developments.

Two Japanese Precipitation Processes

These represent research work from the early 1990s and use neither solvent extraction nor ion exchange (12, 13). The first process (12) elaborated in joint work by university and industrial researchers is aimed both at reprocessing spent fuel and at partitioning HLLW. It suggests that the fuel should be dissolved in HCl or a HCl/HN03 mixture. The solution is then reduced by hydrazine and, after addition of SnCl2, platinoids are precipitated as Cs salts of chlorostannate complexes. Separation of U and Pu from fission products is accomplished in subsequent steps. However, the lack of selectivity and the contamination of the HLLW with HCl and Sn(II) render the process unattractive.

In another process (13), the actinides, fission lanthanides and fission alkaline earth elements are supposed to be precipitated from HLLW as oxalates at 1–3 M HN03. Without being supported by data, the platinoids are said to remain in the supernatant solution together with the alkali elements. The procedure, mentioned here for completeness, holds no promise of platinoid recovery.

Two American Combined Processes

These two processes (14, 15) were suggested as a result of industrial research.

The first process described is aimed at recovering Tc, but also includes optional recovery of platinoids. The simulated HLLW was made alkaline (pH ≥ 9) by Ca(OH)2 to precipitate fission products, among them the platinoids, and to leave Tc(VII) in solution. The precipitate was optionally dissolved in dilute nitric acid and the platinoids were then cathodically deposited. However, some fractions of the platinoids remained in the solution with the Tc(VII) after the addition of Ca(OH)2. These were codeposited cathodically, with the Tc, in another electrolysis step. The deposit was then stripped with 5.3 M HN03, the solution was made alkaline, and Tc(VII) was extracted into 2,4-dimethylpyridine, leaving the platinoids in the aqueous phase (14).

Salination of HLLW with a large amount of Ca(NO3)2 would inadequately increase the amount of solids in the subsequent treatment of the waste and would nowadays be quite unacceptable. Adding Ca(OH)2 might perhaps be acceptable after prior denitrification of the HLLW. However, individual separation of the platinoid is missing from this process, and as the platinoids are split between an electrode deposit and an aqueous raffinate, the process is of no interest.

In the flowsheet of the second process (15), the simulated HLLW was neutralised by 50% aqueous ammonia from an initial 8 M to 0.2 M HN03. The platinoids and Tc(VII) were then cathodically deposited at −0.40 V vs. Ag/AgCl at a current density decreasing from an initial 70 mA cm−2 to a final 0.3 mA cm−2. About 99% of Pd, Rh and Tc and 60% of Ru were plated over a period of ~ 48 hours. Treatment of the deposit with HN03 dissolved the Pd, Ru and Tc, while Rh was converted to flakes suspended in the resulting solution (15).

The same objections as before arise regarding the neutralisation of the HLLW and the incomplete separation. There are no known reports concerned with developing these processes beyond the laboratory scale.

Japanese Combined Process

This is based on a flowsheet developed by university-industrial research in the 1990s (16). It is mentioned here to give an example of a rather confusing concept that is intended to accomplish both the reprocessing of spent fuel and the partitioning of the waste. It utilises the ability of U(VI) and Pu(VI) to form soluble carbonate complexes in order to remove the major part of the fission products as hydroxides or carbonates.

The flowsheet is useless for the recovery of platinoids (and barely useful for its other objectives). Part of the Ru is removed as RuO3, during dissolution of the fuel in dilute nitric or hydrochloric acid under simultaneous oxidation. The remainder of the Ru, and the bulk of the Pd and Rh are distributed into a number of process
streams, such as: the insoluble residue after fuel dissolution; the Cs tetr phenylborate product; the U/Pu product; the waste fraction containing Na, Tc and Mo; and the waste fraction containing Tc, Mo and Zr.

Japanese Electrochemical Process

This platinoid recovery process (17) is one of the results of extended research work performed at the Power Reactor and Nuclear Fuel Corporation (Tokai-mura). The work is aimed at improving the Purex process, for example, by introducing electrochemical operations which reduce the salt content in the HLLW and so facilitate the final waste treatment. Constant-current electrolytic deposition of Pd at the optimal −0.1 V vs. SCE is a promising method to recover Pd from HLLW that contains 3 M HNO₃. In long-term electrolysis > 90% Pd is deposited, but Rh deposition is very slow. Its advantage is that the operation does not produce secondary waste. Thus the operation is of potential use in a future process for partitioning the HLLW, if installed and operated on a large scale.

Hydrometallurgical Separation from Dissolver Solution and Solubilised Dissolver Residue

Japanese Electrochemical Process Option

Without giving details, electrolytic deposition is said to be a candidate method for removing unspecified platinoids (and Tc) from the dissolver solution without producing secondary waste (17).

French Solvent Extraction Process

This process (18) involves extraction of Pd(II) by a 0.034 M solution of 6,9,12-trihexyltridecane in chloroform. As much as 86% Pd is extracted in one phase contact from a solution containing 214 g l⁻¹ U(VI), 0.55 g l⁻¹ Pu(IV), 1 M HNO₃, 15.4 mg l⁻¹ Pd, and 0.84 GBq l⁻¹ gamma radioactivity of fission products. After the extraction and after one scrubbing phase contact with 1 M HNO₃, the level of gamma radioactivity per mg Pd is reduced by a factor of $3 \times 10^5$. A one-step stripping with water yields a solution containing 5 mg l⁻¹ U, < 0.5 mg l⁻¹ Pu, 13.3 mg l⁻¹ Pd, and 2.7 kBq l⁻¹ gamma radioactivity (phase volume ratios have obviously been 1/1 in all steps). It is important that the extraction equilibrium is attained in 5 minutes.

These results lead us to expect good separation and decontamination efficiency when using countercurrent extractors. Indeed, it would be very desirable to replace the chloroform by a less volatile and, preferably, halogen-free diluent. However, the applicability of the process could be hindered by the extractant having insufficient chemical or radiation stability and, eventually, by its high price. It is unfortunate that the source (18) gives no information about the behaviour of Rh.

Japanese Solvent Extraction Process

This method (19) was developed in the late 1980s/early 1990s to be linked with extraction into Pb buttons (see Japanese Extraction Process 1 (21) below). A solution obtained by dissolving a Pb button in dilute nitric acid contains Pd, Rh, Mo, excess Pb, and 0.1–6 M HNO₃. Only Pd(II) is extracted into 10% dibucyl sulfide in dodecane. The Pd(II) is stripped with 1 wt.% thiourea and reduced to metal by a hydride reagent. Acetic acid is added, to a concentration of 20 wt.%, to the aqueous phase left over from the extraction step and ammonia is used to adjust the pH to 8–10. Lead (90–95%) is left in the supernatant and a precipitate containing Mo(VI) and Rh(III) is filtered off and redissolved in diluted HNO₃. These two elements are then separated on an amide oxime chelating resin (CS-346 Sumichelate).

The process, only briefly described in (19), is a plausible completion for a pyrometallurgical process. However, it could be simpler to add the Pb button solution to the HLLW, and then recover all the Pd from the HLLW, provided that the considerable Pb(II) content does not interfere with further waste treatment.

