A quarterly journal of research on the science and technology of the platinum group metals and developments in their application in industry
# Platinum Metals Review

A quarterly journal of research on the platinum group metals and developments in their application in industry

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Editorial Team: **Sara Coles** (Assistant Editor); **Ming Chung** (Editorial Assistant); **Keith White** (Principal Information Scientist)

Platinum Metals Review, Johnson Matthey Plc, Orchard Road, Royston, Hertfordshire SG8 5HE, UK

Email: jmpmr@matthey.com

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Preparation of Dispersed Spherical Platinum Particles with Controlled Size and Internal Structure

Versatile and cost-effective route to platinum powders for large scale electronic applications

Uniform dispersed spherical platinum particles were precipitated by reducing Pt(IV) hexaammine ([Pt(NH₃)₆]⁴⁺) complex ions with L-ascorbic acid in the presence of polymeric dispersants. By varying the nature and the amount of dispersing agent the average diameter of the Pt spheres could be adjusted between 200 nm and 800 nm. Electron microscopy and X-ray diffraction (XRD) evaluations revealed that the final Pt particles were the result of an irreversible aggregation of small (~6 nm) nanoparticles. The size of the constituent crystallites was controllably increased through a subsequent heat treatment process without affecting the shape or the dispersion of the Pt spheres. The method described represents a versatile and cost-effective route for producing Pt powders at the sub-micrometre or micrometre scale with controlled crystallinity for thick film electronic applications.

Introduction
The optical (1), catalytic (2) and adsorptive (3, 4) properties of dispersed matter depend not only on their chemical composition but also on the size, shape and structure of individual particles (5–7). In most applications, particle uniformity is also essential for optimal performance (5, 8–11). For example, highly uniform Pt particles with different sizes and structures are the preferred choice in electronic (10), catalytic (8, 12, 13) and biomedical (11) applications. The most widely used route to prepare such Pt powders is the liquid phase reduction of Pt salts (14, 15). The primary reasons for the popularity of this approach are the simplicity of the experimental setups and the versatility provided by the variety of solvents, dispersants, complexing agents and reductants used. The selection of the latter is particularly important as it offers the possibility of controlling the reaction kinetics and, implicitly, the properties of precipitated...
particles (16). Sodium citrate (17, 18), hydrazine (19) and ascorbic acid (20–26) are often used for this purpose.

While the solution reduction route typically yields uniform and well dispersed single Pt crystals (14, 27), their size is usually very small (less than 10 nm). This is the reason why for applications requiring large Pt crystals (> 1 μm), as is the case of the manufacture of electrodes (28), the Czochralski (29, 30), zone melting (31), or Clavilier (32) methods are preferred (33) despite their poor control of particle size, uniformity, and dispersion. Chemical precipitation methods can also generate sub-micrometre and micrometre size Pt particles under carefully controlled experimental conditions. As a rule, however, they are highly polycrystalline (i.e. formed by aggregation of small nanosize crystallites) (7, 34) and are seldom suitable for electronic applications. The main reason is the overlap of ‘intraparticle’ sintering of constituent crystallites with the ‘interparticle’ mass transport during densification, which leads to electrode defects. Gases resulting from the decomposition of organics trapped in the grain boundaries further compromise the quality of the sintered metallic structures and their adhesion to the substrate. In order to extend the range of their applications, the crystallinity of the precipitated particles needs to be increased.

In this study we show that precipitated polycrystalline Pt spheres can be subjected to a heat treatment process that increases their crystallinity and eliminates the undesired residual organics without causing irreversible particle aggregation. The resulting powders possess all attributes (uniformity, dispersion, purity, and structure) necessary for obtaining the thin and dense Pt sintered structures sought in most electronic applications.

**Experimental**  
**Materials and Reagents**

Hexachloroplatinic acid (H₂PtCl₆) solution containing 25.6 wt% Pt, ammonium hydroxide (NH₄OH) 14.8 N, hydrochloric acid 12.1 N, gum arabic and L-ascorbic acid (C₆H₈O₆) reagent grade were all used as received.

**Particles Precipitation and Heat Treatment**

All precipitation experiments were carried out in a 1 l jacketed glass reactor connected to a constant temperature bath. In the first step, dispersed hexamine Pt complex particles were prepared by delivering over 20 min 24.4 g of concentrated NH₄OH into a stirred H₂PtCl₆ solution. The latter was prepared in the reaction vessel by adding 30.5 g of concentrated H₂PtCl₆ (equivalent to 7.8 g Pt metal) into 275 cm³ of deionised water in which various dispersants (see Table I) were previously dissolved for at least 1 hour. Once the addition of ammonia solution was finished, 27.5 g of L-ascorbic acid crystals were rapidly added to the vigorously stirred Pt complex and the temperature was increased to 68ºC. After maintaining the dispersion at this temperature for 30 min, the polymeric dispersant was hydrolysed to allow the settling and separation of Pt particles. For this purpose, the temperature and pH of the dispersion were adjusted to 83 ± 2ºC and 0.6 ± 0.1 (using concentrated hydrochloric acid solution), respectively, and the stirring was continued for a further 90 min. After settling, the particles were washed several times with deionised water and rinsed with acetone before they were dried at 60ºC in vacuum for 6 h.

**Table I** gives the nature and the amount of polymeric dispersant used along with the key data for the Pt particles obtained, while Figure 1 illustrates schematically the precipitation process.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Dispersing agent</th>
<th>Amount of dispersant, wt% based on Pt</th>
<th>Particle size, nm</th>
<th>Surface area, m² g⁻¹</th>
<th>Weight loss, wt%</th>
<th>Crystallite size, nm</th>
</tr>
</thead>
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<tr>
<td>S1</td>
<td>Gum arabic</td>
<td>10</td>
<td>550 ± 70</td>
<td>0.4</td>
<td>2.3</td>
<td>6.0 ± 0.5</td>
</tr>
<tr>
<td>S2</td>
<td>Gum arabic</td>
<td>20</td>
<td>220 ± 50</td>
<td>1.12</td>
<td>3.4</td>
<td>6.0 ± 0.5</td>
</tr>
<tr>
<td>S3</td>
<td>Sodium alginate</td>
<td>3</td>
<td>820 ± 100</td>
<td>0.3</td>
<td>2.9</td>
<td>6.0 ± 0.5</td>
</tr>
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</table>
subsequent heat treatment step consisted of keeping the dried and screened powders for variable lengths of time in an inert atmosphere at temperatures of up to 500ºC.

**Particle Characterisation**

The size and morphology of the metallic particles were assessed by field emission scanning electron microscopy (FESEM) using a JEOL JSM-7400F instrument. ImageJ software (35) was used to determine their size distribution based on the acquired electron micrographs. At least 200 randomly selected particles were measured for this purpose. The crystalline structure of the particles was evaluated by powder XRD with a Bruker AXS D8 FOCUS diffractometer. For the XRD pattern acquisition, the step width and period were 0.01º and 3 s respectively, while the source, sample and detector slits were 2 mm, 0.6 mm and 1 mm. The diffraction patterns obtained were used to calculate the size of the constituent crystallites based on Scherrer’s equation (36). (Although this approach to determining the subunit size is not very accurate in absolute terms, it was decided that the significant crystallite size increase (up to an order of magnitude) during heat treatment makes XRD an adequate tool to monitor the change in powder crystallinity). Thermal gravimetric analysis (TGA) measurements (Perkin Elmer Pyris 1 TGA) were used to estimate the amount of organic matter incorporated into the Pt powders.

**Results and Discussions**

**Precipitation of Platinum Spheres**

During the slow addition of ammonium hydroxide (Figure 1, Step 2), a yellow precipitate of ammonium hexachloroplatinate was formed, followed by immediate conversion to the bright orange Pt(IV) hexaamine complex. The two consecutive reactions are reflected by Equations (i) and (ii):

\[
\text{H}_2\text{PtCl}_6 + 2\text{NH}_4\text{OH} \rightarrow \text{[NH}_4\text{]}_2\text{[PtCl}_6\text{]}^{2-} + 2\text{H}_2\text{O} \quad (i)
\]

\[
\text{[NH}_4\text{]}_2\text{[PtCl}_6\text{]}^{2-} + 6\text{NH}_3 \rightarrow \text{[Pt(NH}_3\text{)}_6\text{]}^{4+} + 2\text{NH}_4\text{+} + 6\text{Cl}^- \quad (ii)
\]

The immediate colour change to green upon the rapid addition of ascorbic acid crystals (Step 4) indicated the reduction of Pt(IV) to Pt(II) and the formation of [Pt(NH₃)₄][PtCl₄] (‘Magnus’ green salt’) a process formally captured by Equation (iii) (36):

\[
2\text{[Pt(NH}_3\text{)}_6\text{]}^{4+} + 8\text{Cl}^- + 2\text{C}_6\text{H}_8\text{O}_6 \rightarrow \text{[Pt(NH}_3\text{)}_4\text{][PtCl}_4\text{]} + 2\text{C}_6\text{H}_6\text{O}_6 + 4\text{NH}_4\text{Cl} + 4\text{NH}_3 \quad (iii)
\]

**Fig. 1.** Schematics of the precipitation process for preparing the spherical platinum particles used in this study. FR (1 and 2) stand for ‘flow rate’ and indicate pumps used to deliver the reagents in a controlled manner. CPA = hexachloroplatinic acid; L-AA = L-ascorbic acid; DA = dispersing agent

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The green precipitate consists of alternately stacked square planar [PtCl\(_4\)]\(^{2-}\) cations and [Pt(NH\(_3\))]\(^{2+}\) anions, its formal structure usually being given in a simplified manner as PtCl\(_2\)(NH\(_3\))\(_2\). At a higher temperature (68ºC), the excess ascorbic acid slowly but quantitatively reduces the Pt\(^{2+}\) species to Pt\(^0\) as suggested by the gradual change of the dispersion colour from green to grey-black. This process is formally captured by Equation (iv):
\[
\text{PtCl}_2(\text{NH}_3)_2 + \text{C}_6\text{H}_8\text{O}_6 \rightarrow \text{Pt}^0 + \text{C}_6\text{H}_6\text{O}_6 + 2\text{NH}_4\text{Cl} \quad \text{(iv)}
\]

The electron microscopy evaluations of the isolated solids revealed that well dispersed and quite uniform spherical Pt particles were obtained in all experiments (Figure 2). The median size of the particles was influenced by both the nature and the amount of dispersing agent used. The average size of the particles decreased from ~550 nm to ~220 nm when the level of gum arabic was increased from 10 wt% to 20 wt% (Figures 2(a) and 2(b)). This outcome is expected as an increased amount of dispersant favours the formation of a larger number of aggregation centres and reduces the number of constituent nanocrystals captured by each aggregate (38). In the case of sodium alginate, when an even lower amount of polymer was used due to a high viscosity of the starting solution, the average particle size increased to ~800 nm (Figure 2(c)).

The X-ray diffractograms of the three samples were essentially indistinguishable. For illustration, the pattern obtained for the particles obtained in the presence of 10% gum arabic is given in Figure 3(a). The unusually broad peaks for such large particles provided the first indication that the metal spheres may be assemblies of much smaller Pt entities. Indeed, the calculations based on Scherrer’s equation (36) gave a value of ~6 nm for the size of the Pt crystallites. Additional inspection of the particles at high magnification (Figure 3(b)) confirmed both the aggregated nature of the Pt spheres and the calculated size of the constituent crystallites.

Considering the extensive internal grain boundary formed during the aggregation of a very large number of such small entities, it is expected that a significant amount of polymeric dispersant is trapped inside the large spheres. TGA analysis was used to determine not only the total residual amount of organic matter incorporated in the final dry powder but also the dynamics of its decomposition as a function of temperature. The decomposition pattern shown in Figure 4 for gum arabic was typical for both dispersants but the total weight loss recorded at 450ºC...
varied with the type and amount of polymer used. In the case of gum arabic, it increased from ~2.3% to ~3.4% when the polymer amount was doubled from 10% to 20% (Table I, Samples S1 and S2). The increase in the residual organic matter in the latter case is likely the result of a larger external surface area associated with spheres of smaller diameter. Although the particle diameter was comparable to that recorded in Sample S1, in the case of sodium alginate the weight loss was larger (~2.9%). Since the internal grain boundary and external surface area in both cases should be roughly similar (comparable size of both crystallites and spheres), the reason for the difference was likely the higher molecular weight of sodium alginate.

**Heat Treatment of Platinum Nanoparticles**

It is well known that the sintering temperature of nanoparticles is significantly lower than that of much larger entities of the respective materials (39, 40). Since the large precipitated particles contain nanosubunits, finding a temperature where their sintering is confined inside each sphere without intersphere mass transport (and thus powder sintering) taking place could be a viable way to increase particle crystallinity without irreversible particle aggregation. Also, as the sintering temperature of Pt is well above the decomposition point of most organic polymers, another advantage of such treatment would be a significant reduction of the amount of dispersant trapped in the internal grain boundary. In order to find a temperature at which the ‘intraparticle’ and ‘interparticle’ sintering are separated, four aliquots of Sample S1 were kept for 1 hour in an inert atmosphere at 200°C, 300°C, 400°C and 500°C, respectively. XRD analysis revealed a significant increase in the crystallinity of the Pt particles with temperature, as judged both by the width of the diffraction peaks (Figure 5(a)) and the increase in the calculated crystallite size (Figure 5(b) and Table II).
As indicated by the TGA data in Figure 6, the increase in crystallinity was also associated with a significant reduction in the amount of residual organic matter (from ~2.3% to ~0.2%). Compared to the image of the original precipitated particles shown in Figure 3(b), the scanning electron microscopy (SEM) of the heat treated powders (Figures 7(a) and 7(b)) showed a much smoother surface, a clear indication of a significant reduction in the internal grain boundary. It is noteworthy that the exposure to elevated temperature for a relatively long time also causes the merging/sintering to a certain extent of the surface crystallites resulting in the loss of their original morphology. The analysis of multiple micrographs also showed that no interparticle ‘bridging’ took place at temperatures of 400°C or below. In contrast, at 500°C severe interparticle fusion was observed (Figure 7(c)).

These findings suggest two sintering regimes of spherical composite particles taking place at different size scales. At temperatures below 400°C, ‘intraparticle’ coarsening occurs as a result of the growth of constituent subunits and the reduction of internal grain boundaries. At 500°C, interparticle mass transport becomes significant and results not only in the growth of the constituent Pt crystallites, but also severe aggregation of the large Pt spheres. Since the latter cannot be redispersed to form electronic inks capable of depositing smooth and continuous thin Pt films, the optimum temperature at which powders suitable for electronic applications (crystalline and non-aggregated) can be prepared is ~400°C.

**Conclusion**

This study describes a precipitation method for obtaining concentrated dispersions of uniform polycrystalline Pt spheres. By tailoring the reaction conditions it is possible to control the final particle size in the 200 nm to 800 nm range. A heat treatment process capable of increasing the crystallinity of the precipitated spheres and decreasing the content of residual dispersant is also reported. The combination of the two processes makes possible the preparation of reasonably crystalline, uniform and well dispersed Pt spheres, which are suitable for thick film electronic applications. The use of widely available Pt salt, common reagents, and the simple experimental...
setup makes the reported preparation route suitable for the manufacturing of spherical Pt powders on a large scale.

Acknowledgements
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References
7. I. V. Sevonkaev and V. Privman, World J. Eng., 2009, 6, P909
20. H. Borsook and G. Keightley, PNAS, 1933, 19, (9), 875

Further Reading
K.-A. Starz, D. V. Goia, J. Köhler and V. Bänisch, OMG AG & Co, KG, ‘Noble Metal Nanoparticles, a Process for Preparing These and Their Use’, European Appl. 1,175,948; 2002

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Brendan Farrell is a Research and Development Project Leader with Metalor Technologies, USA. He completed his PhD in Physical Chemistry at Clarkson University, Potsdam, New York, USA, under the direction of Professor Dan V. Goia.

Igor Sevonkaev has a PhD in Physics and currently holds a Research Associate position in the Department of Chemistry & Biomolecular Science at Clarkson University, Potsdam. He is primarily involved in industrial projects focused on design and preparation of materials for fuel cell and photovoltaic applications. His expertise is in the development of metallic (gold, silver, platinum, palladium and indium) and non-metallic (lead(II) sulfide and magnesium fluoride) particles of various sizes and shapes for practical applications.

Dan V. Goia is a Professor in the Department of Chemistry & Biomolecular Science/Center for Advanced Materials Processing (CAMP) at Clarkson University, Potsdam. Prior to joining Clarkson in 2001 he was the Research and Development Director in the Electronic Materials Division of Degussa Corporation. His research focuses on the synthesis, characterisation, and modification of fine metallic particles.
“Solid-Phase Organic Syntheses: Solid-Phase Palladium Chemistry”

Reviewed by David W. Knight
Cardiff Catalysis Institute, School of Chemistry, Cardiff University, Main College, Park Place, Cardiff CF10 3AT, UK
Email: knightdw@cardiff.ac.uk

The purpose of this relatively small volume is to provide methods for carrying out representative examples of palladium-catalysed couplings on a solid support, essentially in the style of Organic Syntheses (1). There are contributions from both academic and industrial groups. This is a somewhat specialised area of synthesis, requiring techniques additional to those employed in ‘normal’ organic synthesis. Solid-phase synthesis has a number of pros and cons. The idea of immobilising part of, say, a drug candidate to a solid support on quite a large scale and then coupling a series of ‘second’ parts of the drug target to samples of the initial species can be a very convenient and attractive approach to library synthesis and one which is potentially very efficient and rapid. Alternatively, a diverse series of precursors can be built up on a solid support then cyclised using palladium catalysis. On the downside, it is often rather time-consuming to follow the progress of such syntheses and to manage the inevitable differences in reaction rates between a diverse range of reactants.

Hence, the purpose of this book is to provide experimental guidance across a range of palladium-catalysed coupling reactions of the types which have made such an important impact on organic synthesis in general. These reactions represent a true paradigm shift in the way that organic synthesis is currently viewed and executed.

Palladium-Catalysed Solid-Phase Organic Synthesis

A clear introduction by Carmen Gil (Instituto de Química Médica, Madrid, Spain) delineates the scope of the book. Following a generalised introduction to solid-phase organic synthesis (SPOS), individual representative examples are given to define the Heck, Suzuki, Stille and Sonogashira reactions. Illustrative of this and the style of diagrams in the book are the three diverse routes to indoles developed by Kazuo Yamazaki, Yosuke Nakamura and Yoshinori Kondo.
This is followed by a brief but useful discussion of polymer-bound reagents and catalysts and the cleavage of polymer-bound products using palladium catalysis which, very significantly, can be completely orthogonal to typical acid- or base-catalysed methods.

There follows a collection of five chapters, each giving examples of palladium-catalysed SPOS. The first of these is by Vaibhav Mehta and Erik Van der Eycken (University of Leuven, Belgium) and describes the synthesis of halo-pyrazinones bound to Wang amide resin (Figure 2) and the subsequent homologation of these using Stille and Sonogashira couplings, and finally cleavage from the resin. An alternative strategy combines these steps: pyrazinone derivatives linked to the resin by a sulfur atom undergo coupling with phenylboronic acid at this site with concomitant cleavage from the resin.

A second chapter, by Zheming Ruan et al. (Bristol-Myers Squibb Pharmaceutical Research Institute, Princeton, USA), outlines how to carry out the amidation of polymer-bound allyl esters. Kwangyong Park and Chul-Hee Cho (Chung-Ang University, Seoul, South Korea) then illustrate the coupling of polymer-supported arylsulfonates with aryl Grignard reagents and Wei Zhang (University of Massachusetts, Boston, USA) and Yimin Lu (Fluorous Technologies, Inc, Pittsburgh, USA) show how the methodology can be used to synthesise a series of aminomidazo[1,2-a] pyridines and pyrazines using fluorous sulfonates as leaving groups. A final chapter in this section describes the application of the Sonogashira reaction for resin-to-resin transfer reactions and was written by Judit Tulla-Puche (University of Minnesota, USA; and Institute for Research in Biomedicine, Barcelona, Spain), Rita Majerle and George Barany (University of Minnesota, USA) and Fernando Albericio (Institute for Research in Biomedicine, Barcelona; CIBER-BBN, Networking Centre on Bioengineering, Biomaterials and Nanomedicine, Barcelona; and University of Barcelona, Spain).

