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Editorial

55 Years of Platinum Metals Review

This year marks the 55th anniversary of the first publication of *Platinum Metals Review* by Johnson Matthey. In more than five decades of continuous quarterly publication, *Platinum Metals Review* has covered a wide range of industrial and scientific uses of the platinum group metals (PGMs), emphasising the metals' unique properties in applications ranging from automotive emissions control and efficient industrial processes to anticancer drugs. *Platinum Metals Review* also covers new applications of the PGMs, and regularly features articles on new and emerging technologies such as fuel cells and hydrogen energy. This issue continues these traditions, featuring subjects as diverse as palladium-based membranes for the production of high-purity hydrogen and platinum casting techniques for the jewellery industry. With PGM science more relevant than ever at this time, it gives me great pleasure to be managing this prestigious and respected journal.

2011 also marks a number of important anniversaries for the Johnson Matthey group: the 160th anniversary of George Matthey joining the company which was to become the partnership Johnson and Matthey and eventually Johnson Matthey PLC, and the 150th anniversary of the company being approved as refiners to the Bank of England. It also marks the 85th anniversary of A. R. Powell, then head of Johnson Matthey’s Research Department, perfecting a process for extracting and refining the PGMs from the ores of the Merensky Reef in South Africa. This enabled the successful exploitation of the world’s biggest platinum deposits and helped to develop Johnson Matthey’s close and enduring association with PGMs and with the South African company Rustenburg Platinum Holdings Ltd, which later became Anglo Platinum Ltd, the world’s largest primary producer of PGMs.

Another important milestone has recently passed, the anniversary of the US Clean Air Act Extension in 1970, which led to the development of PGM-based technologies for the control of automotive exhaust emissions. By 1975 model year, platinum-based autocatalysts fitted to cars in the US were instrumental in reducing carbon monoxide and hydrocarbon emissions by 90 per cent compared with 1970 models. 1976 model year cars went on to use two separated PGM-based catalysts to also control NOx emissions. By the early 1980s the first practical systems to use platinum/rhodium three-way catalysts to control all three legislated pollutants were in production.

Almost every country in the world now has automotive emissions regulations which necessitate the use of PGM autocatalysts and this application is currently the single biggest demand sector for platinum, palladium and rhodium. Progress on the development and implementation of PGF catalysts for vehicle emissions control is covered in this issue in our ‘Appreciation’ of one of the pioneers of autocatalysts, Dr Haren Gandhi of Ford, by another autocatalyst pioneer, Dr Martyn Twigg of Johnson Matthey.

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Palladium-Based Alloy Membranes for Separation of High Purity Hydrogen from Hydrogen-Containing Gas Mixtures

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Palladium-based alloys with yttrium, copper, ruthenium or indium additions were investigated. Their specific hydrogen permeability, strength, linear thermal expansion in hydrogen and corrosion resistance in a number of gas media were determined. This allowed effective membrane elements to be developed using membranes made from these alloys, which are used for the separation of high purity hydrogen from hydrogen-containing gas mixtures. Membrane elements with 93.5 wt% palladium-6 wt% indium-0.5 wt% ruthenium alloy membranes were developed by the authors’ research group, and their technical characteristics are described.

Introduction
Hydrogen is an attractive alternative fuel to meet ever-growing energy requirements while reducing the reliance on oil and gas, with their attendant environmental and resource problems. By contrast, hydrogen is potentially an inexhaustible, clean and environmentally sustainable resource. One way to produce high purity hydrogen is by separation from hydrogen-containing gas mixtures produced by catalytic or chemical manufacturing processes.

Hydrogen production volumes vary widely, depending on the end use application. These can range from several cubic metres per hour (m$^3$/h) for micro- and nanoelectronics and portable energy sources such as fuel cells, to tens or hundreds of m$^3$/h for transport and small stationary energy sources, tens of thousands of m$^3$/h for the chemical industry and metallurgical applications, and hundreds of thousands of m$^3$/h for large stationary energy installations and hydrogen production plants.

Recent progress in hydrogen power engineering means that the demand for high purity hydrogen
(>99.9999 vol%) is increasing rapidly. The pressure swing adsorption method is most frequently used in the USA (1). However, this method is energy intensive as high volumes of adsorbents are used, and some of the separated hydrogen is used for adsorbent regeneration, reducing the efficiency of the process for hydrogen purification. Therefore, the best method for the production of high purity hydrogen is currently by separation via selective diffusion through metallic membranes made from palladium-based alloys whose permeability for other gases is infinitely small.

Hydrogen separation installations using palladium-based alloy membranes are more expensive in terms of capital expenditure than installations using polymeric membranes. However, palladium-based membranes have a number of advantages, namely that high purity hydrogen can be prepared in a single step and that the process can be carried out at high temperatures. This allows the hydrogen separation process to be combined with the production of hydrogen-containing gas via the direct incorporation of membranes into membrane catalytic reactors (2–4).

There has been growing interest in the development of palladium-based alloy membranes for hydrogen separation. Analysis of published scientific and patent literature shows a large increase in the number of patent and non-patent publications related to palladium membranes in recent decades (see Figure 1). However, the analysis also shows that the commercial preparation of inexpensive high purity hydrogen remains problematic due to the lack of efficient palladium-based membrane alloys, of systematic data on the properties of membranes, and of original designs of membrane elements and modules.

This article reviews the work undertaken by the authors’ research group to develop high-capacity palladium-based membrane alloys and to design efficient membrane elements and modules based on these alloys for the commercial production of high purity hydrogen.

**Palladium-Based Alloy Membranes**

Efficient hydrogen separation membrane alloys must have high hydrogen permeability, low expansion when saturated with hydrogen, good corrosion resistance, and low hydrogen crossover. Additionally, the effectiveness of the membrane element depends on its design and the fabrication process. Palladium-based alloy membranes meet these requirements due to their unique properties:

1. **High Permeability:** Palladium-based alloys have high hydrogen permeability, which is essential for efficient hydrogen separation.
2. **Low Expansion:** The expansion of the permeating hydrogen is low, which helps maintain the integrity of the membrane.
3. **Corrosion Resistance:** Palladium-based alloys are resistant to corrosion, ensuring durability and long-term performance.
4. **Low Hydrogen Crossover:** The hydrogen crossover is minimized, reducing the overall system efficiency.

**Figure 1.** Global trends in the number of publications in the patent and non-patent scientific literature relating to palladium membranes for hydrogen separation between 1970–2009
resistance and high plasticity and strength during operation at temperatures of 300–700°C. The main problems with membrane reliability are related to their corrosion resistance, changes in their hydrogen permeability and structural changes that occur during operation.

The search for effective alloys was limited to palladium-based solid solutions as these are the only materials which can demonstrate all of the required properties. Palladium alloys of high plasticity are required as they are used in the form of micron-sized foils and tubes. Palladium forms a wide range of solid solutions with many metals. Such palladium-based solid solutions are formed with 10–30 wt% of refractory metals (niobium, molybdenum, ruthenium, tantalum, tungsten, rhenium, vanadium, etc.) and low-melting metals (lithium, magnesium, indium, lead, tin, bismuth, etc.).

An interesting feature of palladium is the existence of wide solid solution regions (around 10–15 wt%) with all rare earth metals except lanthanum and neodymium, for which the regions are around 2 wt%. Palladium alloys with structurally isomorphous metals (iron, cobalt, nickel, copper, silver, gold, etc.) crystallise with the formation of continuous solid solutions. The wide range of palladium-based solid solutions observed in binary systems is also found in ternary systems of these metals.

The purity of palladium with respect to interstitial elements is of primary importance during alloy formation. To avoid the problems of internal oxidation and formation of complex impurity inclusions in the crystal lattice, both the chemical purity of the starting components and the preparation of the alloy must be carefully controlled. Arc-melted palladium alloys, which are pure with respect to interstitial impurities, have adequate plasticity (elongation before fracture, \( \delta \), of >20%). This allows micron-sized foils to be prepared by cold rolling with intermediate vacuum annealing (5, 6).

**Palladium-Silver Alloy Membranes**

Membrane alloys based on the palladium-silver system are well studied and have commercial applications (7). The 77 wt% Pd-23 wt% Ag composition is a plastic alloy with a specific hydrogen permeability of 3.4 Nm\(^3\) mm m\(^{-2}\) h\(^{-1}\) MPa\(^{-0.5}\) at 600°C. However, the high silver content leads to a decrease in hydrogen purity above 450°C, as traces of oxygen are observed in the hydrogen output stream.

Multicomponent palladium-silver-based alloys referred to as ‘B type’ were developed in Russia during the 1970s. The ‘B1’ alloy, whose composition is 80.6 wt% Pd-15 wt% Ag-3 wt% Au-0.6 wt% Pt-0.6 wt% Ru-0.2 wt% Al, is used in industry (8–11) as it shows the optimum combination of membrane characteristics: it is strong, plastic and corrosion-resistant in hydrocarbon gas media. Its specific hydrogen permeability is 2.5 Nm\(^3\) mm m\(^{-2}\) h\(^{-1}\) MPa\(^{-0.5}\) at 600°C. However, non-uniform distribution of alloying components can cause failure of capillaries and membranes made from this alloy. Moreover, palladium-silver alloys are poisoned irreversibly in gas mixtures containing even small amounts of hydrogen sulfide.

**Silver-Free Palladium Alloy Membranes**

Our studies were aimed at the development of silver-free alloys which are easy to manufacture and have a higher hydrogen permeability than that of pure palladium.

An analysis of our experimental results showed that variations in the hydrogen permeability caused by alloying are directly dependent on variations in the lattice parameters of palladium. In particular, alloying with ruthenium, indium, lead, and rare earth metals leads to an increase in the hydrogen permeability of palladium alloy foils, whereas tin slows down hydrogen diffusion. When alloying with copper, low levels of copper addition initially cause a drop in hydrogen permeability, but in palladium alloys with 38–42 wt% copper, which show solid-state ordering below 600°C (12), hydrogen permeability is increased. Changes in the hydrogen permeability of palladium-copper alloys have been studied by a number of investigators (13–15).

**Hydrogen Permeability and Mechanical Properties**

We studied the hydrogen permeability and strength of palladium-copper, palladium-indium, palladium-lead, palladium-yttrium-ruthenium, palladium-indium-ruthenium and palladium-rare earth metal alloys (16, 17). Based on our previous results, we selected the following compositions of membrane alloys for further investigation of their hydrogen permeability, strength, expansion and corrosion resistance:

- 93 wt% Pd-7 wt% Y;
- 60 wt% Pd-40 wt% Cu;
- 94 wt% Pd-6 wt% Ru;
- and 93.5 wt% Pd-6 wt% In-0.5 wt% Ru.

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Preparation procedures and techniques for measuring the strength, hydrogen permeability and expansion are described in a previous paper by Burkhanov et al. (18).

Tables I and II show the mechanical properties and specific hydrogen permeability, respectively, of these alloys. It can be seen from the Tables that the 93 wt% Pd-7 wt% Y alloy has the highest hydrogen permeability and strength but the lowest plasticity of the alloys studied.

Effects of Temperature

Palladium alloys dissolve hydrogen to concentrations of around 0.3–0.6 at% H directly from the gas phase. Stresses resulting from the increase in alloy volume upon hydrogen dissolution are the principal cause of loss of membrane element sealing. Therefore, the study of thermal expansion in the presence of hydrogen is of primary importance in designing membrane elements. Experimental values for linear thermal expansion (ΔL/L, %) of the palladium alloys at a hydrogen pressure of 0.1 MPa are shown in Table III.

The thermal expansion must be kept below 1% and this determines the range of possible operating temperatures of the alloy membranes (see Table III). The lowest thermal expansion is observed for the 94 wt% Pd-6 wt% Ru alloy; the range of its operating temperatures is 150–500°C. The range of operating temperatures for the 60 wt% Pd-40 wt% Cu alloy is 200–450°C; above 450°C, the disordered face-centred cubic (fcc) phase appears and the hydrogen permeability decreases. The range of operating temperatures for the 93 wt% Pd-7 wt% Y and 93.5 wt% Pd-6 wt% In-0.5 wt% Ru alloys is 300–600°C.

Table I

Mechanical Properties of Palladium-Based Membrane Alloys in the Annealed State

<table>
<thead>
<tr>
<th>Composition, wt%</th>
<th>Hardness, HV</th>
<th>Ultimate tensile strength, σ, kg mm⁻²</th>
<th>Relative elongation, δ, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>100% Pd</td>
<td>40</td>
<td>30</td>
<td>28</td>
</tr>
<tr>
<td>93% Pd-7% Y</td>
<td>172</td>
<td>60</td>
<td>16</td>
</tr>
<tr>
<td>60% Pd-40% Cu</td>
<td>120</td>
<td>50</td>
<td>22</td>
</tr>
<tr>
<td>94% Pd-6% Ru</td>
<td>142</td>
<td>55</td>
<td>20</td>
</tr>
<tr>
<td>93.5% Pd-6% In-0.5% Ru</td>
<td>114</td>
<td>48</td>
<td>26</td>
</tr>
</tbody>
</table>

Table II

Specific Hydrogen Permeability of Palladium-Based Membrane Alloys at Different Temperatures

<table>
<thead>
<tr>
<th>Composition, wt%</th>
<th>Temperature, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>200</td>
</tr>
<tr>
<td>100% Pd</td>
<td>–</td>
</tr>
<tr>
<td>93% Pd-7% Y</td>
<td>–</td>
</tr>
<tr>
<td>60% Pd-40% Cu</td>
<td>–</td>
</tr>
<tr>
<td>94% Pd-6% Ru</td>
<td>0.3</td>
</tr>
<tr>
<td>93.5% Pd-6% In-0.5% Ru</td>
<td>–</td>
</tr>
</tbody>
</table>

*Specific permeability is given in Nm⁻³ mm⁻² h⁻¹ MPa⁻⁰.⁵
Effects of Gas Composition

The stability of membranes and membrane elements depends on the hydrogen permeability. Heating palladium-based membrane elements from room temperature to ~300°C in hydrogen-containing gas mixtures and then cooling causes an increase in the membrane volume due to hydrogen absorption. Therefore, the heating and cooling of membranes is typically carried out in either a vacuum or an inert gas atmosphere.

We studied the hydrogen permeability of membrane alloys during heating and cooling in the presence of carbon dioxide in synthesis gas obtained from hydrocarbon fuel conversion. The specific hydrogen permeability was measured at different temperatures during repeated heating and cooling of membranes 50 µm thick in vacuum, then in CO₂, and again in vacuum. Within a selected temperature range of 200–600°C (200–400°C for the palladium-copper alloy), the specific hydrogen permeability was found to be independent of the pressure drop across the membrane (the difference between pressures before the membrane and after it).

With the exception of the 93 wt% Pd-7 wt% Y alloy, there was no change in the specific hydrogen permeability before and after heating and cooling of membranes in CO₂. This indicates that there were no structural changes in the membranes under these conditions within this temperature range. The same results were observed after heating and cooling the membranes in a vacuum. Therefore, we conclude that membrane elements made from 60 wt% Pd-40 wt% Cu, 94 wt% Pd-6 wt% Ru and 93.5 wt% Pd-6 wt% In-0.5 wt% Ru alloys can be heated up to ~300°C in a CO₂ atmosphere. This removes the need for a vacuum or an inert gas atmosphere and consequently allows the process to be simplified and costs to be reduced.

The hydrogen permeability of the 93 wt% Pd-7 wt% Y alloy decreases during heating and cooling in CO₂. Therefore, the heating of this membrane should be carried out in a vacuum or an inert gas atmosphere (19).

Membrane characteristics of the 93 wt% Pd-7 wt% Y, 60 wt% Pd-40 wt% Cu, 94 wt% Pd-6 wt% Ru and 93.5 wt% Pd-6 wt% In-0.5 wt% Ru alloys were studied previously, and recommendations were made for their effective operation in selected gas media (20).

<table>
<thead>
<tr>
<th>Composition, wt%</th>
<th>Temperature, ºC</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>30</td>
</tr>
<tr>
<td>93% Pd-7% Y</td>
<td>3.2</td>
</tr>
<tr>
<td>60% Pd-40% Cu</td>
<td>3.1</td>
</tr>
<tr>
<td>94% Pd-6% Ru</td>
<td>2.74</td>
</tr>
<tr>
<td>93.5% Pd-6% In-0.5% Ru</td>
<td>4.1</td>
</tr>
</tbody>
</table>

*The linear thermal expansion is defined as ∆L/L, %

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**Table III**

Linear Thermal Expansion of Palladium-Based Membrane Alloys in Hydrogen

<table>
<thead>
<tr>
<th>Composition, wt%</th>
<th>Temperature, ºC</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>30</td>
</tr>
<tr>
<td>93% Pd-7% Y</td>
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<td>60% Pd-40% Cu</td>
<td>3.1</td>
</tr>
<tr>
<td>94% Pd-6% Ru</td>
<td>2.74</td>
</tr>
<tr>
<td>93.5% Pd-6% In-0.5% Ru</td>
<td>4.1</td>
</tr>
</tbody>
</table>

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**Behaviour of the Palladium Alloys**

**93 wt% Pd-7 wt% Y Alloy**

Maximum hydrogen permeability and strength are observed for palladium alloys with rare earth metals, in particular with yttrium (21, 22). The optimum composition is 93 wt% Pd-7 wt% Y. At certain temperatures, its hydrogen permeability exceeds that of 77 wt% Pd-23 wt% Ag and B1 alloys by factors of two and three, respectively. Further work is being undertaken to optimise service conditions for this alloy in view of its instability in the presence of CO₂.

Membranes made from the 93 wt% Pd-7 wt% Y alloy have good corrosion resistance and high productivity during operation in gas mixtures of argon and hydrogen, helium and hydrogen, and nitrogen and hydrogen. Thus, the composition shows promise as a membrane alloy for the separation of high purity hydrogen from hydrogen-helium mixtures (purification of helium with respect to hydrogen isotopes),
ammonia dissociation products, and for liquid nitrogen production.

**60 wt% Pd-40 wt% Cu Alloy**
This alloy gives a substantial cost saving due to its high copper content. It is plastic and corrosion resistant during operation in hydrocarbon media. It operates stably at temperatures of 280–320°C for the separation of hydrogen from water vapour-methanol conversion products.

**94 wt% Pd-6 wt% Ru Alloy**
This alloy has the lowest hydrogen permeability and thermal expansion of all the alloys studied. It can operate at low temperatures (from 150°C) in hydrocarbon media and in waste streams from silicon production (H₂ + CH₃SiH₃ + SiCl₄ + HCl + CₙHₙ). (to 18 vol%), CO₂, H₂S (to 1.5 vol%) (19). Test reports demonstrating its performance in hydrogen-containing gas mixtures with up to 1.5 vol% H₂S are available on request by contacting the corresponding author Gennady S. Burkhanov at genburkh@imet.ac.ru.

The ternary alloy may be used to separate high purity hydrogen from synthesis gas produced from hydrocarbon fuel and natural gas conversion (20).

**Hydrogen Purification Modules**
At present, increasing demand for high purity hydrogen means that effective, reliable and low-cost commercial modules for hydrogen production and purification are required. Membrane elements can be constructed in the form of either capillary tubes, flat plates or discs. In terms of ease of manufacture, service characteristics, efficiency and ease of repair it can be demonstrated that disc membranes are the most promising for commercial application (3, 23). The disc structure requires five to ten times fewer joints between membranes and structural elements than does the capillary tube structure, leading to improved reliability.

**Figure 2** shows a hydrogen separation element and its components. The membranes, membrane elements and membrane modules are produced using cold forming and cutting techniques to ensure accuracy at each stage. Joints are sealed by diffusion and argon-arc welding in the absence of solders, pastes, etc., to ensure efficient sealing.
The membrane filtration element is a ‘sandwich-like’ assemblage of two walls in the form of disc membranes either 50 mm or 150 mm in diameter, made from a palladium-based alloy foil 20–50 µm thick and welded onto a stainless steel ring frame by diffusion welding. A porous separator (wire netting) is placed between the walls. After that, the frames are welded circularly with a branch pipe for the output of high purity hydrogen.