Pyrometallurgical Separation from HLLW

Japanese Process

A super-high-temperature process (20) suggests calcination of HLLW at ~ 700°C, followed by the removal of Cs and Rb by sublimation at ~ 1000°C. The platinoids can then be reduced at ~ 1600°C without adding reductants, or can be reduced in
the presence of nitrides, such as AlN, BN, TiN or Si3N4. Experiments with simulated HLLW have shown that a molten metallic phase is formed which, after cooling, contains the platinoids as Pd metal and as a Ru-Fe alloy. The phase also contains Mo in metallic form and corrosion products in the form of Cr-Ni, Fe-Ni and Cr-Fe-Ni alloys. Rh is also expected to be present in the metallic phase, but its behaviour has not been investigated. Stable oxides form the other phase, which contains zirconium, actinides, lanthanides and alkaline earth elements.

Clearly the platinoids are incompletely separated in this process, and it is difficult to assess how many further process steps would be needed to obtain pure products.

**Pyrometallurgical Separation from Dissolver Residue**

**Japanese Extraction Process 1**

This process has been developed by Japanese industrial and university researchers since the 1980s (21). It is based on extraction into a Pb or PbO2 button coexisting with a glass phase. Melting Pb with Na5B4O7 or B2O3 as glass forming constituents, and the dissolver residue, in the ratio 50:10:1 by weight, at 750–1100°C under bubbling air produces a PbO2 button containing the platinoids. The Mo is vaporised during the melting. Melting the above components in an argon (Ar) atmosphere yields a Pb metal button containing 95–98% of the Pd, 87–97% of the Rh and 91–95% of the Ru together with 2–13% of the Mo. CeO2 and Fe2O3 (simulating actinides and crud components) are directed into the glass phase both under bubbling air and in the Ar atmosphere. To remove the Pb, the button can first be melted for 0.5–1 hours with Zn at 650°C in an Ar atmosphere. Subsequent cooling to 390°C removes Pb in liquid form, leaving a solid Zn phase containing 74–90% of the platinoids and Mo. Zn can finally be removed by evaporation.

Alternatively, the Pb or PbO2 button can be dissolved in boiling 3 M or 6 M nitric acid. As much as ~ 90% of the Pd but only ~ 30% of the Rh is dissolved after 3–12 hours. The Rh yield can be improved to ~ 90% by a small addition of Bi at the melting step. The fraction of Ru transferred during the dissolution into solution is as little as ~ 0.024%, both with and without the Bi addition. Pd and Rh can subsequently be separated by an aqueous method, such as described above (19).

A common feature of this and the next two processes is that the platinoids are incompletely separated from each other and from the other fission products, especially Mo. The pyrometallurgical operations serve mainly to solubilise the residue. Further separation steps, with a hydro-metallurgical treatment as an optimal procedure, are necessary. This will make the recovery of the platinoids rather complicated.

**Japanese Extraction Process 2**

This process (22, 23), analogous to Japanese Extraction Process 1 (21) based on extraction into a lead phase, was developed at the Power Reactor and Nuclear Fuel Development Corporation (Tokai-mura) in the 1980s. It was tested in cold runs with simulated residue and in hot runs with true residue. The hot residue contained, in wt. %: 6.1 Pd, 20.6 Ru, 5.5 Tc, 22.1 Mo, 1.85 Pu and 12.0 U (the Rh content was not given). The hot residue was mixed with Pb metal and Na5B4O7 (at a ratio of 1:50-10) and two phases formed during melting at 800°C. As much as ~ 100% of the Pd, most of the Rh, but only 60–80% of the Ru, Mo and Tc were extracted into the Pb phase. Pd and Rh were homogeneously dispersed in the Pb phase. Ru, Mo and Tc were concentrated near the boundary of the Pb phase where Mo formed a mixed oxide with Pb. Pu and U were partitioned to the glass phase and their concentration in the Pb phase was below the detection limit of an electron probe microanalyser. A 3 M solution of HNO3 (probably boiling, but not specified in the source) was then used to dissolve the Pb phase together with most of the Pd and several tens of per cent of Mo. Most of the Rh and Ru and the rest of the Mo remained in a solid residue.

**American Extraction Process**

As mentioned in Part I (1), in 1981 it was suggested that fission Ru could be separated to obtain the radioactive isotopes 103Ru and 106Ru, precursors
Japanese Distillation Process

In the first step of this process (25), performed at ambient temperature, Ru is oxidised to RuO₂ by ozone and distilled off together with Te₂O₇ and part of the Pb oxide. Mo and the remaining Pb are then distilled from the solid residue in an air or oxygen stream at ≥ 1100°C. Finally, Pd is distilled in vacuum at ≥ 1230°C, leaving Rh in the solid. All three platinoids are mutually separated, but the separation efficiency is unknown.

Let us remember the poor applicability of large scale RuO₂ distillation, due to the tetroxide being easily reduced to RuO₃ in the gaseous phase. The dioxide then forms a deposit on the walls of the piping and reaction vessels which is extremely difficult to remove.

Conclusions

Fission platinoids, Pd, Rh and Ru, with Pd and Rh being of most interest, can best be recovered from spent nuclear fuel, namely from the HLLW and the dissolver solution by a hydrometallurgical process. Solvent extraction and electrolytic deposition are the most promising methods, less so are precipitation and ion exchange or extraction chromatography.

While numerous processes have been developed, few have been tested with real HLLW. Indeed, many of the processes developed have not gone beyond the laboratory scale. However, some are promising as a starting point for further research. In some processes the mutual separation of the platinoids is the final goal, but not in others.

To separate the platinoids from the dissolver residue, a pyrometallurgical treatment appears to be the only feasible option. This treatment can convert the residue to a form soluble in dilute nitric acid. However, with the present state of knowledge, the platinoids are neither mutually separated nor decontaminated from other fission products. Subsequent hydrometallurgical separation is therefore needed. One possibility that should be checked is to combine the residue solution with the HLLW, instead of treating it separately.

References

1. Z. Kolarik and E. V. Renard, *Platinum Metals Rev.*, 2003, 47, (2), 74
The Platinum-Enhanced Activity of Antibacterial Silver

Silver (Ag) has valuable antibacterial and purifying properties, and for centuries was used to keep potable liquids pure. It has also been used in many medical applications, ranging from wound dressings to attacking Legionnaires’ disease. Its antibacterial activity depends on the balance between the activity of Ag⁺ ions, which kill the bacteria, and the total amount of Ag released from a coating. If the amount of Ag released is too high, cytotoxicity will result. The released Ag⁺ ions act by displacing other essential metal ions, such as those of calcium or zinc, from biological material. In order to enhance the antibacterial performance of Ag, it is necessary to increase the concentration of Ag⁺ ions relative to that of metallic Ag released from the coating.

Researchers from Enterprise Ireland, and Biomatech in France, have now investigated whether platinum (Pt) could enhance the release of Ag⁺ ions from antibacterial Ag coatings (D. P. Dowling, A. J. Betts, C. Pope, M. L. McConnell, R. Eloy and M. N. Arnaud, Surf. Coat. Technol., 2003, 163–164, 637–640). As Ag is more active than Pt in the galvanic (electrochemical) series, Pt should enhance Ag⁺ ion formation through galvanic action. To evaluate this, chronoamperometric experiments were performed on Ag-Pt alloys (0.5 and 3.0% Pt) in pH 8.0 borax buffer solutions containing 0.02 mol l⁻¹ HCl at 20 ± 2°C. Resulting current-time curves showed that Ag⁺ formation increased with Pt addition by up to 100%.