**Immobilised Catalysts and Ligands**

The third part of the book is concerned with the elaboration of immobilised catalysts and ligands (see Figure 3 for examples). Specific chapters feature detailed descriptions of the preparations of polymer-supported palladium for Suzuki and Heck reactions by Peter Styring (University of Sheffield, UK) and Maria Dell’Anna, Piero Mastrorilli and Cosimo Nobile (Acque e di Chimica del Politecnico di Bari, Italy). Moumita Roy, Pravin Likhar and M. Lakshmi Kantam (Indian Institute of Chemical Technology, Hyderabad, India)
highlight the synthesis of palladium immobilised on polyaniline for use in Suzuki couplings in water, while Katarzyna Glegola and Eric Framery (Université Claude Bernard Lyon 1, France) detail the preparation of a supported arylidicyclohexylphosphine ligand for use in the same reactions. This section is rounded off by a method for the formation of diaminobutane (DAB) dendrimers as supports for palladium catalysts by Karine Heuzé, Agnés Fougeret, Julietta Lemo and Daniel Rosario-Amorin (Université de Bordeaux, France).

**Palladium-Mediated Multifunctional Cleavage**

The fourth part of the book details methods for the palladium-mediated multifunctional cleavage of products from supporting resins. This is illustrated by the work of François Carreaux (Université de Rennes 1, France), Hervé Deleuze (Université de Bordeaux, Talence, France) and Christelle Pourbaix-L'Ebray (Galapagos SASU, Romainville, France) who provide methods for reacting polymer-bound boronic acids with aryl halides, the boronic acids being present as esters formed with a polymer-based diol. Phenol-based resins are the basis of a method for making bound immobilised enol phosphates which undergo smooth Suzuki couplings to provide a range of cyclic aryl enamides as described by Tom Woods (University of Auckland, New Zealand). Sylvia Vanderheiden, Nicole Jung and Stefan Bräse (Karlsruhe Institute of Technology, Germany) show how resin-bound triazines can be cleaved using Heck methodology while Andrew Cammidge and Zainab Ngaimi (University of East Anglia, Norwich, UK) describe the palladium-mediated cleavage of tetrafluoroaryl sulfonate linkers. Richard Brown and Martin Fisher (University of Southampton, UK) next show how allylic amines can be synthesised by palladium-catalysed displacement of aryl-substituted allylic alcohols from hydroxypropylstereone by primary or secondary amines. A final section from

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**Fig. 3. A selection of polymer-bound palladium catalysts**

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the same group (Lynda Brown, Richard Brown and Martin Fisher) show how similar methodology, when carried out intramolecularly, can be used to obtain 4-methylene pyrrolidines.

**Conclusions**

The general style of the narrative throughout the book includes the use of many useful footnotes and, while the methods have not been checked by an independent group, they appear to be thorough, complete and clear. A substantial amount of characterisation data is often, but not always, included, usually along with a sensible discussion and relevant literature references.

Once a few of these methods have been read and understood, a pattern emerges of how to carry out this type of synthesis. I do think the book is perhaps a little short on breadth, although this may be justified by the repetitive nature of the methods. I would have liked to see a little more discussion on how to follow such reactions and also, in some cases, more justification of why one should use solid state methods in preference to more conventional chemistry. Although many of the methods have obvious applications in library synthesis, a few seem to lack practical usefulness – this could perhaps have been discussed further.

Overall, though, the adoption of an *Organic Syntheses* style is an excellent idea and works very well. Along with other related volumes, this collection serves to demystify polymers-supported methods for palladium-catalysed reactions and provides a very useful collection of clear methods. It will certainly be of interest and use to those new to the field. It should be available to anyone contemplating using such methodology, including research students, academics and industrial chemists.

**References**


“Solid-Phase Organic Syntheses: Solid-Phase Palladium Chemistry”

**The Reviewer**

David W. Knight is a Professor of Synthetic Organic Chemistry at Cardiff University, UK. His research interests include the development of novel synthetic methodologies, especially in the area of heterocyclic ring formation and subsequent applications of these in natural product and other target syntheses. He regularly makes use of palladium-catalysed coupling methods, even to the extent of recently optimising a version of the Suzuki-Miyaura method for styrene synthesis. He has published over 300 original research papers.
The 3rd CARISMA International Conference on Medium and High Temperature Proton Exchange Membrane Fuel Cells

Three approaches to better platinum catalysts at biannual conference

Reviewed by Jens Oluf Jensen*, Lars N. Cleemann and Qingfeng Li
Department of Energy Conversion and Storage, Technical University of Denmark, Kemitorvet 207, DK-2800 Kgs. Lyngby, Denmark
*Email: jojen@dtu.dk

The 3rd CARISMA International Conference was held at the Axelborg venue in Copenhagen, Denmark, from 3rd to 5th September 2012. The CARISMA conference series is specifically devoted to challenges in the development and testing of fuel cell materials and membrane electrode assemblies (MEAs) for proton exchange membrane fuel cells (PEMFCs) for operation at intermediate and high temperatures, i.e., above 100°C, for both transport and stationary applications. The conference series was initiated by the European CARISMA Coordination Action for Research on Intermediate and High Temperature Specialised Membrane Electrode Assemblies, with the first two conferences held in 2008 and 2010 at La Grande Motte near Montpellier, France. The scope of the conference series is scientific and its spirit is to encourage the free exchange and open discussion of recent findings in this important area.

The 2012 event in Copenhagen had around 150 participants from 20 countries in five continents. The majority of the audience was academic or from research organisations, but there was also industrial participation from 20 companies to put the research and development in perspective and to strengthen the link between fundamentals and applications. The oral programme comprised 50 speakers of whom 11 were invited. It was organised in 13 sessions, of which two were devoted to fuel cell catalysts and their supports. Other sessions covered membranes, MEAs, alkaline fuel cells, electrodes, system and stacks, and degradation. In addition there were 63 papers within the same fields presented in two poster sessions. The Book of Abstracts including the programme, selected presentations and posters can be downloaded via the conference homepage (1).

The focus of the present review is on a selection of those presentations dealing with platinum group metal
(pgm)-based fuel cell catalysts. Individual references to the presentations are not given. Instead names and titles are provided and the reader is referred to the Book of Abstracts (2).

**PEMFCs at Elevated Temperature**

The idea of operating PEMFCs at elevated temperature dates back a few decades. One of the general advantages of the PEMFC is its low working temperature, conventionally 60–80°C, but there are a number of benefits if the temperature can be increased to above 100°C. The main drivers have been higher tolerance to fuel impurities, easier heat rejection, reduced challenges with water management and a higher value of the produced heat (3).

Catalysts, electrodes and cell architecture of the high temperature PEMFC (HT-PEMFC) are to a large extent shared with the conventional low temperature PEMFC. The major difference is the proton conducting electrolyte membrane, which must be thermally stable and maintain conductivity at the elevated temperature. A well-recognised breakthrough was made at Case Western Reserve University, USA, with the phosphoric acid doped polybenzimidazole (PBI) membrane (4). Hereafter, this and comparable systems have been explored by an increasing number of groups (5). The community of people involved in HT-PEMFCs is growing and a number of commercial enterprises are aiming at commercialisation of the technology on cell, stack and system levels. Many of the leading companies in this industry such as Elcomax (Germany), EnerFuel (USA), Samsung (Korea), Danish Power Systems (Denmark) and Serenergy (Denmark) were present at the conference.

**Catalysts**

Similarly to low temperature PEMFCs and phosphoric acid fuel cells (PAFCs), Pt and its alloys are exclusively used as catalysts in HT-PEMFCs. High surface area carbon blacks (for example, VULCAN® XC72 or Ketjenblack® carbon blacks) have been widely used as the catalyst support, though it is well known from PAFC research that corrosion rates of these carbon materials are unacceptably high for long term operation. Higher operational temperatures impose even more challenges on the catalysts and electrodes. First of all, the doping acid adsorbs strongly on the catalyst surface and slows down electrode reactions. Moreover the high temperature aggravates the corrosion of the carbon support.

The work presented at this conference reflected the main challenges for PEMFC catalysts, namely cost and durability. The presentations can be grouped in the following categories: Pt catalyst structures and application processes, alternative catalyst supports and Pt alloy catalysts. There were also a number of presentations on non-noble metal catalysts that are not included in the present review.

**Platinum Catalyst Structures and Application Processes**

Gustavo Doubek (University of São Paulo, Brazil) and colleagues, in collaboration with Yale University, USA, presented a supportless approach for the design of stable catalyst architectures for HT-PEMFCs. This was done via Pt nanotubes or metallic glass nanowires. The glasses were thermoplastically moulded and subsequently activated through selective dealloying leading to a roughened Pt rich surface. Electrochemical cycling experiments showed that the activities of the metallic glass catalysts were constant or in some cases improved while the activity of a commercial ETEK Pt/C catalyst decreased under the same conditions. However, further development is needed to reach a practical electrode.

Shangfeng Du *et al.* (University of Birmingham, UK) have prepared single crystal Pt nanowires in the [111] direction for catalysts. Their catalyst layer of unsupported Pt nanowires was only 0.5 μm thick (see Figure 1 (6, 7)). In a potential cycling test against a commercial catalyst with methanol as fuel the nanowire catalyst showed higher stability.

An approach to ultra-low Pt anodes prepared via physical vapour deposition (PVD) was presented by

![Fig. 1. Platinum nanowire thin film catalyst electrode (Courtesy of Shangfeng Du, University of Birmingham, UK)](http://dx.doi.org/10.1595/147106713X667740 • Platinum Metals Rev., 2013, 57, (3)•)
Daniel Gonzalez et al. (Tecnalia, Spain). Catalysts were prepared with Pt loadings between 15 and 150 \( \mu \text{g cm}^{-2} \) and particle sizes down to 10 nm. The preparation of anodes with Pt loadings down to 10 mg per kW was envisioned with this technique.

**Alternative Catalyst Supports**

Alternative catalyst supports for Pt were addressed in a number of presentations. Some of these were modified carbon structures. Maria Daletou et al. (Foundation of Research and Technology-Hellas/Institute of Chemical Engineering Sciences (FORTH/ICE-HT), Greece) prepared pyridine functionalised multiwalled carbon nanotubes (MWCNTs), which showed increased Pt active surface utilisation and stable and robust behaviour at 180ºC under hydrogen lean reformate conditions. The pyridine moieties helped distribute the Pt clusters (see Figure 2). The focus was on anode stability and the catalyst was tested with a phosphoric acid doped membrane (polyethers with pyridine units, Advent Technologies SA, Greece).

Henri Perez (Commissariat à l’énergie atomique et aux énergies alternatives (CEA), France) et al. studied the oxygen reduction reaction (ORR) by organically grafted Pt electrocatalysts, carbon nanotubes and N-doped carbon nanotubes in combination. The grafting of the Pt particles was by organic moieties of different sizes bound by sulfur bridges. Test methods for porous electrodes were presented. Naotoshi Nakashima (Kyushu University, Japan) et al. presented PBI-wrapped carbon nanotubes as Pt catalyst support. Treatment with PBI increased the affinity of the support for Pt nanoparticles without prior oxidation. A similar approach on graphene as support was taken by Anastasia Permyakova et al. (Technical University of Denmark). PBI treatment led to well distributed Pt particles. Amrit Chandan (University of Birmingham, UK) et al. made fuel cell electrodes with Pt catalysts supported on graphene oxide. Apparently, the sheet structure of graphene oxide led to poor gas transport properties, but this was solved by mixing in more spherical particles of carbon black.

Supports not based on carbon were the subject of several presentations. Magnus Thomassen et al. (SINTEF, Norway) used antimony-doped tin oxide (ATO) as a Pt support for the ORR. The Pt particles were about 3.5 nm diameter and well distributed. Accelerated testing showed high stability and minimal loss of electrochemically active surface area. The reference catalyst was from Tanaka. Catalyst supports of titanium dioxide and titanium oxy carbide (TiOC) with Pt applied by a colloid method were prepared by Alessandro Zana (University of Copenhagen, Denmark) et al. The electrochemically active surface area was much larger on TiOC than on TiO\(_2\). Specific activity and mass activity were reported to be comparable to commercially available Pt/C catalysts.

Carbide based supports were presented by Min Yin (Changchun Institute of Applied Chemistry, China) et al. and Antonio Luis Tomas Garcia et al. (Technical University of Denmark). Yin used tungsten carbide (WC) as a support for palladium and palladium-cobalt catalysts for formic acid electrooxidation and Tomas Garcia screened carbides of tantalum, molybdenum, niobium and chromium in hot phosphoric acid.

Finally, Jozsef Speder et al. (University of Copenhagen, Denmark) presented the support independent polyol method for Pt nanoparticle synthesis as a suitable way to decouple the particle synthesis from that of the support. This method allows the variation of process parameters to be avoided when applying the catalyst to the support. New catalyst supports can thus be studied without being affected by the Pt particle preparation.

**Platinum Alloy Catalysts**

There were eight presentations on pgm alloys. Pt-Co alloys were presented by Alexander Schenk et al. (Graz University of Technology, Austria) and Ioannis Spanos and Matthias Arenz (University of Copenhagen, Denmark). The work by Schenk was performed in collaboration with Elcomax, a HT-PEMFC producer. Spanos compared eight different ways to prepare the alloy catalyst particles in terms of composition, active surface area and specific activity. Significant
variations were found. A third Co alloy presented was the Pd-Co by Yin et al. (Changchun Institute of Applied Chemistry, China) mentioned above. Gaurav Gupta et al. (University of Birmingham, UK) made Nafion stabilised Pt-Co alloy particles supported on Vulcan carbon black and graphene oxide. The active area was slightly higher for the graphene oxide based catalysts, but quite low in both cases. Nevertheless, the activity was reported to be high.

Jong Hyun Jang et al. (Korea Institute of Science and Technology, Korea) have studied the ORR activity of ruthenium-selenium on carbon in phosphoric acid. The aim was to find ways to mitigate the adsorption of phosphoric acid anions on the catalysts in HT-PEMFCs. A positive effect on the ORR after alloying of Ru with Se was seen in phosphoric acid. A platinum-gadolinium (Pt5Gd) catalyst was presented by Maria Escudero-Escribano et al. (Technical University of Denmark).

This alloy catalyst showed an activity similar to that previously obtained for platinum-yttrium (Pt3Y) (8), which has been identified as the most active Pt-based polycrystalline alloy for the ORR to date. The Pt5Gd catalyst also showed high stability during potential cycling with an upper potential of either 1.0 V or 1.6 V (9). Anton Vassiliev et al. (Technical University of Denmark) and Brian Benicewicz (University of South Carolina, USA) both presented recent work on direct conversion of dimethyl ether in a HT-PEMFC with Pt-Ru anode catalysts.

Conclusions
The conference strongly supported the trend in fuel cell catalyst research towards higher stability and lower cost. Three main approaches can be identified. First, Pt application processes which result in better distribution of the catalyst surface. This includes non-supported nanostructured Pt. Second, the search for new and more stable supports. These can be nanostructured carbon materials or inorganic materials. Third, the development of Pt alloys and de-alloyed structures. It was evident at the third CARISMA International Conference that steady progress is being made in all three directions to improve fuel cell performance.

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References

The Authors
Jens Oluf Jensen is Associate Professor at the Department of Energy Conversion and Storage at Technical University of Denmark (DTU), where he is presently heading the section on Proton Conductors. He obtained his PhD in the field of metal hydrides and his current research is devoted to HT-PEMFCs and water electrolysis. He chaired the third CARISMA International Conference and is a member of the International Scientific Committee of the conference series.

LarsNilauersenCheemannreceivedhisPhDfromDTUin2009,workingonelectrochemicalpromotioninfuelecels. He is currently a post doctoral researcher at DTU working on durability issues in HT-PEMFCs and was a member of the organising committee of the third CARISMA International Conference.

Qingfeng Li received his PhD in Electrochemistry from Northeastern University of China in 1990. He is now Associate Professor at DTU and is involved in research on materials and technologies for electrochemical conversion and storage of energy. He is a member of the International Scientific Committee of the CARISMA International Conference series.
Crystallographic Properties of Osmium

Assessment of properties from absolute zero to 1300 K

The crystallographic properties of osmium at temperatures from absolute zero to the experimental limit at 1300 K are assessed following a review of the literature published between 1935 and to date. Selected values of the thermal expansion coefficients and measurements of length changes due to thermal expansion have been used to calculate the variation with temperature of the lattice parameters, interatomic distances, atomic and molar volumes and densities. The data is presented in the form of Equations and Tables. The density of osmium at 293.15 K is 22,589 kg m⁻³.

This is the seventh in a series of papers in this Journal on the crystallographic properties of the platinum group metals (pgms), following two papers on platinum (1, 2) and one each on rhodium (3), iridium (4), palladium (5) and ruthenium (6). Like ruthenium, osmium exists in a hexagonal close-packed (hcp) structure (Pearson symbol hP2) up to the melting point estimated by the present author to be 3400 ± 50 K (7) for the pure metal. The actual published values of 3318 ± 30 K by Knapton et al. (8) were for metal of only about 99.7% purity and of 3283 ± 10 K by Douglass and Adams (9) for metal of 99.5% purity.

The thermal expansion is represented by three sets of lattice parameter measurements: those of Owen and Roberts (10, 11) (from 293 K to 873 K) and Schröder et al. (12) (from 289 K to 1287 K) in the high-temperature region and those of Finkel’ et al. (13) (from 79 K to 300 K) in the low-temperature region. The latter measurements were only shown graphically and by incorrect equations with the actual data points as length change values being given by Touloukian et al. (14). As shown below the latter measurements are incompatible with the high-temperature data so the high- and low-temperature data were initially treated separately.

Thermal Expansion
High-Temperature Region

Length change values derived from the lattice parameter measurements of Owen and Roberts (10, 11) and Schröder et al. (12) agree satisfactorily and are represented by Equations (i) and (ii) for the a-axis.
and c-axis respectively. On the basis of the standard deviations of ± 0.004 and ± 0.002 respectively, the selected values were extended to a rounded temperature of 1300 K.

**Low-Temperature Region**

The measurements of Finkel’ et al. (13) as given by Touloukian et al. (14) (Figure 1) were fitted to smooth Equations (iii) and (iv). The incompatibility of these measurements with the high-temperature data can be shown by deriving thermal expansion coefficients from these equations at 293.15 K as $\alpha_a = 5.8 \times 10^{-6} \text{K}^{-1}$ and $\alpha_c = 8.8 \times 10^{-6} \text{K}^{-1}$. These values are notably higher than those calculated from Equations (i) and (ii) and as given in Tables I and II. In spite of the high purity claimed for the metal used in the experiments of Finkel’ et al., the c-axis lattice parameter value of 0.43174 nm at 293.15 K is notably lower than all other values given in Table III suggesting that these measurements must be treated with a certain degree of suspicion. Because it does not appear to be possible to reconcile the high- and low-temperature data the measurements of Finkel’ et al. were rejected.

In order to extrapolate below room temperature the procedure given in Appendix A was adopted. This utilises specific heat values selected by the present author (15) as expanded in Appendix C, leading to Equations (vii) and (viii) which were extrapolated in order to represent thermal expansion from 0 K to 293.15 K. Because there are two axes, the values of low-temperature specific heat as given in Appendix C can be substituted into the Equations, removing the need to develop a relatively large number of complimentary spline-fitted polynomial equations to

![Fig. 1. Differences between the measurements of Finkel’ et al. (13) as given by Touloukian et al. (14) and the selected values](image-url)

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(Continued)
Table I (Continued)

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\( ^a \) \( \alpha_{av} = \) average

\( ^b \) Since all values below 293.15 K are estimated they are given in italics
### Table II
Further Crystallographic Properties of Osmium

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(Continued)
Table II (Continued)

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<th>Temperature, K</th>
<th>Lattice parameter, a, nm</th>
<th>Lattice parameter, c, nm</th>
<th>c/a ratio</th>
<th>Interatomic distance, d1, nm</th>
<th>Atomic volume, 10^{-3} nm^3</th>
<th>Molar volume, 10^{-6} m^3 mol^{-1}</th>
<th>Density, kg m^{-3}</th>
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\[ a = d2 \]

\[ b \] Since all values below 293.15 K are estimated they are given in italics

Table III
Lattice Parameter Values at 293.15 K

<table>
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<tr>
<th>Authors (Year)</th>
<th>Reference</th>
<th>Original temperature, K</th>
<th>Original units</th>
<th>Lattice parameters, a, corrected to 293.15 K, nm</th>
<th>Lattice parameters, c, corrected to 293.15 K, nm</th>
<th>Notes</th>
</tr>
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<td>291</td>
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<td>(a)</td>
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<td>(a)</td>
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<td>(a)</td>
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<td>Finkel’ et al. (1971)</td>
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<td>Å</td>
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<td>0.43174</td>
<td>(a), (b)</td>
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<td>Rudman (1965)</td>
<td>(21)</td>
<td>rt(^b)</td>
<td>Å</td>
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<td>(c)</td>
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<td>Swanson et al. (1955)</td>
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<td>Å</td>
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\[ a \] Selected values for the present paper 0.27342 ± 0.00002 and 0.43199 ± 0.00002

\[ b \] rt = room temperature

Notes to Table III
(a) For information only – not included in the average
(b) Lattice parameter values given by Touloukian et al. (14)
(c) The c-axis value was not included in the average
correspond to Equations (vii) and (viii). On the basis of the expression:

\[
100 \times \frac{\delta L}{L_{293.15 \text{ K (experimental)}} - \delta L}{L_{293.15 \text{ K (calculated)}}}
\]

where \( \delta L_{293.15 \text{ K (experimental)}} \) are the experimental length change values relative to 293.15 K as calculated from Equations (iii) and (iv) and \( \delta L_{293.15 \text{ K (calculated)}} \) are the relative length change values as given in Table I, the measurements of Finkel’ et al. for the \( a \)-axis over the range 80 K to 240 K show a bias of 0.005 to 0.006 lower than the selected values. For the \( c \)-axis at 80 K the difference is 0.029 lower with a trend to agree with the selected values with increasing temperature.

