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Studies of Precious Metal Catalysts in the CARMAC Programme

Improved catalyst specificity and selectivity through a combination of chemical engineering and greater understanding of reaction mechanisms

One of the recurrent challenges in catalysis is how to ensure that the right reactions take place. In a recent collaborative programme between academic and industrial partners, some of the key issues relating to reactant specificity and product selectivity in liquid and gas media have been tackled using a combination of computational modelling, catalyst chemistry and chemical engineering. As well as providing solutions to several real-life problems from the chemical manufacturing industry, essential skills required for in situ studies have been established within the academic centres during the course of the programme. These developing skills are intended to have an ongoing impact on the understanding and application of complex multiphase processes, in which platinum group metals and other precious metals are often present as catalysts.

The Scope of the CARMAC Programme

The programme known as Controlling Access of Reactive Molecules to Active Centres (CARMAC) was set up to study and promote catalytic specificity and selectivity. The intended applications include manufacturing processes in which either a specific reactant needs to be consumed from a mixture, or one target product has to be formed selectively from a reactant feed that can undergo several parallel or consecutive reactions. It was planned as a series of complementary projects addressing clearly defined problems, which were grouped under three main themes:

(a) Hydrogenation of difficult molecules in liquid media (where hydrogen can attack different parts of the molecules, but reaction of only one functional group is required);

(b) Overcoming equilibrium limitations to allow one product to predominate;

(c) Enrichment and clean-up of multicomponent gas streams.

In addition to the technical targets, the stated aim of the programme was to improve the catalysis skills base in the UK. This specific aim was endorsed and
supported by one of the UK’s major academic funding bodies, the Engineering and Physical Sciences Research Council (EPSRC), as part of its commitment to building capability in key areas of science, engineering and technology.

From its start in late 2003, CARMAC brought together chemists and chemical engineers from the Universities of Cambridge and Reading and Queen’s University Belfast in the UK and the University of Virginia, USA, along with their counterparts from industry. The industrial partners represented the full range of relevant catalyst application skills, namely catalyst support manufacture (Grace Davison), catalyst production and catalytic process engineering (Johnson Matthey PLC), and catalyst use in chemical manufacture (Robinson Brothers Ltd).

The five-year lifetime of the programme was intentionally longer than the usual duration of a PhD studentship or typical postdoctoral fellowship. This allowed greater continuity, and also encouraged more flexibility in starting, interrupting or even stopping the various experimental and modelling activities within the programme. A loose matrix of overlapping teams, led jointly by academic and industrial project leaders, enabled effective input from all partners into the component projects, and allowed the emergent techniques to be used as transferable resources between the programme themes. Two technical experts, Brian Harrison and Colin Gent, monitored progress throughout and provided feedback to the project partners and to the EPSRC.

Reflecting the broad range of target applications, a diverse range of catalytic materials was studied during the programme. This included base metals for the isomerisation of alkanes (1, 2) and modified zeolites for the methylation of toluene to \( p \)-xylene (3, 4).

However, pgms and other precious metals featured in many of the projects, and it is from this body of work that we have selected the examples that are highlighted below.

**Hydrogenation of Difficult Molecules**

Organo-sulfur compounds, such as mercaptans, are key intermediates in the production of bulk and specialty chemicals. Although aliphatic mercaptans can be produced by the direct reaction of alcohols with hydrogen sulfide over alkali metal catalysts, the same route cannot be used for the manufacture of aromatic mercaptans. Instead, aromatic sulfonic acids or sulfonyl chlorides are reduced either with phosphorus, or with nascent hydrogen formed by reacting a metal with a mineral acid. These reactions are highly selective, but have the drawback of generating phosphoric acid and metal compounds as byproducts. A potential alternative route is by reductive breaking of the sulfur–sulfur bond in the corresponding bis-disulfide, as in Equation (i):

\[
\text{C}_6\text{H}_5\text{S}–\text{S}–\text{C}_6\text{H}_5 + \text{H}_2 \rightarrow 2\text{C}_6\text{H}_5\text{SH} \quad (i)
\]

However, the reducing agent is usually a stoichiometric reagent, such as sodium borohydride, triphenylphosphine or semicarbazide. In attempting to develop an equivalent catalytic reaction, the challenges lay in identifying selective catalysts that would not break the carbon–sulfur bonds, and would not themselves be deactivated by the sulfur compounds.