Antibacterial Ag and Ag/Pt coatings were deposited onto a range of polyurethane and silicone polymers using a combination of magnetron sputtering and neutral atom beam plasma sources. The magnetron sputtering target was prepared from 1% Ag/99% Pt coatings. Cytotoxicity was not observed.

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ABSTRACTS

of current literature on the platinum metals and their alloys

PROPERTIES

An Original Route for the Preparation of Hard FePt
N. H. HAI, N. DEMPSEY, M. VERON, M. VERDIER and D.

Cyclic cold rolling was used to prepare textured Fe/Pt multilayer foils of total thickness ≈ 100 μm and individual layer thicknesses of the order of 10 nm. Ordered f.c.t. FePt (L10) was rapidly formed upon annealing at 450–550°C. Coercivities as high as 0.9 T were measured at room temperature following annealing at 450°C for 48 h. Coercivity decreased with increasing temperature: to 0.37 T at 600 K.

Adsorption and Desorption of Methanol on Pd (111) and on a Pd/V Surface Alloy

Thermal desorption spectroscopy and density functional theory established that a H bond between neighbouring MeOH molecules on Pd(111) is required to break the C–O bond. This leads to formation of CH₄. This reaction pathway is not possible on the Pd/V alloy surface, due to the different electronic structure of the alloy surface. The calculated geometries for Pd(111) and for the Pd/V alloy are very similar.

Effect of Ta Content on Martensitic Transformation Behavior of RuTa Ultrahigh Temperature Shape Memory Alloys

The martensitic transformation (MT) behaviour of RuₓTa₁₋ₓ (x = 46–54 at.%) alloys (1) was investigated by DSC, dilometry, XRD and optical microscopy. The one-stage reversible MT occurs in Ta-poor (1) (Ta < 49 at.%). The two-stage reversible MT takes place in near-equatomic (1). No reversible MT is observed in Ta-rich (1) (Ta ≥ 52 at.%). Ru₀·₅Ta₁₀ exhibited the best MT behaviour.

CHEMICAL COMPOUNDS

Structure and Bonding of the Hexameric Platinum(II) Dichloride, Pt₆Cl₁₂ (β-PtCl₆)

As previously reported, the structure of Pt₆Cl₁₂ (1) is confirmed as a hierarchical variant of the cubic structure type of W (b.c.c.), where atoms are replaced by the hexameric (1) molecules. (1) shows the (trigonally elongated) structure of the classic M₂X₁₃ cluster compounds with (distorted) square-planar PtCl₆ fragments, but without metal-metal bonds.

[Pt₆(CO)₁₀(PtCl₁₀)] and [Pt₆(CO)₁₀(PtCl₁₁)]
Generation of Nanosized Pd₆₃- and Pd₄₃-Core Geometries Containing Interpenetrating Cuboctahedral-Based Metal Polyhedra

[Pt₆(CO)₁₀(PtCl₁₀)] and [Pt₆(CO)₁₀(PtCl₁₁)] were synthesised as byproducts together with [Pt₆(CO)₁₀(PtCl₁₁)] through the deligation of [Pt₆(CO)₁₀(PtCl₁₁)] with CO assistance at the initial stage of the reaction. Their nanosized Pd₆₃ and Pd₄₃ cores are reported to be the first examples of “twinned”-core geometries involving a previously unknown oligomeric growth pattern, comprised of interpenetrating cuboctahedra as building blocks.

Palladium(II) and Palladium(0) Complexes of BINAP(O) (2-Diphenylphosphino)-2’-(diphenylphosphinyl)-1,1’-binaphthyl)
W. J. MARSHALL and V. V. GRUSHIN, Organometallics, 2003, 22, (3), 555–562

The reaction of [MeCN]₂PdCl₂ with BINAP(O) (1) gave [(BINAP(O))PdCl₂] (2), in which (1) is P,O-chelated to Pd. Reduction of (2) with LiBH₄, in the presence of (1) gave a new Pd(0) complex [(BINAP(O))Pd] (3). In (3) both (1) are P-bonded to Pd and one (1) provides π-arene coordination via the C=C bond adjacent to the phosphinyl group.

Rhodium(III) and Rhodium(II) Complexes of Novel Bis(oxazoline) Pincer Ligands

New C₂-symmetric bisoxazoline pincer ligands, benbox and benboxMe₂, were used to prepare coordinate unsaturated Rh(III) complexes. Trapping reactions of [RhCl₂{(S,S)-tb-benbox(Me₂)}] are described. For [RhMe₂{(S,S)-ip-benbox(Me₂)}][BAR₄] Rh-to-aryl methyl migration occurs. Air-stable, mononuclear, paramagnetic Rh(II) complexes [RhCl₂{(S,S)-tb-benbox(Me₂)}(H)] and [RhCl₂{dm-benbox(Me₂)H}] were isolated and characterised.

Crystal Growth of Novel Osmium-Containing Triple Perovskites

Single crystals of Ba₂LiOs₂O₇ (1) and Ba₂NaOs₂O₇ (2) were grown from reactive molten hydroxide fluxes in sealed Ag tubes. (1) and (2) crystallise in the space group P6₃/mmc with lattice parameters of a = 5.8025(1) Å, c = 14.1468(4) Å for (1) and a = 5.8858(1) Å, c = 14.3451(5) Å for (2).
ELECTROCHEMISTRY
Ruthenium Based DSA\textsuperscript{s} in Chlorate Electrolysis—Critical Anode Potential and Reaction Kinetics

Ru-based DSA\textsuperscript{s} were investigated in chlorate electrolyte using rotating discs made from commercial electrodes. The voltammetric charge and \( iR \)-corrected polarisation curves, up to current densities of 40 kA m\(^{-2} \), were recorded on new anodes and on aged anodes after 3 years in use. New anodes for chlorate electrolysis that work at a potential \( E_{\text{cr}} \), determined polarisation curves, up to current densities of 40 kA m\(^{-2} \), will develop an increase in real surface area during the first months of operation.

PHOTOCONVERSION
Room Temperature Phosphorescence from a Platinum(II) Diamine Bis(pyrenylacetylide) Complex

Long-lived, room temperature phosphorescence was observed in Pt(dbbpy)(C=C-pyrene)\textsubscript{2} (dmbpy = 4,4'-di(t~(t-buty1)-2,2'-bipyridine; C=C-pyrene = 1-ethynylpyrene) in fluid solution. The static and time-resolved absorption and luminescence data are consistent with phosphorescence emerging from the C=C-pyrenyl units following excitation into the low energy MLCT absorption bands.


The photodissociation of the axial PPh\(_3\) ligand of (X)(PPh\(_3\))Rh\textsuperscript{III}OEP (1) and (X)(PPh\(_3\))Rh\textsuperscript{III}TPP (2) (X = Cl, Br, I) in toluene was studied by 355 nm laser flash photolysis. The photodissociation yield of PPh\(_3\), \( \Phi \), from (1) is dependent on the nature of X: \( \Phi = 0.79 \) for X = I, \( \Phi = 0.48 \) for X = Br and \( \Phi = 0 \) for X = Cl. Similar trends are observed for (2): \( \Phi = 0.13 \) for X = I and \( \Phi = 0 \) for X = Br, Cl.