The Lattice Parameter at 293.15 K

The values of the lattice parameters, \( a \) and \( c \), given in Table III represent a combination of those values selected by Donohue (16) and more recent measurements. Values originally given in kX units were converted to nanometres using the 2010 International Council for Science: Committee on Data for Science and Technology (CODATA) Fundamental Constants (17, 18) conversion factor for CuK\( \alpha \_1 \), which is 0.100207697 ± 0.000000028. Values given in angstroms (Å) were converted using the default ratio 0.100207697/1.00202 where the latter value represents the old conversion factor from kX units to Å. Lattice parameter values were corrected to 293.15 K using the values of the thermal expansion coefficient selected in the present review. Density values given in Tables I and II were calculated using the currently accepted atomic weight of 190.23 ± 0.03 (19) and an Avogadro constant \((N\_A)\) of \((6.02214129 ± 0.00000027) \times 10^{23} \text{ mol}^{-1}\) (17, 18). From the lattice parameter values at 293.15 K selected in Table III as \( a = 0.27342 ± 0.00002 \text{ nm} \) and \( c = 0.43199 ± 0.00002 \text{ nm} \), the derived selected density is 22,589 ± 5 kg m\(^{-3}\) and the molar volume is \((8.4214 ± 0.0013) \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}\). The difference from the density value for iridium, 22,562 ± 11 kg m\(^{-3}\) (4), at 27 ± 12 kg m\(^{-3}\) is considered to be the proof that osmium is the densest metal at room temperature and pressure.

In Tables I and II the interatomic distance \( d_1 = (a^2/3 + c^2/4) \) and \( d_2 = a \). The atomic volume is \((\sqrt{3} a^2 c)/4\) and the molar volume is calculated as \( N\_A (\sqrt{3} a^2 c)/3\), equivalent to atomic weight divided by density. Thermal expansion \( \alpha_{avr} = (2 \alpha_a + \alpha_c)/3 \) and length change \( \Delta\text{avr}/\text{avr}_{293.15 \text{ K}} = (2 \delta a/a_{293.15 \text{ K}} + \delta c/c_{293.15 \text{ K}})/3 \) (avr = average).

### High-Temperature Thermal Expansion Equations for Osmium (293.15 K to 1300 K)

\[
\delta a/a_{293.15 \text{ K}} = -1.32379 \times 10^{-3} + 4.46595 \times 10^{-6} T + 1.69909 \times 10^{-10} T^2
\]

\[
\delta c/c_{293.15 \text{ K}} = -1.53749 \times 10^{-3} + 4.64427 \times 10^{-6} T + 2.04826 \times 10^{-9} T^2
\]

### Equations Representing the Thermal Expansion Data of Finkel’ et al. (13) (79 K to 300 K)

\[
\delta a/a_{293.15 \text{ K}} = -1.22081 \times 10^{-3} + 3.13600 \times 10^{-6} T + 1.37670 \times 10^{-9} T^2 + 7.27143 \times 10^{-12} T^3
\]

\[
\delta c/c_{293.15 \text{ K}} = -1.71224 \times 10^{-3} + 3.88446 \times 10^{-6} T + 3.26721 \times 10^{-9} T^2 + 1.16202 \times 10^{-11} T^3
\]

\[
\alpha_a (\text{K}^{-1}) = C_p (-3.14503 \times 10^{-8} + 6.95814 \times 10^{-10} T + 1.86500 \times 10^{-5} / T)
\]

\[
\alpha_c (\text{K}^{-1}) = C_p (-7.35814 \times 10^{-8} + 1.16358 \times 10^{-9} T + 2.62261 \times 10^{-5} / T)
\]

### Low-Temperature Thermal Expansion Equations for Osmium (0 K to 293.15 K)

\[
\alpha_a (\text{K}^{-1}) = C_p (1.58546 \times 10^{-7} + 1.09521 \times 10^{-11} T + 6.88982 \times 10^{-6} / T)
\]

\[
\alpha_c (\text{K}^{-1}) = C_p (1.71988 \times 10^{-7} + 1.41412 \times 10^{-10} T + 6.95413 \times 10^{-6} / T)
\]

### High-Temperature Specific Heat Equation (240 K to 3400 K)

\[
C_p (\text{J mol}^{-1} \text{K}^{-1}) = 26.1938 + 2.64636 \times 10^{-4} T + 1.15788 \times 10^{-6} T^2 + 1.599912 \times 10^{-10} T^3 - 150378/T^2
\]
Summary

The number of measurements of the thermal expansion data for osmium is very limited and although the two high-temperature sets of lattice parameter measurements show satisfactory agreement, their usefulness only applies from room temperature to about 1300 K. The low-temperature lattice parameter measurements appear to be completely incompatible with the high-temperature data and were therefore rejected. Instead a novel approach was used to obtain values in the low-temperature region that agreed with the high-temperature data. Clearly the thermal expansion situation for osmium is unsatisfactory and new measurements are required at both low- and high-temperatures.

Appendix A

Representative Equations for Extrapolation Below 293.15 K

Equations (i) and (ii) are considered to be confined within the experimental limits of 289 K to 1287 K except for an extrapolation to a rounded maximum of 1300 K. Therefore in order to extrapolate beyond these limits a thermodynamic relationship is required such as that proposed by the present author to represent a correlation and interpolation of low-temperature thermal expansion data (1). In this case the relationship was evaluated in the high-temperature region and extrapolated to the low-temperature region. Equations (i) and (ii) were differentiated in order to obtain values of $\alpha^*$, the thermal expansion coefficient relative to 293.15 K, with thermodynamic thermal expansion coefficients calculated as

$$\alpha = \alpha^*(1 + \delta L_{293.15})$$

Selected values of $\alpha$ at 293.15 K and in the range 300 K to 700 K at 50 K intervals were then combined with high-temperature specific heat values calculated from Equation (ix) to derive Equations (vii) and (viii). These were then extrapolated to the low-temperature region using the specific heat values given in Appendix C. The range 293.15 K to 700 K was selected since this gave a satisfactory agreement between the derived experimental and calculated values. Length change values corresponding to Equations (vii) and (viii) were obtained by three-point integration.

Appendix B

The Quality of the Density Value for Osmium at 0 K

In view of the novel approach used to estimate the low-temperature properties and the relatively large extrapolation used, an independent estimate of the density at 0 K would be considered as a test of the quality of the procedure used. Such a value can be obtained from the rejected measurements of Finkel’ et al. (13) as given by Touloukian et al. (14). Equations (iii) and (iv) are considered as being confined within their experimental limits of 80 K to 293.15 K and therefore in order to extrapolate beyond these limits a similar approach to that used in Appendix A was applied. This approach led to Equations (v) and (vi) which are applicable between the limits 80 K to 293.15 K and these were extrapolated to 0 K using the specific heat values given in Appendix C. Three-point integration was used to derive values at 0 K of $10^\circ \delta a/a_{293.15} = -0.107$ and $10^\circ \delta c/c_{293.15} = -0.153$ so that the derived density value is thus 22,672 kg m$^{-3}$ which is surprisingly only 11 kg m$^{-3}$ (0.05%) greater than the selected value. It is possible therefore that the true density could lie between these two values although based on the selected value it is considered that the density at 0 K can best be represented as 22,661 ± 11 kg m$^{-3}$.

Appendix C

Specific Heat Values for Osmium

Because of the large number of spline fitted equations that would be required to conform to both Equations (vii) and (viii), a different approach has been used for the non-cubic metals in that specific heat values are directly applied to these equations. However this would require that the table of low-temperature specific heat values originally given by the present author (15) has to be more comprehensive and the revised table is given as Table IV. In the high-temperature region Equation (ix) represents the specific heat essentially from 240 K to the melting point and is obtained by differentiating the selected enthalpy equation given by the present author (15). Selected values derived from Equation (ix) are given in Table V.
Table IV
Low-Temperature Specific Heat Values for Osmium

<table>
<thead>
<tr>
<th>Temperature, K</th>
<th>Specific heat, J mol⁻¹ K</th>
<th>Temperature, K</th>
<th>Specific heat, J mol⁻¹ K</th>
<th>Temperature, K</th>
<th>Specific heat, J mol⁻¹ K</th>
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Table V
Selected High-temperature Specific Heat Values for Osmium

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<tr>
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<th>Specific heat, J mol⁻¹ K</th>
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References
21 P. S. Rudman, J. Less Common Met., 1965, 9, (1), 77

The Author

John W. Arblaster is interested in the history of science and the evaluation of the thermodynamic and crystallographic properties of the elements. Now retired, he previously worked as a metallurgical chemist in a number of commercial laboratories and was involved in the analysis of a wide range of ferrous and non-ferrous alloys.
Study of Copper/Palladium Nanoclusters Using Acoustic Particle Sizer

The preparation and non-destructive characterisation of bimetallic nanoclusters

In the present study polyvinylpyrrolidone (PVP) stabilised copper/palladium bimetallic nanoclusters were synthesised through chemical routes. The prepared Cu/Pd bimetallic nanoparticles were characterised by ultraviolet-visible (UV-vis) spectroscopy, X-ray diffraction (XRD) and transmission electron microscopy (TEM). The UV-vis absorbance band confirmed the formation of complex metal ions triggered by the complexing agent trisodium citrate. The XRD pattern indicated the formation of bimetallic nanoparticles. The TEM images of the synthesised bimetallic Cu/Pd nanoparticles showed that the size distribution of the particles was in the range 5–15 nm. An acoustic particle sizer was then used to analyse the size distribution. The results obtained by the acoustic particle sizer were consistent with the XRD and TEM analyses. These results demonstrate the potential usefulness of the acoustic particle sizer for quick and easy characterisation of nanoparticles in various catalytic, sensor and fuel cell applications.

1. Introduction
Nanoclusters draw much attention in materials science because they show quite different properties from their bulk counterparts due to the so-called ‘quantum size effect’. Nanoclusters are also important in industrial fields such as catalysis, sensors, electronic devices, magnetic materials and optics (1–6). The preparation of stable nanoclusters with monometallic and bimetallic compositions colloidaly dispersed in solution in the presence of protecting polymers has been reported (4, 7, 8).

Bimetallic alloy systems have been known and exploited for many years in various catalytic reactions such as promising anode catalysts for direct formic acid fuel cells (9). The addition of a second metal in a bimetallic particle provides a way to control the activity and selectivity of the resulting particles for a variety of reactions. By varying the ratio of the two constituents, the distribution of the compounds at the surface may also be altered. In this way it is possible to tune the chemical reactivity at the surface of an alloyed particle (10).
Nanoparticles of palladium and its alloys have been successfully applied to catalyse various chemical reactions. One widely known example is the palladium/tin colloidal solution used as an activator for electroless Cu deposition in printed circuit board manufacture. Electroless Cu deposition (11) has been extensively employed in the plating through hole technique in the printed circuit board industry; Cu interconnection for ultra large-scale integration and circuit fabrication for large-scale liquid crystal display panels.

The preparation of bimetallic systems is not trivial. Often not only alloying but also small particle size and a narrow particle size distribution are required. Various preparation techniques are available, for instance, coimpregnation and coprecipitation. More advanced techniques have also been used, such as impregnation with bimetallic precursors or sequential impregnation in which the second precursor is deposited on the surface of the first precursor. If bimetallic particles are not formed during the impregnation step, one may rely on succeeding steps such as calcination and reduction. The bimetallic nanoparticles formed by these techniques usually exhibit tailed structure and high activity.

Ultrasonic non-destructive evaluation techniques are widely used for the characterisation and analysis of physical and thermal properties of various types of materials. Both theoretical and experimental studies using ultrasonic techniques have been performed in the field of materials science (12, 13).

In this paper we report a novel chemical method for the synthesis of Cu/Pd nanoclusters. The method uses sodium citrate as a complexing agent added to the metal precursors. The obtained Cu/Pd nanoparticles had good stability and were well dispersed with particle sizes in the range 5–15 nm. They were characterised by UV-vis spectroscopy, XRD and TEM. An acoustic particle sizer was also used for particle size distribution analysis, and was found to give accurate results comparable to the XRD and TEM data. The advantage of this technique is that no sample preparation is required for the measurement and the instrument is easy to handle.

2. Experimental
2.1 Sample Preparation
Uniformly dispersed Cu/Pd nanoclusters were prepared following a chemical route. All chemicals were used as received without further purification. A fresh homogeneous solution of palladium nitrate (625 μmol) and copper(II) sulfate pentahydrate (31.25 μmol) was prepared in 50 ml deionised water. Complexing agent trisodium citrate anhydrous (0.147 g) was added to this solution. The protecting agent, 0.5 g PVP, was added to the solution and stirred until dissolved. 0.5 ml of formaldehyde and 2 ml of 1N sodium hydroxide solution were mixed with water and then slowly added to the prepared solution. The stirring was continued for 1.5 h. All reactions were performed at room temperature.

2.2 Characterisation Techniques
The absorption spectrum was recorded using a Perkin Elmer LAMBDA™ 35 double beam UV-vis absorption spectrophotometer at the Laser and Spectroscopy Laboratory, University of Allahabad, India. XRD measurement at room temperature was done using a PANalytical X’Pert PRO Materials Research Diffractometer (MRD) (CuKα radiation, λ = 1.5406 Å) at the Nanotechnology Application Centre, University of Allahabad. The particle size and selected area electron diffraction (SAED) pattern were analysed with a Philips CM12 transmission electron microscope (operating at 200 KeV) at the Sophisticated Test and Instrumentation Centre, IIT Bombay, India.

The particle size distribution analysis of the Cu/Pd nanoclusters was carried out using a Matec Applied Sciences APS-100 acoustic particle sizer. This technique consists of propagating ultrasonic waves at a range of frequencies (1–100 MHz) through the particulate system and accurately measuring the attenuation at each frequency. This attenuation spectrum can be converted to particle size distribution data. The lower limit of the APS-100 is 10 nm, and the upper limit is 1 mm. This measurement was carried out at the Ultrasonics Non-Destructive Evaluations & Nanoscience Laboratory, University of Allahabad.

3. Results and Discussion
To confirm whether the metal complex ions were formed after the addition of trisodium citrate, the complexing behaviour was investigated by UV-vis spectroscopy. Figure 1 depicts a strong absorbance band near 250 nm after the addition of trisodium citrate into the copper sulfate solution. Similarly, the UV-vis spectrum of the Pd precursor mixed with trisodium citrate also exhibited an absorption band near 260 nm. This UV-vis absorbance band confirms the formation of metal ion complexes triggered by the complexing agent trisodium citrate. The absence of absorption peaks above 300 nm in all the samples
confirmed the reduction of Pd(II) ions (14). This type of behaviour was also found by Yonezawa et al. (15).

Figure 2 shows the typical XRD pattern for these Cu/Pd nanoclusters, indicating the formation of bimetallic nanoparticles. The obtained peaks were indexed using Joint Committee on Powder Diffraction Standards (JCPDS) files (now renamed the International Centre for Diffraction Data (ICDD)) (JCPDS File No. 04-0836 and 05-0681). One broad main peak located between 2θ = 40º and 43º was observed in the system (Figure 2).
The broadened shape indicates a reduced grain size, as expected for nanoparticles. The location of the peak, between those characteristic of Pd nanoparticles (2θ = 40°) and Cu nanoparticles (2θ = 43°), corresponding to (111) planes, represents the formation of a disordered solid solution between Pd and Cu.

Figure 2 reveals small peaks at 2θ = 31.8° and 45.8° in the system with complexing agent. Comparison of the peaks at 2θ = 31.8° and 45.8° with those found in the JCPDS (No. 46-1211, palladium(II) oxide (PdO): 2θ = 31.7° (200) and 2θ = 45.6° (220)) suggests the existence of a cubic PdO structure. The full width at half maximum of this peak is much smaller than that of the characteristic peak of Cu/Pd nanoparticles, indicating PdO structures with an enlarged crystal size. Since the XRD samples were prepared with all particles in solution (including the large precipitated particles initially formed and the precipitates after centrifugation with the addition of acetone), the PdO peak may have arisen from the large particles initially formed, which were not observed in the TEM. Without complexing agent there was a peak at 34° which was due to the formation of copper(II) hydroxide (Cu(OH)₂). However, Figure 2 reveals no Cu(OH)₂ crystalline structures, implying that the complexing agent may have prevented the formation of Cu(OH)₂ particles, which accounted for the substantially higher stability of Cu/Pd nanoparticles synthesised with the complexing agent. The obtained peaks are well identified by the reference values given in JCPDS (No.48-1551) (11). The crystallite size was also calculated by Debye Scherrer’s formula (16) as 14 nm.

TEM was used to determine the size distribution and morphology of the synthesised nanoparticles and SAED was used to confirm the crystallinity of the samples. The TEM images are shown in Figure 3. The TEM images show that the size distribution of the synthesised bimetallic Cu/Pd nanoparticles is in the range 5–15 nm (Figure 3(a)). It can be observed from this figure that most of the particles are >10 nm, with only a few at ~5 nm. The nanoparticles are well dispersed. The SAED pattern shown in Figure 3(b) corresponds to a crystalline structure – a result consistent with the XRD results.

The acoustic particle sizer was then used to measure the particle size distribution. The results are shown in Figure 4. The lower limit of this technique is 10 nm, which leads to the sharp line seen at this value on the particle size distribution graph. This analysis confirms that the Cu/Pd nanoclusters are in the range 10–15 nm.

APS can be used to perform many repetitive measurements for optimal signal averaging in order to maximise resolution, accuracy and reproducibility. Acoustic attenuation must be measured at multiple spacing for two reasons: (a) high frequency measurements have higher attenuation so they
must be made over short paths, whereas at low frequencies, longer path lengths are required due to much lower attenuations; and (b) the attenuation versus frequency curve must be built with as many data points as possible in order to produce reliable particle size distribution data. The attenuation level, as well as the shape of the acoustic attenuation curve, is related to the particle size distribution. The particle size distributions are calculated from the acoustic attenuation data using software based on Epstein and Carhart theory (17).

4. Conclusions
Cu/Pd nanoclusters have been synthesised successfully in aqueous solution under ambient conditions with the addition of a complexing agent, trisodium citrate. These Cu/Pd nanoparticles were stable in suspension. The TEM image and SAED pattern showed a uniform dispersion of crystalline Cu/Pd nanoparticles. Particle size distribution analysis by the acoustic particle sizer was consistent with the TEM analysis and showed particle sizes in the range 10–15 nm. Hence this technique can be considered a very useful and efficient tool for the non-destructive characterisation of bimetallic nanoclusters. It is hoped that this work will prompt future study and characterisation of bimetallic nanoparticles containing platinum group metals for a variety of applications.

Acknowledgements
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References
1 L. Dai and S. Zou, J. Power Sources, 2011, 196, (22), 9369
11 S. H. Y. Lo, Y.-Y. Wang and C.-C. Wan, J. Colloid Interface Sci., 2007, 310, (1), 190

The Authors

Giridhar Mishra is Assistant Professor at the Department of Applied Physics, Amity School of Engineering and Technology, New Delhi, India. He obtained his PhD in Physics from the University of Allahabad, India. He has worked as a Research Fellow in a project sponsored by the Department of Science and Technology, New Delhi, in the field of materials science. His current research interests are focused on the study of ultrasonic and thermal properties of nanofluids, nanomaterials and other materials.

Dr Devraj Singh is Assistant Professor and Head of the Department of Applied Physics at Amity School of Engineering and Technology, New Delhi. His research interests are in the ultrasonic non-destructive characterisation of condensed materials. Presently, he is working on ultrasonic studies of rare earth materials for engineering applications.

Pramod Kumar Yadava is an Assistant Professor in the Department of Applied Physics, Amity School of Engineering and Technology, New Delhi. He obtained his PhD in Ultrasonics from the University of Allahabad. His research interests are in the ultrasonic non-destructive characterisation of condensed materials and nanofluids.

Satyendra Kumar Verma obtained his MSc in Physics with Condensed Matter and PhD in Physics from the University of Allahabad. He has now been selected as a Physics lecturer in the Technical Education Department (TED) Uttar Pradesh, India. His research interests are in the field of ultrasonic non-destructive characterisation of nanomaterials.