In CARMAC, we showed that, contrary to expectation, palladium-based heterogeneous catalysts are both active and resistant to sulfur poisoning in the hydrogenation/hydrogenolysis of aromatic disulfides. This conclusion came as a result of a fundamental study that was targeted at identifying and understanding the underlying scientific barriers, and not through an empirical trial-and-error approach. In this case, a combination of density functional theory (DFT) calculations and systematic experiments (5), in which the aromatic substituent was varied, provided us with a mechanistic model which allows the disulfide to adsorb in parallel or perpendicular to the palladium surface (Figure 1). The perpendicular conformation allows a high surface concentration of adsorbed hydrogen, which in turn enables a high rate of reaction, and encourages cleavage of the S-S bond by hydrogenation in preference to reduction of the aromatic substituent.

**Overcoming Equilibrium Limitations**

Carbazole (CZ), 1, and its derivatives are valuable chemical intermediates in the production of pharmaceuticals, dyes, pigments and agrochemicals. A key step in the synthesis of CZ is the endothermic liquid-phase dehydrogenation of 1,2,3,4-tetrahydrocarbazole (THCZ), 2, which is carried out catalytically, preferably in a batch reactor. However, the yield is limited by the chemical equilibrium between the forward and reverse reactions. Using Le Chatelier’s principle (6), the simplest means of increasing the yield is by either raising the temperature or continuously removing the \( \text{H}_2 \) coproduct. Raising the temperature has a direct impact on the running costs of the
process, while the physical removal of H₂ requires fundamental changes to the process design, such as operating the reactor in semi-batch mode. Having recognised these inherent limitations in the dehydrogenation reaction, the contribution from CARMAC was to think ‘outside the box’ and recognise that chemical removal of hydrogen using cheap, readily available hydrogen scavengers could also be used to manipulate the equilibrium and improve the yield of the desired product. In the past the most effective additives identified for related reactions have been relatively high-value organic chemicals (7).

Once again, through a combination of experiments and computational studies, we were able to propose a solution based on a mechanistic understanding of the catalytic process (8). Our experiments showed that simple gas-phase hydrogen acceptors, such as ethene, propene and but-1-ene, produce a fivefold increase in the rate of THCZ dehydrogenation at a fixed temperature (135°C) over a supported palladium catalyst. DFT calculations revealed that alkene hydrogenation competes effectively with the back-hydrogenation of the intermediates formed on the catalyst surface, causing the equilibrium to shift in favour of CZ formation. As well as being more cost effective than liquid-phase H₂-acceptors, such as nitrotoluene or diethyl maleate, the alkenes and their product alkanes can be readily separated from the reaction medium.