**Figure 3** shows the appearance of a hydrogen separation unit for the diffusion purification of hydrogen. **Figure 4** shows a membrane module with a hydrogen separation unit containing seven membrane elements. This type of membrane unit can easily be introduced into a production process for the separation of hydrogen from hydrogen-containing gas mixtures or chemical product streams.

Technical characteristics of separation elements made from the 93.5 wt% Pd-6 wt% In-0.5 wt% Ru alloy with membranes 50 mm in diameter (FEL-50) and 150 mm in diameter (FEL-150) are given in Table IV. The hydrogen separation capacity, $Q$, of the optimum hydrogen separation unit containing ten membrane elements with 93.5 wt% Pd-6 wt% In-0.5 wt% Ru membranes 150 mm in diameter was calculated for preset operating parameters: membrane thickness, operating temperature, input hydrogen pressure, output hydrogen pressure, and high purity hydrogen separation coefficient, $\eta$, (which is set as the ratio of the volume of separated pure hydrogen to the partial volume of hydrogen in the gas mixture). Results are given in Table V. The preset membrane area was 0.326 m².

The hydrogen separation capacity of the membrane hydrogen separation units can easily be increased by increasing the differential pressure across the membrane, by increasing the number of membrane elements or by decreasing the membrane thickness. This hydrogen separation unit also allowed the precious metal loading to be reduced compared to that used in capillary tube elements (24).

**Conclusions**

The separation of high purity hydrogen from hydrogen-containing gas mixtures using palladium-based alloy membranes is an effective, environmentally sustainable and economical process for the commercial production of high purity hydrogen.

The membrane composition can be optimised for each gas mixture to ensure maximum stability and service life. During this study, it was found that disc membranes of diameter 150 mm made from 93.5 wt% Pd-6 wt% In-0.5 wt% Ru alloy are the most promising for commercial application for use with synthesis gas derived from hydrocarbon conversion. Modules were designed using this alloy and can be introduced...
into a production process to separate high purity hydrogen from a variety of hydrogen-containing gas mixtures.

Table IV
Technical Characteristics of Hydrogen Separation Elements FEL-50 and FEL-150

<table>
<thead>
<tr>
<th>Property</th>
<th>FEL-50</th>
<th>FEL-150</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen separation capacity, m³ h⁻¹</td>
<td>0.2–0.5</td>
<td>2.4–4.4</td>
</tr>
<tr>
<td>Weight of palladium alloy in the hydrogen separation element, g</td>
<td>2.4</td>
<td>22.0</td>
</tr>
<tr>
<td>Membrane thickness, µm</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>Hydrogen separation element diameter, mm</td>
<td>63</td>
<td>170</td>
</tr>
<tr>
<td>Maximum dimensions of optimum module (10 elements), mm</td>
<td>D = 70</td>
<td>D = 200</td>
</tr>
<tr>
<td>H = 50</td>
<td>H = 80</td>
<td></td>
</tr>
<tr>
<td>Hydrogen purity, vol%</td>
<td>&gt;99.999</td>
<td>&gt;99.999</td>
</tr>
</tbody>
</table>

*Operating conditions: temperature = 600ºC, input pressure = 1.0–5.0 MPa, partial pressure of pure hydrogen = 0.11 MPa*

Table V
Calculated Optimum Hydrogen Separation Capacity of the Palladium-Indium-Ruthenium Alloy Membrane Unit

<table>
<thead>
<tr>
<th>Membrane thickness, µm</th>
<th>Operating temperature, ºC</th>
<th>Input hydrogen pressure, MPa</th>
<th>Output hydrogen pressure, MPa</th>
<th>Hydrogen separation capacity, Q, Nm³ h⁻¹</th>
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<td>0.15</td>
<td>39</td>
<td>36</td>
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</tbody>
</table>

⁺High purity hydrogen separation coefficient, η, defined as the ratio of the volume of separated pure hydrogen to the partial volume of hydrogen in the gas mixture

References
The Authors

Gennady S. Burkhanov received a PhD from the Moscow Steel and Alloys Institute in 1961 and was appointed a lecturer in physics in 1975, Chief of Laboratory in 1984 and Professor in 1986. He received the USSR State Prize in 1968, 1986 and 1989 and was elected as corresponding member of the Russian Academy of Sciences in 2000. He has published about 380 papers, monographs and patents in the field of materials science of refractory and rare metals, single crystals, and superconductors.

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CAFC9: 9th Congress on Catalysis Applied to Fine Chemicals

Selective precious metal catalysts play key roles in value added fine chemicals synthesis

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Fine chemicals have been defined in many ways, but one definition would be that they are chemical products with specific properties which give them a high added value. As a consequence these molecules are, in general, polyfunctional molecules that require highly selective synthetic methods. Therefore, catalysis plays a crucial role in fine chemicals synthesis, and any improvements in catalytic performance can have a very positive impact on the fine chemicals industry.

The Congress on Catalysis Applied to Fine Chemicals (CAFC) is devoted to the application of any type of catalyst (homogeneous, heterogeneous or enzymatic) to the synthesis of fine chemicals, with special emphasis on selectivity. Previous conferences in this series have been held in The Netherlands (2003), Germany (2005) and Italy (2007). The latest, CAFC9, was held in Zaragoza, Spain, from 13th to 16th September 2010 (1), in the magnificent Paraninfo Building of the University of Zaragoza. It was organised by the Heterogeneous Catalysis in Selective Organic Synthesis Group at the university, with financial support from the Spanish Council for Scientific Research (CSIC), the University of Zaragoza and the Government of Aragón.

The scientific programme consisted of nine sessions, with four plenary lectures, five keynote lectures, and 31 oral communications, as well as two poster sessions. Overall, around 125 participants from both academia and industry in 20 countries attended this event. Researchers involved in areas from the synthesis of target molecules in the pharmaceutical industry to catalyst development were able to discuss their work and share their experiences. The contributions covered a wide range of work in fields such as enzymatic catalysis, organocatalysis, solution-phase and supported complexes of a large variety of metals, heterogeneous acids and bases, supported metals, and less conventional subjects such as the application of neoteric solvents (ionic liquids, supercritical carbon dioxide (scCO2), etc.), continuous flow reactions, or metal–organic frameworks. However, for this review only relevant works involving
the use of platinum group metals (PGMs) and gold have been selected. The review has been divided into three categories: homogeneous catalysis, heterogeneous catalysis, and metal nanoparticles, according to the type of catalytic system, although the boundaries between these three categories are not clear in some cases.

**Homogeneous Catalysis**

A good number of contributions, many of them from industrial participants, dealt with the use of precious metals in the form of homogeneous catalyst complexes. Walter Leitner (RWTH Aachen University, Germany) demonstrated in the opening plenary lecture how scCO₂ can be successfully used to carry out continuous-flow reactions, either as the only reaction medium or as part of a biphasic system (liquid-liquid or liquid-solid). The tunable properties of scCO₂ as a solvent allow the efficient design of catalytic reactions, such as the isomerisation of allylic alcohols catalysed by rhodium or ruthenium complexes with phosphines bearing perfluorinated chains. Integrated processes such as the ruthenium-catalysed conversion of levulinic acid (4-oxopentanoic acid) into 2-methyltetrahydrofuran can also be treated in this way. Several examples of biphasic systems of scCO₂ with another liquid phase were also presented. Ionic liquids, such as 1-butyl-3-methylimidazolium hexafluorophosphate, [bmim][PF₆], can be used as a carrier for chiral iridium–phosphinooxazoline or rhodium–quinaphos complexes, active in the enantioselective hydrogenation of imines and alkenes, respectively. It is also possible to immobilise the ionic liquid phase on solids, improving the life of the catalyst. Other liquid phases for biphasic systems can be poly(ethylene glycol) (PEG) or water, provided that a suitable ligand is used to improve the solubility of the complex.

Matt Clarke (University of St Andrews, UK) described the development of carbonylation processes to obtain building blocks for biologically active chiral compounds. The ligand and the method of catalyst preparation play extremely important roles in determining catalyst performance. For example, rhodium-catalysed hydroformylation of alkenes can be carried out with high enantioselectivity using Landis ligands (diazaphospholanes), 1, or Kelliphite ligand (a diphosphite), 2, depending on the substrate. It was also shown how a dipalladium complex with a chiral diphosphine Xyl-Phanephos, 3, is able to efficiently catalyse the enantioselective hydroxy- and alkoxycarbonylation of alkenes for the production of chiral acids and esters.

Christian Müller (Eindhoven University of Technology, The Netherlands) presented work in which the rhodium-catalysed hydroformylation of alkenes was integrated in sequence with a cyclisation reaction to construct complex molecular...
structures based on bicyclic and tricyclic imidazole derivatives. Several rhodium catalysts with phosphorus-containing ligands were used to catalyse the hydroformylation reaction. The cyclisation step was simultaneously accelerated by microwave irradiation, reaching overall yields higher than 95%.

Homogeneous hydrogenations catalysed by different metal complexes were also discussed. Lionel Saudan (Firmenich SA, Switzerland) showed in a keynote lecture how ruthenium complexes with nitrogen–phosphorus ligands, such as 4, could reduce esters to alcohols using a low catalyst loading (0.01–0.05 mol%) under mild conditions. The methodology can be applied to a wide range of substrates with almost quantitative yields and it even allowed the selective hydrogenation of esters in the presence of C=C double bonds with over 95% conversion.

Hans Guentner Nedden (Johnson Matthey, Catalysis and Chiral Technologies, UK) described the industrial application and optimisation of Noyori’s enantioselective ketone hydrogenation methodology. In one process example, the active pharmaceutical ingredient phenylephrine was obtained (Scheme I), using a [Xyl-P-Phos RuCl₂ Daipen] catalyst, 5, without the need for protecting groups, used to date in manufacturing processes.

Laurent Lefort (DSM, The Netherlands) presented two different pathways to obtain chiral amines, which are also important building blocks in the synthesis of high value-added products of industrial interest. Firstly, the enantioselective hydrogenation of enamines with a new rhodium–phosphoramidite chiral catalyst was applied to the synthesis of an anti-obesity drug intermediate. Secondly, the asymmetric reductive amination of β-ketoesters to the corresponding β-amino acid derivatives was achieved by means of a ruthenium–diphosphine catalyst.

An enantioselective hydrogenation, reported in a keynote lecture by Rocco Paciello (BASF, Germany), was the first step in an efficient three-step route to l-menthol from citral (3,7-dimethyl-2,6-octadienal). The conjugated C=C double bond of the α,β-unsaturated carbonyl compound was chemoselectively hydrogenated using a rhodium–chiraphos catalyst. Opti-
misation was possible by using a small amount of carbon monoxide to preserve the active species. This was verified by a density functional theory (DFT) mechanistic study.

Other enantioselective reactions, such as palladium-catalysed allylic substitution and ruthenium-catalysed cyclopropanation and transfer hydrogenation, were presented in several of the posters.

**Heterogeneous Catalysis**

In one of the plenary lectures, Hermenegildo García (Instituto de Tecnología Química, Spain) showed how metal–organic frameworks (MOFs) can act as reusable heterogeneous catalysts for the synthesis of fine chemicals. He proved that, in some cases, MOFs can perform better than the analogous transition metal catalysts in solution or than related zeolitic materials, due to their large surface area, high metal density, site isolation and hindered aggregation. In one of the examples, a palladium 2-hydroxypyrimidinolate MOF (Figure 1) was able to carry out the oxidation of allylic alcohols to aldehydes in an aerobic atmosphere with 99% conversion and 74% selectivity. No palladium leaching was detected and the solid catalyst could be recovered and reused in several consecutive runs.

Several authors showed the use of mesoporous solids as supports for transition metal complexes. Marie Genelot (Institut de Recherches sur la Catalyse et l’Environnement de Lyon (IRCELYON), France), in her keynote lecture, described the preparation of several quinolones and indoxyls through a carbonylative Sonogashira coupling/cyclisation sequence catalysed by palladium complexes immobilised on mesoporous SBA-type silica solids. Together with the palladium catalyst, an immobilised amine or an immobilised phosphine had to be used in order to selectively obtain a six-member or a five-member N-heterocycle, respectively (Scheme II). Palladium leaching was detected and a study of different reaction parameters (solvent polarity, surface treatment and type of catalyst) was carried out to try to reduce this. Suman Sahoo (Stockholm University, Sweden) reported the immobilisation of rhodium complexes onto several silica MCM and SBA mesoporous solids via two strategies: covalent bonding of the N-heterocyclic carbene ligand or hydrogen bonding through a sulfonic group on the phosphine ligand. The catalysts were used to promote the isomerisation of allylic alcohols and the amination of aryl bromides with good activity. Other examples of immobilised complexes, including the ruthenium-BINAP-diamine system on graphite oxide and ruthenium-based Grubbs catalyst on mesoporous silica, were reported in the poster sessions.

Other supports were also used for the immobilisation of metals such as platinum, palladium or gold.

![Fig. 1. (a) A palladium 2-hydroxypyrimidinolate metal–organic framework (MOF) used to catalyse efficient oxidation of allylic alcohols to aldehydes; (b) Palladium 2-hydroxypyrimidinolate subunit. Colour coding: blue = N, red = O, yellow = Pd, grey = C, light blue = Cl (Courtesy of Jorge A. Rodríguez Navarro, Department of Inorganic Chemistry, University of Granada, Spain)](image-url)
Gatla Suresh (Leibniz Institute for Catalysis, Germany) described the preparation of several palladium on titania (Pd/TiO₂) catalysts in order to accomplish the gas-phase acetoxylation of toluene. The influence of precursors, promoters, supports and pretreatment procedures on the reaction was studied. The highest catalytic performance was reached with a palladium-antimony catalyst supported on rutile, which gave a selectivity of 99%. TiO₂ was also used by Katharina Heidkamp (Institute of Agricultural Technology and Biosystems Engineering, Johann Heinrich von Thünen-Institute, Germany) as a support for gold and gold-platinum catalysts, which proved to be active for the oxidation of fatty alcohol ethoxylates to their corresponding carboxylic acids with molecular oxygen. Variable leaching of gold was detected for Au/TiO₂ depending on the preparation conditions. The presence of platinum in a bimetallic Au-Pt/TiO₂ catalyst improved the activity and reduced metal leaching. The screening of other support materials showed that the use of ceria (CeO₂) completely avoided gold leaching and gave very good activity (58 mmol min⁻¹ gAu⁻¹) and selectivity (>99%) under optimised reaction conditions.

Antonio Leyva-Pérez (Instituto de Tecnología Química, Spain) also proposed the use of TiO₂, as well as of silica ITQ-2, for the immobilisation of platinum or palladium. A metal-acid bifunctional solid catalyst was obtained. This was able to promote a cascade process involving a chemoselective hydrogenation-cyclisation-amination reaction, to obtain the antipsychotics olanzapine (Scheme III) and clozapine.

A good number of examples of supported metals were also described in the poster sessions. There were several examples of oxidation reactions, including the oxidation of glucose using hydrogen peroxide (H₂O₂) and gold on alumina (Au/Al₂O₃) catalysts, the dehydrogenation of lignans using palladium on different supports (alumina, activated carbon and mesoporous silicas), and the aerobic oxidation of secondary alcohols using Pt/C. Suzuki and Heck coupling reactions with palladium catalysts were also described, and there were some examples of hydrogenation reactions.

**Metal Nanoparticles**

The use of nanoparticles was described in a number of oral communications and posters. In his keynote

![Scheme II](image)

![Scheme III](image)
lecture. Tamas Mallat (ETH Zurich, Switzerland) described the use of several rhodium and platinum nanoparticles supported on Al₂O₃, SiO₂ or the mixed oxide and modified by cinchonidine or quinine molecules. These catalysts were tested in the enantioselective hydrogenation of several aliphatic and aromatic ketones, and gave enantioselectivities up to 94%. A detailed study of the particle size, crystallographic face and acid-base properties of the support showed the sensitivity of the catalytic performance to all these factors.

Takato Mitsudome (Osaka University, Japan) reported the deoxygenation of epoxides using alcohols as reductants and catalysed by gold nanoparticles stabilised on hydrotalcite. A wide range of epoxides can be deoxygenated to their corresponding alkenes with a selectivity of over 99% and a turnover number (TON) of up to 20,000. The catalysts were recovered by filtration and reused in several reaction cycles without loss of activity.

Pawel K. Plucinski (University of Bath, UK) presented the use of a continuous reactor containing magnetically entrapped nanocatalysts. Magnetite (Fe₃O₄) superparamagnetic nanoparticles were used as carriers to immobilise chiral complexes such as (R,R)-Rh-DUPHOS-SO₃ and (R)-Ru(OAc)₂(BINAP) or palladium nanoparticles on the surface. The catalysts were tested for hydrogenations, Suzuki reactions and even a tandem Knoevenagel condensation-hydrogenation reaction, resulting in excellent catalytic performance.

Organic polymers can also be used to stabilise nanoparticles. Linda Zh. Nikoshvili (Tver Technical University, Russia) presented two methods of formation of nanoparticles in two types of nanostructured organic polymers: amphiphilic block polymers with poly(2-vinylpyridine) units and hypercrosslinked polystyrene. These polymers were prepared containing Pt, Pd, Ru, Au or bimetallic systems such as Pd-Pt, Pd-Zn, Pd-Au or Ru-Pt. After a complete characterisation of the catalysts, they were tested for the triple bond hydrogenation of dehydrolinalool (3,7-dimethyloct-6-ene-1-yne-3-ol) and for the selective oxidation of L-sorbose and D-glucose.

François Quignard (The Institute Charles Gerhardt of Montpellier, France) described alginates (polysaccharides) as stabilisers for palladium nanoparticles. Palladium cations can be exchanged in ionotropic gels of alginates with divalent cations and then reduced to form the supported nanoparticles. The textural properties and particle size were highly dependent on the initial divalent cation in the alginate. The best performance for the Suzuki carbon–carbon coupling reaction was obtained with a black Pd-Cu/alginate catalyst (Figure 2).

Eduardo García-Verdugo (Universitat Jaume I, Spain) reported the use of polystyrene–divinylbenzene copolymers (beads and monoliths) functionalised with imidazolium groups (similar to ionic liquids) as supports for palladium and gold nanoparticles, among other catalysts. As an example, supported palladium nanoparticles were tested as catalysts for Heck reactions. The functionalised polymers can be reused in several reaction cycles without loss of catalytic performance. Pasi Virtanen (Åbo Akademi, Finland) described the immobilisation of palladium nanoparticles in an ionic liquid phase supported on activated carbon cloth. The effect of alkaline modifiers on the catalytic activity of the solids in the hydrogenation of citral (3,7-dimethylocta-2,6-dienal) in a batch reactor was studied. The alkaline modifiers were able to enhance the activity and increase the selectivity to citronellal (3,7-dimethyloct-6-en-1-ol).

Concluding Remarks

Selectivity issues (chemoselectivity, regioselectivity, stereoselectivity and enantioselectivity) are crucial in the synthesis of fine chemicals, and catalysis plays a key role. In the closing plenary lecture of CAFC9, Hans-Jürgen Federsel (AstraZeneca, Sweden) showed how catalysis in general, and in particular that involving precious metals, is a valuable tool in making the fine chemicals industry more sustainable.
both from an environmental and an economic point of view. Improvements to the predictability, scope, selectivity and customisability of catalytic methods will in turn increase the usefulness of catalysis even further, but for this to happen there is a need for a deeper scientific understanding of catalysts and catalytic processes. The CAFC series aims to address this need to the benefit of both the scientific community and industry.