Professor Dr Raja Ram Yadav is presently Professor of Physics at the Department of Physics, University of Allahabad. His research interests are in the non-destructive ultrasonic and thermal characterisation of nanomaterials, lyotropic liquid crystalline materials, intermetallics and semiconductors; the development of nanomaterials for biomedical applications; and theoretical calculations of nonlinear elastic and ultrasonic properties of crystalline materials. He was awarded the prestigious INSA Teachers Award of the Indian National Science Academy for the year 2012.
CAPOC 9: 9th International Congress on Catalysis and Automotive Pollution Control

Progress in emissions control for diesel and gasoline vehicles

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Reviewed by Martyn V. Twigg*

Caxton, Cambridge CB23 3PQ, UK
*Correspondence may be sent via Platinum Metals Review: editorpmr@matthey.com

Introduction
The topical conference series Catalysis and Automotive Pollution Control, generally known by the acronym ‘CAPOC’, has taken place periodically at the Université Libre de Bruxelles, Belgium, since the first one in 1986. The late Professor Alfred (Freddy) Frennet was central in establishing these conferences and for many years he was their guiding force. The first four Proceedings were published as volumes in the ‘Studies in Surface Science and Catalysis’ book series (forever associated with Professor Bernard Delmon of the Université Catholique de Louvain, Belgium) (1–4). Later as the organisational helm was increasingly taken over by Professor Norbert Kruse, who is now the Chairman, they were published as special issues of the journal Topics in Catalysis (5–9).

Since the first conference there have been many, sometimes dramatic, developments in the catalytic control of emissions from both spark ignition (mainly gasoline) and compression ignition (mainly diesel) internal combustion engines. Platinum group metal (pgm) catalysts have been central to many of these advances and they have been discussed by leading workers at these conferences so the Proceedings provide a valuable and easily accessed record of how the increasingly stringent emissions requirements have been met. A key feature of the conferences has been the wide range of attendees, with a high proportion from light-duty (cars and vans) and heavy-duty vehicle manufacturers as well as catalyst companies, in addition to leading academics from around the world. Indeed the main industrial companies have been instrumental in financially supporting the conferences from the start and have also been represented on the Scientific Advisory Boards that select the content of each conference. Another notable feature of the conferences has been the open discussion periods at the end of each session which allow time for clarification and detailed
discussion about particular points. These also provide an opportunity for industrialists to give updates on what is actually happening in ‘the real world’.

The most recent conference, the ninth in the series, took place at the Université Libre de Bruxelles from 29th to 31st August 2012 and was a great success, attracting 240 attendees from 36 different countries and involving almost 30 oral presentations and more than 130 posters. The main current challenges involve control of fine particulate matter (PM) from diesel engines and soon some gasoline engines as well, and the reduction of nitrogen oxides (NOx) (nitric oxide (NO) and nitrogen dioxide (NO2)) under lean conditions. Development and the present understanding of the basic science in these areas were covered during the conference as were fuel alternatives and innovative technologies. The technical lecture programme is reviewed in the order of the final published programme.

**Introductory Session**

The first session had three presentations that provided a technical context for the conference. They covered legislation, particulate and NOx control technologies. Nikolaus Steininger (European Commission, Brussels, Belgium) reviewed the successes and failures of European emissions legislation. There are major concerns that many locations in Europe have ambient air quality that is not improving in line with the increasingly stringent emissions standards. It appears that while gasoline cars follow standards in type approval during on road driving, this may not be the case with the increasing number of diesel cars. For instance, the actual emissions for Euro 3 diesel cars on the road may be as much as four or five times higher than they are in the test cycle standards (emissions factors). As a result, and in spite of tightening legislation, there has been relatively little actual change in the total NOx emissions over the last fifteen years or so. Thus the main problem with real driving emissions (RDE) is high NOx (and NO2) emissions outside of the test cycle conditions.

With the introduction of ammonia selective catalytic reduction (SCR) NOx control systems and especially with Euro 6 certified vehicles that can provide good NOx control outside of cycle conditions it may be expected that the overall ambient NOx levels could improve as Euro 6 compliant vehicles are introduced. The European Commission will monitor the situation, and consideration will be given to amending test procedures, using portable emissions measuring systems (PEMS) and the use of ‘not to exceed limits’ should this become necessary. The work of the Real-Driving Emissions–Light-Duty Vehicles working group and especially the use of PEMS in random test cycles was discussed and some legal difficulties in adopting such procedures highlighted, as were the concerns associated with NOx emission, though as NOx emissions in test cycle and RDE tend towards very low levels so will the NO2 emissions.

The amount of research on ultra-fine PM emissions and particularly particle number (PN) measurements of exhaust gas from internal combustion engines has been growing tremendously and it is generally considered that these tiny particles represent a serious health hazard. The Euro 5 PM standard (2 mg km–1) forced fitment of diesel particulate filters (DPFs) on diesel cars in 2009, and with the introduction of Euro 6 legislation in 2014 and 2017 there will also be PN standards. There was discussion about the use of the Particle Measurement Programme (PMP) test procedure, originally developed for use with diesel engines fitted with filters, and its use in the measurement of exhaust PN from gasoline engines that do not have filters. Here there may be huge numbers of solid ultra-fine particles including material derived from lubrication oil and fuel additives that are below the 23 nm cut-off of the PMP procedure, see for example (10). Thus it may be appropriate to use an improved PN measurement procedure, and this is an active area of research. Some form of filtration will have to be used on direct injection (DI) gasoline engines, and it is yet to be confirmed how efficient they will be if the filters remain effectively clean. Special filters may have to be developed for these applications.

The second presentation, by Claus Vögt (NGK Insulators Ltd, Japan), continued the theme of actual ambient pollutant levels being relatively high in many parts of Europe, with the focus being on PM. Ceramic wall-flow filters have been increasingly fitted to European diesel cars since their first introduction on some 2000 model year cars, and to all Euro 5 compliant diesel cars since 2009. At first silicon carbide filters were used and more recently aluminium titanate ones have been introduced. Initially bare filters were used with an inorganic fuel additive (11) that facilitates soot combustion during periodic high-temperature filter regenerations. Then a few years later smaller catalysed filters incorporating platinum and/or palladium catalysts were introduced that did not require a fuel additive and the associated storage tank, dosing pump etc. In some instances not even an additional
oxidation catalyst is needed (12). These cost effective filter units are relatively small since they do not have to accommodate additional ‘inorganic ash’ from a fuel additive (Figure 1).

Now filters incorporating a NOx control functionality are required and this puts an increased emphasis on producing higher porosity filters of sufficient strength that are able to accept within the wall structure an adequate amount of NOx control catalyst and still have a low backpressure and high filtration efficiency. Backpressure affects turbocharger efficiency and the all important fuel economy which must be optimised to meet legislated carbon dioxide emissions standards. New filter designs are able to meet these demanding requirements and some details about them were presented. An example was given of a new filter loaded with a Johnson Matthey SCR catalyst which had 20% lower backpressure than a similarly loaded traditional filter.

As noted earlier, it has become clear that in future filters will be required not only for diesel cars but also for some gasoline cars. The first gasoline engines to have them will be DI downsized engines developed for low carbon dioxide emissions where DI and turbocharging enables power to be available for events such as harsh accelerations when required. It was suggested that these engines will be the predominant Euro 6 technologies, and their filters are referred to as gasoline particulate filters (GPFs) by analogy with the well established DPFs. Filter manufacturers are now providing advanced designs for these applications.

The final presentation in the opening session was a review by the present reviewer on control of NOx emissions from automotive engines. The approach was chronological, starting with the rich NOx reduction catalysts used on mid-1970s gasoline engines, the introduction of three-way catalysts (TWCs) for stoichiometric engines in the early 1980s, and more recently the most challenging NOx control in lean exhausts, first by NOx-trapping catalysts containing platinum and rhodium on lean-burn gasoline engines in the 1990s and now by NOx-trapping and low-temperature ammonia SCR technologies on lower temperature diesel engine cars. The earlier introduction of SCR NOx control on the higher temperature heavy-duty diesel engines was easier because existing vanadium-based SCR catalysts could be used. For use on diesel cars that can have remarkably low-temperature exhaust gas, reflecting their exceptional fuel economy (especially compared to their gasoline counterparts), special new low-temperature zeolite-based ammonia SCR catalysts had to be developed.

Ammonia is important in several areas of NOx control, and this is because it can react with NOx to form ammonium nitrite which for more than 150 years has been known to readily decompose to nitrogen and water, Equation (i). It was one of the reactions used to produce ‘chemical nitrogen’ during the discovery of argon in air some hundred and twenty years ago (13). Indeed, even the so called ‘fast catalytic SCR’ reactions, first reported in the 1980s (14, 15) involving equimolar amounts of NO and NO2 that are so much a part of modern low-temperature SCR NOx control technology, have long been known as an aqueous solution reaction forming ammonium nitrite. And it has been reported, see for example (16), as a route for producing ammonium nitrite, perhaps according to Equation (ii).

\[
\text{NH}_4\text{NO}_2 \rightarrow N_2 + 2\text{H}_2\text{O} \quad \text{(i)}
\]

\[
2\text{NH}_3 + \text{NO} + \text{NO}_2 + \text{H}_2\text{O} \rightarrow 2\text{NH}_4\text{NO}_2 \quad \text{(ii)}
\]

Interestingly ammonia can be formed during the reductive regeneration of NOx-trapping catalysts, and a downstream SCR catalyst can utilise this to convert additional NOx to nitrogen so improving the overall NOx conversion. Already this system has been used on series production diesel cars (17).

Today, pgm-based TWCs are outstandingly efficient at controlling all three pollutants found in gasoline exhaust: carbon monoxide (CO), hydrocarbons (HCs) and NOx, as illustrated in Equations (iii), (iv) and (v). One possibility is that NOx is reduced directly to nitrogen because a clean rhodium surface dissociatively adsorbs NO to adsorbed oxygen and nitrogen atoms. The weakly adsorbed nitrogen atoms combine and are released as dinitrogen into the gas.

Fig. 1. A compact catalysed particulate matter filter mounted directly on the turbocharger of a small diesel engine (Image copyright Martyn V. Twigg)
phase, ultimately leaving a strongly bound oxygenated surface that has to be reductively cleaned for the NO dissociation process to continue.

\[
\text{CO} + \text{O}_2 \rightarrow \text{CO}_2 \quad \text{(iii)}
\]

\[
\text{C}_n\text{H}_m + (n+m/4)\text{O}_2 \rightarrow n\text{CO}_2 + m/2\text{H}_2\text{O} \quad \text{(iv)}
\]

\[
2\text{NO} + 2\text{CO} \rightarrow \text{N}_2 + 2\text{CO}_2 \quad \text{(v)}
\]

It was speculated that an alternative process might also take place. With exhaust gas composition oscillating around the stoichiometric point the catalyst surface might be sufficiently rich (i.e. low in oxygen) for short periods of time for surface-bound ammonia to be formed, and there would then be the possibility for NOx to be reduced to nitrogen during the lean phase via ammonia nitrite, as in Equation (i). Although this suggestion is very speculative, ammonia can be formed from NOx over pgm catalysts, and in fact this often took place in early two stage three-way systems with rich NOx control. Ammonia that was formed over the rhodium-containing NOx reduction catalyst was oxidised back to NOx over the downstream pgm oxidation catalyst thus lowering the overall NOx conversion. Such speculation is based on insight now available about the mechanisms of various NOx control reactions (see below).

**NOx Control Technologies**

There were six presentations in the initial session concerned with NOx control, and the first entitled ‘DeNOx Performance and Reaction Mechanism of the DiAir System’ was given by Mikio Inoue (Toyota Motor Corp, Japan). This system uses a NOx-trapping type catalyst with continuous rapid short pulse injections of HCs into the exhaust gas for regeneration. Since this does not depend on the storage of bulk NOx derived compounds their thermal stability is unimportant. Only surface species are involved, so operation at higher temperatures than with conventional NOx-trapping is possible. This paper discussed some of the surface reaction mechanisms from the standpoint of the contribution of HC and the reaction intermediates. Good NOx conversion at 800°C has been demonstrated, performance reminiscent of TWC behaviour, and again the possibility of surface ammonia should not be overlooked. However, direct NOx dissociation is likely with the short rich pulses keeping the surface free of adsorbed oxygen atoms, in keeping with investigations made several years ago by Nakatsuji and co-workers when this kind of behaviour was first reported in detail (18–20).

This was followed by a joint contribution by Todd Toops (Oak Ridge National Laboratory, USA) and colleagues from Chalmers University of Technology, Sweden, and Cummins Inc, USA, in which the reactions taking place along the channels of a monolithic SCR catalyst were monitored by taking gas samples at different positions through fine capillary tubes. The ammonia adsorption equilibrium is faster than the SCR reactions, and with increasing temperature the SCR reaction zone, as might be expected, moves closer to the front of the monolith, and rate determining steps may change.

Over recent years there has been a lot of academic interest in the activation of silver/alumina catalyst in HC SCR reactions, and a paper by Sebastian Fogel (Haldor Topsøe A/S, Denmark, and the Technical University of Denmark) and colleagues reported the use of such a silver catalyst in combination with an iron zeolite in a hydrogen-assisted ammonia SCR system. The best combination was to have the silver catalyst upstream of the iron catalyst, and NOx formed by oxidation seems to play a role. Of course it would have been interesting to have available the comparison with an upstream platinum oxidation catalyst followed by ammonia injection before the iron SCR catalyst. Robbie Burch’s group (Queen’s University Belfast, UK) also working with silver catalysts reported that very high HC SCR activity could be obtained at low temperature if the catalyst was prepared by dry ball milling rather than the conventional wet impregnation method. The calcination temperature (650°C) was critical and the final ball milled catalyst had a high silver dispersion. The underlying reasons for the improvement are not completely clear, but a combination of ball milling and the correct calcination temperature was needed to get silver clusters having the right size for optimum NOx conversion.

A paper from Hannes Kannisto and Hänna Harelind (Chalmers University of Technology, Sweden) highlighted the practical difficulties associated with marine SCR applications. One of the important factors is the incredibly high sulfur content of most marine diesel fuels that could be described as organic sulfur compounds! There then followed an outstanding contribution presented by Luca Lietti (Politecnico di Milano, Italy) on a study using labelled 15NO with a model platinum barium-based NOx storing catalyst that provided a real insight into the complex chemistry involved in NOx storage and reductive regeneration.
Unlabelled NOx was stored in the catalyst at 150°C and when this was exposed to $^{15}$NO there was facile exchange with the stored nitrite and nitrate with the former being easier. This process was inhibited by CO suggesting that platinum is involved in the exchange process. This was confirmed by an experiment with a non-reacting platinum-free formulation. The hydrogen reduction of stored nitrite and nitrate paralleled the NO exchange behaviour indicating that platinum probably has a role. Reaction of unlabelled NH$_3$ with stored labelled $^{15}$NOx produced $^{14}$N$^{15}$N in agreement with the reaction involving surface NH$_4$NO$_2$ species, and nitrous oxide (N$_2$O) was formed when NO was present at high concentrations. One of the remarkable features of this work was that it demonstrated the ease with which surface NOx derived species interconvert, and this was later taken up in a subsequent paper from the same institute (see below).

### NOx Control Mechanisms

The next session had five presentations and continued the theme of the mechanisms of NOx control processes. The first paper was from Mike Harold (University of Houston, USA) and concerned dual layer catalysts in which the lower layer was a NOx storing formulation and the upper layer a copper- or iron-based zeolite ammonia SCR catalyst. The concept can work well but the two functions must be separated rather than just mixed together, and the addition of ceria has several benefits.

The next paper was from Enrico Troconi (Politecnico di Milano, Italy), and examined the importance of the oxidation of NO to NO$_2$ in ammonia SCR reactions. It had been proposed that this was the rate limiting step in the NO SCR reaction. It was shown that over copper zeolite NO oxidation is slow, while the activity for the standard SCR reaction is high; over an iron zeolite catalyst there is more NO oxidation although this is still slower than the NO SCR reaction. Moreover water inhibits NO oxidation but not the SCR reaction. Based on the present results and much published information a redox mechanism was proposed in which Fe(III) nitrite decomposes to Fe(II) liberating NO$_2$, and the resulting Fe(II) is then oxidised back to Fe(III), by oxygen. This is illustrated by Equations (vi)–(ix). Thus NO oxidation and the standard SCR reaction share the same initial reaction, which is not the SCR rate determining step but perhaps a rapidly formed pre-equilibrium. The rate determining step is probably the re-oxidation of iron(II) to iron(III) (Equation (ix)).

\[
\begin{align*}
\text{Fe(III)}\text{OH} + \text{NO} &\rightarrow \text{Fe(II)} + \text{HNO}_2 \quad \text{(vi)} \\
\text{Fe(III)}\text{OH} + \text{HNO}_2 &\rightarrow \text{Fe(III)ONO} + \text{H}_2\text{O} \quad \text{(vii)} \\
\text{Fe(III)ONO} &\rightarrow \text{Fe(II)} + \text{NO}_2 \quad \text{(viii)} \\
2\text{Fe(II)} + \text{H}_2\text{O} + \frac{1}{2}\text{O}_2 &\rightarrow 2\text{Fe(III)OH} \quad \text{(ix)}
\end{align*}
\]

HCs are known to inhibit NO oxidation over platinum catalyst, and a presentation by William Epling (University of Waterloo, Canada) in collaboration with the University of Houston, USA, provided information to understand more about this phenomenon. The reactivity of surface nitrates in the oxidation of propene was examined, and diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) experiments showed that surface nitrate was reduced to linear nitrite by propene. Gas phase NO$_2$ also reacted with a series of HCs in the reactivity order: dodecane > xylene > propene. Rather surprisingly it was found that over a platinum catalyst propene was oxidised faster by oxygen than by NO$_2$ although the comparison involved experiments with 6.5% oxygen and with 0.1% NO$_2$. Perhaps the HC inhibition of NO oxidation can be interpreted by the fact that any NO$_2$ formed will be consumed oxidising HC and therefore only when there is no reactive HC present will NO$_2$ be observed.

If there is insufficient reductant available to fully reduce NOx to N$_2$ or the temperature is too low for this to take place N$_2$O may form, and this is undesirable because it is a very powerful greenhouse gas having more than three hundred times the global warming potential of carbon dioxide (by weight over a hundred years). A paper from Šárka Bártová (Institute of Technology, Prague, Czech Republic) and colleagues from Oak Ridge National Laboratory, USA, discussed a model for N$_2$O formation during regeneration of a NOx storage catalyst with hydrogen, CO and HCs. Two kinds of N$_2$O emission were identified. The primary emission takes place before the reductant has broken through the catalyst, and a secondary emission sometimes takes place when conditions return to lean and surface intermediates are oxidised to N$_2$O. Reforming reactions producing hydrogen and CO can decrease the amount of N$_2$O released and increase overall NOx conversion.

The last paper in this session was a joint French contribution given by Arnaud Frobert (IFP Energies nouvelles, France) with PSA Peugeot Citroën, France, on the coupling of the rather unusual ethanol SCR
with ammonia SCR derived from the first stage that had upstream injection of ethanol over a silver on alumina catalyst. The ethanol is oxidised to acetaldehyde by oxygen and NO₂ at quite low temperatures, other products include hydrogen cyanide. The second catalyst was a traditional iron zeolite SCR catalyst. However, this added little to the overall NOX conversion and had essentially no effect on the hydrogen cyanide content which was found to be particularly detrimental to the NOx sensor. So for several reasons in the present form this is not the basis of a practical NOx control system.

Sorption Mechanisms and Ageing

The first paper in this section was by Ines Lezcano-Gonzalez (Materials innovation institute (M2i), Delft, The Netherlands, and Utrecht University, The Netherlands), and resulted from a collaboration between these two institutions plus Ghent University, Belgium. It examined the protonation of zeolites and their copper exchanged counterparts using Fourier transform infrared (FTIR) spectroscopy, temperature programmed desorption (TPD) and theoretical calculations. FTIR and TPD experiments showed that there are three types of surface ammonia species: those coordinated to copper centres, those coordinated to extra framework aluminium atoms, and ammonium cations at Brønsted sites. There was reasonable agreement between calculated and observed infrared absorptions confirming their assignments, and it was concluded that isolated coordinated ammonia at copper sites reacted quickly compared to ammonium ions at Brønsted sites. However, when coordination sites are present the ammonium cations react more quickly, and it is thought that this is where ammonia is stored.