**Enrichment and Clean-Up of Gas Streams**

**Preferential Combustion of Carbon Monoxide**

Maleic anhydride, 3, is used mainly in the production of unsaturated polyester resins, but it is also an intermediate in the production of pesticides, reactive plasticisers and lubricating oil additives. In the manufacture of maleic anhydride, the catalytic partial oxidation of butane is usually performed under single-pass conditions of high conversion, but relatively low product selectivity (9). In principle, the process could be operated under less wasteful conditions, where the per-pass conversion would be lower but the selectivity much higher. However, before recycling the unconverted butane back to the catalytic reactor, any carbon monoxide contaminant would have to be removed (or converted to carbon dioxide) to avoid poisoning the vanadium-based partial oxidation catalyst.
Prior to CARMAC, collaborative work between Queen’s University Belfast and Johnson Matthey had shown that a continuous NaA zeolite membrane, grown over the active sites of a platinum-iron catalyst supported on silica, would allow CO to be preferentially combusted in the presence of butane (10). The growth of the crystalline membrane (estimated to be 50 nm to 70 nm thick) required pretreatment of the 3 mm-diameter Pt-Fe/SiO$_2$ particles with a polyelectrolyte to reverse the surface charge, before the zeolite was hydrothermally synthesised in situ over the particles at high pressure. The coherence of the membrane was attributed to the fact that it was crystallised from a precursor gel that, following the charge-reversal step, perfectly wetted the catalyst surface. The specificity of the membrane could be simply related to the pore size of the NaA zeolite (0.4 nm), which allowed entry and egress to molecules with a small enough kinetic diameter (CO: 0.376 nm; O$_2$: 0.346 nm; CO$_2$: 0.33 nm) while excluding butane (0.43 nm).

In CARMAC, a similar degree of discrimination between CO and butane was achieved by forming a largely amorphous aluminium–silicon–oxygen layer (about 500 nm thick) over the catalyst particles (Figure 2), using a much simpler preparative route (11). Following pretreatment to reverse the surface charge, the particles were immersed in the NaA zeolite precursor gel, before simply being heated in open air. The increase in path length from the gas phase to the active sites, which results from applying the amorphous layer, seemed to explain why the molecule with the higher diffusivity (CO) was preferentially oxidised. However, it became clear that the presence of this physical barrier is not the sole reason for the molecular discrimination. We demonstrated that chemical modification of the Pt-Fe catalyst by the Na$^+$ ions present in the precursor gel also plays a part, by altering the specificity of the active sites (Figure 2).

**Reactive Removal of Oxygen**

Dehydrogenation reactions are widely used for converting low value feedstocks (e.g. alkanes) to higher value intermediates (e.g. alkenes). One of the most promising means of promoting dehydrogenation of hydrocarbons over a pgm catalyst is by the inclusion of oxygen, which can shift the equilibrium, cause an adiabatic temperature rise and prevent soot formation on the catalyst surface. Combustion is suppressed either by limiting the proportion of O$_2$ in the feed (12) or by using very high space velocities (13). However, traces of unreacted O$_2$ can remain in the product stream, which may interfere with or inhibit any subsequent reaction. For example, even parts per million (ppm) concentrations of residual O$_2$ will have a detrimental impact on ethene polymerisation.

Prior to CARMAC, the only reported study of the selective removal of O$_2$ by reaction with excess H$_2$ in the presence of light alkenes was described in a patent that disclosed the use of a partially-poisoned Pd catalyst at relatively high temperatures (>350°C) (14). In CARMAC, a range of potential precious and base metal catalysts was screened for low-temperature activity, with silver emerging as the best candidate for
Further development and scale-up (15). Silver had been included in the screening on the basis that it is known to: (a) activate oxygen (16); (b) be a poorer hydrogenation catalyst than platinum and palladium (17); and (c) inhibit ethene hydrogenation when added to palladium-based acetylene hydrogenation catalysts (18). In our tests, a catalyst containing 7.6% (by weight) silver dispersed on alumina gave full conversion of O2 at 50°C, with negligible loss of the alkene, when either ethene or propene was used in the gas stream.

**Increasing the Hydrogen Concentration in Reformate**

When mainstream hydrocarbon fuels or biofuels are reformed to produce hydrogen, the product stream (reformate) invariably contains CO, CO2 and water in addition to H2 (19). If the reformer is to be coupled with a low-temperature fuel cell as part of an integrated power source, the CO concentration has to be reduced from per cent levels to below 50 ppm to prevent the fuel cell anode being poisoned (20). The most efficient way to do this is by converting as much CO as possible to CO2 using the water-gas shift (WGS) reaction, which increases the hydrogen concentration at the same time (Equation (ii)):

![Equation](https://doi.org/10.1002/prmt.200820221)

Although thermodynamically favoured at low temperatures (21), the reaction requires a highly active WGS catalyst to reduce the CO concentration to 0.5%. The remainder can then be removed by preferential oxidation or methanation, either of which will consume some of the H2.