As a summary of the Congress, a selection of contributions will be published in a special issue of *Catalysis Today* in 2011 (3). Finally, it was decided that CAFC10 will be held in Turku (Åbo) Finland in 2013.

**References**

3 *Catalysis Today*, Special Issue: 9th Congress on Catalysis Applied to Fine Chemicals (CAFC9), to be published in 2011

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**The Reviewers**

José M. Fraile is currently a Research Scientist of the Spanish Council for Scientific Research (CSIC) in the Instituto de Ciencia de Materiales de Aragón (ICMA) at the University of Zaragoza, Spain. He obtained his PhD from the University of Zaragoza in 1992. He worked as a postdoctoral researcher in the École Nationale Superieure de Chimie de Montpellier, France. His research interests focus on the preparation and application of heterogeneous catalysts based on metals such as copper, palladium, indium, ruthenium, etc. for selective organic synthesis, mainly chiral catalysts for enantioselective processes.

Clara I. Herrerías is currently a lecturer at the University of Zaragoza, Spain. She obtained her degree and PhD from the same university under the supervision of Dr J. A. Mayoral and Dr J. M. Fraile. She worked as a postdoctoral researcher in Dr C.-J. Li’s group at McGill University, Canada, and later, in Dr M. A. Pericas’ group at the Institute of Chemical Research of Catalonia, Spain. She is involved in the development of compatible heterogeneous catalysts based on metals including copper, palladium, titanium, etc. for multi-step reactions and in the synthesis and applicability of new multitopic chiral ligands, able to form complexes with several metals at the same time.
The Role of Process Parameters in Platinum Casting

Investigation of optimised casting parameters for two platinum jewellery alloys

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http://www.platinummetalsreview.com/

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Platinum is a challenging material for casters because of its physical properties, which result in possible crucible and flask reactions during melting and casting, high shrinkage porosity and difficulties in filling of filigree items. This paper summarises the results of a collaborative research effort by several industrial partners and FEM on the influence of casting process parameters. Two common platinum jewellery alloys (platinum with 5 wt% cobalt and platinum with 5 wt% ruthenium) and four different investment materials were used for casting experiments with variation of atmosphere, casting and flask temperature, tree design and centrifugal machine parameters. Detailed sample investigation found shrinkage porosity and surface defects to be the main problems. Optimised process parameters for heavy and filigree items were identified. Future research on platinum casting should focus on casting simulation in order to reduce experimental effort and costs.

Introduction

In recent years articles on the casting properties of platinum have been published (1, 2). Different aspects such as suitable alloys for casting (3–6), tree design (7–10) and investment reactions (11, 12) have been discussed, as well as the effect of centrifugal casting parameters for different alloys and investments (12–14). Platinum with 5 wt% cobalt (Pt-5Co) was identified as a very versatile casting alloy, showing excellent form filling of filigree parts even for flask temperatures as low as 100°C (12). Platinum with 5 wt% ruthenium (Pt-5Ru) on the other hand showed poor form filling of filigree parts for flask temperatures below 800°C (12). Besides casting properties, functional alloy properties such as colour, hardness, ductility and magnetic properties have to be taken into account for jewellery. In this regard Pt-5Ru is more versatile compared to Pt-5Co or platinum with 5 wt% copper (Pt-5Cu), and can be used for all jewellery applications.
The present project focused on Pt-5Ru and Pt-5Co as the most commonly used jewellery alloys. Investment casting experiments were carried out as part of a research project commissioned by Platinum Guild International (PGI), USA, in cooperation with several industrial partners and FEM. This paper summarises the results given in a presentation at the 24th Santa Fe Symposium® on Jewelry Manufacturing Technology in 2010 (15).

Experimental
Casting experiments were carried out using a TopCast TCE10 vacuum centrifugal casting machine with induction heating and a power of 10 kW and a working capacity of 1500 g. Metal temperature during heating and melting was monitored using a quotient pyrometer. Most of the casting trees used a 'diablo' type setup. A typical tree containing some standard items (ball rings and grid) is shown in Figure 1. Four different investments from different suppliers were tested. Table I gives an overview of the properties of the investments and briefly describes the experience of working with them.

A number of casting experiments were carried out to analyse the influence of casting parameters (melt temperature, flask temperature, casting atmosphere, casting machine type), alloy and investment material by using standard sample geometries such as ball rings and grids. The grid represents filigree items and demonstrates form filling ability. The ball ring represents heavy section pieces. With the large ball acting as a hotspot it was expected to provoke investment reactions and to be prone to shrinkage porosity. The as-cast samples were evaluated in terms of surface quality, shrinkage porosity and investment reactions by optical microscopy, metallography and scanning electron microscopy (SEM).

Results and Discussion
Alloy Properties
The alloys differ in their dendrite morphology, segregation behaviour and melting temperature. Solidus and liquidus temperature were calculated using the Thermo-Calc® software package with the Scientific Group Thermodata Europe (SGTE) noble metal alloys database (SNOB1), and are in accordance with Reference (16). The calculated phase diagrams give the same melting range for both alloys, but due to segregation the melting range of Pt-5Co is actually about twice that of Pt-5Ru. This is one possible reason for the better form filling ability of Pt-5Co. However, segregation of Co to the melt promotes oxidation of Co and investment reactions, even for vacuum casting.

Form Filling
Form filling is a critical issue for filigree items and was determined on standard grids (Figure 2). Pt-5Co clearly has superior form filling ability to that of Pt-5Ru and shows excellent results for a flask temperature of 850°C. For Pt-5Ru, form filling considerably increases with increasing centrifugal speed and flask temperature. Its optimum flask temperature is 950°C for filigree items. Vacuum casting allowed complete filling of filigree items with two-part investments for both alloys, as did overheating of the melt for Pt-5Ru. However, this also promoted investment reactions.
<table>
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<th>Working time, min</th>
<th>Burnout time, h</th>
<th>Burnout temperature, °C</th>
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<td>12.5</td>
<td>871</td>
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<tr>
<td>No. 2</td>
<td>Lane PT120</td>
<td>Two-part</td>
<td>Paper base and liner</td>
<td>20–25</td>
<td>10–12</td>
<td>12.0</td>
<td>870</td>
<td>Curing does not start at room temperature, extended working time possible</td>
</tr>
<tr>
<td>No. 3</td>
<td>Gold Star Platin Cast</td>
<td>One-part/ fibre</td>
<td>Rubber base</td>
<td>8</td>
<td>5–7</td>
<td>11.5</td>
<td>900</td>
<td>Cold water required to reach upper working time limit; high viscosity</td>
</tr>
<tr>
<td>No. 4</td>
<td>SRS Platinò</td>
<td>One-part/ fibre</td>
<td>Rubber base</td>
<td>8</td>
<td>5–7</td>
<td>10.0</td>
<td>900</td>
<td>Cold water required to reach upper working time limit; high viscosity, risk of bending of filigree parts, especially plastic parts</td>
</tr>
</tbody>
</table>
Surface of Cast Parts

The surface quality of cast parts is affected by investment reactions, inclusions of investment particles and rough or matt appearing surfaces. Table II compares the behaviour of the two alloys using the different investments at different flask temperatures.

The best surface quality was observed for Pt-5Ru. This alloy did not show any investment reactions despite its high casting temperature. Investment reactions were observed for Pt-5Co independent of casting atmosphere and resulted in a blue layer of cobalt silicate (Figure 3).

Investment inclusions (Figure 4) on the surface were observed, especially in the case of the one-part investment No. 4. With increasing flask temperature the surface became rougher and the inclusions more frequent. For the two-part investments No. 1 and No. 2, inclusions were seldom observed, probably due to their lower porosity and higher stability. Therefore, the surface quality achieved using these investments was usually superior to that obtained with investment No. 4.

The cast parts often showed matt and glossy areas. The matt areas showed a dendritic-like surface and

<table>
<thead>
<tr>
<th>Investment</th>
<th>Devesting performance</th>
<th>Surface quality of Pt-5Co alloy at the flask temperature, ºC</th>
<th>Surface quality of Pt-5Ru alloy at the flask temperature, ºC</th>
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</tr>
<tr>
<td>No. 2</td>
<td>+++</td>
<td>++</td>
<td>++</td>
</tr>
<tr>
<td>No. 3b</td>
<td>++</td>
<td>+</td>
<td>+++</td>
</tr>
<tr>
<td>No. 4</td>
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<td>+</td>
</tr>
</tbody>
</table>

*+++ (best); ++ (medium); + (worst)

bNo. 3 was only used for casting trials with Indutherm MC 15 tilting machine
Fig. 3. (a) Investment reactions of Pt-5Co (flask temperature 850°C); (b) and (c) energy dispersive X-ray (EDX) analysis of reaction products on position 1 (cobalt oxide) and position 2 (cobalt-magnesium silicate).

Fig. 4. Inclusions of investment material (black) on the surface of Pt-5Ru alloy.
were observed on the heavy sections (Figure 5) of the affected parts. The matt surface was caused by shrinkage of isolated melt volumes during solidification.

**Shrinkage Porosity**
Shrinkage porosity was the main problem for both heavy bulk and lightweight filigree patterns in the casting trials performed. The effects of casting parameters and the position on the tree were found to be relatively small.

Table III and Table IV show shrinkage porosity in the Pt-5Co and Pt-5Ru alloys, respectively. In general, shrinkage porosity was less pronounced for Pt-5Ru. There was a significant difference in shrinkage pore morphology between the two alloys. Pt-5Co showed few but large pores while Pt-5Ru often showed scattered pores built by intersecting dendrites (Figure 6).

Flask temperature and casting atmosphere had little influence. The investment material was found to influence shrinkage porosity and the lowest levels were achieved with investment No. 4. This is probably an effect of the lower thermal conductivity of this investment, resulting in slower and more homogeneous cooling of the melt.

**Effect of the Casting Machine**
A comparison of two types of casting machine, a centrifugal (TopCast TCE10) and a tilting machine (Indutherm MC 15, capacity 200 g), showed that centrifugal casting produced superior results for form filling of filigree items. Defect-free castings of the ball ring were obtained for the Pt-5Co alloy at 950ºC under vacuum using the tilting machine, which was not possible by centrifugal casting under comparable conditions.

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**Table III**

<table>
<thead>
<tr>
<th>Flask temperature, ºC</th>
<th>Casting atmosphere</th>
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*a+++ (low = best); ++ (high = medium); + (very high = worst)*

**Table IV**

<table>
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<th>Flask temperature, ºC</th>
<th>Casting atmosphere</th>
<th>Investment</th>
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*a+++ (low = best); ++ (high = medium); + (very high = worst)*

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Fig. 5. Matt surface of a Pt-5Ru casting with dendritic surface
Pt-5Ru was difficult to cast in the tilting machine, because of the low heating rate in the specific model used, which resulted in hot tearing of the parts. Machines with higher power and sufficiently short melting time may enable successful casting of Pt-5Ru.

**Conclusions**

In this study shrinkage porosity was found to be the main problem for both bulk and filigree casting patterns using Pt-5Ru and Pt-5Co alloys. The best results in terms of shrinkage porosity were obtained with Pt-5Ru alloy using investment No. 4.

In order to solve the problem of shrinkage porosity, sprue design and tree setup are most important. Directional solidification has to be assured. The usefulness of techniques such as increasing the flask temperature is limited by the thermal stability of the investment materials. However, optimisation of casting behaviour solely by experimental means remains challenging.

**Recommendations for Future Work**

In recent years, casting simulation has been demonstrated to be a valuable tool for gold and silver casting (17, 18). Sophisticated software packages are available to determine form filling and shrinkage porosity depending on alloy, tree setup, melt and flask temperature, allowing optimisation by computer simulation. This would be especially valuable for optimising the casting parameters for platinum due to its high price and extreme casting and flask temperatures.

Detailed knowledge of the thermophysical properties of the alloys and investments are required. Such data are currently scarce and they must be determined. Benchmark experiments with sophisticated thermal recording during the centrifugal casting process should be performed to calibrate the casting simulation results.

Investment materials were found to play an important role in form filling and shrinkage porosity. It is assumed that properties such as gas permeability and thermal conductivity are responsible for this behaviour. Therefore, the influence of the water:powder ratio, burnout cycle, flask temperature and casting atmosphere requires further investigation to understand how the physical properties of the investments can be tailored.

**Acknowledgements**

The authors are grateful for the financial support of PGI, with special thanks to Jurgen Maerz. C. Hafner GmbH and Co, Germany, provided platinum alloys, which is kindly acknowledged. The companies Ransom & Randolph, USA, Lane Industries LLC, USA, and Specialist Refractory Services Ltd (SRS) UK, are acknowledged for providing investment materials and Indutherm GmbH, Germany, is acknowledged for casting trials. Special thanks to Dieter Ott (FEM, Germany) for fruitful discussions of the project results and to the staff members of the metallurgy department at FEM, especially to Franz Held and Ulrike Schindler for casting trials and metallography.

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Tiziana Drago has a BSc in Materials Engineering with specialisation in surface treatments from the Politecnico di Milano, Italy, and an MSc in Materials Science from the University of Pisa, Italy. She works in the Department of Physical Metallurgy at the Research Institute for Precious Metals and Metals Chemistry (FEM) in Schwäbisch Gmünd, Germany.
The 10th International Symposium on the Scientific Bases for the Preparation of Heterogeneous Catalysts (‘PREPA10’) was held in Louvain-la-Neuve, Belgium from 11th–15th July 2010 (1). It was attended by over 270 delegates from 34 countries, of whom more than 20% were from industry. A scientific committee consisting mainly of industrial representatives refereed all published submissions and selected the presentations, which gave the symposium a strong industrial focus. The symposium included the following session topics: scaling up, shaping and macrostructured catalysts; basic understanding and innovations in unit operations; nanostructured catalysts; hierarchical porous supports and hybrid catalysts; and in situ spectroscopic analysis during catalyst preparation. In addition, almost 200 posters were presented in two sessions.

**Catalyst Preparation**

The plenary speaker was Galen Stucky (University of California, Santa Barbara (UCSB), USA) who presented on a range of topics, including the use of zeolites to prevent fatal blood loss. Of more relevance to catalysis, he presented some work on the AcHE (acetic acid, hydrochloric acid and ethanol) sol-gel method (2) which generates high surface area metal oxide materials from metal ethoxides.

The highlights of the first session included several presentations on the coating of metallic substrates with catalytic materials. Among these, Francesco Basile (Università di Bologna, Italy) presented an interesting approach to coating iron-chromium-aluminium alloy (FeCrAlloy®) substrates. Precursors of nickel or rhodium catalysts on hydrotalcite type supports were electrochemically deposited on FeCrAlloy (the working electrode) from nitrate solutions, followed by calcination to obtain the final catalysts. Catalyst loadings of up to 5 wt% were achieved after 1000 seconds of electrochemical deposition (3).

Also in the first session was an intriguing presentation by Bair S. Bal’zhinimaev (Boreskov Institute of Catalysis, Russia) on the use of glass fibre materials as
catalyst supports (Figure 1) (4). Zirconium silicate glass was shown to be a suitable support for platinum and palladium catalysts, which were impregnated as the metal–amine complexes, [M(NH₃)₄]²⁺, and formed subsurface metallic clusters after calcination. The presence of the metallic clusters below the surface was proposed to provide selectivity, due to differing diffusion properties of various gases through the zirconium silicate network. A number of catalytic applications were investigated for these materials including sulfur dioxide (SO₂) oxidation, nitrogen oxides reduction (deNOₓ) and acetylene selective hydrogenation (5, 6). In the deep oxidation of ethylbenzene, a higher activity was achieved for a glass fibre supported Pt catalyst at a Pt loading of 0.02 wt% than for a Pt/Al₂O₃ catalyst at a loading of 0.56 wt%.

Stefania Specchia (Politecnico di Torino, Italy) opened the second session with a talk on the use of solution combustion synthesis (SCS) as an intriguing way to produce palladium on zirconia-stabilised lanthanum manganese oxide perovskite, Pd/(LaMnO₃·2ZrO₂), on FeCrAlloy gauzes for catalytic combustion of methane in commercial boilers. SCS allowed the preparation of highly porous materials with a very high dispersion of zero-valent palladium clusters (determined by the low-temperature adsorption of carbon monoxide onto the material). An in situ spray pyrolysis method, in which a solution of the catalyst precursors was sprayed onto the hot (400°C) FeCrAlloy support, was developed to overcome the scale-up difficulty associated with exothermic heat generation in the SCS process.

The use of high-temperature combustion methods for the synthesis of highly dispersed catalysts was continued in the poster sessions. Of note were two posters from Elena Golubina (Moscow State University, Russia) detailing the formation of nanocomposite metal-on-carbon materials (metal: Ni, Pd or Ni-Pd alloy) and Pd on ultradispersed diamond (UDD), and the application of these to the hydrodechlorination (HDC) of chlorobenzenes. Both types of material required forcing reaction conditions: nanocomposite metal-on-carbon materials were formed by heating the metal in a closed system to 2000°C in a hydrocarbon/argon gas mixture, while UDD was formed using a detonation method involving the explosion of trinitrotoluene (TNT) (7). High HDC activity was achieved for the catalysts; in the case of the Pd/UDD catalysts it was found that support defects enable the stabilisation of highly dispersed, partially oxidised palladium particles (8).

Nanostructure and Size Control
The use of carbon nanofibre supports was one of the recurring themes of the conference. Krijn de Jong (Utrecht University, The Netherlands) presented his work on the preparation of Pt-loaded, mechanically stable nanofibres (9). He claimed that loading increased with the number of acid sites on the nanofibres, with a maximum of 4 wt% (10). Heat treatments in nitrogen were found to decrease the number of acid sites and refluxing in hydrogen peroxide or nitric acid was used to increase the number. Another interesting talk came from Chen Jin (Ruhr-Universität Bochum, Germany) who presented the use of nanotube-supported sulfided Rh catalysts (Figure 2) for the oxygen reduction reaction in HCl (11). The well dispersed catalysts, which were found by X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD) analysis to consist of Rh cores with surface Rh–S species, displayed high electrochemical stability in the corrosive electrolyte.

Peter Witte (BASF, The Netherlands) presented some work on surfactant-stabilised Pt, Pd and Pt-Pd nanoparticulate catalysts deposited on carbon or titaniam silicate supports. These catalysts, which were developed as lead-free alternatives to the Lindlar catalyst, are now commercial products, successfully used in the semi-hydrogenation of substituted acetylenes, although possible Pd and surfactant leaching may affect the catalyst performance.

Keizo Nakagawa (The University of Tokushima, Japan) presented a talk about silica-coated Pt on carbon and its potential in selective hydrogenation

![Fig. 1. A view of the glass fibre support used for platinum and palladium catalysts (Reprinted from (4) with permission from Elsevier)](image-url)
Fig. 2. Electron micrographs of carbon nanotube-supported rhodium sulfide catalysts with rhodium loadings of (from top): 4.3 wt%, 6.4 wt%, 16.1 wt% and 21.9 wt%. Images (a)–(d) are scanning electron micrographs; (e)–(h) are transmission electron micrographs (Reproduced from (11) by permission of The Royal Society of Chemistry).

applications (12). Siloxane precursors of different sizes were used to control the pore size of the silica formed, in the order: methyltriethoxysilane (MTES) > phenyltriethoxysilane (PhTES) > triethoxysilane (TEOS). Catalysts prepared using MTES as silica precursor allowed benzene absorption, while PhTES resulted in pores too small for benzene activity but allowed methane activation. Loïc Rouleau (Institut
Français du Pétrole, IFP-Lyon, France) reported on the preparation of hierarchical supports by coating 1.6 mm diameter α-alumina spheres with γ-alumina and subsequent impregnation with Pd. A tight Pd eggshell and high Pd dispersion were achieved, as demonstrated by the high selectivity of the catalyst in the partial hydrogenation of styrene to ethylbenzene.