Twenty years or so ago there were in-field problems with some TWCs that were prone to deactivation due to phosphorous poisoning derived from lubrication oil, and this was shown to be due to cerium phosphate formation and hence a decreased oxygen storage capacity (OSC). The next paper, from Angelos Efstathiou (University of Cyprus), returned to this topic. Phosphorous was impregnated into mixed oxides (30 mol%, 50 mol% and 70 mol% cerium) as ammonium dihydrogen phosphate ((NH₄)H₂PO₄) and calcined, which is rather different to what happens in an exhaust, but it enabled interesting information to be obtained. X-Ray photoelectron spectroscopy (XPS) showed a major decrease in surface percentage of Ce(IV) that in itself goes a long way to explain the reduced activity of phosphate poisoned catalyst, and scanning electron microscopy/energy-dispersive X-ray spectroscopy (SEM/EDAX) showed a general depletion of cerium upon phosphation. ¹⁸O exchange experiments showed that for the original mixed oxides the amount of exchangeable oxygen at a particular temperature changed little with composition, and as expected it increased with temperature. For the ‘poisoned’ samples at a particular temperature composition again had little effect, but there was less than half the amount of exchangeable oxygen. All of these data refer to the mixed oxides themselves, and this reviewer believes that a similar study is needed with materials containing pgms, especially rhodium and palladium.

The oxidation of methane in exhaust gas is becoming increasingly important, and this is usually best done over a palladium-based catalyst. The nobility of palladium is such that it exists under reaction conditions either as oxide or metal depending on the catalyst formulation and the operating temperature, and it is usually considered that the oxide form is more active than is the metallic form. A density functional theory (DTF) and surface X-ray diffraction study from Henrik Grönbeck (Chalmers University of Technology, Sweden) and colleagues at Lund University, Sweden, focused on the dissociation of methane on the surface and concluded that PdO(101) and Pd metal have the highest activities, although there is no immediately obvious way in which this helps with the practical problem of lowering the temperature needed for methane oxidation.

The last paper in this session was from Davide Ferri et al. (Swiss Federal Laboratories for Materials Science and Technology (EMPA), Dübendorf, Switzerland) with colleagues from the European Synchrotron Radiation Facility, Grenoble, France, on modulation excitation spectroscopy (MES), an exciting new dynamic X-ray technique enabled by bright cyclotron radiation, that permits detailed monitoring of structural changes in catalysts such as palladium or rhodium on Al₂O₃ or ceria/zirconia mixed oxide. The element specific results are profound and provide time resolved information about parameters such as oxidation state, coordination environments, crystallinity and phase composition under conditions close to real world operating conditions, for instance of TWCs. The results presented included alternate exposure of palladium and rhodium to CO and NOx. Rhodium remained metallic under CO but was partially oxidised by NO. In contrast when palladium was exposed to CO
Similarly the sharp resonance of an empty soot filter alternative on-board diagnostic (OBD) measurement, fully reduced, implying that this could be used as an 0.5 GHz and dramatically broadened when it was oxidised TWC were shifted down about catalyst properties. For instance, the sharp resonance of a fully oxidised TWC were shifted down about 0.5 GHz and dramatically broadened when it was oxidised. Clearly these new techniques will provide tremendous insight into pgm-catalysed reactions taking place in automotive pollution control systems in the future.

**Fuel Alternatives and Innovation Technologies**

In this, the penultimate session, there were three papers of general interest. The first was on the microwave monitoring of the condition of automotive catalysts from Ralf Moos (University of Bayreuth, Germany) and colleagues from Umicore AG & Co KG, Germany. Using a simple robust antenna system it is fairly easy to expose monolith catalysts and filters to microwave radiation and measure the resonance absorption parameters that may be present. This has been done for a variety of catalysts and it has been shown that the resonance frequencies and ‘Q’ linked half-height absorption widths can be related to meaningful catalyst properties. For instance, the sharp resonance of a fully oxidised TWC were shifted down about 0.5 GHz and dramatically broadened when it was fully reduced, implying that this could be used as an alternative on-board diagnostic (OBD) measurement. Similarly the sharp resonance of an empty soot filter gradually shifted down frequency and broadened as it was loaded with soot, and the amount of ammonia on an SCR catalyst could be monitored. However, the NOx-trapping catalysts do not appear to be amenable to this technique. Already one instrument is commercially available (from General Electric, USA) and it will be interesting to see if this gains acceptance in the industry.

The second paper was from Akira Obuchi (National Institute of Advanced Industrial Science and Technology (AIST), Japan), and was about the use of a heat exchanger to enhance the operating temperature associated with exothermic reactions. Exhaust gas was heated by effluent evolved from sequential catalytic oxidation, particulate filtration and ammonia SCR after urea solution injection. The design was shown to work well over the Japanese 10-15 mode test driving cycle, providing SCR operating temperatures in the region of 300°C that gave 98% NOx conversion. The potentially serious problem associated with the development of very high temperatures during filter regenerations was not discussed.

The last paper in this section was from Djamela Bounechada (Politecnico di Milano, Italy) and Ecocat Oy, Finland, and was concerned with the performance of a rhodium/palladium TWC containing an oxygen storage component for natural gas exhaust, and the effects of lambda oscillations on methane conversion. At 450°C it was shown that during symmetrical lambda oscillations the methane conversion was markedly higher during the rich phases than during the lean phases, and that there was a narrow region where both methane and NOx conversions were significantly enhanced. These changes were attributed to the oxidation state of the palladium – metal or oxide. At higher temperatures the palladium was not reoxidised to palladium oxide, in keeping with the known thermodynamics of palladium oxide prevailing under such conditions. Lambda scan experiments showed that the effects of increasing the cycle period depended on the available OSC present, and that during long cycle periods there was insufficient OSC to complete the oxidations of HCs and CO to water and carbon dioxide. Hydrogen was then formed from carbon monoxide via the water gas shift reaction, Equation (x).

\[
\text{CO} + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{CO}_2 \quad (x)
\]

Increasing the water content increased the amount of hydrogen formed under rich conditions, and inhibited methane conversion under lean conditions. The presence of NOx inhibited methane conversion under lean conditions. Interestingly these experimental results might indicate that a partially reduced palladium oxide surface is a very active phase, as suggested by some surface science studies.

**Particulate Matter Control**

The final session was on particulate control. The first of six papers was from Alexander Yu. Stakheev (Zelinsky Institute of Organic Chemistry, Moscow, Russia) and colleagues from Haldor Topsøe A/S, Denmark, and was concerned with integration of soot and SCR NOx removal in a DPF. An iron zeolite SCR catalyst was combined in various ways and locations with a ceria/zirconia mixed oxide to mediate soot combustion. To optimise the carbon oxidation and SCR functions a carbon black was used as a soot substitute in loose contact with ceria/zirconia mixed oxide powder. Thermogravimetric analysis (TGA) experiments showed that this mixture had a significantly lower oxidation temperature (about 420°C) than the same carbon
black mixed with inert alumina (about 600°C). When iron zeolite SCR catalyst was added to the mixture the effect was slightly reduced (488°C). Synergistic effects were found and were attributed to NO oxidation to NO₂ over the ceria/zirconia which optimised the SCR process via the fast SCR reaction, Equation (x). This probably also facilitated low-temperature soot oxidation, as in a Continuously Regenerating Trap (CRT®), Equation (xii), although the effect over platinum is more pronounced. Addition of a small amount of manganese to the ceria/zirconia mixed oxide enhanced the NO oxidation capability, and this parameter was optimised as was the positioning of the oxidation catalyst so as to minimise the detrimental oxidation of ammonia to NOx, Equation (xiii). Base metal systems of this type are usually sensitive to sulfur poisoning but no mention of such sensitivities was mentioned.

\[
\text{NO} + \text{NO}_2 + 2\text{NH}_3 \rightarrow 2\text{N}_2 + 3\text{H}_2\text{O} \quad \text{(xi)}
\]

\[
\text{CH(soot)} + \text{NO}_2 \rightarrow \text{CO}_2/\text{CO} + \text{H}_2\text{O} + \text{NO} \quad \text{(xii)}
\]

\[
2\text{NH}_3 + 4\text{O}_2 \rightarrow 2\text{NO} + 3\text{H}_2\text{O} \quad \text{(xiii)}
\]

There followed a presentation from Oliver Kröcher (Paul Scherrer Institute, Villigen, Switzerland) on ammonia SCR reactions over the same carbon black that was used in the previous study and also actual diesel soot. The results suggested that the NO₂/NH₃ and ‘fast’ SCR reaction take place on soot, and that the presence of sulfuric acid accelerates NOx reduction (confirming earlier work by the present reviewer). A particularly interesting feature was the consideration given to the processes taking place on the carbon surface, and how for instance hydrogen cyanide might be formed from surface carboxylic acids via the formation and dehydration of surface amides. One possible mechanism is shown in Equations (xiv)–(xvi):

\[
\text{Soot}–\text{CH}_2\text{CH}_2\text{COOH} + \text{NH}_3 \rightarrow \text{Soot}–\text{CH}_2\text{CH}_2\text{CONH}_2 + \text{H}_2\text{O} \quad \text{(xiv)}
\]

\[
\text{Soot}–\text{CH}_2\text{CH}_2\text{CONH}_2 \rightarrow \text{Soot}–\text{CH}═\text{CH}_2 + \text{HCN} \quad \text{(xv)}
\]

\[
\text{Soot}–\text{CH}_2\text{CH}_2\text{CN} \rightarrow \text{Soot}–\text{CH}═\text{CH}_2 + \text{HCN} \quad \text{(xvi)}
\]

The next contribution, from Kiyoshi Yamazaki (Toyota Central R&D Laboratories, Inc, Japan), provided more details about what appears to be a rather special form of silver/ceria which catalyses the soot combustion reaction. This material, as shown by a transmission electron microscopy (TEM) image (Figure 2), has metallic silver cores surrounded by small ceria particles producing an overall spherical particle. The high activity is attributed to the close silver/ceria contacts leading to availability of ‘atomic oxygen species’. The preparation of this material involves ammonia coprecipitation of cerium(III) and silver(I) nitrates under neutral conditions in which silver ammine is reduced by cerium(III) to silver metal and ceria, as shown in Equations (xvii)–(xix). An unusual variant on the silver mirror reaction! And of course anyone carrying out this procedure should be aware of the explosive nature of silver nitride that can inadvertently be formed from ammonial silver nitrate.

\[
\text{Ag}^+ + 2\text{NH}_3 \rightarrow \text{Ag(NH}_3)_2^+ \quad \text{(xvii)}
\]

\[
\text{Ce}^{3+} + 4\text{OH}^- \rightarrow \text{Ce(OH)}_4 + \text{e}^- \quad \text{(xviii)}
\]

\[
\text{Ag(NH}_3)_2^+ + \text{e}^- \rightarrow \text{Ag} + 2\text{NH}_3 \quad \text{(xix)}
\]

As discussed previously the PN standards for gasoline DI engines are going to become the same as those for diesel cars fitted with filters within Euro 6 legislation. There will be a transition period starting in 2014, with $6 \times 10^{12}$ particles km⁻¹, and then in 2017 the limit will be tightened to $6 \times 10^{11}$ particles km⁻¹. This will force DI gasoline cars to be fitted with some form of filter. At the moment it appears that ceramic filters, perhaps incorporating some TWC functionality, and having at least 75% filtration efficiency will be needed to meet the standard. There is however concern that the additional backpressure caused by a filter will be detrimental to the turbocharger efficiency of the small downsized engines that are capable of providing the fuel economy necessary for the low carbon dioxide emissions requirements. A presentation by Stephanie Spiess et al. (Umicore AG & Co KG, Germany) on the emissions performance of a 2 litre turbocharged DI
gasoline engine in a family size car equipped with an under-floor GPF having an equivalent amount of pgm to the current series production vehicle, distributed between a close coupled flow-through TWC and the GPF. The NOx conversion was improved compared with the series arrangement, and over 160,000 km the PN emissions were better than the required 6 × 10^{11} particles km^{-1}. Importantly, there was no measurable impact on fuel consumption or carbon dioxide emissions, highlighting the likelihood of this technology being optimised and implemented on European gasoline powered cars in the future.

The penultimate paper from Bengt Andersson (Chalmers University of Technology) was on the reactivity of different soots, especially towards oxidation. Soot from gasoline DI, gasoline port fuelled, ethanol port fuelled and diesel engines were compared with the behaviour of a commonly used synthetic soot. The oxidative reactivity in 2% oxygen increased in the order: synthetic < diesel < gasoline port fuelled, gasoline DI < ethanol port fuelled soot. A number of differences were identified, and particularly interesting was the variation of activation energy with conversion although the range was within that previously reported for diesel soot. It could be worthwhile to compare with the results obtained by Andrea Strzelec (now at Texas A&M University, USA) and her colleagues showing that the rate of oxidation of diesel soot in the presence of 10% oxygen is directly proportional to the surface area. NOx oxidation is different, perhaps because the reaction rate is so rapid that diffusion effects are important.

The final presentation from Marcial Valencia et al. (Galician Automotive Technology Centre, Spain) and colleagues at the University of Alicante, Spain, dealt with forming Ce_{0.5}Pr_{0.5}O_{2} species within a DPF via impregnation of the corresponding nitrates followed by calcinations to catalyse regenerative soot combustion. Both cordierite and silicon carbide filters were used, and data were collected on a commercial 1.6 litre Euro 5 engine. The backpressure of the catalysed filter was consistently higher than that of an uncoated version, and in regeneration experiments only at 550°C did the backpressure of the catalysed filter reduce to match that of the uncoated filter. Of course 550°C is the temperature at which soot burns in air, suggesting that the catalyst in the filter is not particularly effective. However, other experiments using pre-sooted filters indicated that the ‘balance point’ may be around 400°C, although the experiments were only run for a few minutes. Again this work showed that ceria can catalyse the oxidation of NO to NO_{2}. It is a pity that a commercial pgm-catalysed DPF was not included in this work to provide a meaningful benchmark.

Conclusions
There are concerns about the lack of significant air quality improvements in parts of Europe over recent years, and increasingly stringent standards and other measures will be introduced to correct this situation. The papers presented at this important conference illustrated that tremendous technical advances are being made especially in the key areas of PM and NOx emissions control. Developments are being made with filters for PM control, and increasing amounts of catalyst are being incorporated into filters for NOx control (especially in the form of ammonia SCR for diesels), and TWC for upcoming gasoline applications that will require higher porosity filter materials. In practical systems pgm catalysts provide durable high activity for oxidation of CO and HCs to CO_{2} and H_{2}O, and of NO to NO_{2} for ‘fast SCR’ and passive low-temperature soot oxidation, as well as several functions in NOx-trapping catalysts.

At present copper and iron are being used in combination with small pore zeolites for low-temperature ammonia SCR NOx control. Here it appears that an important factor is the elimination of HC species from the active metal sites in zeolite channels, and it would be interesting to know how pgm centres would perform in such situations since in more traditional catalysts they have outstanding low-temperature performance, although their selectivity is less than desired for this application.

Finally, the organising committee, and especially Professor Norbert Kruse (Chairman), Jean-Marie Bastin (Treasurer) and Thierry Visart de Bocarmé (Secretary) are to be congratulated for organising an excellent conference.

References
3 “Catalysis and Automotive Pollution Control III, Proceedings of the Third International Symposium


12 M. V. Twigg, ‘Compact Diesel Filters’, Ingenia, March 2009, (38), pp. 35–39

13 ‘Argon, a New Constituent of the Atmosphere’, Lord Rayleigh and W. Ramsay, Proc. R. Soc. Lond., 1895, 57, 265. Lord Rayleigh showed the density of ‘nitrogen from the air’ was slightly less dense than that of ‘chemical nitrogen’. Sir William Ramsay went on to identify argon in air was the cause of the discrepancy and he went on to discover other inert gases that fitted in with the then evolving Periodic Table. This work led to the award of the 1904 Nobel Prize in Chemistry to William Ramsay.


The Author

Martyn Twigg retired as the Chief Scientist of Johnson Matthey in 2010. Dr Twigg was previously European Technology Director for the Environmental Catalysts and Technologies Division of Johnson Matthey in Royston, UK. He has authored or co-authored many research papers, written numerous chapters in encyclopaedic works, and edited and contributed to several books. He edits the book series ‘Fundamental and Applied Catalysis’, and a series on the kinetics and mechanisms of inorganic and organometallic reactions. He is on the editorial board of several journals, and maintains active associations with universities in the UK and elsewhere, with honorary positions at some.
Platinum Alloys: A Selective Review of the Available Literature

Introduction
More than half of the platinum that is produced around the world each year currently finds use in automotive and other areas of industry as a catalyst and as a major constituent in various engineering alloys (Figure 1) (1). Platinum also has a place in jewellery manufacturing. The objective of this article is to review the existing phase diagrams and known properties of some platinum alloys that are used in industrial and jewellery applications, and also to present published data on some less used platinum alloys which nevertheless have interesting properties. The alloys covered are of platinum with palladium, iridium, rhodium, ruthenium, gold and nickel.

The data on mechanical properties of the platinum alloys presented in Tables I–VII are obtained from the monograph by R. F. Vines (2) published in 1941, still the most comprehensive source, from The PGM Database (3) hosted by Johnson Matthey, and from the internal database and website of Sigmund Cohn Corporation (4), a US pgm alloy fabricator. To keep the uniformity of units of measure all tensile strength (TS) data is presented in psi, and all the hardness data is presented in Vickers hardness (HV) (some of these values are converted from MPa and Brinell respectively). All alloy compositions are given in weight per cent (wt%) unless otherwise specified.

Platinum Alloys for Jewellery
Platinum alloys containing other platinum group metals (pgms), gold and some base metals present a variety of workable materials that demonstrate high strength, increased hardness and springiness. Many of these alloys are used for making jewellery (5), as they exhibit platinum’s desirable white colour, and can be cast (6), extruded (7), rolled, drawn and formed (8).

A moderate brightness in combination with low red and yellow colour components make the colour of platinum a unique and attractive jewellery material that effectively accents the reflectivity of precious stones. Table 1 compares the colour of platinum with that of fine silver and typical 18 carat and 14 carat white golds using CIELAB colour coordinates, as measured by the author using a Macbeth Color-Eye® spectrophotometer model M2020PL. Platinum and its alloys show brightness L* about 85, neutral a* and fairly low b* components. Silver shows a* and b* values similar to those of platinum but a much higher brightness L*, about 95. The L* and a* values of white golds are similar to those of platinum but a much higher brightness L*, about 95. The L* and a* values of white golds are similar to those of platinum, however such alloys exhibit much higher yellow components b* of at least 9.0 and most of them require rhodium plating.

The Santa Fe Symposium presentation by Jurgen Maerz in 1999 provides a comprehensive review of common platinum jewellery alloys (5). The legal requirements of minimum platinum content narrow the alloy range and prohibit the utilisation of the enhanced mechanical properties of many alloys outside this range.

Fig. 1. Platinum demand by application. Industrial applications include chemical, electrical, glass, petroleum and other (1)
One of the key factors affecting the properties of an alloy is the crystalline structure of the pure metals of which it is composed. The crystalline structures of the pgms are shown in Figure 2. Four elements, Pt, Pd, Ir and Rh, have a face-centred cubic (fcc) structure, where the atoms are positioned at each corner and in the centre of each face of the cube. In general, the fcc metals are soft in the annealed condition and are quite workable, similar to gold, silver and copper. The structure of the other two pgms, Ru and Os, is the more complex hexagonal close-packed (hcp) structure, similar to that of zinc. Such a major difference in crystalline structure suggests the significant hardening effect of Ru and Os when alloyed with Pt. In fact, additions of Os to Pt make the resultant alloys extremely hard and practically unworkable.

It is not surprising that binary phase diagrams (9) of Pt-Pd, Pt-Ir and Pt-Rh (Figures 3, 4 and 5 respectively) show similarity, whereas the Pt-Ru (Figure 6) phase diagram has a different and more complex form. Pd, Ir and Rh show solubility in Pt for the entire compositional range at high temperatures and miscibility gaps are seen at lower temperatures. In contrast, Pt-Ru is a peritectic system. Ru has solubility in Pt within certain compositional ranges (10). The miscibility gap feature is a potential mechanism for age hardening of Pt-Pd-Ir-Rh alloys, although little published data is available, probably because of fairly slow ageing kinetics (11).

### Platinum-Palladium Alloys
Pt-Pd alloys are soft and workable. Figure 7 shows that the hardness and tensile strength of Pt-Pd alloys reach their maximum values at about 40% Pd. The mechanical properties of pure Pt, Pd and some of their alloys are compared in Table II. Pt and Pd are very similar: both have low hardness and tensile strength in annealed and cold worked conditions. The additions of 10% and even 40% Pd to Pt increase the hardness and strength somewhat; however these values still remain fairly low. The use of Pt-Pd alloys is therefore quite limited. It is remarkable that when 6% Ru is alloyed with Pt in addition to 10% Pd, the resultant alloy shows significantly increased hardness and strength, and retains good ductility (25% elongation) and excellent resistance to corrosion.