Commercial low-temperature WGS catalysts are generally copper-based, but these need to be carefully activated by reduction, kept in their reduced state, and protected from contact with air, with which they can react pyrophorically. Therefore, for fuel cell applications, a new generation of WGS catalysts has to be developed. Initial screening of potential catalysts identified a number of promising candidate catalysts in which either platinum or gold was the preferred metal, and oxides with redox character (such as cerium oxide) were the preferred supports (Figure 3).

The development of improved catalysts was based on fundamental investigations of the nature of the active catalyst, the mechanism of deactivation, and the mechanism of the WGS reaction itself. Supported by DFT calculations (22) the experimental work in CARMAC provided a complete mechanistic model for the WGS reaction over the most active catalysts (gold supported on cerium zirconium oxide (Au/CeZrO4) in which it was proposed that a key intermediate was a surface carboxylate species (23, 24). Although such a species could not be detected experimentally, it provides a feasible route from COads to CO2(ads) by reaction with OHads, and with hindsight seems much more plausible than the widely favoured ‘formate model’ (25). In the latter, a C–H bond is formed through the (energetically very difficult) step of insertion into an O–H bond but then, in order to generate CO2, this C–H bond has to be broken again.

![Figure 3. Water-gas shift activity of gold catalysts compared to platinum](https://doi.org/10.1002/prmt.200820221). The results show that the performance of the gold catalysts is very sensitive to the metal loading and the support material used (▲ = 2%Pt/CeO2; • = 2%Au/TiO2; ▲ = 2%Au/CeO2; ○ = 0.2%Au/CeZrO4; ● = 2%Au/CeZrO4). Platinum catalysts are much less sensitive (23).
Detailed experimental work, using fast transient kinetic isotope techniques coupled with infrared spectroscopy and mass spectrometry (26), showed that the formate species seen by infrared are not relevant to the main reaction pathway on any of the very active low-temperature catalysts developed in this programme (27, 28).

Although the Au/CeZrO₄ catalysts are extremely active they have a tendency to deactivate under reaction conditions. By undertaking a detailed investigation of their structure, primarily using extended X-ray absorption fine structure (EXAFS), X-ray absorption near edge structure (XANES) and high-pressure X-ray photoelectron spectroscopy (XPS), again supplemented by DFT calculations (29), we began to realise that the high activity of gold supported on redox oxides requires a strong interaction with the support. The loss in activity of the catalyst appears to be caused by a change in morphology of the gold particles, leading to the breakdown of this strong interaction (Figure 4), rather than a loss of exposed gold surface area (30). Armed with this knowledge, further experimentation was focused on developing precious metal catalysts that would enhance the formation of such strong interactions, and on maintaining these interactions by optimising the process conditions.

A further important outcome of the multidisciplinary research in CARMAC has been the recognition that the definition of an ‘active site’ in heterogeneous catalysis is non-trivial. Frequently, we think of an active site as a single entity such as a few atoms on a metal crystal (possibly differentiating between planar, edge or corner atoms), a cation or an anion, or a Lewis or Brønsted acid or base site. In fact, for almost all heterogeneously catalysed reactions the active ‘site’ is much more complex. For example, for the low-temperature WGS reaction on supported gold catalysts, it now seems that the active site requires metallic gold atoms in a specific arrangement, probably with cationic gold to connect the metallic gold atoms to the support with sufficient strength of interaction to activate the gold/oxide interface, and oxygen vacancies adjacent to this interface. As each component may be involved in one or several reaction steps, the absence of any one component can completely eradicate the low-temperature activity. By comparison, the structurally simpler platinum analogues are easier to stabilise, but have yet to match the performance of gold at temperatures below 200°C (31).