Spectroscopic Analysis

Several interesting presentations were given in the final session on in situ spectroscopic analysis of catalysts during and after preparation. Ursula Bentrup (Leibniz-Institut für Katalyse, Universität Rostock, Germany) presented work detailing the online monitoring of molybdate catalyst precursors using simultaneous X-ray and spectroscopic methods in situ (13). She presented an impressive technique that uses an ultrasonic trap to levitate droplets of reaction solution into laser or X-ray beams in order to mimic spray drying and characterise species formed during this process. Leticia Espinosa-Alonso (Utrecht University, The Netherlands) reported on in situ tomographic energy dispersive diffraction imaging (TEDDI) measurements (14) which allow time and space resolved concentration maps of crystalline and amorphous phases to be monitored across a support body during catalyst impregnation or calcination (Figure 3).

Concluding Remarks

The exciting developments in catalyst characterisation concluded a diverse 10th Symposium which addressed current issues in catalyst preparation as well as original catalysts for the future. A book of abstracts is available containing further information about the talks and posters presented (15).

References


Fig. 3. Raw tomographic energy dispersive diffraction imaging (TEDDI) images obtained from mapping of a catalyst body: (a) a ‘Y’ map generated from continuous measurement of one-dimensional ‘Y’ scan-lines in the centre of the catalyst body during calcination; (b) a two-dimensional ‘XY’ map of a pellet at a selected temperature point during the calcination process (to relate the XY map to a specific temperature point the sample is rapidly quenched to 25°C after the selected temperature is reached); and (c) typical total spectrum contained in one pixel of a TEDDI image. The blue pixels represent spectra with a low number of total counts, and the red pixels represent regions with a high number of counts (Reprinted with permission from (14). Copyright 2009 American Chemical Society)
The Reviewer

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“Metathesis in Natural Product Synthesis”


Reviewed by Valerian Dragutan* and Ileana Dragutan**
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“Metathesis in Natural Product Synthesis” subtitled ‘Strategies, Substrates and Catalysts’ benefits from a foreword by Robert H. Grubbs, joint recipient of the 2005 Nobel Prize in Chemistry for his work on the development of the metathesis method in organic synthesis. This timely publication focuses on developments in the synthesis of natural products which use as a key step the versatile metathesis reaction catalysed by transition metal complexes, especially ruthenium. While reference to metathetic pathways in obtaining natural products or their mimics is encountered sporadically in many books and articles which primarily deal with metathesis as a catalytic process, to the best of our knowledge this is the first monograph devoted entirely to a systematic treatment of metathesis applications in natural product synthesis. The field has direct relevance for the drug industry, and currently receives a great deal of attention due to the pharmacological activity found in many natural compounds. Therefore, this volume promises to be a very helpful resource.

Total Synthesis of Natural Compounds
Taking full advantage of the wide range of synthetic possibilities offered by alkene and alkyne metathesis, the book illustrates how a great variety of natural compounds with small, medium or macrocycles can now be routinely obtained through considerably shorter and more efficient protocols than in the past. A major problem in total synthesis of natural compounds is the numerous reaction steps needed, resulting in a modest overall yield and proceeding only with moderate to low product selectivity. The ability of metathesis to selectively lead to a desired biologically active stereoisomer or enantiomer makes it an efficient approach which can considerably improve the outcome of otherwise difficult natural product syntheses. The advances showcased in the book have been stimulated by the parallel introduction of a
A wide variety of well-defined metathesis catalysts (1–10), many of which are ruthenium-based systems which tolerate a range of functional groups and reaction conditions.

After an inspiring foreword by Grubbs, a detailed table of contents and the concise preface by the editors, the book begins with a list of structures of the main catalysts involved in the synthetic work, which is fully cross-referenced with the book’s index. Then, in thirteen chapters and roughly 400 pages, it progresses to an in-depth look at synthetic strategies which use metathesis reactions as crucial steps in sequential and cascade sequences applied to natural product synthesis. The information is up to date and is organised by the editors according to carbocycle size, the nature of the heteroatom incorporated into the heterocyclic moiety of the targeted compounds, the type of metathesis reaction (ring-closing metathesis (RCM), cross-metathesis (CM), ring-opening metathesis (ROM), etc.) and the techniques used. The first chapters report on RCM as the first, and still most widely used, type of metathesis reaction for natural product synthesis.

In Chapter 1, Nicolas Blanchard and Jacques Eustache (Université de Haute Alsace, France) depict the synthesis of naturally occurring molecules focusing on the construction by RCM of medium-sized carbocycles (five- to ten-membered rings) and complex spiro, bicyclic or polycyclic structures. In this chapter the reader quickly becomes acquainted with a plethora of natural compounds having diverse pharmacological properties that can be accessed easily by RCM. Novel reaction sequences such as [3,3]-sigmatropic rearrangement/RCM and RCM/fragmentation are also discussed as efficient routes to natural compounds.

Some examples of metal–alkylidene metathesis catalysts:
Biologically Active Compounds

An impressive array of products with five- and six-membered nitrogen heterocycles is illustrated in the next chapter, by the well-known group of authors Sebastiaan (Bas) A. M. W. van den Broek, Silvie A. Meeuwissen, Floris L. van Delft and Floris P. J. T. Rutjes (Radboud Universiteit Nijmegen, The Netherlands). Several important alkaloid families (pyrrolidine, pyrrolizidine, piperidine, indolizidine and quinolizidine), many of them recognised for their potent and versatile biological activity, are shown to become available by efficient ruthenium-catalysed RCM, carried on appropriate diene substrates, to yield the five- and six-membered heterocyclic units incorporated into their respective molecules. See for instance swainsonine (Scheme I) and castanospermine (Scheme II). The less frequently encountered cyclisation by RCM to seven- and eight-membered N-heterocycles, as in balanol and manzamine A, respectively, is also highlighted.

Interesting applications of RCM in synthesis of natural products containing medium-sized O-heterocycles are introduced by Jon D. Rainier (University of Utah, USA) in Chapter 3. Supported by beautiful graphic representation of intricate chemical structures, the illustrated compounds include members of the poly cyclic ether family (brevetoxins, ciguatoxins, etc.), the laurenccins, and heliannuol A, along with representatives from the eunicellin diterpene family. Typical specimens for eight-membered ring lactones (octalactin A) and ten-membered ring lactones (microcarpalide and herbarum III) are presented as well. Additionally, data on the related carbonyl olefination cyclisation using a stoichiometric titanium reagent are included.

In Chapter 4, Christopher D. Thomas and Paul R. Hanson (University of Kansas, USA) demonstrate the role played by RCM in the construction of sultone and phosphate heterocycles, thus providing an effective method in which both sulfur and phosphorus serve as temporary tethers to mediate several selective transformations. The sultone motif has been applied by Janine Cossy and coworkers in the synthesis of the originally proposed structure of (+)-mycothiazole to access 1,3-dienols possessing an internal Z-olefin. Further, Hanson et al. used phosphate tethers in the construction of asymmetric 1,3-anti-diols to build the C1–C14 and C15–C30 subunits of dolabelide.

The next chapter, coauthored by Ana Gradillas and Javier Pérez-Castells (Universidad CEU San Pablo, Spain), presents the RCM-based synthesis of natural products containing macrocyclic cores. Following the biogenetic classification, the authors address the synthesis of biologically important macrolactones, as divided into the main family groups: resorcinyllic, salicylates, other antibiotic macrolides, macrocyclic musks (Scheme III), epothilones (Scheme IV), amphidinolides (Scheme V), other polyketides and natural cyclophanes, and then terpenoids, followed by the macrocycles resulting from amino acid

Schemes I and II. Ruthenium-based ring-closing metathesis in synthesis of swainsonine and castanospermine
metabolism (lactams, depsipeptides and alkaloids); and finally the macrocyclic glycolipids. Examples of macrolactone synthesis are described, revealing important aspects concerning control of the RCM process; in doing so, novel insights into factors affecting RCM, such as the influence of the catalyst, solvent, temperature and reactant concentrations are provided.

**Development of Novel Synthetic Strategies**

Extension of enyne metathesis to the synthesis of various natural products is concisely outlined by Miwako Mori (Hokkaido University, Japan) in Chapter 6. Starting from the first application of enyne RCM to the total synthesis of (−)-stemoamide, the author describes the development of this delicate strategy for production of a broad range of important natural compounds such as (−)-longithorone A, allocolchicine, (−)-galanthamine, (−)-anthramycin, lancelodilactone G, etc. Next, the alternative formation of 1,3-dienes from alkyne and ethylene using cross-metathesis is demonstrated for the synthesis of anolignans, vitamin D receptor antagonists and amphidinolide E. Finally, transition metal-catalysed, in particular ruthenium-, palladium- and platinum-catalysed, skeletal rearrangements and reorganisations are illustrated for the formal total synthesis of streptorubin B, metacycloprodigiosin, roseophilin and related compounds.

The following chapter, by Paul W. Davies (University of Birmingham, UK) examines the meaningful application of ring-closing alkyne metathesis (RCAM) in natural product synthesis. After introductory remarks on RCAM, the author overviews the catalyst systems, emphasising the potential of RCAM-based strategies for obtaining many biologically relevant molecular targets, in particular dianiminosuberic acid derivatives, oligopeptides, glycophanes, cyclic β-turn mimics, lantibiotic nisin Z mimics and alkyne-linked glycocarno acids. The author describes two major strategic routes using RCAM macrocyclisation: (a) RCAM/hydrogenation protocols for the synthesis of macro-
cyclic musks, prostaglandin lactones, sophorolipid lactones, epothilone A, cruentaren A, latrunculins and myxovirescin; and (b) RCAM/sequential transformations for the synthesis of citreofuran by RCAM/cycloisomerisation and of amphidinolide V by RCAM/ene-yn metathesis (Scheme VI). The RCAM approach can accommodate a broad range of functionalities, comparable to RCM. However, further developments in catalyst design are needed in order to improve understanding and broaden the applicability of the RCAM strategy for natural product synthesis.

An excellent account of temporary silicon-tethered RCM (TST-RCM) reactions, mainly promoted by ruthenium-based catalysts, is to be found in Chapter 8, written by P. Andrew Evans (University of Liverpool, UK). This approach avoids the problems frequently associated with entropically unfavourable reactions and offers a practical way to achieve target-directed synthesis. Examples of O-SiR₂-O tethered substrates (symmetrical and unsymmetrical silaketals), O-SiR₂-C tethered substrates (allyl- and vinylsiloxanes), and enyne and diene TST-RCM, are given to illustrate the versatility of this strategy for the synthesis of challenging structures encountered in total synthesis protocols.

Applications of RCM involving a relay process (RRCM), initiated at a remote site within the substrate, are surveyed in Chapter 9 by Thomas R. Hoye and Junha Jeon (University of Minnesota, USA). After a basic presentation of the relay concept, the authors deal with the first successful use of RRCM in natural product synthesis (oximidine III), then expand the discussion of the efficiency of RRCM to the synthesis of new valuable products such as longithorones, trienomycin, mucocin, phoslactomycin B, tricholomenyn A, asperpetyn and harveynone. For a better understanding of this innovative technique, particular cases in which the desired relay process is prevented by interference from a truncation event or premature macrocyclisation are highlighted.

**Cross-Metathesis**

The importance of CM for functionalising terminal alkenes, appending a side chain to the core of a complex compound, or coupling two fragments in order to build the entire framework of the target molecule, is shown in Chapter 10 by Joëlle Prunet (Ecole Polytechnique, Palaiseau, France) and Laurence Grimaud (Ecole Nationale Supérieure des Techniques Avancées, Paris, France). Many natural compounds (including histrionicotoxin, colletol, cylindramide A, isoaltholactone, amphidinol, chlorotonil A, lasonolide A, and asimicin) have been prepared by combining this unique method with more conventional synthetic procedures. Moreover, employing CM in tandem or cascade ruthenium-based metathesis processes (ROM/CM, ROM/CM/RCM, ROM/RCM/CM, CM/RCM, and ring-closing enyne metathesis (RCEYM)/CM) and on enyne and alkyne substrates has proved to be a very fruitful concept leading to other products such as cylindrocyclophanes, squamostolide, routien nocin and anthramycin.

With these useful principles of CM reactions in mind, the reader is well prepared to navigate easily...
through the next chapter on cascade metathesis reactions in natural product synthesis, authoritatively written by Marta Porta and Siegfried Blechert (Technische Universität Berlin, Germany). The enormous potential of these transformations is given a fresh look in a collection of elegant syntheses of selected natural products, for example: panaxytriol, securinine, swainsonine (Scheme VII) castanospermine, *ent*-lepadin B (Scheme VIII), etc., obtained via ingeniously designed cascade reactions. Insights into the ROM/CM, RCM/CM, ene-yne RCM/RCM and RCM/RCM cascades, and how to steer selectivity in ene-yne-ene metathesis cascade, prove the efficiency and versatility of these methods for building the carbocyclic, heterocyclic and polycyclic units found in natural products. The authors conclude that, given the advantages of metathesis cascades in terms of atom economy and catalytic productivity, further significant applications of these processes are to be expected, contributing to the wider usefulness of olefin metathesis in natural product chemistry.

**Novel Pathways**

In a brief yet essential account (Chapter 12), Amir H. Hoveyda, Steven J. Malcolmson, Simon J. Meek and Adil R. Zhugralin (Boston College, USA) point out the crucial role of enantioselective olefin metathesis in the synthesis of natural products. Total syntheses of coniine (Scheme IX), africol (Scheme X) and tipranivir (Scheme XI) by RCM using enantiomerically pure chiral molybdenum catalysts are presented. Also highlighted is the enantioselective synthesis of quebrachamine by RCM with a chiral molybdenum catalyst and that of baconipyrone C through ROCM promoted by a chiral ruthenium catalyst. These few examples of catalytic enantioselective olefin metathesis, selected by the well-known Hoveyda group, clearly indicate that more active and robust stereoselective metathesis catalysts still need to be discovered in order to achieve the maximum potential of this method in natural product synthesis.

The final chapter, by Sofia Barluenga, Pierre-Yves Dakas, Rajamalleswaramma Jogireddy, Gaëlle Valot and Nicolas Winssinger (Université Louis-Pasteur Strasbourg I, France), is devoted to a topic which is currently gaining in importance due to growing demand for more cost-effective processes, namely solid-phase organic synthesis via metathesis reactions promoted by ruthenium catalysts. Relevant issues concern RCM with cleavage of the substrate.
Schemes VII and VIII. Synthesis of swainsonine and ent-lepadin B by ring-rearrangement metathesis cascade

Schemes IX–XI. Enantioselective synthesis of coniine, africanol and tipranavir by ring-closing metathesis
from the resin support, synthesis of small rings and macrocycles on the resin via RCM, dimerisation of polymer-bound small molecules by metathesis, RCM to construct peptide conformations, and solid-phase CM and ene-yne metathesis. Cyclorelease cleavage to obtain biologically active products can be used to prepare tetrapeptide macrocycles, epothilones, lactams and β-turn mimics. By using these solid-state techniques, with their inherent ease of separation, purification and manipulation, diversity-oriented synthesis based on metathesis aimed at chemical biology is expected to gain momentum.

Concluding Remarks
The book highlights how the available library of functional group-tolerant and robust ruthenium metathesis catalysts, along with the highly active and air sensitive molybdenum–alkylidene complexes, has been successfully applied in total syntheses of numerous biologically active natural products, all having in common metathesis reactions as key steps. Nowadays, the application of ruthenium-based catalysts in natural product synthesis is one of the fastest growing metathesis domains, with great potential for drug development.

This valuable publication will be of great interest to academic and industrial specialists working in the areas of alkene or alkyne metathesis, transition metal catalysis, and the synthesis of natural products and biologically active compounds. Despite some minor errors in the text, overall the book is of high quality. The editors are well-recognised authorities in the field, and the contributions are written by highly-qualified authors. Throughout the text, the volume displays attractive, well-designed schemes and diagrams that substantially contribute to the high quality of this work. The book will be informative for professionals and will also be useful for teaching staff, graduates and undergraduates in organic and medicinal chemistry and in materials science.
Johnson Matthey released its latest market survey of platinum group metal (pgm) supply and demand, “Platinum 2010 Interim Review”, on 16th November 2010.

**Platinum**

**Platinum Market Forecast to Be in Small Surplus in 2010**

Gross platinum demand was forecast to rise by 11 per cent to 7.56 million oz in 2010. Recycling of platinum in the autocatalyst, jewellery and electrical sectors was expected to increase by 31 per cent to 1.84 million oz. Supplies of platinum from current mining operations were set to remain almost flat at 6.01 million oz. As a result, net platinum demand was expected to increase by 6 per cent to 5.72 million oz, putting the market in a small annual surplus of 290,000 oz.

**Autocatalyst Platinum Demand to Rise**

Global demand for platinum in autocatalysts was expected to strengthen by 37 per cent to 2.99 million oz as vehicle production recovered. Gross demand for platinum in European autocatalysts was expected to increase by 46 per cent to 1.42 million oz due to increased purchases of diesel vehicles with platinum-containing exhaust aftertreatment systems. In North America, platinum loadings were set to rise on some heavy-duty diesel vehicles as manufacturers fitted platinum ammonia slip catalysts in NOx aftertreatment systems. Global recycling of platinum from spent autocatalysts was expected to rise by 32 per cent to 1.1 million oz, stimulated by higher platinum prices and the returns from car scrappage schemes.

**Jewellery and Investment Demand for Platinum Set to Decline**

Gross global demand for platinum in the jewellery sector was forecast to drop by 14 per cent in 2010 to 2.42 million oz as retailers and consumers reduced purchasing in response to higher prices in 2010. Higher platinum prices were anticipated to lift recycling levels by 30 per cent to 735,000 oz. Despite the popularity of platinum exchange traded funds (ETFs), identifiable physical investment demand for platinum was forecast to fall by 34 per cent to 435,000 oz in 2010. Higher prices were expected to reduce demand for platinum coins and bars, and encourage redemption of ETF positions in the more mature funds.

**Palladium**

**Palladium Market to be Close to Balance in 2010**

The palladium market was forecast to be in a very small annual surplus of 45,000 oz in 2010. Gross demand for palladium was set to rise by 15 per cent to 8.94 million oz in 2010 on the back of strong automotive and industrial demand. Recovery of palladium medical components with a sewing needle for scale (Copyright 2010 Johnson Matthey PLC)
Palladium from scrapped autocatalysts, jewellery and electronics was expected to increase by 29 per cent to 1.85 million oz. Net demand was therefore forecast to increase by 12 per cent to 7.10 million oz. Supplies of palladium were set to be almost flat at 7.14 million oz.

Automotive Palladium Demand Set to Increase
Demand for palladium in autocatalysts was forecast to increase by 27 per cent to 5.15 million oz in 2010. Recovery of light-duty vehicle production in all regions, and particularly rapid growth in production of gasoline vehicles in China, was expected to drive this increase in demand. European gasoline catalysts now contain, on average, a ratio of 97:3 per cent palladium:platinum, while diesel formulations typically have a ratio of around 25:75 per cent palladium:platinum. Together with higher vehicle sales, this helped to lift gross automotive demand for palladium. Recovery of palladium from spent autocatalysts was forecast to increase by 37 per cent to 1.32 million oz as a higher palladium price and car scrappage schemes stimulated recycling.

Industrial Palladium Demand to Benefit from Recovery in Electrical Sector
Gross demand for palladium in industrial applications was expected to rise by 8 per cent to 2.49 million oz, returning close to its 2008 level. Palladium use in multilayer ceramic capacitors was expected to be boosted by increased purchasing of consumer electronics, bringing demand for palladium by the electrical sector to 1.41 million oz. Recycling of palladium from scrapped electrical devices was forecast to increase by 11 per cent to 440,000 oz, driven mainly by legislation on electronic waste. Chemical demand for palladium was expected to benefit from the wider recovery in the manufacturing sector in 2010, with demand amounting to 385,000 oz.