Extending the Luminescence Lifetime of Ruthenium(II) Poly(pyridine) Complexes in Solution at Ambient Temperature

Synthesised Ru(II) poly(pyridine)s have a central diethynylated pyrene moiety separating the 2,2'-bipy and 2,2':6',2'-terpyridine-based terminals. The mononuclear complex, having only bipy coordinated with the metal cation, and the corresponding binuclear complex show remarkably similar luminescence properties in deoxygenated MeCN at room temperature. Two emission bands are present in the spectrum. The phosphorescence lifetimes are significantly longer than those of the parent complexes. At low temperature, only the MLCT triplet is observed.

ELECTRODEPOSITION AND SURFACE COATINGS
Nucleation and Growth of Electroless Palladium Deposition on Polycrystalline TiN Barrier Films for Electroless Copper Deposition

The nucleation and growth of electrochemically deposited Pd on DC magnetron sputtered polycrystalline TiN thin films (1) were investigated. The growth of the Pd nuclei on (1) was 3D island growth. Plan-view TEM images of electrochemically nucleated Pd on (1) for 5 s showed that the Pd nuclei were mainly formed on the grain boundaries of (1), especially on the grain boundary triple points.

Iridium Coatings Grown by Metal–Organic Chemical Vapor Deposition in a Hot-Wall CVD Reactor

Ir thin films (1) were deposited on W substrates by thermal decomposition of Ir(COD)(MeCp) in H\(_2\) or O\(_2\). The growth was carried out in a horizontal hot-wall MOCVD reactor under reduced pressure at 573–673 K. The process is more difficult to control using H\(_2\). O\(_2\) avoids C incorporation in layers of (1) and significantly enhances the growth rate. However, codeposition of Ir and IrO\(_2\) was observed on using a high O\(_2\) excess. (1) with uniform thickness (1–2 \( \mu \text{m} \)) over a length of \( \sim 15 \text{ cm} \) were achievable.

Ruthenium Thin Films Grown by Atomic Layer Deposition

High quality Ru films (1) were grown by atomic layer deposition at 275–400°C using RuC\(_2\) and O\(_2\) precursors. (1) were deposited on thin Al\(_2\)O\(_3\) and TiO\(_2\) films on glass. XRD analysis indicated that (1) were polycrystalline metallic Ru and SEM showed that (1) had excellent conformality. (1) grown at 350°C contained < 0.2 at.% C, < 0.2 at.% H and < 0.4 at.% O, and had resistivity of 13 \( \mu \Omega \text{ cm} \).

APPARATUS AND TECHNIQUE
On the Platinum Sensitization of Nanosized Cerium Dioxide Oxygen Sensors

O sensors using nanosized CeO\(_2\) had improved sensitivity and response time, \( \tau_0 \), compared with those using coarse-grained CeO\(_2\). Pt incorporated into CeO\(_2\) also increased the sensitivity and decreased \( \tau_0 \) at 1081–1178 K, the optimum operating temperature. This is due to its catalytic role and its presence making O vacancy formation favourable.
Preparation of Thin and Highly Stable Pd/Ag Composite Membranes and Simulative Analysis of Transfer Resistance for Hydrogen Separation


Composite Pd/Ag membranes on an α-Al₂O₃ substrate were prepared by sequential electroless plating. SEM showed that the Pd/Ag film was of columnar form perpendicular to the substrate. Annealing the separate Pd and Ag deposited layers at > 600°C in H₂ gave homogeneous Pd/Ag alloy films. H₂ fluxes ≤ 0.35 mol m⁻² s⁻¹ and H₂/N₂ selectivities of 4500 were obtained. Long term thermal cycling tests at two pressures showed that the membranes are stable.

High-Performance Taste Sensor Made from Langmuir–Blodgett Films of Conducting Polymers and a Ruthenium Complex


A sensor array consisting of nanostructured LB films can be used as an electronic tongue capable of identifying sucrose, quinine, NaCl and HCl at the ppb level. The sensing units comprise LB films from conducting polymers and n(rr-RuCl₃(dpbb)(py) = (dpbb = PPh₂(CH₃)₂PPh₂; py = pyridine) transferred onto Au interdigitated electrodes. Impedance spectroscopy is used in the detection.

HETEROGENEOUS CATALYSIS

Study of Structure-Function Relationships in Platinum-Silica Catalysts Using Hydrocarbon Hydrogenation as a Probe Reaction


Solid-state NMR and Raman spectroscopy were used to characterise Si environments in the structure of 0.5 wt.% Pt/SiO₂ supported in particular strained ethene and ethyne hydrogenation reactions with (1) as catalysts. The results indicate that catalytic activity is influenced by outermost metal surface area, which is controlled by the method of metal deposition. The selectivity of ethene hydrogenation to ethane appears to correlate with the structure of the SiO₂ surface.

Direct Synthesis of Propylene Oxide with CO₂ as the Solvent


CO₂ was used as the sole solvent for the clean one-step generation of propylene oxide (PO) from H₂, O₂ and propylene over the catalyst Pd/Ti silicalite (TS-1). CO₂ can solubilise large quantities of gases, is miscible with both propylene and PO, and is chemically inert to the PO product. Therefore MeOH is not required for the efficient production of PO from propylene and H₂O₂ produced in situ as was previously suggested.

Reductions of Aromatic Amino Acids and Derivatives


The reduction of aromatic amino acid derivatives to the corresponding cyclohexyl compounds without racemisation of the amino acids was achieved with H₂ at low pressure over Rh/Al₂O₃ or Rh/C catalyst. The Rh/C catalyst was only effective under acidic conditions (HCl, H₂SO₄, H₃PO₄). The procedure can be scaled up to prepare multikilogram quantities of the products.

Highly Efficient Liquid-Phase Oxidation of Primary Alcohols to Aldehydes with Oxygen Catalysed by Ru–Co Oxide


Ru³⁺-Co⁵⁺ (1:1.5) binary oxide (1), prepared by coprecipitation, was found to be a highly efficient catalyst for the oxidation of primary alcohols to aldehydes (76–95% selectivity at 54–100% conversion) with O₂ or air. The oxidation was carried out under atmospheric pressure at 80–110°C in solvents such as toluene, acetonitrile or dichloroethane; toluene being the best solvent. (1) was reusable, but with gradually declining activity. The Co may have a significant role in the activation of O₂ in catalyst reoxidation.

HOMOGENEOUS CATALYSIS

Dispersing Palladium Nanoparticles Using a Water-in-Oil Microemulsion—Homogenization of Heterogeneous Catalysis


Pd nanoparticles (1) were dispersed in a H₂O/ AOT/ n-hexane microemulsion by H₂ gas reduction of PdCl₂. TEM showed the presence of spherical Pd metallic particles with diameters of 4–10 nm. (1) are very efficient catalysts for hydrogenation of olefins such as 1-phenyl-1-cyclohexene, methyl trans-cinnamate and trans-stilbene in n-hexane. (1) are stable for ~ 15–20 minutes. (1) could be separated from the n-hexane solution by filtration.
A Novel Methodology for Efficient Removal of Residual Palladium from a Product of the Suzuki-Miyaura Coupling with Polymer-Supported Ethylenediamine Derivatives


Polymer-bound ethylenediamines (1) were used to remove residual Pd from the crude 2'-cyanobiphenyl obtained by the Suzuki-Miyaura coupling of an optically active bromobenzene derivative with a boronate using PdCl2(PPh3)2 catalyst. Treatment with (1) reduced the Pd content of the crude product from 2000–3000 to 100–300 ppm. Subsequent purification by salt formation with di-p-toluoyl-D-tartaric acid gave a low Pd content of < 10 ppm.