**New Preparative and Investigative Techniques**

In tackling the technical challenges posed in the individual projects, CARMAC also had the key objectives of: (a) advancing catalyst design, (b) developing state-of-the-art techniques for studying catalysts under reaction conditions, and (c) improving collaboration between chemists and engineers.

Using a new preparative technique, in which a surfactant was used to pre-form a platinum-containing...
microemulsion (32), chemists at the University of Reading were able to encapsulate platinum nanoparticles in ceria (Figure 5), rather than disperse them over the surface. The resulting catalyst was more active than conventionally prepared Pt/CeO$_2$ for the WGS reaction, and had the added advantage of not forming any methane when tested in a gas stream rich in H$_2$ (i.e. representative of a reformate). Detailed characterisation at the University of Reading and Queen’s University Belfast, showed that encapsulating the platinum inhibited the strong CO adsorption that can lead to the non-selective methanation reaction taking place, and indicated that the WGS reaction was taking place exclusively on the ceria shell. As ceria on its own has low WGS activity, the results imply that the platinum nanoparticle core exerts (electronic) control over the metal oxide shell (33).

Mechanistic studies of heterogeneously catalysed gas-phase processes, such as those described above for the WGS reaction, require measurements that are made on a relevant timescale. In the study of the WGS reaction, Queen’s University Belfast developed in situ infrared spectroscopy (Figure 6) to study catalyst surfaces under real reaction conditions with a time resolution of around 10 s (34). When combined with kinetic experiments on a similar timescale, the spectroscopic measurements provided us with unequivocal information (27), where previously several plausible but often conflicting mechanisms had been proposed.

Throughout the programme, chemical engineers at the University of Cambridge used and, in some cases, developed new, in situ magnetic resonance techniques to measure the characteristics of catalysts. Novel measurements included spatial mapping of both chemical composition (35) and fluid transport within a working catalytic reactor (36). We were able to monitor the distribution of liquid throughout the inter-particle space (Figure 7), and calculate the average concentration gradient between the outside and the inside (i.e. within the pores) of the catalyst particles. We believe these are the first direct measurements of concentration gradients across the inter- and intra-particle space of a reactor resulting from mass transfer limitations. This knowledge can be used to guide the selection of the porosity and shape characteristics of catalyst particles, and the operation of the reactor. The results were correlated with molecular models from the University of Virginia together with kinetic measurements and characterisation studies from Queen’s University Belfast creating a cross-scale representation of the events taking place in a packed bed of catalyst particles within a liquid medium (37) and providing insights into catalyst deactivation and regeneration (38).

Pulsed-field gradient nuclear magnetic resonance (PFG-NMR) was also used to demonstrate the first spatially-resolved, chemically-specific measurements of the diffusion coefficients of reactants and products during reaction. The reaction considered was the esterification of ethanol with acetic acid over an ion-exchange resin. It was even possible to discriminate between diffusion inside and outside the ion-exchange resin catalyst particles.

Other developments included the application of PFG-NMR techniques to directly measure two distinct
molecular diffusion coefficients within the pore space of a catalyst. In collaboration with Queen’s University Belfast, it was possible to compare these experimental data directly with the results of molecular simulations. Remarkably good agreement was obtained between the two approaches. The simulation showed evidence of a strongly-influenced surface layer of molecules which was characterised by diffusion processes at least an order of magnitude slower than the molecular diffusion in the bulk of the internal pore space of the catalyst. Related to this work was the development of NMR relaxometry (the determination of spin-lattice relaxation time, $T_1$, and spin-spin relaxation time, $T_2$). It was demonstrated that the attenuation of the $T_1$ and $T_2$ values, characteristic of a liquid when it is contained within the catalyst, can be used as a direct indicator of the strength of the surface interaction between the catalyst and the particular liquid molecule under consideration. This method opens up the possibility of probing competitive adsorption processes inside the pore space of catalysts (39).