### Platinum-Iridium Alloys
Pt-Ir alloys are noticeably harder and stronger than Pt-Pd. Pure Ir is fairly hard. Additions of Ir to Pt result in a rapid rise in alloy hardness and strength as shown in Figure 8. Pt-Ir alloys with about 30% Ir and higher become extremely springy and practically unworkable – probably that is why the data in Figure 8 is limited to 30% Ir.

The mechanical properties of pure Pt and Ir and some of their alloys are listed in Table III. Even though the hardness of the annealed Ir is about four or five times higher than that of Pt, Ir shows a tensile strength similar to that of Pt and a fairly good percentage elongation of 21%. Pt-5% Ir and Pt-10% Ir are common jewellery alloys. Pt-20% Ir alloy is much harder, stronger,
Fig. 3. Platinum-palladium phase diagram (9)

Fig. 4. Platinum-iridium phase diagram (9)
Fig. 5. Platinum-rhodium phase diagram (9)

Fig. 6. Platinum-ruthenium phase diagram (9)
Table II

Mechanical Properties of Platinum, Palladium and Their Alloys in the Annealed\(^a\) and Cold Worked\(^b\) Conditions

<table>
<thead>
<tr>
<th>Metal or alloy</th>
<th>Vickers hardness, HV(_{\text{ann}})</th>
<th>Tensile strength, TS(_{\text{ann}}), psi</th>
<th>Percentage elongation, (%E_{\text{ann}})</th>
<th>Vickers hardness, HV(_{\text{cw}})</th>
<th>Tensile strength, TS(_{\text{cw}}), psi</th>
</tr>
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<tbody>
<tr>
<td>Pt</td>
<td>40</td>
<td>18,100</td>
<td>40</td>
<td>90</td>
<td>49,300</td>
</tr>
<tr>
<td>Pd</td>
<td>40</td>
<td>27,500</td>
<td>40</td>
<td>100</td>
<td>47,000</td>
</tr>
<tr>
<td>Pt-10% Pd</td>
<td>80</td>
<td>21,300</td>
<td>25</td>
<td>140</td>
<td>49,700</td>
</tr>
<tr>
<td>Pt-40% Pd</td>
<td>100</td>
<td>50,000</td>
<td>–</td>
<td>180</td>
<td>–</td>
</tr>
<tr>
<td>Pt-10% Pd-6% Ru</td>
<td>200</td>
<td>75,000</td>
<td>25</td>
<td>320</td>
<td>90,900</td>
</tr>
</tbody>
</table>

\(^a\) ann = annealed

\(^b\) cw = cold worked

and still maintains good ductility (20% annealed elongation). In the sheet form it can be rolled down to 0.0005” (0.0127 mm) thickness. In the wire form it can be drawn to 0.001” (0.0254 mm) diameter. This pgm alloy is used for precision machining of parts for implantable medical devices.

Pt-30\% Ir alloy shows extreme hardness and strength. This alloy is not easily workable. Its main application is found in medical devices as a spring wire. The mechanical properties of Pt-20\% Ir alloy can be enhanced by adding 10\% Rh. The Pt-20\% Ir-10\% Rh alloy is less springy than Pt-30\% Ir, shows good
Table III
Mechanical Properties of Platinum, Iridium and Their Alloys in the Annealed\(^a\) and Cold Worked\(^b\) Conditions

<table>
<thead>
<tr>
<th>Metal or alloy</th>
<th>Vickers hardness, HV(_{\text{ann}})</th>
<th>Tensile strength, TS(_{\text{ann}}), psi</th>
<th>Percentage elongation, (%E_{\text{ann}})</th>
<th>Vickers hardness, HV(_{\text{cw}})</th>
<th>Tensile strength, TS(_{\text{cw}}), psi</th>
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<tbody>
<tr>
<td>Pt</td>
<td>40</td>
<td>18,100</td>
<td>40</td>
<td>90</td>
<td>49,000</td>
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<tr>
<td>Ir</td>
<td>210</td>
<td>18,000</td>
<td>21</td>
<td>–</td>
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</tr>
<tr>
<td>Pt-5% Ir</td>
<td>85</td>
<td>36,500</td>
<td>35</td>
<td>145</td>
<td>65,000</td>
</tr>
<tr>
<td>Pt-10% Ir</td>
<td>110</td>
<td>51,000</td>
<td>30</td>
<td>185</td>
<td>70,000</td>
</tr>
<tr>
<td>Pt-20% Ir</td>
<td>190</td>
<td>100,000</td>
<td>20</td>
<td>240</td>
<td>188,500</td>
</tr>
<tr>
<td>Pt-30% Ir</td>
<td>280</td>
<td>159,500</td>
<td>20</td>
<td>315</td>
<td>269,500</td>
</tr>
<tr>
<td>Pt-20% Ir-10% Rh</td>
<td>–</td>
<td>120,000</td>
<td>20</td>
<td>–</td>
<td>200,000</td>
</tr>
</tbody>
</table>

\(^a\) ann = annealed
\(^b\) cw = cold worked

workability and retains good ductility (20% annealed elongation).

**Platinum-Rhodium Alloys**
Pt-Rh alloys are primarily used in thermocouples for operation at high temperatures (up to 1700°C) in an oxidising or inert environment. Type S consists of Pt versus Pt-10% Rh, type R of Pt versus Pt-13% Rh and type B of Pt-6% Rh versus Pt-30% Rh. The standard wire sizes that are used to manufacture these thermocouples range between 0.001" (0.0254 mm) and 0.032" (0.813 mm). Table IV lists the mechanical properties of Pt, Rh and
some of their alloys. Rh is very difficult to work and anneal. As a result, the published tensile properties of annealed Rh are inconsistent; its strength is reported between 81,000 psi and 125,000 psi, and the elongation between 9% and 33% (3). Pt-Rh alloys, however, are quite ductile, and show consistent and moderate rise in hardness and strength as the Rh content increases. The elongation stays practically constant at between 30% and 35% with Rh content up to at least 40 wt%. Pt-20% Rh alloy shows good hardness and strength, and excellent machining properties. It is used for precision part fabrication for the aerospace industry. Replacing some Rh with Ru, such as in Pt-15% Rh-5% Ru alloy, enhances the strength, but also results in the loss of some ductility from 33% to 18% elongation.

Platinum-Ruthenium Alloys
The hardening effect of Ru additions to Pt was first recognised by Adolph Cohn almost a century ago (12). Since then Ru-containing Pt alloys have become widely used in a variety of applications especially jewellery. Table V lists hardness, tensile strength and percentage elongation values for Pt, Ru, and two Pt alloys containing 5% and 10% Ru respectively. This data shows that alloying Ru with Pt yields much harder and stronger alloys without compromise in ductility.

Table IV
Mechanical Properties of Platinum, Rhodium and Their Alloys in the Annealed* and Cold Workedb Conditions

<table>
<thead>
<tr>
<th>Metal or alloy</th>
<th>Vickers hardness, HV&lt;sub&gt;ann&lt;/sub&gt;</th>
<th>Tensile strength, TS&lt;sub&gt;ann&lt;/sub&gt;, psi</th>
<th>Percentage elongation, %E&lt;sub&gt;ann&lt;/sub&gt;</th>
<th>Vickers hardness, HV&lt;sub&gt;cw&lt;/sub&gt;</th>
<th>Tensile strength, TS&lt;sub&gt;cw&lt;/sub&gt;, psi</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt</td>
<td>40</td>
<td>18,100</td>
<td>40</td>
<td>90</td>
<td>49,000</td>
</tr>
<tr>
<td>Rh</td>
<td>100</td>
<td>81,000–125,000</td>
<td>9–33</td>
<td>215,000</td>
<td></td>
</tr>
<tr>
<td>Pt-10% Rh</td>
<td>90</td>
<td>45,000</td>
<td>35</td>
<td>200</td>
<td>133,500</td>
</tr>
<tr>
<td>Pt-20% Rh</td>
<td>115</td>
<td>68,000</td>
<td>30</td>
<td>235</td>
<td>152,000</td>
</tr>
<tr>
<td>Pt-30% Rh</td>
<td>130</td>
<td>71,000</td>
<td>30</td>
<td>290</td>
<td>178,000</td>
</tr>
<tr>
<td>Pt-40% Rh</td>
<td>145</td>
<td>83,500</td>
<td>30</td>
<td>–</td>
<td>200,000</td>
</tr>
<tr>
<td>Pt-15% Rh-5% Ru</td>
<td>–</td>
<td>95,000</td>
<td>18</td>
<td>–</td>
<td>200,000</td>
</tr>
</tbody>
</table>

*<sup>a</sup> ann = annealed
<br>b<sup>b</sup> cw = cold worked

Platinum-Gold Alloys
The addition of Au for hardening Pt was first suggested by Adolph Cohn in 1919 (13). The Pt-Au phase diagram in Figure 9 shows a fairly broad liquidus–solidus melting range and a miscibility gap with the peak close to the solidus. A wide range of Pt-Au alloys undergo spinodal decomposition within the miscibility gap as shown in Figure 10. The tensile properties as a function of Au content are shown in Figure 11. Although both Pt and Au are very soft, Au acts as an extremely effective hardener for Pt (14). Table VI lists the mechanical properties of Pt, Au and Pt alloys with low Au content. The hardness and strength rise with the Au content; however the percentage elongation dramatically decreases. This limits the practical use of such alloys. The deterioration of elongation is attributed mainly to grain growth during solution annealing (15).

It is found that small Rh additions broaden the miscibility gap and displace it up towards the solidus line forming a peritectic-type system (15). Small Rh additions to Pt-Au alloys not only enhance the hardness and strength but also improve ductility by increasing the elongation as illustrated by the Pt-3.5% Au-1% Rh alloy. A similar effect of Rh additions is also observed at higher Au concentrations. Pt-Au alloys with small additions of Rh are hardenable (14–16).
Table V
Mechanical Properties of Platinum, Ruthenium and Their Alloys in the Annealed\(^a\) and Cold Worked\(^b\) Conditions

<table>
<thead>
<tr>
<th>Metal or alloy</th>
<th>Vickers hardness, (HV_{\text{ann}})</th>
<th>Tensile strength, (TS_{\text{ann}}), psi</th>
<th>Percentage elongation, (%E_{\text{ann}})</th>
<th>Vickers hardness, (HV_{\text{cw}})</th>
<th>Tensile strength, (TS_{\text{cw}}), psi</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt</td>
<td>40</td>
<td>18,100</td>
<td>40</td>
<td>90</td>
<td>49,000</td>
</tr>
<tr>
<td>Ru</td>
<td>250</td>
<td>65,200</td>
<td>3</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Pt-5% Ru</td>
<td>130</td>
<td>65,000</td>
<td>30</td>
<td>200</td>
<td>115,000</td>
</tr>
<tr>
<td>Pt-10% Ru</td>
<td>185</td>
<td>123,000</td>
<td>30</td>
<td>220</td>
<td>150,000</td>
</tr>
</tbody>
</table>

\(^a\) ann = annealed  
\(^b\) cw = cold worked

Fig. 9. Platinum-gold phase diagram (9)

Platinum-Base Metal Alloys
A fairly detailed review of Pt-base metal alloys was compiled by R. F. Vines (2). Pt-tungsten and Pt-cobalt alloys have been most studied; and these alloys are commonly used for industrial applications (16, 17). A variety of Pt-base metal alloys such as those containing copper, cobalt, nickel and gallium effectively respond to age hardening (18, 19). Ni, however, finds limited use as an alloying element with Pt even though it belongs to the same group in the Periodic Table. The Pt-Ni phase diagram in Figure 12 shows the solubility of Ni in Pt for the entire compositional range.

Table VII lists the mechanical properties of pure Pt, Ni and their alloys. It is evident that the hardening effect of Ni on Pt is more pronounced than that of Ir: compare with Table III. The phase diagram also shows that alloys containing as little as 10% Ni undergo order-disorder transformation, a typical mechanism for age
Fig. 10. Platinum-gold phase diagram (9) – spinodal curve

Fig. 11. Tensile properties of solution treated platinum-gold alloys (14)
Table VI
Mechanical Properties of Platinum, Gold and Their Alloys in the Annealed\textsuperscript{a} and Cold Worked\textsuperscript{b} Conditions

<table>
<thead>
<tr>
<th>Metal or alloy</th>
<th>Vickers hardness, HV\textsubscript{ann}</th>
<th>Tensile strength, TS\textsubscript{ann}, psi</th>
<th>Percentage elongation, %\textsubscript{E\textsubscript{ann}}</th>
<th>Vickers hardness, HV\textsubscript{cw}</th>
<th>Tensile strength, TS\textsubscript{cw}, psi</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt</td>
<td>40</td>
<td>18,100</td>
<td>40</td>
<td>90</td>
<td>49,000</td>
</tr>
<tr>
<td>Au</td>
<td>20</td>
<td>15,500</td>
<td>40</td>
<td>60</td>
<td>31,000</td>
</tr>
<tr>
<td>Pt-2.5% Au</td>
<td>70</td>
<td>31,000</td>
<td>26</td>
<td>138</td>
<td>49,000</td>
</tr>
<tr>
<td>Pt-5% Au</td>
<td>85</td>
<td>45,000</td>
<td>20</td>
<td>155</td>
<td>63,500</td>
</tr>
<tr>
<td>Pt-10% Au</td>
<td>130</td>
<td>77,500</td>
<td>12</td>
<td>–</td>
<td>91,500</td>
</tr>
<tr>
<td>Pt-3.5% Au-1% Rh</td>
<td>90</td>
<td>36,000</td>
<td>30</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

\textsuperscript{a} ann = annealed

\textsuperscript{b} cw = cold worked

Fig. 12: Platinum-nickel phase diagram (9)
hardening. For example, an ageing heat treatment increases the tensile strength of Pt-10% Ni alloy from 230,000 psi up to 300,000 psi (TSht in Table VII). The magnetic transformation curve in Figure 12 indicates that Pt-Ni alloys with Ni content below 40% are practically non-magnetic. This is in contrast with Pt-Co alloys which show magnetism even at 5% Co.

Conclusions

Platinum alloys play a significant role in industry and in jewellery manufacture. It is apparent that there is a wealth of information available from a range of sources and suppliers, and some of it is more readily available than others. The present paper is an attempt to bring together, in convenient form, the basic data that exists in the literature for some of these alloys and to emphasise their interesting properties for industrial and jewellery applications.

GRIGORY RAYKHTSAUM
LeachGarner, 49 Pearl St, Attleboro, Massachusetts 02703, USA
Email: graykhtsaum@leachgarner.com

References


Table VII

Mechanical Properties of Platinum, Nickel and Their Alloys in the Annealed\(^a\) and Cold Worked\(^b\) Conditions and After Heat Treatment\(^c\)

<table>
<thead>
<tr>
<th>Metal or alloy</th>
<th>Vickers hardness, HV(_{\text{ann}})</th>
<th>Tensile strength, TS(_{\text{ann}}), psi</th>
<th>Percentage elongation, %E(_{\text{ann}})</th>
<th>Vickers hardness, HV(_{\text{cw}})</th>
<th>Tensile strength, TS(_{\text{cw}}), psi</th>
<th>Tensile strength, TS(_{\text{ht}}), psi</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt</td>
<td>40</td>
<td>18,100</td>
<td>40</td>
<td>90</td>
<td>49,000</td>
<td>–</td>
</tr>
<tr>
<td>Ni</td>
<td>85</td>
<td>45,000</td>
<td>45</td>
<td>220</td>
<td>90,000</td>
<td>–</td>
</tr>
<tr>
<td>Pt-5% Ni</td>
<td>130</td>
<td>66,500</td>
<td>26</td>
<td>–</td>
<td>100,000</td>
<td>–</td>
</tr>
<tr>
<td>Pt-10% Ni</td>
<td>220</td>
<td>118,000</td>
<td>28</td>
<td>380</td>
<td>230,000</td>
<td>300,000</td>
</tr>
<tr>
<td>Pt-20%Ni</td>
<td>280</td>
<td>132,000</td>
<td>–</td>
<td>–</td>
<td>250,000</td>
<td>–</td>
</tr>
</tbody>
</table>

\(^a\) ann = annealed
\(^b\) cw = cold worked
\(^c\) ht = heat treated
13 A. Cohn, ‘Alloy’, US Patent 1,323,834; 1919
14 A. S. Darling, Platinum Metals Rev., 1962, 6, (2), 60
15 A. S. Darling, Platinum Metals Rev., 1962, 6, (3), 106
16 A. G. Knapton, Platinum Metals Rev., 1980, 24, (2), 64

The Author

Grigory Rakhtsaum is Director of Metallurgy at LeachGarner in Attleboro, Massachusetts, USA. He holds an MS degree in Physics from the Polytechnic Institute in St. Petersburg, Russia. He also studied Materials Science at Northwestern University in Evanston, Illinois, USA. He has worked in the precious metals industry since 1984, focusing on gold and pgm alloy and process development, quality assurance and failure analysis. This paper was written while with Sigmund Cohn Corp in Mount Vernon, New York, USA. He has coauthored 12 patents and about 40 publications, as well as giving numerous presentations at venues including the Santa Fe Symposium on Jewelry Manufacturing Technology, the International Precious Metals Institute and Manufacturing Jewelers and Suppliers of America.
In a recent article in *Platinum Metals Review* (1), the section on jewellery states that a platinum rod which is 10 cm long and 1 cm in diameter can be drawn into a wire approximately 2777 km long. This should be a factor of 10 higher at 27,778 km (see calculation below).

The wire length was based on calculating a constant volume from the starting rod, based on the final wire thickness of 0.0006 mm (2).

**Calculation:**

Volume of a cylinder = $\pi r^2 l$

where $r$ = radius and $l$ = length.

Therefore, volume of a cylinder 1 cm diameter (corresponding to 0.5 cm radius) by 10 cm length is $\pi \times 0.5^2 \times 10 = 7.854$ cm$^3$.

For thin wire, diameter = 0.0006 mm or 0.00006 cm.

Therefore, $l = \frac{7.853}{(\pi \times 0.000032)}$

\[
\begin{align*}
  l &= \frac{7.853}{(\pi \times 0.000032)} \\
  &= 2.7778 \times 10^9 \text{ cm} \\
  &= 2.7778 \times 10^7 \text{ m} \\
  &= 27778 \text{ km}
\end{align*}
\]

**References**


Johnson Matthey's latest survey of the platinum group metal (pgm) markets, "Platinum 2013", was released on 13th May 2013. The trends in supply and demand in 2012 are covered and the short term outlook on the status of the pgm market is reported.

**Platinum**

The Platinum Market Was in Deficit in 2012

A decline in output from South Africa caused a deficit in the platinum market of 375,000 oz in 2012. Supplies of platinum fell by 13% to 5.64 million oz and its total demand in 2012 was down by 0.6% to 8.05 million oz. The recycling of platinum was marginally less than in 2011 at 2.03 million oz.

Supplies Were at a Twelve Year Low

Primary supplies of platinum, at 5.64 million oz, were at a 12 year low, with platinum shipments by South African producers down by 16% to 4.10 million oz in 2012. Legal and illegal strikes, safety stoppages and the closure of some marginal mining operations caused the loss of at least 750,000 oz of production.

Demand in Autocatalysts Rose

Gross demand for platinum in autocatalysts rose by 1.7% to 3.24 million oz. European demand was weak due to depressed light vehicle output and a lower market share for diesel vehicles; however, this was offset by higher demand in Asia and North America and increased demand for platinum autocatalysts for non-road diesel engines.

Demand for Platinum Jewellery Has Improved

Gross demand for platinum for jewellery manufacturing grew by 12% in 2012 to 2.78 million oz. This was helped by expansion of the retail jewellery distribution network in China. Manufacturers also took advantage of the relatively weak platinum price to increase stocks.

Platinum Demand for Industrial Uses Fell

In 2012, platinum demand for industrial applications fell by 21% to 1.57 million oz. This was caused by a slowing of expansion in the glass industry, reduced production of hard disk drives in the electrical industry and a decrease of inventory in both sectors. Chemical demand was slightly lower compared to 2011.

Demand for Platinum in Investment Was Steady

Net identifiable physical demand for platinum in the investment sector reached 455,000 oz in 2012, only 5,000 oz lower than in the previous year. A fall in demand for large bars in Japan was offset by strong investor interest in North America and a rise in the minting of platinum coins.

**Palladium**

The Palladium Market Was in Deficit

In 2012, the palladium market moved into a deficit of 1.07 million oz following a surplus of 1.19 million oz in 2011. This was due to lower primary and secondary supplies, record demand for palladium autocatalysts and a large swing in investment demand from heavily negative in 2011 to strongly positive in 2012.
Supplies of Palladium Fell During 2012
In 2012, there was a decrease of 11% in supply of palladium to 6.55 million oz, the lowest since 2002. Russian newly-mined supply fell by 3% to 2.63 million oz and sales from state stocks dropped by two-thirds to 250,000 oz as Russia’s palladium reserves neared depletion.