Palladium Investment Demand to Remain Strong, Jewellery Demand to Fall
Identifiable physical investment demand for palladium, particularly in ETFs, was expected to rise to 670,000 oz in 2010. Redemptions in the more mature funds were anticipated to limit the increase in new demand. Demand for palladium jewellery was forecast to fall by 19 per cent in 2010 to 630,000 oz, with most of the decline due to weaker trade interest in China.

Other Platinum Group Metals
“Platinum 2010 Interim Review” gives supply and demand data for rhodium as well as demand data for ruthenium and iridium for 2010. The rhodium market was forecast to be in a modest surplus of 79,000 oz, with gross demand climbing by 22 per cent to 876,000 oz as recovery in autocatalyst and industrial demand took place. Supplies of rhodium were expected to fall by 7 per cent to 716,000 oz.

Ruthenium demand was set to increase by 83 per cent to 1.05 million oz, driven by strong purchasing by the electrical sector, especially for use in hard disk drive manufacture.

Iridium demand was forecast to more than double to 204,000 oz in 2010 on the back of rising industrial demand. This included iridium crucibles for the growth of single crystals of sapphire, used as a substrate in the production of light-emitting diodes (LEDs), as well as the upgrading of the Chinese chlor-alkali industry from older mercury-based technology to ruthenium-iridium membrane cell technology. The upswing in the global automotive industry also led to increased demand for iridium in spark plugs.

Special Feature
This edition’s Special Feature on ‘Platinum in Medical Applications’ reports on medical uses for platinum, including anticancer drugs and components for implanted biomedical devices such as pacemakers and catheters. Demand for platinum in medical applications, including the dental industry, was forecast to be 255,000 oz in 2010.

Availability of “Platinum 2010 Interim Review”
The book is available, free of charge, as a PDF file in English, Chinese or Russian, or as a hard copy in English, by visiting the Platinum Today website at: http://www.platinum.matthey.com/publications/pgm-market-reviews/archive/platinum-2010-interim-review/ or by sending a request to the Email address: ptbook@matthey.com.

By Martyn V. Twigg
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Throughout his long and distinguished career with the Ford Motor Company Haren Gandhi was concerned with controlling tailpipe pollutants from cars, and through his work this article reviews the huge amount of progress made during his four-decade career. His early work with gasoline engines embraced all of the major developments ranging from the first platinum-based oxidation catalysts through nitrogen oxides (NOx) reduction using platinum-rhodium catalysts and the later introduction of palladium into three-way catalysts (TWCs) via ‘trimetal’, palladium-rhodium and palladium-only formulations. Gandhi’s other work included the interactions of poisons with catalysts as part of maintaining their in-use performance, the potential for using ruthenium in NOx control in gasoline TWCs and NOx adsorbing catalysts (NACs) for lean-burn engines, and the use of zeolite-based selective catalytic reduction (SCR) catalysts for effective diesel engine NOx control. Gandhi received many awards and honours in recognition of his technical achievements and a selection is mentioned here. Haren Gandhi is remembered with tremendous fondness and respect throughout the automotive industry concerned with exhaust gas emissions control and his technical contributions towards improving the quality of the air we breathe will continue to benefit us all.

Haren Gandhi: An Appreciation
Harendra Sakarlal Gandhi (Haren, as he was known) (Figure 1), was born into a large family in Calcutta, India, on 2nd May 1941 and raised in Bombay (Mumbai), the capital of the State of Maharashtra and then the most populous city in the world. He obtained a first class honours degree from the Department of Chemical Technology at the University of Bombay in 1963. Later he moved to the USA where he attended
the University of Detroit, and on 15th February 1967 he joined the Ford Motor Company in Dearborn, Michigan, as a Research Engineer while still studying. In the same year he was awarded a Master of Science degree, and in 1971 he gained a doctorate in Chemical Engineering with a thesis entitled “Adsorption of Nitric Oxide on Transition Metal Oxides”. By the time Gandhi had completed his doctoral research, the US 1970 Clean Air Act had been signed. This required a 90% reduction of carbon monoxide (CO) and hydrocarbon (HC) emissions from 1970 model year levels by 1975, and a 90% reduction of nitric oxide (NO) emissions from 1971 model year levels by 1976. These requirements were major challenges to the car industry, and Gandhi joined a research team dedicated to achieving them.

Haren Gandhi spent his working life with Ford, first as a research engineer and, after a number of engineering and scientific positions in the area of automotive catalysis and emissions control, as a Henry Ford Technical Fellow overseeing Ford’s worldwide emissions control projects. He had a keen awareness of the social benefits that result from improved urban air quality delivered by emissions control catalysts, and he wished to extend these benefits around the world and especially to developing countries. He began early in the catalytic control of exhaust pollutants, and his successes were driven by a love and enthusiasm for his work that was supported by always having a creative research group of excellent scientists and engineers at Dearborn, coupled with the strong technical links that he developed with leading scientists from global catalyst manufacturers. He was a visionary leader with openness to new ideas and an ability to translate science and research into innovative products that went to series production. He worked closely with US government organisations such as the Environmental Protection Agency (EPA) and the California Air Resources Board (CARB), as well as national laboratories and universities. Haren Gandhi is shown in Figure 1 when, on one of his regular European visits, he was invited to the UK House of Lords to help clarify the detrimental effects sulfur from fuel has on the performance of automotive emissions control systems.

Gandhi was always a most honourable person with a strong professional appreciation of the ethics associated with commercial dealings. Through his successes he raised the profile of all those who innovate and are responsible for introducing new technologies, especially those associated with transportation. Haren Gandhi passed away on 23rd January 2010 and will be deeply missed by his many friends around the world, although his technical contributions towards improving the quality of the air we breathe will continue to benefit us all. Above all Haren Gandhi was a family man, and many technical meetings with him started with talk about his most recent family holiday or how his grandchildren were developing; he leaves his wife Yellow, his daughter Sangeeta and his son Anand.

Recognition and Awards
Apart from his earliest research, almost all of Gandhi’s work involved the application of platinum group metals (pgms), and his successes were largely based on the tremendous catalytic activity these metals can have in optimally formulated practical catalysts. Gandhi was keenly aware of the unique roles pgms have in controlling tailpipe emissions. He often recalled the experience of visiting a pgm mine and

Fig. 1. Dr Haren Gandhi photographed on 18th July 1996 prior to attending a meeting accompanied by the present author in the House of Lords with Lord Porter and Lord Lewis, to discuss the impact of fuel sulfur levels on catalytic emissions control systems.
seeing for himself the very low levels of these metals in the ore that necessitate extensive concentrating and refining to provide pure salts of the metals for the manufacture of catalysts.

One of the earliest awards Gandhi received was the Chemical Engineer of the Year Award from the Detroit Section of the American Institute of Chemical Engineers (1984). This was followed by others including the UK Institution of Mechanical Engineers (IMechE) Crompton Lanchester Medal (1987), the Society of Automotive Engineers (SAE) Ralph R. Teetor Industrial Lectureship Award (1988–1989), the Technological Innovation Award by Discover Magazine (1990), the Award for Excellence in Catalysis by Exxon (1992) and his election to the US National Academy of Engineers (1999). He heads the list for the number of Henry Ford Technological Awards, with the last, in 2009, being for the development and integration of virtual design and optimisation of global diesel after-treatment systems. But his chief award, and most prized by him, was the US National Medal of Technology for research, development and commercialisation of automotive exhaust catalyst technology and precious metal utilisation that he received from President George W. Bush in 2002.

Contributions to Catalytic Emissions Control Systems

Oxidation Catalysts

In anticipation of the 1975 implementation of the 1970 Clean Air Act several approaches were investigated to meet the demanding HC and CO tailpipe reduction targets. These included non-catalytic means such as running gasoline engines lean and having post-engine thermal combustion devices. But it became appreciated that the initial requirements could be met by using an oxidation catalyst in conjunction with an air pump to ensure that the exhaust was sufficiently lean (containing excess oxygen) for the oxidation of residual HC and CO to small amounts of carbon dioxide (CO₂) and water (H₂O), Equations (i) and (ii), to take place.

\[
2\text{CO} + \text{O}_2 \rightarrow 2\text{CO}_2 \quad (i) \\
2\text{C}_m\text{H}_n + (2m + \frac{1}{2}n)\text{O}_2 \rightarrow 2m\text{CO}_2 + n\text{H}_2\text{O} \quad (ii)
\]

Base metal catalysts were inadequate in terms of long-term activity and poison resistance (1) while platinum-based ones performed well, and once sufficient durability was demonstrated catalytic oxidation was successfully introduced into production. At this time a profound decision of lasting importance was to use coated monolithic ceramic honeycomb catalyst structures, rather than traditional catalyst pellets initially employed by some other companies which lacked long-term physical durability. The addition of a second pgm to oxidation formulations was used by catalyst manufacturers to provide improved durability by inhibiting sintering of the very small catalytically-active platinum crystallites under lean conditions. This could be done with either palladium or rhodium and for technical reasons Johnson Matthey used small amounts of rhodium. Later this took on special significance when NOx emissions also had to be controlled – NOx refers to the combined NO and nitrogen dioxide (NO₂) emissions. The control of tailpipe emissions with just an oxidation catalyst only lasted a short time because the need to reduce NOx emissions by 1976 required implementation of more complex catalyst systems.

**NOx Reduction**

It was apparent that engine measures alone, such as exhaust gas recycle (EGR) used to moderate the formation of NOx in an engine by reducing the levels of oxygen present during combustion, would not be sufficient to meet the NOx emissions limits by 1976. It would be necessary to convert NOx to inert nitrogen (N₂) to meet the demanding legislation, and a huge amount of research was directed to understanding how this difficult transformation could be achieved. At Dearborn, Ford was in the thick of NOx reduction research. A key scientist there, who became very important, was Mordecai Shelef with whom Haren Gandhi worked (2, 3). The possibility of using base metal catalysts had appeal and this approach was thoroughly explored; indeed Gandhi’s doctoral work was concerned with some of the relevant fundamental chemistry. Although dissociation of NO into its elements is thermodynamically favoured, under practical lean conditions this could not be done. The most active surfaces for NO dissociation are metallic, and dissociative adsorption of NO, Equation (iii), can be followed by rapid desorption of N₂, Equation (iv). However, oxygen atoms remain strongly adsorbed on the catalyst surface, and soon coverage by oxygen is complete and this prevents further adsorption of NO so its dissociation is halted. Effectively the surface is poisoned by adsorbed oxygen atoms, and under the prevailing conditions they can only be removed through reaction with a reductant, for example with...
hydrogen, as illustrated in Equation (v), or with CO as in Equation (vi), to provide a clean active surface for further NO dissociation.

\[
\begin{align*}
2\text{NO} & \rightarrow 2\text{N}_{\text{ads}} + 2\text{O}_{\text{ads}} \quad \text{(iii)} \\
\text{N}_{\text{ads}} + \text{N}_{\text{ads}} & \rightarrow \text{N}_2 \quad \text{(iv)} \\
\text{O}_{\text{ads}} + \text{H}_2 & \rightarrow \text{H}_2\text{O} \quad \text{(v)} \\
\text{O}_{\text{ads}} + \text{CO} & \rightarrow \text{CO}_2 \quad \text{(vi)}
\end{align*}
\]

These equations do not imply intimate mechanistic detail, but rather highlight the key role that surface oxygen plays in inhibiting NO dissociation. Consequently, at that time NO emissions could only be controlled by reduction to N\(_2\) in the absence of oxygen. It was found that the most catalytically active metals for this process were rhodium and ruthenium, and Gandhi explored the use of both. The reduction of NO became a theme that ran throughout his career.

**Reduction/Oxidation Systems**

The first practical system to control all three pollutants from cars used two separated pgm-based catalysts (4), the first reduced NO\(_x\) to N\(_2\) and the second oxidised HC and CO to CO\(_2\) and H\(_2\)O. The upstream catalyst operated under rich conditions and, after addition of excess oxygen from an air pump, HC and CO were oxidised over the downstream catalyst. However, chemical complexities including over-reduction of NO\(_x\) to ammonia (NH\(_3\)) by the first catalyst took place with some formulations, with remarkably high selectivity and high conversion (5–7). NH\(_3\) emissions are undesirable, although any NH\(_3\) formed in this way would almost certainly be oxidised back to NO\(_x\) over the downstream oxidation catalyst, causing significant overall NO\(_x\) conversion inefficiency. To combat this, catalyst selectivity was improved and operating conditions were kept not too rich. Such two-catalyst systems for controlling HC, CO and NO\(_x\) emissions were effective, but the catalyst and ancillary equipment cost was high.

**Three-Way Catalysts (TWCs)**

Fundamental work on conversion of the three pollutants HC, CO and NO\(_x\) as a function of air to fuel ratio showed that if a gasoline engine is operated around the stoichiometric point (an air to fuel ratio of about 14.7) a single platinum-rhodium catalyst could remove the three pollutants simultaneously, and this concept was christened the three-way catalyst (TWC) (8, 9) (**Figure 2**). There was a strong drive for the introduction of TWCs because of improved cost and efficiency, but well-controlled stoichiometric engine operation required implementation of three new key technologies:

(a) An oxygen sensor to determine whether the exhaust gas is on the lean or rich side of the stoichiometric point;

(b) An electronic fuel injection (EFI) system to permit metering precise amounts of fuel into the engine to maintain stoichiometric operation;

(c) A microprocessor for closed-loop feedback control of the overall system.

By the late 1970s all these features had become available, and TWCs came into production in the early
1980s as the technology of choice for controlling all three legislated pollutants (10). Subsequent addition of components such as air mass flow meters, better oxygen sensors, substantial microprocessor and software improvements and major catalyst improvements enabled TWCs to be integrated into the engine management system with remarkable results. Today TWCs can achieve almost complete removal of the three legislated pollutants, while an onboard diagnostics (OBD) system monitors their performance via measurement of oxygen storage capacity with two oxygen sensors. Table I illustrates trends in Californian emissions limits set by CARB since 1993 (11) that for several years guided the direction of Gandhi’s work. The SULEV hydrocarbon limit after 120,000 miles’ driving (0.010 g mile⁻¹, and significantly less than this when the vehicle is new) can be compared with the 15 g mile⁻¹ of a typical mid-1960s US car to provide a direct indication of the progress made in controlling emissions over three and a half decades. Indeed, tailpipe emissions of regulated pollutants from gasoline cars can now be less than levels in ambient air, so it could be said that during Gandhi’s career the situation moved from these emissions being a major

<table>
<thead>
<tr>
<th>Year</th>
<th>Category</th>
<th>Emissions (g mile⁻¹, FTP Test)</th>
</tr>
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<tbody>
<tr>
<td></td>
<td></td>
<td>HC</td>
</tr>
<tr>
<td>1993</td>
<td></td>
<td>0.25</td>
</tr>
<tr>
<td>1994</td>
<td>Tier 1</td>
<td>0.25</td>
</tr>
<tr>
<td>2003</td>
<td>Tier 1</td>
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</tr>
<tr>
<td>2004</td>
<td>TLEV₁, ²</td>
<td>0.125</td>
</tr>
<tr>
<td></td>
<td>LEV₂, ²</td>
<td>0.075</td>
</tr>
<tr>
<td>2005</td>
<td>LEV₁, ²</td>
<td>0.075</td>
</tr>
<tr>
<td></td>
<td>LEV₂, ²</td>
<td>0.040</td>
</tr>
<tr>
<td>2006</td>
<td>ULEV₁, ²</td>
<td>0.040</td>
</tr>
<tr>
<td></td>
<td>ULEV₂, ²</td>
<td>0.001</td>
</tr>
<tr>
<td>2007</td>
<td>ZEV₁</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>ZEV₂</td>
<td>0</td>
</tr>
</tbody>
</table>

²FAN MOG = fleet average NMOG reduced progressively from 1994–2003
³LEV₁ type emissions categories phased out 2004–2007
⁴LEV₂ type emissions limits phased in 2004 onwards
⁵ULEV₂ standards have same emission limits for passenger cars and trucks <8500 lb gross weight
⁶SULEV₁ onwards 120,000 miles durability mandated

Note: TLEV = transitional low emission vehicle, LEV = low emission vehicle, ULEV = ultra low emission vehicle, SULEV = super ultra low emission vehicle, ZEV = zero emission vehicle.

CARB = California Air Resources Board, FTP = Federal Test Procedure

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contributor to atmospheric pollution to one in which car use could help to reduce their levels in the air! And this was achieved with no more pgm per car than originally employed (Figure 3), thanks to the tireless efforts of Gandhi and other catalyst scientists in the automotive industry.

**Ruthenium Catalysts**

Although platinum-rhodium-based catalysts were discovered to be effective in NOx reduction, during the search for NOx reduction catalysts it was found that ruthenium was particularly effective and had the advantage of being cheaper than rhodium. However, the major problem encountered with ruthenium (and also to a lesser extent with iridium) catalysts is metal loss via volatile higher oxidation state oxides. Gandhi with his colleagues undertook research aimed at stabilising ruthenium catalysts against metal loss by forming stable ruthenates, and this was the subject of some of Gandhi’s first patents (12–16). There was some success (17–19), although real-world performance and durability proved insufficient to displace rhodium from platinum-rhodium TWC formulations.

**Palladium Catalysts**

The pgms have outstanding catalytic activity and ruthenium was one of the cheapest for NOx reduction, but because of durability concerns it was inappropriate for autocatalyst applications. The next most cost-effective metal was palladium, but it is very sensitive to poisoning by lead and sulfur. Unleaded gasoline was introduced to allow the use of catalysts, and when fuel sulfur levels were reduced in the early 1990s, it became feasible to incorporate palladium into platinum-rhodium catalysts to form commercially successful ‘trimetal’ TWCs (20). These still contained a high proportion of platinum. Palladium-rhodium formulations were later developed that actually outperformed the older, more costly platinum-rhodium TWCs. Gandhi became a strong advocate for the development of ‘palladium-only’ formulations that provided very good HC control and sufficient NOx control to meet the legislative requirements of the time. Gandhi pushed catalyst manufacturers to develop palladium-only TWC formulations with exceptional thermal durability and this was achieved, allowing durable palladium-only products to enter series production in the mid-1990s (21). The increased demand for palladium caused its price to increase and this, together with more demanding legislation that required tighter NOx control, took rhodium back into TWC formulations (see Table 1). However, the experience and knowledge obtained in the development of palladium-only catalysts was
transferred by catalyst manufacturers to developing advanced palladium-rhodium formulations (22) that led to remarkable TWCs for super ultra low emission vehicles (SULEVs) with astonishing performance and durability using relatively low pgm loadings (23).

Sources and Effects of Catalyst Poisons

Throughout his career Gandhi was involved with understanding the effects of poisons on automotive catalysts. In fact, the introduction of catalytic control of exhaust pollutants was only possible once unleaded gasoline was made available (for many years significant levels of toxic tetraethyl lead (TEL) were used to enhance the octane rating of gasoline). Lead is a powerful catalyst poison that blocks surface active sites and forms inactive alloy phases with pgms (24). Sulfur, a common catalyst poison, originates from gasoline and also lubrication oil (25). Other poisons derived from lubrication oil include calcium, zinc and phosphorus compounds. Phosphorus can form glassy surface layers on the catalyst that prevent gases reaching the active components (26) as well as being responsible for other problems (27, 28). Some TWCs are also susceptible to forming redox-inert cerium phosphate that degrades washcoat structure and depletes its vital oxygen storage capacity (29). Addressing these problems, which forms part of ensuring that in-use catalyst activity is maintained, concerned Gandhi. In this area he was also much troubled by the use of the lead-substitute octane enhancer methycyclopentadienyl manganese tricarbonyl, because manganese oxide deposits which form from it degrade engine performance by fouling the spark plugs and engine internals (30). In the exhaust system these deposits can inhibit the behaviour of the oxygen sensors which are instrumental in the proper running of the engine and OBD measurements. Catalyst performance can also be impaired through a surface coverage/blocking process (31–37). Recently the manganese fuel additive was reported to form ultra-fine nanoparticle tailpipe emissions (38, 39) that may themselves give rise to health concerns (40).