**Achievements of the CARMAC Programme**

One of the major achievements of CARMAC was the creation, within the academic centres, of a suite of ‘state of the art’ scientific and engineering
competencies, which were designed to address specific technical problems in collaboration with industry. These competencies allowed us to investigate and understand the heterogeneously-catalysed target reactions in the liquid and gas phases. It is significant that many of the catalysts identified, designed or developed in this programme were pgm or other precious metal formulations. With their low loadings of highly dispersed metal, often interacting with the support, these catalysts were the most difficult to study. However, they challenged us to develop cutting-edge methodologies that will allow us to understand catalytic function across the length scales, from molecular rearrangements on the surface of metal nanoparticles to mass transfer in a catalytic reactor.

The programme also enhanced the transfer of knowledge and technology between academia and industry, and provided trained and highly skilled researchers for both sectors. In terms of direct technology transfer it is worth remarking that at the end of the ‘normal’ three-year PhD or two-year post-doctoral project there would have been few results that could have been transferred to industry. During the CARMAC programme much more time was available, and as a result it achieved practical outputs for industry by first identifying the key questions and then providing the knowledge required to address those questions. This process typically took four years.

Beyond CARMAC: The CASTech Programme

So, what happens next? A new five-year programme, Catalytic Advances through Sustainable Technologies (CASTech), is already underway, having started as CARMAC finished. Most of the partners from CARMAC (including the University of Cambridge, Queen’s University Belfast, Johnson Matthey PLC and Robinson Brothers Ltd) have been joined by several new members: the University of Birmingham, Borregaard, Forestry Commission Research Agency, Questor Centre and Sasol Technology Research Laboratory. Again, the academic centres are largely funded by the EPSRC, with industry contributing substantial in-kind support. In CASTech, the individual projects relate to renewable energy, protecting our environment, and developing truly benign chemical manufacturing processes. Led by industry and building on the core competencies created in the CARMAC programme, we believe that CASTech has the capability and momentum to take on some of the current ‘grand challenges’ in science and technology.

Precious metal catalysts are likely to feature strongly once again, particularly in the challenges associated with processing complex bio-feedstocks, and with the generation and storage of renewable energy. A key aim throughout will be designing or re-engineering the catalyst manufacturing processes to ensure that they too are pollution-free.

Dedication

This article is dedicated to the memory of Colin Gent (former Head of Catalysts at ICI and Technical Director of the Institute of Applied Catalysis (IAC), London) who, as an advisor to the programme, contributed greatly to the successes of CARMAC.

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The Authors

Professor Robbie Burch OBE was the Programme Manager of CARMAC, based at Queen’s University Belfast, UK, where he is now Emeritus Professor of Physical Chemistry. His research is concerned with developing a fundamental understanding of catalytic processes of industrial importance, including automotive emissions control, hydrocarbon processing for fuel cell applications and clean organic synthesis.

Professor Lynn Gladden CBE was the Principal Investigator for CARMAC at the University of Cambridge, UK, where she is Head of the Department of Chemical Engineering and Biotechnology. Her group’s primary research interest is in the development of magnetic resonance techniques to study research problems in chemical engineering.

Professor Stan Golunski, who was at the Johnson Matthey Technology Centre at Sonning Common in the UK at the time, was the Programme Director of CARMAC. He is now Deputy Director of the Cardiff Catalysis Institute, Cardiff, UK. His research interests lie in the field of gas-phase heterogeneous catalysis.
The Catalysis Society of South Africa (CATSA) is an organisation that aims to promote the advancement of catalysis amongst academia and the chemical industry in South Africa (1). The history of CATSA dates back to the late 1970s, when Dr Wim Mandersloot from the Council for Scientific and Industrial Research (CSIR) began organising annual meetings for catalysis researchers in South Africa. From a handful of people, the attendance at these annual conferences had grown substantially, and as a result CATSA was founded in 1990. Catalyst research in South Africa is 'alive and well' with the following programmes playing a substantial part in growing the field:

- c*change™ (the South African Department of Science and Technology – National Research Foundation (DST-NRF) Centre of Excellence in Catalysis)
- HySA (Hydrogen South Africa, the DST's National Hydrogen and Fuel Cell Technologies Research, Development and Innovation Strategy)
- Project AuTEK (an Anglogold Ashanti, Goldfields, Harmony Gold and Mintek sponsored project to find industrial uses for gold).