Development of a 9-Borabicyclo[3.3.1]nonane-Mediated Solid-Phase Suzuki Coupling for the Preparation of Dihydrostilbene Analogs


A novel 9-borabicyclo[3.3.1]nonane (9-BBN)-mediated solid-phase Suzuki coupling was used to prepare dihydrostilbenes and related derivatives. Under optimised conditions (20 mol% PdCl2(dppf), 10 equiv. Et3N and 10 equiv. olefin/9-BBN in DMF/H2O (9:1) at 50°C for 18 h) high conversions were achieved. This methodology was applied to the preparation of a combinatorial library.

New P,N-Ferrocenyl Ligands for Rhodium-Catalyzed Hydroboration and Palladium-Catalyzed Allylic Alkylation


Nine new chiral P,N-ferrocenyl ligands (1) were prepared and used in metal-catalysed enantioselective reactions. The Pd-catalysed asymmetric alkylation of 1,3-diphenylallylic systems (≤ 94% ee) gave good results. The Rh-catalysed hydroboration of styrene with catechol borane proceeded with high regioselectivity (≤ 97:3) or with high enantioselectivity (≤ 92% ee) depending on the catalyst. Fine tuning of (1) had a significant influence on the performance.

Synthesis of a Conjugated Star Polymer and Star Block Copolymers Based on the Living Polymerization of Phenylacetylenes with a Rh Catalyst


1,4-Diethynylbenzene was used as linking agent in the living polymerisation system of phenylacetylene by [(nbd)RhCl2]/Ph3C=C-(Ph)Li/Ph3P (nbd = norbornadiene). The Mn and arm number of a typical star polymer formed by this system were 145,000 and 25, respectively. The arm number of the star polymer increased with increasing concentration of the linking agent, temperature of the linking reaction and with decreasing DP, of the linear polymer.

Hydroformylation Studies Using Nafion Supported Rhodium Based Homogeneous Catalysts


[Rh(C2NBD)BF4] (1) and [Rh(L-L)NBD]BF4 (2) (L = a phosphine ligand; L-L = a diphosphine ligand; NBD = norbornadiene) were prepared. (1) and (2) were incorporated into Nafion by ion exchange. These supported catalysts were compared with their homogeneous precursors for their activity as catalysts for hex-1-ene hydroformylation. The overall yield and ratio of normal heptanal to branched products are reduced in all cases by the supported catalysts.

Transition-Metal Nanocluster Catalysts: Scaled-up Synthesis, Characterization, Storage Conditions, Stability, and Catalytic Activity before and after Storage of Polyoxoanion- and Tetrabutylammonium-Stabilized Ir(0) Nanoclusters


Isolated, 3.8 ± 0.6 nm Ir(0) nanoclusters (1) (~ 1 g), stabilised by P2W18O62− and (c6-C6H6)2N+, in propylene carbonate solvent, have been synthesised. (1) retain ~ 65% of their as-formed catalytic activity for cyclohexene hydrogenation. (1) maintain their activity to within ± 15% for 6 weeks when stored as a solid under N2 in a ≤ 5 ppm O2 drybox. (1) are more stable when stored under 40 psig H2.

Dimethyl Carbonate–Water: an Environmentally Friendly Solvent System for Ruthenium Tetraoxide Oxidations


Dimethyl carbonate–H2O was used as solvent in RuO4 oxidations of alkenes, alkynes, arenes, alcohols, ethers and aldehydes. Either hydrated RuCl3 or hydrated RuO4 was used as the source of Ru. Suitable cooxidants include Na periodate, bleach and Oxone®. RuO4 with bleach as cooxidant, may find use in the oxidative degradation of organic pollutants.

FUEL CELLS

High Performance Carbon-Supported Catalysts for Fuel Cells via Phosphonation


Pt/C was phosphonated using 2-aminoethylphosphonic acid to give Pt/carbon-CH2CH2PO3H2 catalysts. (1) have largely enhanced proton conductivity and performed substantially better than the untreated counterparts in PEMFCs. Even with 10% less Nafion, the phosphonated catalyst has 20% higher performance over the entire current density region. The highest power densities achieved by phosphonated and unphosphonated catalysts were 0.57 and 0.47 W cm−2, respectively.
Methanol Electrochemistry at Carbon-Supported Pt and PtRu Fuel Cell Catalysts: Voltammetric and In Situ Infrared Spectroscopic Measurements at 23 and 60°C


The electrochemical oxidation of MeOH (50–200 mM) in 0.1 M HClO₄ on thin films of Pt (10 wt.%) (1) and PtRu (30 wt.% Pt, 15 wt.% Ru) (2) supported on Vulcan XC-72R C on bulk Au was investigated. MeOH electrooxidation was more sluggish on (1) than on either bulk polycrystalline Pt or (2). (2) was more resistant than bulk PtRu to CO adsorption.

Preparation of Methanol Oxidation Electrocatals: Ruthenium Deposition on Carbon-Supported Platinum Nanoparticles


MeOH oxidation electrocatalysts were prepared by Ru electrochemical or spontaneous deposition on Pt nanoparticles/Vulcan XC72 C. The maximum electrocatalytic activity for MeOH oxidation at room temperature was observed at lower Ru coverage (θRu ~ 10%) for spontaneous deposition than for electrodeposition (θRu ~ 20%). However, higher current densities for MeOH oxidation were obtained with electrodeposited Ru.

Electrocatalytic Enhancement of Methanol Oxidation at Pt-WO₃ Nanophase Electrodes and In-Situ Observation of Hydrogen Spillover Using Electrochromism


Pt–WO₃ and WO₃ thin film electrodes were grown using RF magnetron cosputtering. The Pt–WO₃ nanophase electrode had enhanced electrocatalytic activity compared to Pt itself for MeOH oxidation and exactly the reverse change in optical signal intensity with respect to electrochemical cell potential, compared with an electrochromic WO₃ electrode.

MEDICAL USES

The First Examples of Platinum Amine Hydroxamate Complexes: Structures and Biological Activity

T. W. FAILES, M. D. HALL and T. W. HAMBLEY, Dalton Trans., 2003, (8), 1596–1600

{[Pt(en)]₂(bha)ClO₄H₂O} and {[Pt(R,R-chxn)]₂(bha)NO₂H₂O} have two Pt centres that are bridged through the bha ligand via (O,O) and (C,N) coordination modes, the latter mode occurring through deprotonation of the ortho C of the phenyl ring. The cytotoxicities of these dinuclear complexes were tested. Both complexes were less active than their corresponding dichloro parent complexes.