Lean-Burn Gasoline Engines

Over the last decade or so there has been growing interest in the reduction of greenhouse gas emissions. Widespread use of lean-burn engines, especially diesel engines (see below), with improved fuel economy could make significant contributions to lowering emissions of the main greenhouse gas, CO₂, and starting in the mid-1990s lean-burn gasoline engines had a revival for this reason. The possibility of operating gasoline engines under lean conditions with direct injection of fuel into the cylinder has a number of attractions, including increased power and fast response as well as some fuel economy benefits. Several lean-burn direct injection gasoline engines in cars followed Mitsubishi’s 4G93 1.8 litre engine which was first used in Japan and came to Europe in the Mitsubishi Carisma model in 1995. The fuel mixture is stratified in the cylinder of these engines so that it can be ignited by the spark plug, and progressively the mixture is leaner further away from the ignition point, so overall the combustion is lean. Thus the main emissions challenge was to control NOx emissions under lean conditions. Because of these considerations, controlling pollutants from lean-burn engines became the focus of some of Gandhi’s latest work at Ford.

The typical catalytic emissions control system for a direct injection lean-burn gasoline engine, illustrated
in Figure 4, has in practice a close-coupled TWC for use when the engine runs stoichiometrically (usually when starting and during acceleration) and an oxidation catalyst to control HC and CO emissions when the engine runs lean (41). NOX is then removed by a cooler downstream NOx absorbing catalyst (NAC) (also known as a lean NOx trap (LNT)) through a process involving oxidation to NO2 over a platinum component followed by its reaction with an alkaline component to form a nitrate phase, as illustrated in Equations (vii) and (viii). Before the absorbing catalyst is saturated with nitrate the exhaust is enriched, causing the nitrate to destabilise and decompose, Equation (ix), liberating NO that is reduced to N2 over a rhodium component in much the same way as in a TWC. Under operating conditions the alkaline component (M), usually the alkaline earth metal barium, when not nitrated is present as a carbonate, Equation (x). The overall process is called ‘regeneration’ and typically takes place every minute or so, with enrichment lasting around a second (Figure 5) (42).

\[
\begin{align*}
\text{NO} + \frac{1}{2}\text{O}_2 & \rightarrow \text{NO}_2 \quad \text{(vii)} \\
\text{MCO}_3 + \text{NO}_2 & \rightarrow \text{MNO}_3 + \text{CO}_2 \quad \text{(viii)} \\
\text{MNO}_3 & \rightarrow \text{MO} + \text{NO} + \frac{1}{2}\text{O}_2 \quad \text{(ix)} \\
\text{MO} + \text{CO}_2 & \rightarrow \text{MCO}_3 \quad \text{(x)}
\end{align*}
\]

In a typical Gandhi way he embraced these concepts with energy and vigour (43–45), and even returned to his desire to use ruthenium-based catalysts – one of his recent patents uniquely uses ruthenium in NAC formulations (46). He considered lean operation of gasoline engines under a variety of situations, including when idling, as a way to help improve real-world fuel economy. However, none of these approaches have yet gained widespread acceptance, perhaps because of technical complexity and the cost of direct injection. However, the combination of an upstream NAC over which NH3 can be formed during regeneration if the exhaust is sufficiently rich, followed by an SCR catalyst (see the section on Diesel Engines) that uses this NH3 to reduce residual NOx, may well gain acceptance in diesel engine NOx control (47) as evidenced by several recent publications (48–51).

**Diesel Engines**

The ultimate lean-burn concept is the diesel engine, and during the last decade Gandhi gave attention to the control of diesel engine emissions, especially NOx (52). In the 1990s major diesel engine developments took place in Europe. The bottom-end torque and driving characteristics of new turbocharged direct injection diesel-powered vehicles, coupled with their outstanding fuel economy (low CO2 emissions) resulted in them becoming very popular. Around half of all new passenger cars in Europe are currently diesels. The two most difficult to control diesel engine emissions are particulate matter (PM) or soot, and NOx. By 2000 diesel particulate filters in combination with fuel-borne catalyst (to enhance periodic burning of PM retained in the filter) were introduced on some European cars (53, 54). This was followed by the introduction of catalysed particulate filters that do not need the fuel-borne catalyst and its associated equipment. By 2005, small compact catalysed filters had been developed that fit directly on the engine’s turbocharger and perform all the catalytic and filtration functions necessary to control HC, CO and PM (55).

Diesel NOx control has all the problems associated
with lean-burn direct injection gasoline engines, exacerbated by lower-temperature operation. Formulation modifications enabled NACs to be used on diesel engines (56), but Gandhi generally favoured selective catalytic reduction (SCR) of NOx with NH3 derived from hydrolysis of urea supplied as an aqueous solution, Equation (xi). NO and NO2 react differently with NH3, Equation (xii) and Equation (xiii), and equal amounts of both react faster than either individually, so the SCR catalyst is usually located downstream of an oxidation catalyst to adjust the NO:NO2 ratio for optimum NOx control performance.

\[
\begin{align*}
(NH_2)CO + H_2O & \rightarrow 2NH_3 + CO_2 \\
4NH_3 + 4NO + O_2 & \rightarrow 4N_2 + 6H_2O \\
4NH_3 + 2NO + 2NO_2 & \rightarrow 4N_2 + 6H_2O
\end{align*}
\]

Since the 1970s SCR technology has been used to remove NOx from the flue gas of power stations and the off-gases from industrial processes such as the manufacture of nitric acid (HNO3) from NH3. Here the catalyst is vanadium-based and requires quite high temperatures, close to those available on heavy-duty trucks, and over recent years these catalysts have been increasingly used in these mobile applications. However, the lower temperatures on cars mean that catalysts of much higher activity are required to be effective. Gandhi over several years pushed catalyst manufacturers to achieve this remarkably difficult target through the use of new zeolite-based SCR catalysts whose performance is remarkable in the light of previous technologies, and they are being introduced into series production (57).

Conclusions

Throughout his entire career Haren Gandhi was deeply engaged in the technical aspects of emissions control, and he led the catalyst manufacturers to continually produce technically better products to meet increasingly demanding legislative requirements. He saw tailpipe emissions go from being relatively out of control (compared to today) and a cause of major environmental problems, to being well controlled by innovative catalytic technologies. However, and as he appreciated, there are always new challenges and demands in this area, as evidenced by the recent growth of advanced diesel engines in cars in Europe with their unique emissions control requirements, and the growing need to reduce CO2 emissions.

Unlike most in the automotive industry, Gandhi remained in his specific chosen area, and saw a series of major objectives achieved. Because of his wide experience and depth of knowledge he became known as a practical emissions control guru. In many ways Gandhi was unique in the industry and all of those who knew and worked with him mourn the loss of a very special friend.

Acknowledgements

The author gratefully acknowledges and thanks the many people who helped to complement his own recollections of working with Haren Gandhi for almost two decades, by sharing recent and more distant memories of collaborations with him, some that stretched over almost four decades. There are too many people to thank individually, although particular special thanks are due to Barry Cooper and to Barb Rutkowski, who was for many years Gandhi's personal assistant.

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US Patent 5,750,082; 1998


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Martyn Twigg was the Chief Scientist of Johnson Matthey PLC and before that the Technology Director for the Environmental Catalysts and Technologies Division. He has authored or co-authored many original research papers, holds many patents, has written numerous chapters in encyclopedic works, and edited and contributed to several books. He edits the book series Fundamental and Applied Catalysis, and has academic positions at several universities.
34th Annual Conference of Precious Metals

A strong theme of sustainability at the IPMI’s annual conference

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On 12th June 2010 over 500 delegates from around the world met at the JW Marriott Starr Pass Resort in Tucson, Arizona, USA, for the 34th Annual Precious Metals conference of the International Precious Metals Institute (IPMI) (1). The resort, located close to the magnificent Saguaro National Park and its forests of giant cacti, overlooks the historic city of Tucson.

The technical programme consisted of either two or three parallel sessions on each day of the conference with the most relevant sessions to platinum group metals (pgms) being:

– Session C: New Trends in Refining and Analyzing Precious Metals;
– Session E: The Future of Precious Metals: Business and Technology;
– Session F: Analysis of Precious Metals;

There was a strong theme of sustainability with many talks revolving around recovery and recycling of pgms and pgm-containing materials.

Recovery and Recycling of PGMs

Thomas Trin (W. C. Heraeus GmbH, Germany) spoke about the increasing need for innovative metal recycling technologies. This is partly due to a wider variety of materials with differing levels of pgm content becoming available for recycling, and partly due to changing economic and legislative conditions. Specific examples of platinum and ruthenium recovery from magnetic data storage media and emerging gas to liquid (GTL) or coal to liquid (CTL) catalyst systems using platinum and ruthenium were given. Two Heraeus processes were described, namely HeraCYCLE®, a proprietary thermal reduction process which allows accurate sampling and precious metal content determination after milling, and HeraSAMPLE®, a new method of providing accurate sampling for precious metal content determination prior to thermal reduction. In addition, Heraeus in collaboration with PhosphonicSTM Ltd offers precious metal scavengers to improve metal recovery from...
low-grade process and waste streams containing from 1 ppm to 500 ppm precious metal.

Christian Hagelüken (Umicore Precious Metals Refining, Germany) provided an update on changes in precious metals refining since the shock of the financial crisis in 2008. Precious metal prices have since recovered to a great extent from the sharp downturn due to demand, underlining once again the role that precious metals play in many important technologies. In parallel, there have been growing concerns about their long-term availability. After comparable exercises in Japan and North America, in November 2008 the European Commission started the Raw Materials Initiative which aims to secure access to ‘high-technology metals’ including pgms as well as cobalt, rare earth metals and titanium. Improved recycling can make a crucial contribution to ensuring supply security at affordable metal prices.

Steven Izatt (IBC Advanced Technologies, Inc, USA) reviewed general trends in precious metal recycling and presented a number of examples demonstrating the use of molecular recognition technology (MRT) to recover metals from low-grade resources. The increasing use of low concentrations of metals (notably rhenium, cobalt, indium, bismuth, germanium and molybdenum) in association with pgms in catalysis, energy generation, pollution abatement, electronics, and advanced materials, as well as the presence of these non-pgm metals in primary pgm ores of decreasing quality, requires highly efficient separation and purification processes to recover the metal value. Such processes must also be economically viable, be environmentally friendly and have minimal carbon footprints.

Corby Anderson (Colorado School of Mines (CSM), USA) spoke about programmes underway at the CSM Kroll Institute for Extractive Metallurgy (KIEM) and the National Science Foundation (NSF) Center for Resource Recovery and Recycling (CR3). These centres are playing a vital role in furthering the implementation of precious metal recycling in the USA.

Dan Cleroux (Sabin Metal Corp., USA) described the processes in operation for precious metal recovery from low-grade secondary ores, primarily through gravity, magnetic and flotation circuits.

He Xiaotang, Wu Xilong, Han Shouli, Wang Huan and Li Yong (Kunming Institute of Precious Metals, China) described a new process for the preparation of chloroiridic acid from iridium-containing organic waste liquids. The organic waste is first treated with aqua regia, thereby transferring iridium into aqueous chloride/nitrate media. Then iridium is separated in the form of Ir(OH)3 and Ir(OH)4 by hydrosolysis with sodium hydroxide, followed by dissolution of Ir(OH)3 and Ir(OH)4 in hydrochloric acid. Silica impurities are removed by adjusting acidity, and base metal impurities (nickel, copper and lead) are removed by ion exchange. Pure chloroiridic acid is obtained after further impurities are removed via ammonium chloride precipitation, re-dissolving the precipitate in aqua regia, and removing nitrate.

Paul Miranda (Center for Advanced Mineral and Metallurgical Processing, Montana Tech of The University of Montana, USA) described the development and application of a mineral liberation analyser for the analysis and quantification of minerals, slags and other phases using back scatter scanning electron microscopic techniques along with energy dispersive X-ray analysis (EDX). Robert M. Ianniello (BASF Catalysts, USA) described results of a research programme to concentrate and recover sub-ppm levels of platinum, palladium and rhodium in mine tailings and high-magnetite ore. The analytical method involves firstly a tellurium collection procedure followed by inductively coupled plasma mass spectrometry (ICPMS) measurement, chosen because of its high sensitivity and dynamic range. Tellurium collection followed by AAS or ICP measurement is considered to provide the best combination of precision, accuracy, speed and repeatability.

**Emerging Applications**

Richard Seymour (Johnson Matthey Technology Centre, UK) spoke about the use of patent mapping as a tool for monitoring competitor and customer activity, and identifying new market opportunities and technology trends. The vast and constantly growing volume of global patent data has led to the development of visualisation tools capable of analysing many thousands of patents. Examples of their application in the analysis of the pgm patent literature were presented, including the identification of developing or emerging technologies such as OLEDs and photovoltaic cells, the activities of specific companies, and how technology trends have changed over time. The use of iridium in medical applications was one area identified by the patent mapping exercise (Figure 1).

In an illuminating presentation Sven Jantzen (Umicore Platinum Engineered Materials, Germany) described how Umicore’s Process Excellence Model
has been applied in a number of product and process developments. These included:

(a) Physical modelling for new products used in the specialist glass industry, such as stirrers;
(b) Rhodium-free bushings for the fibre glass industry, which has seen the introduction of FKS platinum, a fine grain-stabilised material with increased mechanical strength, corrosion resistance and creep resistance at lower cost than conventional rhodium-containing materials;
(c) Improved pgm recovery systems for the nitric acid industry, especially suited to high-pressure plants which are particularly subject to pgm losses.

The Reconi™ catchment gauze from Umicore, a three-dimensional knitted gauze, is a new solution for platinum and rhodium recovery in this process (Figure 2).

Bill Gleason (Center for Advanced Mineral and Metallurgical Processing, Montana Tech, USA) presented his work on autocatalytic electroless reduction of palladium for preparation of membranes for hydrogen purification. The successful adoption of hydrogen as a clean fuel will depend on the development of effective methods of hydrogen purification, such as membrane purification using palladium and palladium alloys. While such membranes have been demonstrated to pass hydrogen while blocking other gas species, work is still required to produce a membrane that is stable, cost effective and durable. Montana Tech is developing a membrane based on autocatalytic reduction of palladium from solution onto a porous substrate. Different palladium salts have been found to give varying substrate coverage, and the self-catalytic reduction reaction gives a range of possible morphologies (Figure 3). While still at a developmental stage, the project has demonstrated that it is possible to produce a cheap, robust, scaleable membrane, offering the potential for a versatile, high-volume hydrogen purification membrane for fuel cell applications.

David Lupton (W. C. Heraeus GmbH, Germany), in his talk reviewing the use of Heraeus’ ammonia oxidation catalysts for optimum nitrous oxide (N₂O) abatement, began with a history of the Ostwald process since it was first introduced in the early part of the 20th century. Warp-knitted gauzes, introduced in the 1990s, have largely replaced earlier woven gauzes due to their higher mechanical elasticity, tear resistance and increased effective surface area. Since 1996, the Heraeus Functional Total Control (FTC)
system has been commercially available, comprising an integrated gauze/catchment pack consisting of platinum-rhodium gauze at the top and platinum-palladium gauze at the bottom. In 2000, N₂O emissions were reduced by 20–30% over a gauze campaign by the introduction of FTCplus, in which a specially designed supported precious metal catalyst is installed immediately beneath the FTC pack. N₂O is a major greenhouse gas, which has 298 times more impact per unit weight than carbon dioxide. The story continues to this day with a new wafer catalyst manufactured not from pgm wires but from fine pgm fibres extracted directly from the melt and sintered to form mechanically stable wafers. Lupton believes this new catalyst will offer the industry a number of new advantages in the future.
IPMI Awards
Among the many award winners were Professor James Dumesic (University of Wisconsin-Madison, USA), who received the Junichiro Tanaka Distinguished Achievement Award for the advancement of the precious metal industry, specifically on spectroscopic, microcalorimetric and kinetic techniques to study the surface and dynamic properties of heterogeneous catalysts, and most recently the use of heterogeneous catalysis for the conversion of renewable biomass resources to hydrogen, liquid hydrocarbons and intermediates for the chemical industry. John Steger (BASF Corp, USA), received the Henry J. Albert Award for contributions to the preparation and application of platinum-, palladium- and rhodium-containing heterogeneous catalysts for emissions control applications.

Concluding Remarks
The IPMI 34th Annual Conference demonstrated the importance of sustainability in pgm applications, with improved metal recovery and recycling being seen as vital now and for the future. With its record high attendance representing 24 countries, the event was considered to be a great success by all. Conference proceedings have been published and can be purchased from the IPMI (1). The 35th Annual IPMI Conference will be held in San Antonio, Texas, USA, on 11th–14th June 2011 (1).

Reference

The Reviewer
Richard Seymour is the Head of Technology Forecasting and Information at the Johnson Matthey Technology Centre, Sonning Common, UK. He is interested in the use of information in the areas of competitive intelligence and commercial development.

IPMI Student Awards 2011
The International Precious Metals Institute is accepting nominations from faculty members for its 2011 Student Award Program. The awards will be made to students who have started or plan to do research or development projects in the field of precious metals and will not have graduated before June 2012. There are 7 awards worth US$5000 each. Details of how to apply, the selection criteria and a list of past winners can be found through the IPMI website: http://www.ipmi.org/awards/index.cfm.
BERLIN–PM’2010

“Platinum Metals in Modern Industry, Hydrogen Energy and Life Maintenance of the Future”

The Fourth International Conference “Platinum Metals in Modern Industry, Hydrogen Energy and Life Maintenance of the Future” (Berlin–PM’2010) took place from 31st May to 4th June 2010, in Berlin, Germany. The International Organisation “Professor E. I. Rytvin Foundation” was the event’s patron and it was supported by the Chamber of Commerce and Industry of the Russian Federation and the International Informatization Academy.

The 60 invited participants included academic and industrial scientists as well as representatives of business groups and public bodies from the UK, Germany, China, Russia, Israel and the Ukraine. The conference programme included 29 reports and communications. All of the papers have been published in the Conference Proceedings (1), which are available from the organisers.

The papers and communications presented at this conference reflect the state of the art in the production, processing and applications of platinum group metals (pgms) and pgm products, with a particular focus on their uses in the production of nitric acid, glass and basalt fibres and other products for the chemical and glass industries. Applications in medicine and energy were also discussed.

The conference provided an opportunity for networking among the participants and allowed manufacturers and end users of precious metal-based materials and equipment to discuss their business needs. This interaction was also expected to promote further scientific and technical progress and ensure positive competition in these areas.

Hydrogen Energy and Global Economy

The conference covered a range of themes from hydrogen energy to social and educational aspects of the precious metals industry. As well as issues relating directly to the pgms, the participants discussed the wider context affecting the precious metals markets.

The problems of implementing hydrogen energy are closely connected with the problems of saving energy and increasing energy efficiency, topics which are of increasing importance due to growing concern over climate change. These questions were considered at the level of individual countries and regions as well as in the context of global development. The basic provisions of the 13th Report on the Development of Human Potential in Russia, “Energy and Stable Development”, formulated within the framework of the United Nations’ Development Programme, were taken into account, as was the energy sector’s influence on the growth of human capital and the global economy.

Innovative technologies involving the pgms which can have a bearing on economic development were presented during the conference. One such example was a project entitled ‘Nano-Structural Catalysts for Hydrogen Energy’, presented by Professor Vladimir N. Fateev (Deputy Director, Russian Research Centre (RRC) “Kurchatov Institute”).