Purchases for Autocatalysts Have Increased
Gross demand for palladium in autocatalysts increased by 7.5% to a new high of 6.62 million oz. Demand strengthened for several reasons: recovering car output in Japan after the natural disasters of 2011; further growth in China; and a boom in new registrations in North America as consumer confidence and economic activity continued to improve.

Demand of Palladium for Industrial Uses Has Decreased
Industrial demand for palladium fell by 4% to 2.37 million oz in 2012. Demand for palladium in chip capacitors, its main electrical application, decreased due to thrifting and competition from base metal alternatives. Demand for palladium chemical process catalysts grew, however, particularly in Asia.

Consumer Demand for Palladium Jewellery Has Declined
There was a decrease of 12% to 445,000 oz in gross world demand for palladium in jewellery manufacturing. Poor consumer demand for palladium jewellery in China resulted in fewer manufacturers and retailers producing it or carrying stock. In most other regions, palladium demand was steady and it was slightly higher in Europe, supported by its use in wedding rings for men.

Investment Demand Has Switched from Negative to Positive
Net physical investment in palladium switched from a negative 565,000 oz in 2011 to a positive 470,000 oz in 2012. In the first half of the year, flows of palladium into ETFs were strong. The launch of a new investment trust in the USA in December 2012 added significantly to demand.

Special Features
There are two special features in “Platinum 2013”. In the first, the disruption to platinum mining in South Africa caused by strikes, safety stoppages and mine closures in 2012 is analysed. At least 750,000 oz of production of platinum was lost. A timeline of the various disruptions is also included. The second special feature covers the components of autocatalyst demand. Emissions control from vehicle exhaust using catalysts is the largest single application for pgms and accounted for 56% of gross world demand for platinum, palladium and rhodium combined in 2012. The demand values for platinum and palladium are separated into their main components of light-duty gasoline, light-duty and heavy-duty diesel and diesel non-road mobile machinery. The historical long-term drivers and future opportunities for the use of pgms in each of these automotive applications are examined.

The Availability of “Platinum 2013”
The book can be downloaded, free of charge, as a PDF file in English, Chinese or Russian from Platinum Today at: http://www.platinum.matthey.com/publications/pgm-market-reviews. The English version can be ordered in hard copy by filling in the form at: http://www.platinum.matthey.com/publications/pgm-market-reviews/market-review-request, by emailing: pbook@matthey.com, or by writing to: Johnson Matthey Precious Metals Marketing, Orchard Road, Royston, Hertfordshire SG8 5HE, UK.
New Ruthenium Complexes for Dehydrogenation Reactions

Johnson Matthey and Alfa Aesar support new platinum group metals research

About the Research

Ruthenium complexes with N-heterocyclic carbene (NHC) ligands are of much interest in homogeneous catalysis. We synthesised unusual cationic tetrakis-carbene complex \([\text{RuH(IMe)}_4][\text{BEt}_4]\) (1, Figure 1), which features an NHC ligand (IMe) that displays four methyl substituents. This complex has a square pyramidal structure with a vacant coordination site that may be exploited advantageously for the coordination of molecules such as \(\text{H}_2\). Using the iso-propyl-substituted ligand IPr we isolated the complex \([\text{RuCl(IPr)}(\text{PCy}_3)]_2\) (2, Figure 1), which is formed via the unusual activation of three iso-propyl C–H bonds. We are currently investigating the potential of these and related complexes as catalysts for dehydrogenation reactions. Another important aspect is the ability of complex 1 and related compounds to activate small molecules such as \(\text{H}_2\), \(\text{CO}_2\) and \(\text{P}_4\).

About the Researcher

* Name: Robert Wolf
  * Position: Professor of Inorganic Chemistry
  * Department: Institute of Inorganic Chemistry
  * University: University of Regensburg
  * Street: Universitaetsstr. 31
  * City: Regensburg
  * County: Bavaria
  * Post or Zip Code: 93047
  * Country: Germany
  * Email Address: robert.wolf@ur.de
  * Website: http://www.uni-regensburg.de/chemistry-pharmacy/inorganic-chemistry-wolf/index.html

![Fig. 1. New NHC ruthenium complexes](image)
Polynuclear hydridoruthenium complexes show the remarkable ability to activate unreactive substrates in a cooperative fashion whereby two or more metal atoms participate. Literature examples include cyclopentadienyl-substituted complexes that effect very unusual, multiple C–H and C–C bond activations. Despite such spectacular examples, suitable, reactive polyhydrides are still very scarce, however. In this project, we investigate novel polynuclear polyhydrides of ruthenium that can be utilised for the cooperative activation of unreactive bonds and in homogeneous catalysis. Figure 2 shows a range of complexes we have recently prepared. We are currently investigating the reaction chemistry and catalytic applications of these complexes. Some of them display unusual spectroscopic and magnetic properties, such as a high-spin ground state for the 3d metal ion in the paramagnetic complexes with $M = \text{Cr–Ni}$. Furthermore, we are currently extending our studies to other electron-rich transition metals such as rhodium and iridium.

**Recent Publications**


Publications in Brief

BOOKS

“Catalysis by Ceria and Related Materials”, 2nd Edition
Edited by A. Trovarelli (Università di Udine, Italy) and P. Fornasiero (Università di Trieste, Italy), Catalytic Science Series, Vol. 12, Imperial College Press, London, UK, 2013, 908 pages, ISBN: 978-1-84816-963-0, £124.00, US$188.00

This book follows the 2002 edition which was the first book entirely devoted to ceria and its catalytic properties. Since then a great amount of work has been carried out in the field, and ceria has gained a more prominent position in catalysis. Special emphasis is given in this 2nd edition to nano-engineered and nano-shaped systems. The book covers recent advances in emerging and traditional large-scale applications of ceria in catalysis, such as the treatment of emissions from diesel and gasoline engines where ceria is widely used in conjunction with a pgm washcoat.

“Catalytic Process Development for Renewable Materials”

This book is the first to combine the fields of high throughput experimentation and catalytic process development for biobased materials. It describes the entire workflow from idea, approach, research and process development, right up to commercialisation by application of advanced methodologies and technologies. Reactor and process design models are covered in detail. Palladium and ruthenium catalysts are featured. The contributions are from scientists and technologists at leading companies.

“Nanomaterials in Catalysis”
Edited by P. Serp and K. Philippot (Toulouse University, Laboratoire de Chimie de Coordination, Toulouse, France), Wiley-VCH Verlag GmbH & Co KGaA, Weinheim, Germany, 2013, 516 pages, ISBN: 978-3-527-33124-6, £125.00, €150.00, US$175.00

Following an introduction of the concepts in nanocatalysis, the fabrication of nanocatalysts in various media is discussed in several chapters including nanoparticles in aqueous phase, nanoclusters and colloids as catalysts precursors, nanoparticles in ionic liquid and supercritical fluids, dendrimers that serve as polymeric supports for nanoparticles and finally nanocatalyst recovery, which addresses the problem of deactivation and regeneration. A section is dedicated to nanoparticle supports like carbon nanotubes and nano oxides. The last chapter reviews modelling of nanocatalysts to show the foundation of theoretical treatment of nanocatalysis and nanomaterials that are used as catalysts. There are examples of all of the pgms as nanocatalysts.


With minimal use of ‘legal jargon’ this book provides researchers with the assistance and advice they require to understand the legal complexities that they may encounter before and during a patent application. It details the reasons behind patents, their importance and relevance to all researchers and the strategy needed for filing for a patent. The book discusses the responsibilities of the researcher after patent applications have been filed and the role the researcher can play in the maintenance of a global patent estate. The author has over 30 years of experience in areas such as process engineering and operation, research and development, and applications research. He has been working in patent matters for over 20 years and is registered to practice before the United States Patent and Trademark Office.

“Writing Science: How to Write Papers That Get Cited and Proposals That Get Funded”

This book treats writing technical papers and proposals...
as part of the literary tradition and focuses on structuring the story of the paper rather than focusing on just sentences. The book targets the internal structure of a paper, explaining how to write clear and professional sections, paragraphs and sentences. It draws upon the author's years of experience as an author, reviewer and editor, offering tools that any scientist can use to communicate.

**JOURNALS**

**Environmental Science & Technology Letters**

Editor: J. Schnoor (University of Iowa, Iowa City, USA); American Chemical Society; ISSN: 2328-8930

ACS Publications announces *Environmental Science & Technology Letters (ES&T Letters)*. This new journal will include brief communications on experimental or theoretical results in all aspects of environmental science (pure and applied) and short reviews on emerging environmental science and technology topics. Among the areas the journal will cover are:

(a) Characterisation of natural and affected environments;
(b) Energy and the environment;
(c) Environmental aspects of nanotechnology;
(d) Environmental measurements methods;
(e) Environmental processes;
(f) Novel remediation and control technologies.

**Journal of CO₂ Utilization**

Editor-in-Chief: S.-E. Park (Laboratory of Nano-Green Catalysis and Nano Center for Fine Chemicals Fusion Technology, Department of Chemistry, Inha University, Incheon, South Korea); Elsevier; ISSN: 2212-9820

The *Journal of CO₂ Utilization* is a new journal from Elsevier. It will publish novel research in the field of carbon dioxide re-use. This includes CO₂ as a feedstock in the chemical, energy and materials sectors, and utilisation in general to help minimise environmental impact. The coverage includes:

(a) Materials for CO₂ activation and adsorption;
(b) Heterogeneous and homogeneous catalytic reactions involving CO₂;
(c) CO₂ conversion to generate synthetic fuels, polymers, organic carbonates and intermediate products;
(d) Supercritical CO₂ utilisation in natural product extraction, catalysis and separation;
(e) Use of CO₂ as an oxidant;
(f) Electrochemical conversion of CO₂;
(g) Photoelectrochemical, photocatalytic and photochemical conversion of CO₂;
(h) Biological conversion of CO₂;
(i) Integrated processes for CO₂ conversion and reduction.

**Metallurgical and Materials Transactions E: Materials for Energy Systems**

Principal Editor: D. E. Laughlin (Carnegie Mellon University, Pittsburgh, Pennsylvania, USA); Springer; ISSN: 2196-2936; e-ISSN: 2196-2944

ASM International and TMS (The Minerals, Metals and Materials Society) through Metallurgical and Materials Transactions are launching a new joint quarterly journal on energy materials. *Materials for Energy Systems* will publish original research and review articles focused on the science of materials applied to or being investigated to address unique aspects of current and emerging energy technologies, to include: battery, biomass, fuel cell, geothermal, hydrocarbons, hydrogen storage, nuclear, solar cell, supercapacitor, thermal conversion, thermochemistry, thermoelectricity and wind energy systems.

**Sustainable Chemical Processes**

Editor-in-Chief: M. Gupta (Indian Institute of Technology Delhi, India); Chemistry Central; e-ISSN: 2043-7129

*Sustainable Chemical Processes* is a new open access journal from Chemistry Central covering both scientific and engineering aspects of sustainable approaches in chemistry. The scope of the journal includes:

(a) Green routes to isolation, purification and synthesis of organic, inorganic or organometallic compounds and materials;
(b) All aspects of catalysis and biocatalysis that lead to sustainable processes;
(c) Biomass conversion and use of renewable resources;
(d) Biofuels, biorefineries and other alternative sources of energy (such as hydrogen generation and storage, solar cells, fuel cells and photovoltaic cells);
(e) Process intensification including flow chemistry;
(f) Green metrics and sustainability assessment of products and processes (including LCA methods);
(g) Microwave and ultrasonic assisted reactions;
(h) Nanotechnology that enhances the sustainability aspects of processes;
(i) Green electronics and sensors;
(j) Approaches to reduce water consumption in chemical processes;
(k) CO₂ capture processes.

Special Issue: Homogeneous Catalysis

ChemCatChem, 2013, 5, (5), 1037–1210

Based on the 18th International Symposium on Homogeneous Catalysis (ISHC-18), held from 9th–13th July 2012 in Toulouse, France, this special issue on homogeneous catalysis is extended to organocatalysis, enzymatic catalysis, bioinspired catalysis, nanocatalysis and heterogenised homogeneous catalysis. Articles of interest include ‘Palladium(II) Complexes with Small N-Heterocyclic Carbene Ligands as Highly Active Catalysts for the Suzuki–Miyaura Cross-Coupling Reaction’, ‘Synthesis of Poly(silyl ether)s by Rhodium(I)–NHC Catalyzed Hydroamination: Homogeneous versus Heterogeneous Catalysis’ and ‘Ruthenium(II)-Catalyzed Hydrogen Generation from Formic Acid Using Cationic, Ammoniomethyl-Substituted Triarylphosphine Ligands’.

ON THE WEB

Buchwald Technical Forum

Johnson Matthey Catalysis and Chiral Technologies has made its powerful Buchwald phosphine ligand technology available on gram to commercial scale. The intellectual property is available on either ‘price per kilo’ or sublicense options. Additionally the Buchwald Technical Forum gives information about Buchwald Technologies at commercial scale along with the full ligand and palladacycle offering.
Find this at: http://www.jmct.com/buchwald

Changing Market Dynamics for Research Chemicals, Metals and Materials: An Interview with Julie Butterfield

Interview Conducted by Kal Kaur, AZoM™ – The A to Z of Materials, 11th March 2013

Julie Butterfield, General Manager of Alfa Aesar, a Johnson Matthey Company, talks to AZoM in this Insights from Industry interview about the changing market dynamics for research chemicals, metals and materials. This includes a brief introduction to Alfa Aesar, their product range, research application areas and manufacturing processes.
Find this at: http://www.azom.com/article.aspx?ArticleID=8308

Johnson Matthey Prices App

Johnson Matthey has launched a pgm prices application, ‘JM Prices’, which is available to download now on the Apple App Store and Android Market, coming soon to Blackberry App World. This free app provides access to the Johnson Matthey Base Prices for platinum, palladium, rhodium, iridium and ruthenium, which are updated throughout every trading day. As an extension to the prices facility on the Platinum Today website, JM Prices is designed to allow quick access to current
and historical price data, create interactive charts or view daily and monthly prices back to 1992, as well as linking through to News, Weekly Price Bulletins and Monthly Price Bulletins on Platinum Today. Find this at:

**Water Electrolysis & Renewable Energy Systems**

Fuel Cell Today launched its report “Water Electrolysis & Renewable Energy Systems” at All-Energy 2013 in Aberdeen, UK, on 22nd May 2013. The report describes how the electrolysis of water to generate hydrogen can be used in conjunction with renewable energy sources to provide a number of benefits. It begins with a brief summary of the fundamentals of water electrolysis and the available electrolyser technologies. It then looks at how electrolysis has been applied in the past and its applicability to, and suitability for, energy use. Find this at: http://www.fuelcelltoday.com/analysis/surveys/2013/water-electrolysis-renewable-energy-systems
Abstracts

CATALYSIS – APPLIED AND PHYSICAL ASPECTS

Fabrication of Noble-Metal Catalysts with a Desired Surface Wettability and Their Applications in Deciphering Multiphase Reactions
Pt and Pd catalysts with a wide range of surface wettabilities were fabricated through an electrochemical method and were characterised with SEM, EDX spectroscopy, TEM and AFM. No surfactant was required. The control of the macroscopic properties of the Pt and Pd catalyst layers led to very different performances in the electrooxidation of hydrogen peroxide and sodium formate or the reduction of oxygen in alkaline solutions. This study demonstrated that wettability not only influences the performance of a solid catalyst, but can also help decipher multiphase reaction mechanisms.

Ru Particle Size Effect in Ru/CNT-Catalyzed Fischer-Tropsch Synthesis
CNT-supported Ru NPs with mean sizes 2.3 nm to 9.2 nm were prepared using different post-treatments and investigated for Fischer-Tropsch synthesis. With shorter contact times, the TOF for CO conversion was dependent on the mean size of the Ru particles; TOF increased with the mean size of Ru particles from 2.3 nm to 6.3 nm and then decreased slightly. The selectivities to C5+ hydrocarbons increased gradually with the mean size of Ru particles up to 6.3 nm and then remained almost unchanged with a further increase in Ru particle size. With longer contact times, C10–C20 selectivity increased significantly at the expense of C21+ selectivity.

Confinement of the Grubbs Catalyst in Alkene-Functionalized Mesoporous Silica
Grubbs I catalyst, [RuCl2(κ=CH2)(Ph)(PCy3)2], was incorporated into ordered mesoporous SBA-15 silica materials functionalised with alkenyl-trichlorosilanes with different C chain lengths, e.g. vinyl- (C2), allyl- (C3), hexenyl- (C6) and octenyl- (C8) trichlorosilanes. The obtained materials, before and after interaction with Grubbs I, were characterised and the investigations revealed a pronounced dependence of the Grubbs catalyst stability on the alkyl chain length of the grafted moieties. The nature of the immobilised Ru-based species was a function of the surface modification, i.e. chain length of the alkenyl-silane.

CATALYSIS – INDUSTRIAL PROCESS

Rapid Analysis of Residual Palladium in Pharmaceutical Development Using a Catalysis-Based Fluorometric Method
A fast and inexpensive high-throughput approach has been found for the detection of residual Pd in pharmaceutical intermediates to support laboratory or pilot plant Pd removal. The approach was based on the Pd-catalysed Tsuji–Trost deallylation of an allylic ether substrate to produce a highly fluorescent product. Excellent sensitivity and linearity were found with Pd standards, and a reasonably good ability to quantify Pd (80–110% of actual) was observed for samples in which appropriate pretreatments with aqua regia and NaBH4 were performed. A streamlined assay procedure involving a predispensed reagent cocktail that was stable for a day at room temperature (and for months in the freezer) is described.

Industrial Scale-Up of Enantioselective Hydrogenation for the Asymmetric Synthesis of Rivastigmine
Two processes for the preparation of rivastigmine via asymmetric hydrogenation using the chiral spiro catalyst Ir(S)-SpiroPAP3-Me, have been developed. The first route was easy to scale up and provided (S)-3-(1-dimethylaminoethyl)phenol, which is a suitable intermediate for the manufacture of rivastigmine in API demand. The second route was convenient for operation and purification, giving rivastigmine in four steps in 84% overall yield.
**FUEL CELLS**

Platinum Monolayer Electrocatalysts: Tunable Activity, Stability, and Self-Healing Properties


Pt monolayer nanostructured electrocatalysts were developed for the ORR. These were nm scale core–shell particles with monolayers of Pt supported by metal, metal alloy or nanostructured noble metal/non-noble metal cores. In addition to an ultralow Pt content (one monolayer) and high Pt utilisation (all atoms can participate in the reaction), these catalysts exhibited very high activity and stability induced by the supporting NP cores, by the ability to tune the catalytic activity of the Pt monolayer depending on the properties of the top atomic layer of the cores, and by self-healing. Examples of tunable activity include a Pt monolayer on smooth core surfaces, Pd tetrahedral NPs, Pd nanowire and hollow Pd NP cores.

**METALLURGY AND MATERIALS**

High-Temperature Mechanical and Shape Memory Properties of TiPt–Zr and TiPt–Ru Alloys


To try to improve the shape memory properties and strength of Ti-50Pt (in at%) alloys at high temperature, the effects of partial substitution (e.g. 5 at%) of Ti with Zr and of Pt with Ru were investigated. The compressive strength and shape memory properties at high temperature were improved by these partial substitutions, e.g.: 1468 MPa for TiPt–Zr, 712 MPa for TiPt–Ru and 485 MPa for TiPt alloys. Furthermore, Ti-50Pt-5Zr alloy exhibited much higher strength and a better shape memory effect than Ti-45Pt-5Ru alloy.

**APPARATUS AND TECHNIQUE**

Temperature-Activated Reverse Sensing Behavior of Pd Nanowire Hydrogen Sensors


H₂ sensors based on individual Pd nanowires (NWs) were fabricated by integrating Pd NWs across microelectromechanical system electrodes, followed by assembling and bonding them to a chip carrier platform. Measurements with these sensors showed reverse sensing behaviours between the temperature zones 370–263 K and 263–120 K.

**CHEMISTRY**

From Osmium Hydrido Vinylidene to Osmacycles: The Key Role of Osmabutadiene Intermediates


Osmium hydrido vinylidene is a versatile and powerful reagent in the synthesis of asymmetric hydrogenation. Researchers have explored the key role of osmabutadiene intermediates in the asymmetric hydrogenation process, which involves the use of osmium hydrido vinylidene. This process is crucial in the preparation of chiral compounds, which are essential in various fields such as medicine, agriculture, and materials science.
Os hydrido vinylidene, 2, showed diverse cyclisation reactivity with activated terminal alkynes. Treatment of 2 with HCC=CCOR (R’ = OEt and Me) gave osmafurans via osmium alkenyl/vinylidenes. Also, 2 reacted with HCC(CH(OH))C≡CH to yield an osmabenzene, in which the alkynol acted as a C₅ fragment to cyclise with 2.