Synthesis and Antitumour Activity of DNA Binding Cationic Porphyrin–Platinum(II) Complexes


DNA binding 5,10,15-tris(N-methyl-4-pyridiniumyl)porphyrin (TrisMPyP)-Pr(II) conjugates (1) were synthesised, in which different spacer ligands were used for appropriate coordination to Pt(II) complexes. (1) exhibited high antitumour activity superior to cisplatin and an elevated tumour-localising effect (tumour: muscle ratio > 2) compared to carboplatin.

Synthesis and Characterisation of Some Water Soluble Ruthenium(II)–Arene Complexes and an Investigation of Their Antibiotic and Antiviral Properties


Complexes [Ru(η₆-p-cymene)X₂] (X = Cl, Br, I, NCS), [Ru(η₅-p-cymene)X₆(pta)] [pta = 1,3,5-triazine-7-phosphatricyclo[3.3.1.1Ⅽ]decane] and the tetraruthenium cluster [H₂Ru₂(η₅-p-benzene)₂]²⁺ (1) were prepared and their antimicrobial properties evaluated. The antimicrobial activity of these complexes may be due to their specific interactions with proteins, but appears not to be correlated with DNA binding. (1) inhibited the growth of the Polio virus but did not affect the growth of human cells.

Ruthenium(III) Polyaminocarboxylate Complexes: Efficient and Effective Nitric Oxide Scavengers


Two RuIII polyaminocarboxylate complexes, AMD6245 (1) and AMD6221 (2), and their nitrosyl analogues, AMD6204, AMD6263 and AMD3689, were prepared and characterised. Upon reaction with NO, (1) and (2) formed a linear, diamagnetic (RuNO)₄ complex. (1) and (2) have an impact on the amount of nitrite accumulation in cell media in the RAW264 murine macrophage assay (an estimation of the NO scavenging ability).
NEW PATENTS

ELECTROCHEMISTRY

Cermet Electrodes for Oxygen Reduction
ROBERT BOSCH Gmbh European Appl. 1,303,753
Pt-cermet electrodes, used for the electrochemical reduction of O₂, have a ceramic portion containing stabilised ZrO₂ as the main component. The composition of the electrodes is designed to reduce their polarisation resistance.

Rhodium Sulfide Electrocatalyst
DE NORA ELETRODI SPA World Appl. 03/040,435
A Rh sulfide electrocatalyst (1) for reduction of O₂ in industrial electrolysers is produced by heating an aqueous solution of a Rh salt to obtain a steady distribution of isomers and then sparging H₂S into the solution. (1) is supported on highly dispersed C black and is highly resistant towards corrosion and poisoning by organic species. Thus (1) is particularly suitable for use in aqueous HCl electrolysis, even when in an acid containing organic contaminants. The activity and consistency of (1) is substantially improved.

Low-Sulfur Platinum Aluminide Layers
GENERAL ELECTRIC CO U.S. Patent 6,551,423
A method for preparing coated Ni-base superalloy, used in high-temperature applications, lowers the S content of the surface of the metallic coating layers. This improves the adhesion of the coating layers to the article. A first layer, of Pt, is deposited to overlay the surface of a substrate, followed by a second layer, of Al, over the Pt. The article is desulfurized by heating in H₂ and a small amount of surface material exposed during the heating is removed. A ceramic layer may be deposited over the desulfurised article.

APPARATUS AND TECHNIQUE

Spark Plug with Yttrium-Stabilised Platinum Alloy
FEDERAL-MOGUL CORP European Appl. 1,312,144
A spark plug with ground and centre electrodes includes a firing tip (1) formed from an alloy containing Pt, W and Y oxide. (1) can be a pad, a rivet, a ball or wire, etc., and can be welded in place on the electrode. (1) gives good erosion resistance, a reduced spark voltage, good welding and forming characteristics, as well as a minimal occurrence of alloy oxidation at the weld area.

Iridium Ultramicroelectrode Array
TRUSTEES OFail COLLEGE U.S. Patent 6,527,930
An Ir ultramicroelectrode (1) includes: a Si substrate; a Si oxide insulating layer; a Ti adhesion layer; and an Ir layer deposited over and insulated from the substrate. Part of the Ir surface (the ultramicroelectrode) is exposed. Also included are: a Au bond pad layer; a Ti adhesion layer; and a SiO₂ insulating layer. Preferably, (1) does not include Hg. (1) and devices using (1) can determine levels of Cu⁺⁺ or Hg⁺⁺ using square wave anodic stripping voltammetry.

Catalytic Removal of Oxygen from Sealed Packages
JOHNSON MATTHEY PLC U.S. Patent 6,562,258
Small quantities of entrained O₂ are removed from sealed packages containing an oxidisable product, such as a perishable foodstuff, using a particulate catalyst (1) with high activity for combining H₂ and O₂. (1) can be a Pt group metal supported on a porous inert carrier with the particles being partially encapsulated on a surface of a H₂O-insoluble adhesive on an inside surface of the sealed package. The adhesive material can be poly(vinylbutyral), nitrocellulose, ethyl cellulose, a polyurethane or a Si rubber.

HETEROGENEOUS CATALYSIS

Highly Selective Shell Impregnated Catalyst
SAUDI BASIC IND. CORP European Appl. 1,303,471
A highly active Al-modified C-supported Pd catalyst (1) on a SiO₂ support, with improved space time yield (STY) for vinyl acetate (VA) production, has a Pd loading of 1.8–7.2 g l⁻¹ and a Au:Pd weight ratio of 0.3:2.0. The support can be further impregnated with K acetate. At 140–160°C and a gas hourly space velocity of 4500 h⁻¹ at 120 psig, (1) has VA selectivity of ≥ 90% when operated under a STY of ≥ 600.

Aluminium-Modified Palladium/Carbon Catalyst
COUNCIL SCI. IND. RES European Appl. 1,308,206
A highly active Al-modified C-supported Pd catalyst (1) is prepared by simultaneously impregnating activated C with 2–6 wt.% Pd precursor and 1–50 wt.% Al precursor both with respect to the C support. (1) is useful for the hydrodechlorination of dichlorodifluoromethane to produce difluoromethane with 85% conversion rate at atmospheric pressure.

Eliminating NOx by a Laminated Structure
INST. FRANCAIS DU PETROLE World Appl. 03/009,918
Material (1) comprising mixed oxides with metals in octahedral coordination are linked to make a laminated structure. (1) are used to remove NO and NO₂ from ICE exhaust gas. (1) contains Mn, W, Zr, etc.; Al, Zn, Cd, etc.; and Pt, Pt-Rh, Pd-Rh, etc.; supported on SiO₂, Al₂O₃, etc. The ICE operates in a medium containing oxidants above stoichiometric level, and NOx can be absorbed and later desorbed by a temperature rise. Pt metals with (1) can eliminate NOx adsorbed by reduction in a rich mixture.