Educational programmes for schools and universities were a new topic for discussion at the Berlin conference. An international programme for schools on the application of resources and energy generation has been introduced, with the motto: “think globally, act locally”. Schools from seventeen countries in the Commonwealth of Independent States (CIS) and Eastern Europe participate in this programme.

Finally, the wider context of the precious metals industry was considered, following the approach taken at the third conference in this series held in Xi’an, China, in 2008, when a declaration on the ‘Development of Interregional Scientific and Educational and Humanitarian Cooperation in the...
Hi-Tech Branches of Economy’ was adopted on Supermetal’s initiative, and supported and updated later in Berlin. This declaration shows the potential for further growth in international cooperation between the participants of this conference series. Innovations in nanotechnology, information sharing and energy generation will contribute towards achieving a uniform process of stable development across the participating regions.

Foundation Award
At the Conference, the International Organisation “Professor E. I. Rytvin Foundation” awarded Professor Richard W. W. Pollock (Department of Russian Studies, Faculty of Humanities, University of Manchester, UK) a Foundation Diploma and a Memorable Silver Medal for his contributions to the development of cooperation in the field of production and application of precious metals and for organising the International Conferences “PM’2005–2010”.

Closing Remarks
The Organising Committee of the Conference has received two offers regarding the next (fifth) international conference “Platinum Metals in Modern Industry, Hydrogen Energy and Life Maintenance of the Future”, and thanks go to Keqin Yin, General Director of Wuxi International Platinum Co, Ltd, China, for his offer to hold the Fifth International Conference in the city of Wuxi, Jiangsu Province, China, in 2012, and to D. Rytvin, General Director of OSEWLT GmbH, Germany, and President of the “Professor E.I. Rytvin Foundation”, for his invitation to hold the conference in the city of Tel Aviv, Israel. The Organising Committee will consider the offers at a correspondence meeting of the Organising Committee in December 2010.

SUPERMETAL, MOSKOW OZERKOVSKAYA NAB., 22/24, H.2, 115184 MOSCOW, RUSSIA
E-mail: info@supermetal.ru

Reference

List of English Abstracts

In order of appearance

Precursors for Obtaining Hydrogen Energy Electrocataysts
T. M. Buslayeva, E. V. Volchkova, E. K. Lyutikova, V. N. Fateyev and E. S. Komandina, Moscow State Academy of Fine Chemical Technology; and Institute of Hydrogen Energy and Plasma Technology of Russian Research Center “Kurchatov Institute”, Moscow, Russia
The purpose of this research was to synthesise precursor complexes for obtaining hydrogen energy electrocataysts. The composition of salts has been selected containing Co(III) in the cation composition and Pt(II) or Pt(IV) in the anion composition.

Precious Metals of Ural Group of Companies Ural Innovative Technologies JSC (GC Dragotensie Metally Urala, JSC Ural’skie Innovatsionnye Tekhnologii)
S. V. Nikiforov, E. V. Terentiev and A. V. Ermakov, Ural Innovative Technologies JSC, Ekaterinburg, Russia
The Precious Metals of Ural Group of Companies (PMU GC) is a rapidly developing group of Ural-based companies. Today, the group provides a wide range of services and products made of precious metals for use in different industries: vehicle manufacturing, glass, electric engineering, hydrocarbon processing, nitrogen and nitrogen compound making, jewellery, medical, etc., where platinum group metals (pgms), gold and silver are used.

Nanostructural Platinum Electrocataysts for Hydrogen Energy
V. N. Fateev, Deputy Director of RRC “Kurchatov Institute”, Moscow, Russia
Fuel cell systems with proton exchange membrane (PEM) compositions are usually based on catalytic pgms or their oxides. The application of new nanocatalysts and nanostructured membranes can reduce the consumption of pgms up to three times, increase specific productivity up to 50% and increase the lifetime up to two times.

Production of Catalyst and Catchment Systems for Ammonia Conversion According on the Umicore AG & Co KG Technology
S. V. Gakh and D. A. Savenkov, OJSC “SIC ‘Supermetal’”, Moscow, Russia; and Umicore AG & Co KG, Business Unit PEM, Hanau, Germany
Platinum alloy catalysts are the best ones for selective ammonia oxidation to nitric oxide. In 2008, a state-of-the-art high-tech line was launched on the platform of OJSC “SIC ‘Supermetal’” in cooperation with Umicore AG & Co KG for the production of platinum alloy-based catalyst systems for ammonia oxidation in the production of nitric acid.
Precious Metals in the Production of Preparations for the Decoration of Ceramics and Glass

O. Galushko and A. Dokuchaev, OOO “NPK ELEFOR”, Andreevka, Russia

Precious metals find application as colourants for products made of ceramic, porcelain and glass. These colourants typically contain sulforesinates, mercaptides or powders of precious metals (Au, Ag, Pd, Pt); organic compounds to improve adhesion and hardening; and organic solvents or oils to allow easy application of preparations to products.

Technological Aspects of Obtaining Platinum Group Metal Coatings by Metal Organic Chemical Vapour Deposition

N. V. Gelfond, I. K. Igumenov and N. B. Morozova, Nikolaev Institute of Inorganic Chemistry SB RAS, Novosibirsk, Russia

Metal layers were deposited by different modifications of the MOCVD technique (atmospheric pressure MOCVD, low pressure MOCVD and pulse MOCVD) using volatile metal complexes as precursors, mainly metal \( \beta \)-diketonate derivatives. Metal coatings of Pt, Ir, Pd, Ru, Rh as well as Au, Re, Ni, Cu and their composites were deposited.

Hydrogen–Palladium Temporary Gradient Material. Form Changes Laws and Nature of the Phenomenon

M. V. Goltsova and E. N. Lyubimenko, Donetsk National Technical University, Donetsk, Ukraine

To study mechanical hydrogen elasticity phenomena a new hydrogen-vacuum device (HVD-4) was planned and constructed. This made possible an investigation of the hydrogen elastic deformation of metals (for example palladium) at \( T > 150^\circ C \), i.e. in the wider region of \( \alpha \)-solid solutions of hydrogen in palladium.

Prospects of Hydrogen Membrane Technology: Technical and Market Aspects

V. A. Goltsov, M. V. Goltsova, G. I. Zhirov, L. F. Goltsova, V. V. Vasekin and L. A. Sportsmen, Donetsk National Technical University, Donetsk, Ukraine; and Federal State Unitary Enterprise “Scientific and Industrial Complex “Supermetal” named after E. I. Rytvin”, Moscow, Russia

High-purity hydrogen is essential for many hydrogen technologies. Membrane technology can be used for high-purity hydrogen production. The main characteristics of palladium alloys for hydrogen diffusion filters and the construction peculiarities of diffusion elements and hydrogen membrane apparatuses (HMA) were presented.

Technological Aspects for Platinum Alloy Thermocouple Wire Production at JSC Krastsvetmet

P. A. Khorikov, S. N. Mamonov, A. I. Yeskin, V. N. Yefimov and D. R. Shulgin, JSC Krastsvetmet, Krasnoyarsk, Russia

JSC Krastsvetmet is developing a new product, platinum and platinum-rhodium alloy fine wire, to be applied in thermocouples and resistance thermometers. It has been shown that the quality depends both on the usage of high-grade starting metals and improvements in alloy production technology, resulting in a more homogeneous structure and distribution of rhodium in platinum.

Experience in Pyro-Processing of the Precious Metal Secondary Raw Materials at OJSC “SIC ‘Supermetal’”

S. D. Levchenko and L. E. Morozova, OJSC “SIC “Supermetal”, Moscow, Russia

Improvements to processing technologies for secondary raw materials and pyrometallurgic refining of precious metal alloys have been shown. Significant reduction of losses of precious metals and application of complex technologies of secondary raw material processing were demonstrated.

Process Excellence Model

J. Leyer, Umicore AG & Co KG, Hanau, Germany

Umicore’s business unit Platinum Engineered Materials (PEM) is one of the world’s leading producers of platinum equipment for the production of high-quality glass and platinum-based catalysts for the chemical industries. This paper gives an overview of Umicore’s activities in the field of platinum-based products and catalysts.

The High Temperature Creep Behavior of Dispersion Strengthened Pt-5Rh Composite

X. Ming, L. Ji, H. ChangYi, L. WeiPing, Z. YanMing and Z. Jiming, Kunming Institute of Precious Metals, Kunming, Yunnan, China

High-temperature tensile tests were performed on dispersion strengthened Pt-5%Rh alloy prepared by a large plastic deformation technique. High-temperature creep properties of the dispersion strengthened Pt-5%Rh alloy were found to be better than those for conventional alloy materials.

MOCVD Precursors of Pt Group Metals for Forming Thin Layers for Microelectronic Applications

N. B. Morozova, I. K. Igumenov and N. V. Gelfond, Nikolaev, Institute of Inorganic Chemistry SB RAS, Novosibirsk, Russia

Thin layers of pgms and gold were obtained by the MOCVD technique using volatile metal complexes with different ligands as precursors. The principles of precursor choice for obtaining thin metal films by means of MOCVD are described.

Effect of Electrochemical Coatings on the Corrosion of Dental Alloys

V. Parunov, I. Lebedenko, M. Stepanova and D. Beljakov, Moscow State University of Medicine and Dentistry, Moscow, Russia

In the last few years, there has been an increase in the number of investigations of the biological properties of prostodontic materials and the interaction of these materials with living tissue. Increasing intolerance of base metal alloys means that there is a need to find an adequate substitute. Taking into account the technological complexity of titanium dentures and the insufficient
strength of ceramic crowns and dental bridges, alloys of precious metals are likely to be the best replacements for base metals.

Members of Inter-Regional Association, Manufacturers of Industrial Products of Precious Metals, Keep Industrial Activity in the Conditions of Crisis
O. V. Pelevin and V. Yu. Preis, Inter-Regional Association of Precious Metals Producers, PZCM-Vtormet LLC, Russia

The Inter-Regional Association of Precious Metals Producers was established in 2000 as a noncommercial partnership and includes refining plants, large plants producing high-tech industrial precious metal products, enterprises processing precious metal scrap and waste, and banks. Its members aim to maintain and develop the commercial production of precious metal goods and services in Russia without government support during the economic crisis.

Plasma Welding Particularities and Possibilities of Platinum and Noble Metals Goods
D. M. Pogrebisky, Jerusalem, Israel

General aspects of plasma arc welding of comparatively thin metal materials, especially platinum and other noble metal alloys, are discussed. Plasma welding of various glass melting apparatuses and devices, including those made of laminated and dispersion strengthened materials, is still not exhausted, and the technique can also be used for dental and jewellery applications.

Properties of the Alloys of Gold with Platinoids
V. V. Vasekin and D. S. Tykochinsky, OJSC “SIC Supermetal”, Moscow, Russia

The effect of platinum, palladium and other alloying elements on the properties of gold alloys has been investigated to obtain data for designing a frame material for ceramic-metal dentures. The efficiency of pgms as strengtheners of gold alloys was estimated and compared with other conventional alloying elements.

A Novel Eptaplatin-Analogue with Improved Antitumor Efficacy
L. Weiping, L. Liguang, C. Xizhu, Y. Qingsong and H. Shouqian, State Key Lab of Advanced Technologies for PGMs, Kunming Institute of Precious Metals, Kunming, Yunnan, China; and Shanghai Institute of Materia Medica, Chinese Academy of Sciences, Shanghai, China

A novel water-soluble analogue of eptaplatin has been chemically synthesised and biologically evaluated in animals. It shows more activity and less toxicity than its parent drug eptaplatin, exhibiting great potential for further development.

Platinum-Based Composites
V. A. Yastrebov, OJSC “SIC Supermetal”, Moscow, Russia

One of the ways to improve the efficiency and economy of platinum and its alloys is the development and application of composite materials. Examples include ceramic products coated with platinum or its alloys and platinum-based dispersion strengthened alloys.

Development and Production of New Jewellery 950 and 990 Palladium Based Alloys at JSC Krastsvetmet
V. N. Yefimov, S. N. Mamonov, D. R. Shulgin and S. I. Yeltsin, JSC Krastsvetmet, Krasnoyarsk, Russia

To diversify the product range at JSC Krastsvetmet, a number of new 950 and 990 palladium jewellery alloys were made. To produce the palladium alloys induction melting in an inert atmosphere and melt pouring into a copper mould was used. The heat treatment conditions and semi-finished jewellery plastic deformation parameters were determined.

The Ordered Phases in the Pd–Sn–Cu and Pd–Sn–Au Systems
G. P. Zhmurko, M. A. Stepanova, E. G. Kabanova, V. N. Kuznetsov and V. V. Vasekin, Chemical Department of Moscow Lomonosov State University, Moscow, Russia; and Open Joint Stock Company Scientific and Industrial Complex “Supermetal” named after E. I. Rytvin, Moscow, Russia

Alloys of palladium containing gold form a basic system for the development of new dental alloys. The aim of the present study was to investigate the solubility of tin in the face-centred cubic solid solutions Pd–Au and Pd–Cu as well as the nature of phases coexisting with those solid solutions in the ternaries at 800°C and 500°C.
Publications in Brief

BOOKS

“Electrocatalysis: Computational, Experimental, and Industrial Aspects”


The book reviews four main electrochemical processes: hydrogen production, oxygen electrochemistry, energy conversion/production, and fine electroplating. It provides extensive coverage of the electrocatalytic reaction; presents the design and preparation of electrocatalysts based on new concepts such as surface roughness; and covers classical quantum models and new possibilities of ab initio methodology in electrocatalysis.

“Innovations in Fuel Cell Technologies”


This book reviews the state of the art in low- and high-temperature fuel cells, across all the types applied in the field today, and assesses current trends in development. The main technology problems are discussed and current gaps to market success identified.

“Microwave Heating as a Tool for Sustainable Chemistry”


The book begins with an introduction to microwave heating, the physical concepts behind it, its application in synthetic chemistry, and commercially available microwave equipment. It shows how microwave heating can be used to facilitate the clean and sustainable synthesis of organic compounds and includes examples which employ pgm catalysts. Other applications are described in detail.

“Solvent Extraction Chemistry of Precious Metals”, 2nd Edition


The 1st Edition of “Solvent Extraction Chemistry of Precious Metals” was published in 2005, and was purchased in a number of countries. Many papers and patents about solvent extraction and the separation of precious metals have been published in the five years since. For this edition, the editor reviewed the new literature, rewrote Chapter 2, renewed the content of other chapters, increased the references, and revised errors in the 1st Edition. The preface to the new edition is by Professor You Xiaozeng of the Chinese Academy of Sciences, who is also honorary director of the Coordination Chemistry Institute and the chairman of the Academic Committee of the State Key Laboratory of Coordination Chemistry at Nanjing University, China.


This guide discusses patentability and explains important concepts of patent law such as novelty, non-obviousness, and freedom-to-operate. Through examples from case law as well as real-world situations with which a researcher might be faced, this book provides readers with a better understanding of how to put that knowledge into practice.
Electrocatalysis

Electrocatalysis is a new journal from Springer, aiming to stimulate the development of electrochemical technologies and invites submissions in subject areas such as:

(a) Theoretical and experimental aspects of the mechanisms and kinetics of electrochemical reactions;
(b) Electrochemical generation of gases;
(c) Electrochemical reactions in fuel cells;
(d) Electrosynthesis, organic electrochemistry, and electrocatalytic hydrogenation;
(e) Electrochemical reactions taking place at matrix-supported electrocatalysts;
(f) Electrode reactions occurring in electrochemical sensors;
(g) Electrochemical degradation of pollutants.

ON THE WEB

Platinum Drugs Take Their Toll


Interest in synthesising new platinum-based structures has been growing, but clinical development may tax the reserves of small firms struggling to make their compounds the new standard in cancer therapy.

Collaboration Yielded a New Class of Cancer Drugs


An account of how an academic research institute, a metals producer, and a pharmaceutical firm developed new platinum compounds on the basis of a serendipitous discovery.

Pedagogy on Platinum Drugs


A timeline of platinum anticancer drug development.

Find these articles at: http://pubs.acs.org/cen/
CATALYSIS – APPLIED AND PHYSICAL ASPECTS

Terminal C≡C Triple Bond Hydrogenation Using Immobilized Wilkinson’s Catalyst


Phenylacetylene was selectively hydrogenated to styrene and 3-phenylpropyne to allylbenzene using Wilkinson’s catalyst immobilised by ionic exchange on hectorite and montmorillonite or by covalent bonding on MCM-41 and SBA-15. Heterogeneous catalysis was more selective than homogeneous catalysis for phenylacetylene hydrogenation. The type of immobilisation had no influence on activity or selectivity.

Osmium(III) Complexes with POP Pincer Ligands: Preparation from Commercially Available OsCl₂·3H₂O and Their X-ray Structures


Os complexes with phosphine ligands such as dbf(PPr₂)₂, xant(PPr₂)₂ or xant(PPh₂)₂ were obtained in high yields by reaction of the corresponding diphosphine with OsCl₂·3H₂O. The corresponding Ru(III) complexes were similarly obtained from RuCl₃·3H₂O in moderate yields. The X-ray structures of dbf(PPr₂)₂ and the synthesised Os complexes are also reported.

Synthesis and RCM Reactions Using a Recyclable Grubbs–Hoveyda Metathesis Catalyst Activated by a Light Fluorous Tag


A recyclable Grubbs–Hoveyda second-generation catalyst activated by a light fluorous tag was prepared. The catalyst exhibited higher activity than the parent or previous reported variant for RCM reactions and could be routinely recovered. The light fluorous tag in the catalyst served as both an activator and a handle for separation and recovery by fluorous solid-phase extraction.

CATALYSIS – INDUSTRIAL PROCESS

Pilot-Plant Study of the PCB Degradation at Ambient Temperature and Pressure


A continuous pilot plant for the degradation of polychlorinated biphenyls (PCBs) by Pd/C-catalysed hydrogenation in the presence of NEt₃ (see the Figure) was designed and constructed. Undiluted PCBs from a capacitor and diluted PCBs with desulphurised trans oil could be decomposed at ambient temperature and pressure. This degradation method can be combined with catalytic desulphurisation technology for the purification of gasoline and kerosene.

EMISSIONS CONTROL

Loading and Aging Effects in Exhaust Gas After-Treatment Catalysts with Pt as Active Component


Several close-to-production DOCs with Pt loadings between 22–130 g ft⁻³ were hydrothermally aged between 700–950°C and characterised by BET, HR-SEM, HR-TEM and CO-TPD. The pollutant conversion could be predicted for DOCs and NSCs with different Pt loadings and under different ageing conditions by determining the catalytically active surface area using CO-TPD.

Simulation of a Nonisothermal Modern Three-Way Catalyst Converter


A 2D nonisothermal monolith reactor model based on intrinsic detailed reaction kinetics was developed to simulate the performance of a commercial TWC.
The model predicts TWC performance for both Pd (front) and Pt/Rh/Ce (rear) monolith bricks. The reactor model was further validated by predicting the TWC performance of the dual-bed reactor under the steady-state sweep test (ss-ST) condition varying the air:fuel ratios from 14.23 to 15.03 at different reaction temperatures.

**FUEL CELLS**

**A One-Step Continuous Synthesis of Carbon-Supported Pt Catalysts Using a Flame for the Preparation of the Fuel Electrode**


A single-step method for continuous production of up to 60 wt% Pt/C catalysts for the fuel electrode of a PEMFC is reported. An acetylene-air diffusion flame was used as the source of both heat and C, and Pt(acac)2-containing xylene droplets were injected into the flame. Size was controlled at 2–7 nm. The electrochemical activity was >74.9 m² g⁻¹ Pt, more efficient than an equivalent commercial (E-TEK 10 wt% Pt) catalyst.