**Complexation to [Ru(bpy)₂]²⁺: the Trick to Functionalize 3,3’-Disubstituted-2,2’-Bipyridine**


The synthesis and chemical transformations of x,x’-disubstituted-2,2’-bipyridine with x = 4, 5 or 6 are often reported. This is not the case when x = 3. Several [(2,2’-bipyridine)₂Ru(3,3’-dialkylated-2,2’-bipyridine)]⁺ complexes were prepared highlighting surprising chemical behaviour by the 3,3’-disubstituted-2,2’-bipyridine ligand.

**ELECTRICAL AND ELECTRONICS**

**Spin Wave-Assisted Reduction in Switching Field of Highly Coercive Iron-Platinum Magnets**


Extremely low-field magnetisation switching was experimentally demonstrated in highly coercive FePt by using a spin wave excited in a soft magnetic permalloy (Ni₈₁Fe₁₉), where the permalloy was exchange-coupled to FePt through the interface. The switching field could be tuned by varying the magnitude and frequency of the radio frequency magnetic field, and a decrease in switching field by one order of magnitude was achieved under optimum conditions. Spin wave-assisted magnetisation switching is therefore promising as an ultralow-energy magnetisation manipulation technique.

**PHOTOCONVERSION**

**A Deep-Blue Emitting Charged Bis-cyclometallated Iridium(III) Complex for Light-Emitting Electrochemical Cells**


A cationic Ir(III) complex showed deep-blue emission in a concentrated film and could be used in light-emitting electrochemical cells (LECs). The complex was based on the 2’,6’-difluoro-2,3’-bipyridine skeleton as the cyclometallating ligand and a bis-imidazolium carbene-type ancillary ligand; bulky tert-butyl substituents were used to limit the intermolecular interactions. LECs were driven both at constant voltage (6 V) and constant current (2.5 mA cm⁻²). The performances were significantly improved with the latter method.

**Wideband Dye-Sensitized Solar Cells Employing a Phosphine-Coordinated Ruthenium Sensitizer**


Efficient DSSCs that exploit near-IR spin-forbidden singlet-to-triplet direct transitions in a phosphine-coordinated Ru(II) sensitizer, DX1, were fabricated. A DSSC using DX1...
generated a photocurrent density of 26.8 mA cm$^{-2}$. A tandem-type DSSC employing both DX1 and the sensitisier N719 was shown to have a power conversion efficiency of >12% under 35.5 mW cm$^{-2}$ simulated sunlight.

REFINING AND RECOVERY

*Recovering Palladium from Its Surplus Complexes in Research Laboratories by Solid State Thermal Treatment*


A method for the recovery of Pd from research laboratory wastes is based on heating Pd complexes to 900ºC in a dynamic air atmosphere to get a Pd residue of purity ~95%. The purity of the metal in the final residue depended on the nature of the Pd complexes; when the sample did not contain P ligands the recovery of Pd was stoichiometric. This was thought to be related to the remarkable inhibition of PdO formation exerted under these conditions by P ligands, free or coordinated to Pd, that was observed in this study.
Patents

CATALYSIS – APPLIED AND PHYSICAL ASPECTS

Palladium Hydrogenation Catalyst
Shell Internationale Research Maatschappij BV, European Appl. 2,570,470; 2013
A monolithic- or honeycomb-based Pd catalyst comprises Pd and two other metals, where the first metal is Pt and the second metal is Bi or the first metal is Ag and the second metal is Mn. The support is Al₂O₃ or a modification thereof. The weight ratio of Pd to the total of the first and second metals is 2:1 to 1:4. This Pd catalyst is used in the selective hydrogenation of unsaturated hydrocarbons which includes acetylene.

CATALYSIS – INDUSTRIAL PROCESS

Platinum-Palladium Alloy Plate for Nuclear Power Plant
Nuclear Power Institute of China, Chinese Appl. 102,744,062; 2012
A catalysis plate comprises a transition layer, prepared from (in wt%) 85–95 Al₂O₃ and 5–15 CeO₂, set on the surface of the base plate, which is FeCrAl heat-resistant steel with a thickness of 0.04–0.12 mm. There is a catalysis layer on the transition layer. The catalysis layer is prepared by mixing (in wt%) 5–25 Pt and 75–95 Pd. The catalysis plate is set on a vertical slot of the catalyst bed drawer situated at the hollow end-opening shell of a hydrogen recombiner. The advantages of the catalysis plate are good low-temperature and low hydrogen concentration running performances, and high-temperature thermal stability.

Palladium Catalyst for Synthesising Paracetamol
Ural Federal University, Russian Patent 2,461,543; 2012
A simplified process for producing paracetamol in high yields involves the reduction of p-nitrosophenol in ethyl acetate in the presence of a Pd/C-containing catalyst by H₂ at 2–4 atm and 20–50°C. This is followed by acylation of the intermediate p-aminophenol and the end product recovery.

CATALYSIS – REACTIONS

Preparation of Halogenated Pyridines
Lonza Ltd, World Appl. 2013/020,938
A continuous method for preparing 1, where 2 is contacted with a metal catalyst or a metal catalyst on a support or a mixture, preferably Pd(0) or Ru(0), at 150–800°C in gaseous phase. R¹ and R² are identical or different and selected from H, halogen, C₁₋₆ alkyl, CN, C_F₃, C₁₋₆ alkoxy or C₁₋₆ alkoxy carbonyl and X¹ is F, Cl or Br. The support is selected from C, Al₂O₃, BaSO₄, SiO₂, aluminosilicate and mixtures thereof.

Production of Alcohols
Celanese International Corp, US Appl. 2013/0,035,517
The process for producing alcohols consists of: (a) converting a first feed composition comprising acetic acid in a hydrogenation reactor in the presence of a first catalyst selected from Ru/SiO₂, Pd/C or Fe/C to produce a product containing acetone; (b) hydrogenating a second feed composition comprising acetone, produced in the first step, in the presence of a second catalyst in a second reactor to produce a hydrogenation effluent comprising isopropanol and acetone; and (c) separating at least a portion of the acetone from the isopropanol and returning the acetone to the second reactor. The second catalyst is selected from Pt/Sn, Pt/Ru, Pt/Re, Pd/Ru, Pd/Re, Co/Pd, Co/Pt, Co/Cr, Co/Ru, Co/Sn, Ag/Pd, Cu/Pd, Cu/Zn, Ni/Pd, Au/Pd, Ru/Re and Ru/Fe.

Continuous Production of Arylamine by Palladium
Xerox Corp, US Appl. 2013/0,046,110
A method for producing an arylamine product involves a continuous Buchwald-Hartwig reaction of an arylamine reactant, e.g. 3-methoxy diphenylamine, with dibromobiphenyl, a sodium tert-pentoxide and dichlorobis(di-tert-butylphenylphosphine)palladium(II) in toluene in a continuous fluid conduit device. The arylamine product is continuously produced at a space time yield of ~100 g l⁻¹ h⁻¹ with a rate product of ~0.6 g min⁻¹. The diameter of the continuous fluid conduit is >1 mm, the pressure is ~6–25 bar and the temperature is between room temperature and ~200°C.
EMISSIONS CONTROL
Wall Flow Type Exhaust Gas Purification Filter
NGK Insulators, Ltd., European Appl. 2,565,408; 2013
A wall flow type exhaust gas purification filter consists of a honeycomb structure which has porous ceramic partition walls forming cells which function as exhaust gas passages. The opening ends of alternate cells are plugged. There is a large pore region with average pore size ≥15 μm and a small pore region with average pore size ≤8 μm and they each have an area of ≥0.1 mm². The catalysts are selected from at least two of Pt, Pd and Rh and a ternary catalyst containing at least one of Al₂O₃, CeO₂ or ZrO₂; these are coated on the internal portions and surfaces of the partition walls.

FUEL CELLS
Platinum Loading for Fuel Cell Electrode
UTC Power Corp, World Appl. 2013/009,275
The electrode for PEMFC comprises a Pt catalyst, C support particles and an ionomer. The Pt loading for both anode and cathode is <0.2 mg cm⁻² and the ionomer-to-carbon ratio is between ~0.5–~0.9. The electrode has a thickness of ~2–~5 μm.

Fuel Cell Catalyst Layer
National Taiwan University of Science and Technology, US Appl. 2013/0,065,155
A catalyst layer for a fuel cell consists of a catalyst support comprising TiₓM₁₋ₓO₂, where M is selected from Group 2, Group 5, Group 6, Group 7, Group 8, Group 9, Group 10, Group 11, Group 12 and Group 13 metal; 0 < x ≤ 0.9; and a catalyst comprising Pt or Pt alloys. The Group 8, Group 9 and Group 10 metals are selected from Pd, Rh, Ir, Os, Ru, Fe, Co and Ni. The method for making the catalyst layer involves: (a) a hydrothermal synthesis of a first precursor, Ti halide and a second precursor, an oxoanion- or polyoxometalate-containing salt, to form the TiₓM₁₋ₓO₂ catalyst support; (b) dispersing the catalyst support into a solvent, selected from water, ethylene glycol, DME, acetonitrile and butanol; and (c) adding a Pt or Pt alloy catalyst to form a mixture. This is then microwave heated to form the catalyst layer. The stability and performance of the cell can be enhanced.

Palladium Catalyst Fine Particles
Toyota Motor Corp, Japanese Appl. 2013-013,878
The catalyst particles consist of Pd-containing centre particles, which include Pd(111) face, coated with Pt-containing outermost layers. The process for manufacturing the catalyst particles includes: (a) preparing the precursors in which the Pd-containing particles with Pd(111) face are coated with Pt-containing outermost layers; (b) putting the coated particles in contact with an acid solution to dissolve ≥1 atom layer of Pd(111) face in dissolution-precipitation equilibrium state of Pt; and (c) depositing Pt on the fcc site of the Pd(111) face. The catalyst particles are used in fuel cells.

METALLURGY AND MATERIALS
Synthetic Diamonds from Platinum Carbonyl Compounds
I. V. Fedoseev et al., Russian Patent 2,469,952; 2012
Synthetic diamonds are obtained by the decomposition of solid Pt carbonyl compounds in a hermetic container at 310–800ºC for 1–2 h. The ratio of the Pt carbonyl compounds to container volume is 1:1.1 to 1:100 in a neutral atmosphere. After opening the container, the diamonds are separated by treating with aqua regia. The advantage of this process is an increase in the size of the obtained diamonds.

Jewellery and Industrial Alloys with Palladium
Hochschule Pforzheim University, German Appl. 102,011,011,448; 2012
A Pt-, Pd- or Au-based alloy consists of metals or metalloids, each of the alloy with at least 10 ppm and boron which hardens the alloy. The typical examples are (in wt%) 95Pt-4.85Pd-0.15 B and 75Au-15Pd-9.7Ag-0.28 B. The alloys are used as catalysts, materials for crucibles or devices for the glass and chemical industries as well as materials for clock cases or jewellery.

APPARATUS AND TECHNIQUE
Platinum in Nanobiosensor
X. Wang, Chinese Appl. 102,749,355; 2012
The nanobiosensor consists of an electrode, made from one or a combination of Pt, Au, Ag, Cu, graphite or glass, wrapped by a nano gel or nanotube array nanocarrier which is attached to a biosensing assembly, a current amplifier and a display alarm device. The nanobiosensor has high sensitivity and a high performance/price ratio and can be used in air quality detection.

ELECTROCHEMISTRY
Platinum Electrode for Lithium-Air Battery
Inha-Industry Partnership Institute, US Appl. 2013/0,022,529
The method for preparing Pt-MnO₂/C complex consists of: (a) preparing MnO₂/C by dispersing C in...
KMnO₄, applying microwaves for ~5–10 mins, filtering and drying the solution to obtain MnO₂/C; and (b) preparing Pt-MnO₂/C by dispersing MnO₂/C in ethylene glycol, adding a Pt precursor, chloroplatinic acid, and applying microwaves for ~5–10 mins to obtain Pt-MnO₂/C complex. Pt-MnO₂/C is used in the positive electrode material of a Li-air battery where 20 parts by weight of the Pt precursor is used per 100 parts by weight of C.

**PHOTOCONVERSION**

**Binuclear Phosphorescent Iridium Complex**

Nanjing University of Posts and Telecommunications, *Chinese Appl.* 102,617,652; 2012

The preparation of the binuclear phosphorescent Ir complex with two-photon absorption characteristic comprises: (a) preparing an aromatic group substituted N,N ligand via the Sonogashira coupling reaction; (b) obtaining bromo phenylquinoline via the Friedlander condensation reaction; (c) reacting with butyllithium at ~78°C in THF to obtain mesitylboryl group-containing C,N ligand; and (d) obtaining the corresponding complex product via coordination reaction. The binuclear phosphorescent Ir complex has a strong two-photon absorption characteristic between 730–840 nm and up conversion phosphorescence. This complex can be used in two-photon excitation induced fluoride ion probe, time-resolved imaging, two-photon fluorescence microscopy imaging and biological fluorescence sensors.
The use of platinum and its alloys is well established in the automotive, chemical, glass, electrical and dental industries. However, many of these applications require high-temperature operation of the alloys. At high temperatures conventional platinum group metals (pgms) are subject to grain growth and, therefore, are weak and subject to creep deformation. They can also be subject to contamination failure.

Johnson Matthey developed zirconia grain stabilised (ZGS) platinum that is resistant to grain growth and contamination and deformation at high temperatures (1). Applications include glass manufacturing equipment (2) as well as a range of laboratory apparatus (3).

ZGS platinum materials are produced by incorporating fine ZrO\textsubscript{2} ceramic particles, dispersed uniformly throughout the platinum metal matrix, a process called dispersion strengthening. These particles slow down the process of degradation in the alloy by pinning dislocation networks formed during thermomechanical processing, so inhibiting the movement of these dislocations to the grain boundaries (Figure 1) (2). Microstructural degradation is effectively restricted, giving extended operating lives compared to conventional pgms and alloys.

The principle of grain stabilisation has been established in the base metal world for some time (4). The difficulty had always been in achieving production of grain stabilised material on a large scale and with a stable dispersion of particles of the correct composition and size to be effective that does not coarsen or dissolve at the operating temperature. Johnson Matthey developed a unique process to meet those requirements, and have been using it for over 20 years.

ZGS platinum offers significantly improved performance over conventional platinum materials for use at elevated temperatures as the following examples show.

**How ZGS Alloys Behave at Working Temperature**

Figure 2 illustrates graphically the improvement in high-temperature life achieved by grain stabilisation. The time to failure at 1400°C under a stress of approximately 10 MPa shows that ZGS Pt lasts up to ten times as long as the conventional Pt-Rh alloy and ZGS Pt-10% Rh lasts more than ten times as long as ZGS Pt. In terms of the rate of deformation before failure, the load to cause a deformation rate of 0.1% h\textsuperscript{-1} is approximately twelve times higher for ZGS
platinum compared to Pt-20% Rh, while at 1% h⁻¹ it is three times higher (1).

Other properties of the ZGS platinum alloys are summarised in Tables I and II (2). All data given is for sheet.

**ZGS Platinum Applications**

ZGS platinum and platinum alloys find particular application in products where high temperature causes creep, distortion and ultimately failure of unsupported conventional platinum and its alloys. Their principle application is in the glass manufacturing industry where their improved properties allow less material to be used while simultaneously improving equipment lifetimes.

ZGS platinum-rhodium baseplates for bushings, used for the production of continuous filament glass fibre, resist creep-induced sagging and eliminate the need for extra structural platinum supports. ZGS platinum alloys can also be used for glass carrying apparatus designed with thinner wall sections and lower rhodium content; such apparatus can have 50% greater useful life and the reduced rhodium content reduces the potential for discolouration of the glass. Lightweight thermocouple sheaths can be fabricated with walls half the conventional thickness, saving on costs. ZGS platinum can make possible the elimination of molybdenum and ceramic cores for glass stirrers, improving service life and reducing potential inservice problems. ZGS platinum-5% gold is used for crucibles and casting dishes for XRF analysis using borate fluxes.

The recommended maximum operating temperatures for the ZGS platinum and ZGS platinum alloy materials are typically 50–100ºC above those of the conventional alloys. Table III (3) shows the maximum temperatures recommended for all applications.

---

**Table I**

How ZGS Platinum and Platinum-Rhodium Alloy Behave at Room Temperature Compared to Conventional Platinum and Its Alloys

<table>
<thead>
<tr>
<th>Property</th>
<th>ZGS Pt</th>
<th>ZGS Pt-10% Rh</th>
<th>100% Pt</th>
<th>Pt-10% Rh</th>
<th>Pt-20% Rh</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific gravity, g cm⁻³</td>
<td>21.4</td>
<td>19.8</td>
<td>21.4</td>
<td>20.0</td>
<td>18.8</td>
</tr>
<tr>
<td>Electrical resistivity at 20°C, µΩ cm</td>
<td>11.12</td>
<td>21.2</td>
<td>10.6</td>
<td>19.2</td>
<td>20.8</td>
</tr>
<tr>
<td>Temperature coefficient of electrical resistivity per ºC</td>
<td>0.0031</td>
<td>0.0016</td>
<td>0.0039</td>
<td>0.0017</td>
<td>0.0014</td>
</tr>
<tr>
<td>Ultimate tensile strength, annealed, kg mm⁻²</td>
<td>19</td>
<td>36</td>
<td>13</td>
<td>34</td>
<td>49</td>
</tr>
<tr>
<td>Vickers hardness, annealed sheet</td>
<td>60</td>
<td>135</td>
<td>40</td>
<td>90</td>
<td>115</td>
</tr>
</tbody>
</table>

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Table II
Ultimate Tensile Strength (Annealed) at Elevated Temperatures of ZGS Platinum and Platinum-Rhodium Alloy Compared to Conventional Platinum and Its Alloys

<table>
<thead>
<tr>
<th>Temperature, ºC</th>
<th>Ultimate tensile strength, kg mm⁻²</th>
<th>ZGS Pt</th>
<th>ZGS Pt-10% Rh</th>
<th>100% Pt</th>
<th>Pt-10% Rh</th>
<th>Pt-20% Rh</th>
</tr>
</thead>
<tbody>
<tr>
<td>1000</td>
<td></td>
<td>5.2</td>
<td>16.7</td>
<td>2.4</td>
<td>8.4</td>
<td>23.5</td>
</tr>
<tr>
<td>1100</td>
<td></td>
<td>4.6</td>
<td>14.3</td>
<td>1.7</td>
<td>6.2</td>
<td>16.5</td>
</tr>
<tr>
<td>1200</td>
<td></td>
<td>3.8</td>
<td>12.8</td>
<td>1.3</td>
<td>4.8</td>
<td>10.1</td>
</tr>
<tr>
<td>1300</td>
<td></td>
<td>3.6</td>
<td>9.4</td>
<td>0.8</td>
<td>3.9</td>
<td>7.0</td>
</tr>
<tr>
<td>1400</td>
<td></td>
<td>2.9</td>
<td>8.5</td>
<td>0.4</td>
<td>3.0</td>
<td>5.0</td>
</tr>
<tr>
<td>1500</td>
<td></td>
<td>2.4</td>
<td>7.2</td>
<td>–</td>
<td>2.4</td>
<td>3.9</td>
</tr>
</tbody>
</table>

Conclusions
ZGS platinum resists contamination failure for extended periods and extends the life of crucibles and other equipment. ZGS platinum also offers an opportunity to reduce the component weight while maintaining material integrity. Standard products including crucibles and dishes are available in ZGS platinum, ZGS platinum-10% rhodium and ZGS platinum-5% gold. Other alloys are available upon request from Johnson Matthey Noble Metals.

Reference

Table III
Recommended Maximum Operating Temperatures for ZGS Platinum Materials Compared to Conventional Platinum and Its Alloys

<table>
<thead>
<tr>
<th>Material</th>
<th>Temperature, ºC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt</td>
<td>1400</td>
</tr>
<tr>
<td>ZGS Pt</td>
<td>1500</td>
</tr>
<tr>
<td>Pt-10% Rh</td>
<td>1550</td>
</tr>
<tr>
<td>ZGS Pt-10% Rh</td>
<td>1600</td>
</tr>
<tr>
<td>Pt-5% Au</td>
<td>1300</td>
</tr>
<tr>
<td>ZGS Pt-5% Au</td>
<td>1400</td>
</tr>
</tbody>
</table>

The Authors
Dominic Morris is a Product Specialist in Sales at Johnson Matthey Noble Metals in Royston, UK. He works with industrial products, which incorporate pgm manufactured products including wire, tube, laboratory equipment and complex fabrications used in high-temperature applications and environments.

Rob McGrath is a Principal Metallurgist at Johnson Matthey Noble Metals. His areas of interest include manufacturing techniques and industrial applications for pgm products, pgm alloy development and coatings technology.
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Keith White
Principal Information Scientist

Email: jmpmr@matthey.com

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