Low Surface Acidity Catalysts
JOHNSON MATTHEY PLC World Appl. 03/013,728
A catalyst (1) suitable for the dehydrogenation and hydrogenation of hydrocarbons comprises a first metal of a Pt group metal(s) and a second metal comprising Sn, Ge, Pb, etc., bound to a support material. The support, containing Al₂O₃, spinel, SiO₂, etc., has an overlayer to block acidic sites on the support. (1) is also substantially chloride free. A preparation method for (1), that uses K₂[Pt(C₂O₄)₂] and Sn(BF₄)₂ precursors in citric acid solution, is also disclosed.
High-Activity Isomerisation Catalyst
UOP LLC World Appl. 03/020,420
A catalyst and process is disclosed to selectively upgrade a paraffinic feedstock to an isoparaffin-rich product for blending into gasoline. The catalyst comprises at least one Pt group metal component, preferably Pt, on a support of a sulfated oxide or hydroxide of a Group IVB (IUPAC 4) metal, and a lanthanide element or an Y component, preferably Yb.

Exhaust System with Hydrocarbon SCR Catalyst
JOHNSON MATTHEY PLC World Appl. 03/033,118
Exhaust gas in an ICE containing NOx and hydrocarbons is reduced in an exhaust system that comprises two hydrocarbon selective catalytic reduction (HC-SCR) catalysts. The first HC-SCR catalyst contains a transition metal on a support selected from Al₂O₃, TiO₂, ZrO₂ or non-zeolite SiO₂-Al₂O₃, etc. The second Pt-based HC-SCR catalyst is placed with and/or downstream of the first HC-SCR catalyst, wherein the exhaust system has means for coking the catalyst during normal engine operation.

Exhaust Line for an ICE
JOHNSON MATTHEY PLC World Appl. 03/037,507
An exhaust system for an ICE comprises a catalysed particulate filter (1) having a NOx absorbent, such as an alkali metal, an alkaline earth metal and a rare earth metal, capable of absorbing NOx in an exhaust gas (2) when its composition is lambda > 1, and capable of releasing the NOx absorbed in the NOx component when the composition of (2) is 1 ≥ lambda. (1) further comprises a Pt and/or Pd oxidation catalyst and Rh capable of oxidising NO to NO₂ when the air:fuel ratio of (2) is lean.

Double Bond Hydrogenation in Unsaturated Carboxyls
CHEMI SPA World Appl. 03/037,506
A process is described for preparing a Rh-based catalytic system (1) heterogenised on an organic or mineral support. It involves the reduction of a Rh derivative with a valence state > 0 in an ether or aromatic solvent and in the presence of a compound chosen from the group consisting of lipophilic tertiary amines, lipophilic tertiary amides and lipophilic quaternary ammonium salts. The mixture obtained is adsorbed onto a suitable organic or mineral support. (1) is used in the hydrogenation of a C=C double bond of an α,β-unsaturated carboxyl compound.

Tin Promoted Iridium Carbonylation Catalyst
EASTMAN CHEMICAL CO U.S. Patent 6,548,444
A carbonylation catalyst (1) contains a solid component with 0.1–10 wt.% Ir and 0.1–10 wt.% Sn in contact with an activated C catalyst support, and a vaporous halide component selected from HI, MeI, etc. (1) is used for producing esters and carboxylic acids from reactants including lower alkyl alcohols, lower alkyl alcohol generating compounds, such as ether and ester derivatives of the alcohols, and their mixtures in a vapour phase carbonylation process.

Hydrogenated Polymers
KURARAY CO LTD U.S. Patent 6,559,241
A hydrogenated polymer is prepared from a polymer having C=C bonds and a hydroxy group and/or a functional group, which is convertible into a hydroxy group or into a hydroxymethyl group, in the presence of a Pd and/or Pt catalyst supported on a base activated C (1). (1) is prepared by treating an activated C with a base and depositing on it a Pd or Pt salt, which is converted to metal by hydrogenation. (1) removes the sites of unsaturation in the polymer and thus improves the low heat resistance and weatherability of the polymer.

Conversion to Hydrogenated Fullerenes
NATL. INST. ADV. IND. TECHNOL. Japanese Appl. 2003/012,572
The conversion of a fullerene comprises converting C₆₀ fullerene to a hydrogenated fullerene (1) using a catalyst obtained by impregnating Ru, Pd, Ir, Pt or Co into an active Al₂O₃. Conversion of the fullerene to C₆₀H₁₈ or C₆₀H₃₆ occurs in high efficiency under mild hydrogenation conditions. The method allows efficient production of (1) as a H storage material.

Carboxylic Acid Ester Production
ASAHI KASEI CORP Japanese Appl. 2003/024,782
A catalyst (1) for producing a carboxylic acid ester (2) from an aldehyde, an alcohol, and O₂ comprises Pd/active C. The Pd is supported on an active C carrier that has specific surface area 500–1500 m². The particle size of the carrier is 75–600 mesh, the bulk density is 0.3–0.8 g ml⁻¹, and the Pd has specific surface area of ≥50 m² g⁻¹. (1) has high reactivity and (2) is produced at lower cost.

Ruthenium Complexes Containing Carboids
BASF AG European Appl. 1,311,520
Ru carboid-containing complexes, used as catalysts in metathesis polymerisation reactions (ROMP, ADMET, etc.) of olefins comprise: H or optionally substituted C₁–20 alkyl, C₆–20 aryl or C₇–20 alkylaryl radicals; and independent neutral electron donor ligands coordinated at the Ru centre as carboids and which can be linked by a bridge W with 0–20 C atoms. The bridge can be a constituent of a cyclic or aromatic group and can be split by heteroatoms, except C₅N-heterocyclic five-membered ring systems.

Infusion of Cyclic Olefin Resins into Porous Materials
MATERLAINC World Appl. 03/020,504
Compositions are claimed comprising porous materials infused with polymers obtained from metathesis reactions, for example, ROMP derived polymers and ADMET derived polymers. Cyclic olefin monomers, including Ru or Os carbene metathesis catalysts, are useful to infuse the porous materials. A method for preparing the porous materials infused with the cyclic olefin resin formulations is described.
Improvements Relating to Prostaglandins
JOHNSON MATTHEY PLC World Appl. 03/037,857
A selective reduction of the 13,14-double bond (in the presence of the 5,6-double bond and unprotected hydroxyl groups) of certain prostaglandin C-1 esters, particularly PGA₂, PGD₂, PGE₂, etc., and their analogues, can be achieved directly by the use of homogeneous catalysts (1), (1) coordinate with the 15-hydroxyl group and selectively deliver up H to the 13,14-double bond. (1) include Wilkinson’s Rh catalyst, Crabtree’s Ir catalyst and Evans’ Rh catalyst.

Ruthenium Compound Catalysts
CHUBU CHELEST CO U.S. Patent 6,548,688
H₂O-soluble diammonium Ru diethylentetramine-pentacacetates or hydrates are produced. They are excellent in handling and exhibit very high, long-term stability both in air and in aqueous solution. The Ru compounds are useful as catalysts for the synthesis of NH₃, the hydrogenation of carbonyl or aromatic compounds, and as raw material for the production of Ru-base metal oxide ceramics.

Oxidative Carboxylation of Toluene
R. L. DU PONT DE NEMOURS CO U.S. Patent 6,548,698
The oxidative carboxylation of toluene, catalysed by Rh or Ir complexes in the presence of an oxidant, such as K₂S₉O₆, H₂O₃, trifluoroperacetic acid, etc., and under mild conditions, produces toluic acid (1) with para-selectivity ≤ 98%. The Rh compound may be [XRh(CO)₅], where X is an anionic ligand selected from acetylacetonate, trifluoroacetylacetonate, hexafluoroacetylacetonate, etc. The Ir compound may be IrₓXₙH₂Oₙ, where n = 0–10, and X is an anion selected from F⁻, Cl⁻, Br⁻ and I⁻.