**Improvement of Platinum Adhesion to Carbon Surfaces Using PVD Coatings**


Adhesion of Pt to modified C surfaces was assessed experimentally using a micro scratch test, and the bond strengths were calculated by first principles simulations. Pt adhesion to graphite could be improved by applying thin interfacial layers of Au, Ti or Cr, which may enhance the Pt catalyst durability in PEMFCs. Pt adhesion to non-hydrogenated diamond-like C was strong enough without the application of these thin layers.

**Colloidal Synthesis and Characterization of Carbon-Supported Pd–Cu Nanoparticle Oxygen Reduction Electrocatalysts**


Colloidal synthesis was used to prepare monodisperse Pd-Cu alloy nanoparticles with average diameter 3 nm for the as-prepared particles and 5–10 nm after removal of the capping agents. The resulting nanoparticles were deposited on high surface area C to form Pd-Cu/C catalysts. Their ORR activity in acidic electrolyte was high and depended on composition and heat treatment conditions.

**METALLURGY AND MATERIALS**

**Effect of Modification by Pt and Manufacturing Processes on the Microstructure of Two NiCoCrAlYTa Bond Coatings Intended for Thermal Barrier System Applications**


Pt was added to two NiCoCrAlYTa coatings made by different manufacturing processes. XRD, SEM, EDS and TEM analyses showed that the Pt layer caused Al uphill diffusion from the NiCoCrAlYTa bulk to the Pt-rich surface during heat treatment. This is expected to provide good oxidation and hot corrosion resistance. The final microstructure was also influenced by the manufacturing process.

**ELECTROCHEMISTRY**

**Observing Iridium Oxide (IrOₓ) Single Nanoparticle Collisions at Ultramicroelectrodes**


The electrochemical detection of single IrOₓ nanoparticle collisions on a NaBH₄-treated Pt ultramicroelectrode (UME) was carried out for the electrocatalytic water oxidation reaction. IrOₓ transiently sticks to the electrode, causing a reversible ‘spike’ in the current. The frequency of spikes was directly proportional to particle concentration, and the peak current increased with applied potential. The observed current was sensitive to the material and surface state of the measuring electrode; a NaBH₄-treated Pt UME was important for reproducibility.

**NANOTECHNOLOGY**

**Shape Control of Platinum and Palladium Nanoparticles for Catalysis**


This mini review surveys solution-phase methods for preparing shaped Pt and Pd nanoparticles with specific crystallographic facets. Catalytic studies of the shaped nanoparticles and results of their activity and
selectivity are highlighted. Aspects of synthesis and catalysis to be considered for the future development of more efficient and effective catalysts are given. (Contains 94 references.)

Electrochemical Pd Nanodeposits on a Au Nanoisland Template Supported on Si(100): Formation of Pd–Au Alloy and Interfacial Electronic Structures

Pd nanoparticles (Pd NPs) were electrodeposited on a H-terminated Si(100) substrate and on a Au nanoisland template (NIT) supported on Si(100). As-deposited Pd NPs on H:Si consisted primarily of a metallic Pd core with Pd$_x$Si at the Pd and Si interface. Annealing the Pd NPs to 700ºC in air promoted formation of PdO with an overlayer of PdO$_2$. Pd NPs on supported Au NIT formed a Pd-Au alloy at room temperature at the metallic Pd and Au nanoisland interface. This was further enhanced by post-annealing at 700ºC.

PHOTOCONVERSION

Red-Phosphorescent OLEDs Employing Iridium (III) Complexes Based on 5-Benzoyl-2-phenylpyridine Derivatives

A series of red phosphorescent Ir(III) complexes based on 5-benzoyl-2-phenylpyridine derivatives was synthesised. Their photophysical and electrophosphorescent properties were investigated. Multilayered OLEDs with efficient red emissions were fabricated. The maximum luminance was 14.200 cd m$^{-2}$ at 14.0 V. Luminous, power, and quantum efficiency were 10.40 cd A$^{-1}$, 3.44 lm W$^{-1}$ and 9.21% at 20 mA cm$^{-2}$, respectively. The peak electroluminescence wavelength was 607 nm, with CIE coordinates of (0.615, 0.383) at 12.0 V. The device also showed a stable colour chromaticity with various voltages.

Heteroleptic Ruthenium Antenna Dye for High-Voltage Dye-Sensitized Solar Cells

A new Ru photosensitiser, CYC-B7 (see the Figure), with an electron-rich bithiophene and a bis-heptyl-substituted carbazole substituent was found to increase the open-circuit voltage ($V_{oc}$) of a dye-sensitised solar cell (DSSC) device to 788 mV, with an overall conversion efficiency ($\eta$) of 8.96%. The MLCT transition band was centred at 551 nm and the molar absorption coefficient was $2.19 \times 10^4$ M$^{-1}$ cm$^{-1}$.

SURFACE COATINGS

Atomic Layer Deposition of Ru/RuO$_2$ Thin Films Studied by In Situ Infrared Spectroscopy

Ru(Cp)(CO)$_2$Et and O$_2$(g) were used as reactants for the deposition of Ru thin films. Sample temperature, precursor pulse length and precursor gas pressure were varied to achieve self-terminated surface reactions on H-terminated Si(111) surfaces. Higher growth rates (~1.5–3 Å/cycle) were obtained compared to those typical of ALD of metals (~0.5–1 Å/cycle) under saturation conditions. The deposition rate was linear and the film became metallic after 22 cycles. Thick films (45 nm) grown with short pulses produced metallic polycrystalline Ru with hcp structure.
CATALYSIS — APPLIED AND PHYSICAL ASPECTS

Platinum Nanoparticles Supported on Bacterial Cells
Japan Atomic Energy Agency, Japanese Appl. 2010-162,442

A cost-effective method for producing 0.1–50 nm nanoparticles of pgms, specifically Pt, is claimed. Aerobically-cultured iron-reducing bacteria such as *Shewanella putrefaciens* are contacted under aerobic conditions with a solution of Pt ions and either an organic acid or H₂(g) as electron donor. Pt nanoparticles are precipitated on the surface of the bacterial cells, which can in turn be deposited on a support such as diatomaceous earth, and are suitable for use as hydrogen isotope exchange reaction catalysts.

CATALYSIS — INDUSTRIAL PROCESS

‘Self-Activating’ Catalysts for Mercury Oxidation

Two classes of catalysts for Hg removal from industrial off-gas are described: metallic Ir or 5–10 wt% Ir-Pt alloy, which are corrosion resistant; and partially combusted coal with 20–80 wt% ash, which is disposable. Both are easily regenerated and are found to be activated in situ by exposure to HCl and Cl₂. The catalysts promote the oxidation of Hg to HgCl₂, allowing it to be removed by conventional scrubbers or precipitators.

CATALYSIS — REACTIONS

Novel Ruthenium-Based Olefin Metathesis Catalysts
Idenix Pharmaceuticals, Inc, World Appl. 2010/090,976

Phosphinate Ru complexes of general formula 1 and their use as catalysts for olefin metathesis and RCM are claimed. Typical molar ratios of catalyst to olefin are ≤0.5, preferably ≤0.01. The complexes may deliver benefits such as better yield, improved chiral purity and less metal contamination of the product.

Iridium Complexes for Imine Hydrogenation
Cheminova A/S, World Appl. 2010/094,164

A process for the hydrogenation of imines at 10–70°C and 10–100 bar in the presence of 0.001–5 mol% of an Ir-based catalyst with one ditertiary phosphine ligand and 0.01–1 mol% of a co-catalyst with a C–halogen bond is claimed. Specifically, the process can be used for the asymmetric hydrogenation of a prochiral ketimine, in the presence of a chiral Ir catalyst of formula for example 2, with one diphosphine ligand of formula for example 3, to produce an optical isomer of an amine with ee >80%.
Osmium-Catalysed Hydrogenolysis of Sugar Alcohols
Chemtex Italia Srl, World Appl. 2010/119,351
Hydrogenolysis of polyalcohols such as sorbitol to lower diols, specifically propylene glycol, is conducted by contacting the alcohol with a suspension of a heterogeneous Os catalyst in water in the presence of a base such as Ba(OH)_2 and in the absence of any phosphine, at 30–90 bar and 180–250ºC for 1–6 h. The Os catalyst is prepared by reducing OsCl_3 or OsO_4 with H_2 at 50–300ºC to metallic Os dispersed at 1–6 wt% on a high surface area (>700 m^2 g^-1) support such as activated C or zeolite NH_4Y.

Ruthenium-Catalysed Water Photolysis
Honda Motor Co, Ltd, Japanese Appl. 2010-158,627
A process for the production of H_2 from water uses Ru-based photocatalysts selected from soluble compounds of Ru with OAc– and Cl– or BF_4–, or insoluble compounds of Ru with terephthalate and Cl–, BF_4–, PF_6– or Br–. These are added to water containing a solution of a photosensitiser such as Ru(bpy)_3Cl_2, a sacrificial electron donor such as disodium EDTA, and an electron-conducting substance such as methylvio-logen, and the mixture is irradiated with visible light of wavelength >420 nm. Depending on the compound, TONs of 3.9–93.4 were demonstrated experimentally.

EMISSIONS CONTROL
Exhaust System with Optimised Rhodium Activity
A catalyst system comprising a close-coupled catalyst, 1, and an underfloor catalyst, 2, is formulated to prevent oxidation and deactivation of Rh under fluctuating air-fuel ratios by restricting Rh-doped Ce-Zr-Nd mixed oxide to catalyst 2. The dissolved Rh is then reduced to active metal by HC and CO passing through catalyst 1 unreacted. Catalyst 2 further contains Pt/Al_2O_3 to convert HC to CO for more effective reduction. Catalyst 1 has a lower layer containing undoped Ce-Zr-Nd mixed oxide and supported Pd, and an upper layer with supported Rh.

NOx Oxidation and Storage Catalyst
An oxidation catalyst for use in a catalytic system to control lean-burn engine emissions and its method of production are claimed. A washcoat of Pt and/or Pd is applied to the first zone of a substrate. A mixture of 50–100% Pt and Pd is applied to the rear or second zone of the substrate with an additional NOx storage material such as BaO and/or K_2O. Zone 1 oxidises CO and HC, while zone 2 oxidises NO and stores NO_2 until it can be released for downstream SCR (which occurs optimally at equimolar NO:NO_2).

FUEL CELLS
Platinum Alloy Catalyst for PAFC
Johnson Matthey Plc, World Appl. 2010/092,369
A ternary alloy particularly suitable for use as an ORR catalyst in PAFCs consists of (in at%): 46–75 Pt; 1–49 of Ni, Co, Cr, Cu, Ti or Mn; and 1–35 Ta or Nb, but excluding the alloys 66 Pt-20 Cr-14 Ta and 50 Pt-25 Co-Ta.

Platinum Phosphide Catalyst
Daimler AG, World Appl. 2010/105,187
A PtP_2 PEMFC catalyst with a cubic crystal structure and the method of its manufacture are claimed, with the catalyst described to exhibit enhanced activity and stability in an acidic environment. The PtP_2 is formed by combining Pt catalyst with a phosphiding agent such as elemental P, PH_3(g), trioctylphospine or a phosphide, and may form a surface layer on a Pt or Pt-transition metal core, where the transition metal is one or more of Co, Fe, Ni and Cu.

Ternary Alloy Fuel Cell Catalyst with High Activity
UTC Power Corp, World Appl. 2010/107,426
Pt, a first alloy metal and a second alloy metal are successively deposited on a carbon support by reduction of appropriate precursors and alloyed by subsequent calcination. Alloy composition is: 40–60 mol% Pt, 5–30 mol% of one or more of Ir, Rh and Pd, specifically Ir, and 20–50 mol% of one or more of Ti, Mn, Co, V, Cr, Ni, Cu, Zr and Fe. The alloy has an average particle size of <60 Å, and a lattice constant of ~3.78–3.83 Å.

APPARATUS AND TECHNIQUE
Application of Palladium Salt to Cut Tobacco
A low-pH method of Pd salt addition to tobacco for the removal of polycyclic aromatic hydrocarbons from smoked product minimises the number of processing steps required. A solution of Na_2PdCl_4, K_2PdCl_6 or (NH_4)_2PdCl_6 is sprayed onto tobacco cut filler at 12–45% oven volatiles and at a mass loading of 0.01–0.15% relative to tobacco weight. The ratio of Pd:Cl is controlled to maintain >99% Pd solubility.
ELECTRICAL AND ELECTRONICS

Palladium Diffusion to Alter Semiconductivity Type
ABB Technology AG, European Appl. 2,234,144 (2010)
A wafer with two or more layers of different conductivity types is formed by: (a) depositing a 1 nm to 10 µm-thick layer of Pd on the first main side of an n-doped wafer; (b) irradiating this side to create defects at a depth controlled by the energy of radiation; and (c) diffusing the Pd into the wafer at 600–650ºC to create a p-doped layer by replacing the defects. The process can be repeated at different depths and on the opposite side, and lateral variation can be achieved by using a thicker layer of Pd (<150 µm) as a radiation mask. Electrical contacts are then created on opposite main sides of the wafer to form a power semiconductor device.

ELECTROCHEMISTRY

Aluminium Battery with Platinum Cathode
Equos Research Co, Ltd, Japanese Appl. 2010-129,495
A battery based on the principle of an air battery has an Al plate anode and a Pt plate cathode, both immersed in a non-aqueous ionic liquid as the electrolyte, and separated by a gel membrane which is impermeable to ions other than OH⁻. The electrolyte is a mixed molten salt of 1-ethyl-3-methylimidazolium chloride and anhydrous AlCl₃, in a molar ratio of 1:2 on the anode side of the membrane, and 2:1 on the cathode side. O₂ is bubbled over the Pt plate from a gas introduction pipe to facilitate the electrochemical reaction, which is found to proceed safely and efficiently.

MEDICAL AND DENTAL

Palladium-Titanium Braze for Ceramic-Titanium Bond
A method and material for forming an hermetic seal between ceramic and titanium sections of the housing of an implantable medical device is claimed. An interlayer comprising a Pd foil and a Ti foil, or a Ti foil sandwiched between two Pd foils, is placed at the interface of the two sections and pressure is applied during heat treatment under vacuum or inert gas. After melting and subsequent cooling, the interlayer forms an eutectic bond with the Ti and wets the ceramic for a complete seal.

PHOTOCONVERSION

Blue-Shifted Phosphorescent Iridium Complex
Pusan National University: Industry-University Cooperation Foundation, World Appl. 2010/090,362
Ir complexes containing a pyridyl triazole ligand with at least one substituent on the pyridine ring, for example 4 and 5, exhibit improved phosphorescent quantum yields, particularly at short wavelengths. Wavelengths of peak intensity are typically ~456 nm and ~486 nm. The Ir complexes are used in the emissive layer of OLEDs, with or without a host material. Synthesis methods are described.

SURFACE COATINGS

Platinum ‘Paint’ for Thermal Barrier Coating
Snecma Moteurs, US Appl. 2010/0,247,755
A pre-layer is formed on the binding sub-layer of a thermal barrier coating on a turbine blade and allows for efficient localised repair of the coating without stripping or modification. A suspension of pgm powder, specifically Pt, in water, oil or hydrocarbon liquid is applied to an aluminide sub-layer using a brush or spray gun or by dip-coating, and is diffusion heat-treated to form a layer of thickness 1–30 µm, preferably 2–10 µm.
**Electrolytic Etching for Microstructure Detection in Platinum Alloys**

The most convenient way to reveal the microstructure of platinum alloys used for jewellery or other applications is by electrolytic etching (1–6). The most widely used electrolytic solution is a saturated solution of sodium chloride in concentrated hydrochloric acid (37%). Other solutions can also be used (see Table I).

Electrolytic etching can be considered as ‘forced corrosion’ where the previously polished specimen surface corrodes inhomogeneously, revealing the different microstructural features which vary from area to area. The surface corrodes selectively as a consequence of different grain orientations, crystal defects such as dislocations and grain boundaries, cold-worked regions and second phases.

Electrolytic etching is usually carried out by means of a DC power supply where the specimen works as the anode. However, for platinum alloys in the saturated NaCl/HCl solution, the best results are obtained with an AC power supply. The degree of electrolytic etching depends on the applied voltage and the etching time. The counter-electrode can be graphite. Better results are obtained if the voltage scale can be varied from 0.1 V to 10 V and the power supply can provide a current of at least 10 A. The specimen dipped in the solution must be kept under a fume hood and must be put in electrical contact with the second electrode.

One of the advantages of electrolytic etching is that the process can be stopped whenever necessary to check the achieved results and started up again to reach the optimal result gradually, a practice that is not always feasible with chemical reagents.

**Other Equipment**

In order to carry out metallographic analyses, a laboratory must be equipped with a grinding and polishing machine which allows the use of grinding papers and polishing cloths, and a metallographic optical microscope with a digital image acquisition system. A precision saw with diamond wafering blade can be very useful to prepare small specimens. Some laboratories may have more sophisticated equipment such as automatic systems for specimen preparation and more powerful optical microscopes.

**Metallographic Investigation of Microstructure**

Work hardening and thermal treatments cause significant changes to the microstructure of alloys with respect to the as-cast condition. In particular, dendrites are no longer visible. The recrystallisation structure resulting from thermal treatments carried out after work hardening is well revealed in most platinum alloys by electrolytic etching solution 1 (Table I). This information is fundamental when

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**Table I**

Electrolytic and Chemical Etching Solutions for Use with Platinum Alloys

<table>
<thead>
<tr>
<th>Etching solution</th>
<th>Composition</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>100 cm³ HCl (37%) + 10 g NaCl</td>
<td>Electrolytic, 3–6 V AC</td>
</tr>
<tr>
<td>2</td>
<td>10 cm³ HCl + 90 cm³ H₂O + 1 g FeCl₃</td>
<td>Electrolytic, 3–6 V AC</td>
</tr>
<tr>
<td>3</td>
<td>100 cm³ HCl (37%) + 3–6 g CrO₃</td>
<td>Chemical*</td>
</tr>
</tbody>
</table>

*Etching solution 3 is chemical, so the specimen can simply be dipped into the solution and no power supply is required. However, it is dangerous for both the operator and the environment as it contains hexavalent chromium. It must be handled with care. This solution is not effective for pure platinum.
setting up working cycles, in order to control the grain size. Furthermore, the metallographic analysis is necessary to characterise possible defects, such as inclusions, porosities, cracks etc.

**Case Study: Microstructure of Two Commercial Platinum Alloys**
The microstructures of as-cast 95% platinum-5% copper jewellery alloy and 70% platinum-29.8% iridium high-temperature alloy for industrial use were investigated by electrolytic etching. Etching solution 1 (Table 1) was used in both cases. Figures 1 and 2 show the crystal grains of the two as-cast alloys. They are very different in shape and dimension. The grains are in both cases microsegregated and dendritic. When work hardened and heat treated the alloy recrystallises, as shown in Figure 3. Using metallography, the temperature and duration of thermal treatments can be adjusted to obtain a suitable grain size.

**Limitations of the Etching Technique**
It is worth remembering that metallographic preparation may not be able to reveal all the microstructural features in each case. Therefore, it is often necessary to use other analytical techniques such as scanning electron microscopy (SEM), transmission electron microscopy (TEM) or X-ray diffraction (XRD) to get full knowledge of the microstructure.

Note: this is a revised extract from a paper presented at the 24th Santa Fe Symposium (7).

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**Fig. 1. Etched sample of as-cast 95 wt% platinum-5 wt% copper alloy. The alloy shows large dendritic grains with copper microsegregation.**

**Fig. 2. Etched sample of as-cast 70 wt% platinum-29.8 wt% iridium alloy. Grains are smaller than in the case of the platinum-copper alloy in Figure 1, and show microsegregation of iridium.**

**Fig. 3. Sample of 95 wt% platinum-5 wt% copper alloy after work hardening and annealing, showing the material recrystallisation. Compare with the as-cast microstructure in Figure 1**

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**References**


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