Production of Aycyclic Olefins
DEGUSSA AG U.S. Patent 6,552,139
Acyclic olefins with two or more C atoms and/or cyclic olefins are prepared using homobimetallic and heterobimetallic alkylidene complexes of Ru containing N-heterocyclic carbene ligands. The Ru complexes also contain: an anionic ligand, a mono- dentate to tridentate ligand which contains a metal and is nonionically bound to the Ru centre, and radicals which may be identical or different and are each H or and/or a hydrocarbon group, but may also form a ring, and the N-heterocyclic carbene ligand.

Mixture of Isomers of Hydrogenated Bisphenol
MARUZEN PETROCHEM CO LTD Japanese Appl. 2003/002,853
Mixtures of hydrogenated bisphenol A isomers (1) containing isomers: cis-cis, cis-trans and 36-45% trans-trans forms are produced by subjecting bisphenol A to catalytic hydrogenation using a Ru catalyst in the presence of a solvent (aliphatic alcohol-based and/or glycol ether-based) at 100–130°C, under pressurised H₂. (1) has excellent compatibility with other resin raw materials and paint solvents and is used as raw material for polyester resin-based paints.

1-Boryl-4-stannyl-1,3-diene Compound
JAPAN SCI TECHNOL CORP Japanese Appl. 2003/026,692
1-Boryl-4-stannyl-1,3-diene compound (1), in which substituted diamino groups are bound to a B atom, is produced by reacting an alkyne compound with a borylstannane compound in the presence of a catalyst comprising Pd and a phosphite ligand. (1) is used as an intermediate for medicines and agrochemicals or as raw material for producing fine chemicals.

FUEL CELLS
Methanol Decomposition Reactor
GENERAL MOTORS CORP U.S. Patent 6,541,142
A fuel cell system contains a MeOH decomposition reactor (1) used to solve cold startup and problems with transient operating conditions. A catalyst containing 10–20 wt.% Pd/ZrO₂ is particularly suitable for MeOH low temperature decomposition. MeOH is charged into (1) and heat is supplied to decompose MeOH (endothermic reaction) to H₂ and CO. The H₂ produced is used by the fuel cell stack.

Electrode Structure for Solid Polymer Fuel Cell
HONDA MOTOR CO LTD Japanese Appl. 2002/367,629
A polymer electrolyte film (1) for the electrode structure of a SPFC, has repeating units composed of a sulfonated compound of a polye ther group of molecular weight 10,000–1,000,000. An electrode catalyst layer contains 0.01–0.6 mg Pt cm⁻², and the average diameter of the C grain is 10–100 nm. (1) has excellent power generating property at reduced cost.

Hydrogen Gas Generation
ULVAC JAPAN LTD Japanese Appl. 2003/012,301
A composition for H₂ gas generation is made by dif fusing ≥ 0.1 wt.% Al into an Ir-Ga alloy, the alloy being adhered to the Al surface. This is brought into contact with H₂O to produce H₂ gas. The apparatus (1) for H₂ gas production consists of a vessel which houses the alloy and various piping. High purity H₂ gas is obtained from the convenient, lightweight production. By combining (1) and a fuel cell, the generated H₂ gas can be used as the H₂ source.

ELECTRICAL AND ELECTRONIC ENGINEERING
Composite Iridium Barrier with Oxidised Refractory
SHARP LAB AMERICA INC U.S. Patent 6,566,753
An Ir—M—O composite film (1) (M includes a variety of refractory metals), that effectively prevents O₂ diffusion and is resistant to high temperature annealing in O₂ is claimed. When used with an underlying barrier layer of oxidised M transition metals, Ir diffusion into underlying Si substrates is suppressed, and Ir silicides are not formed. (1) remains conductive, not peeling or forming hillocks, during high temperature annealing. Conductive electrode/barrier structures with (1) are useful in nonvolatile MFMIS memory devices, DRAMs, capacitors, pyroelectric IR sensors, etc.
Engine Oils and Additives

High-performing engine oil is essential to the smooth functioning of an engine. Engine oil comprises a base oil and additives. But there is concern, that future advanced platinum metals-containing emission control systems and catalysts on vehicles might be sensitive to and react adversely with some of the complex components in the oil.

The primary function of engine oil is to form and maintain a lubricating film between moving engine parts when subjected to high temperatures, mechanical stresses and contamination from ‘condensate’ and chemical compounds. It also helps to keep engine parts clean while the engine is creating soot, ‘varnish’, water and numerous deposit-forming substances. It must also seal areas between pistons, rings and cylinders to prevent gases escaping from the combustion chamber.

One of the most important properties of engine oil is its viscosity, that is, its resistance to flow. The Society of Automotive Engineers (SAE) has an internationally accepted classification system for grading oils according to their viscosity at various temperatures. The ability of an engine to start (crank) reliably on cold winter mornings depends largely on oil viscosity, as does preventing metal to metal contact at high temperatures. Friction, and therefore relative fuel consumption, are at their highest in the first few minutes of engine running, so thinner oils, which circulate more quickly around the engine, will lower the fuel consumption especially during start-up. Modern multigrade engine oils combine low- and high-temperature viscosity properties, so the same oil can be used all year round. Oils are graded with a number, for example, 5W-30; the first value, 5W (winter), is a measure of its cold temperature ‘thinness’, while the second value, 30, refers to its high-temperature properties and indicates oil thinness when hot, ascertaining it will not become too thin – so avoiding engine wear at prolonged high speed operation.

To enable multigrade oils to maintain their properties for long mileages a variety of additive packages are added to the base mineral/synthetic oil. These are mixtures of inorganic and/or organic compounds formulated to enhance specific properties of the oil. Examples of organic additives are: viscosity modifiers to reduce the rate of viscosity change with temperature, friction modifiers and dispersants to keep insoluble contaminants dispersed in the oil. Metallo-organic compounds, such as zinc dialkyl dithiophosphate (ZDDP), are used in the antiwear, antioxidant and corrosion inhibitor packages, while metallo-organic compounds of sodium, calcium and magnesium (among others) contribute to detergent packages to keep surfaces free from deposits.

The demands and thus stress on engine oils have become increasingly severe with the development of high performing modern engines. There is also demand for longer mileage periods between oil changes. Thus thinner oils with more complex additives and highly advanced base stock oils are necessary. Higher performance needs have usually been met by increasing the additive package, but tightening emission standards require more advanced emission control systems and catalysts on vehicles. These systems could be sensitive to additives, and there are particular concerns about levels of phosphorus, sulfur and ash (from detergents) in the additives. Phosphorus from the ZDDP antiwear package is a well-known catalyst poison, but while phosphorus levels have been reduced slightly, no effective replacement for ZDDP has been reported. Sulfur levels in oil may also become a concern now that sulfur is being reduced in fuel. Particulate filters for diesel vehicles are already in production and their use is expected to increase. Ash from the oil could block the filter and reduce engine performance.

Such issues are currently being discussed by the oil, additive and automotive industries aimed at defining suitable oils for the future. A. J. J. WILKINS

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