There has also been much 'contracted' and public research funded by South African companies such as Sasol and PetroSA.

The latest annual CATSA conference, CATSA 2009, took place at the Goudini Spa outside Cape Town, South Africa, from 8th–11th November 2009. The meeting was sponsored by BASF, PetroSA, Poretech (local Micromeritics agent), Sasol and Süd-Chemie. Stellenbosch University hosted the event, which was attended by approximately 250 delegates from both academic and industrial backgrounds. All thirty oral presentations were conducted in a single session spread over three days, and there was a single poster session comprising 103 posters.

As well as good coverage of South African research, there was a strong international flavour at this conference with nine of the thirty oral presentations given by non-South African based speakers. In addition, the CATSA Eminent Visitor Award, which aims to bring international researchers to South Africa, was bestowed on Professor Bert Weckhuysen (Utrecht
University, The Netherlands). His Plenary Lecture focused on in situ spectroscopy of heterogeneous molybdenum-, iron- and cobalt-based catalysts as well as zeolites.

The scientific programme focused on the main interests of the local community; namely heterogeneous catalysis, homogeneous catalysis and biocatalysis.

Given Sasol’s prominent position in South Africa’s petrochemical industry, it was unsurprising that the majority of oral presentations and posters in the area of heterogeneous catalysis were devoted to the Fischer-Tropsch process and associated issues regarding feed and product clean-up. There were however a few oral presentations on environmental catalysis. This selective review describes some of the highlights relevant to the platinum group metals (pgms) as well as gold.

Carbon Monoxide Oxidation

The major issues regarding the use of supported gold nanoparticle catalysts for CO oxidation are catalyst deactivation and precious metal cost. Furthermore, it is well known that these nanoparticles are difficult to characterise by standard techniques. Dean Barret, Mike Scurrell and Paul Franklyn (University of the Witwatersrand, Johannesburg, South Africa) reported on efforts to prevent the sintering of gold nanoparticles on silica and titania by the addition of platinum. A series of supported gold-platinum bimetallic catalysts of varying precious metal ratios were synthesised and characterised by powder X-ray diffraction (PXRD), in situ variable-temperature powder X-ray diffraction (VT-PXRD) and high-resolution transmission electron microscopy (HRTEM). Results showed that the addition of platinum stabilised the gold nanoparticles, and thus the bimetallic gold-platinum nanoparticles are more resistant to high temperatures than monometallic gold nanoparticles. This bodes well for the application of such materials at high temperature (100–600°C).

The thrifting of precious metal from gold catalysts using cyanide leaching was explored by Mike Scurrell (University of the Witwatersrand, Johannesburg, South Africa) reported on efforts to prevent the sintering of gold nanoparticles on silica and titania by the addition of platinum. A series of supported gold-platinum bimetallic catalysts of varying precious metal ratios were synthesised and characterised by powder X-ray diffraction (PXRD), in situ variable-temperature powder X-ray diffraction (VT-PXRD) and high-resolution transmission electron microscopy (HRTEM). Results showed that the addition of platinum stabilised the gold nanoparticles, and thus the bimetallic gold-platinum nanoparticles are more resistant to high temperatures than monometallic gold nanoparticles. This bodes well for the application of such materials at high temperature (100–600°C).

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Deactivation and Commercial Issues

The issues of catalyst deactivation and regeneration were highlighted by Robert Parry (BASF Catalysts, Haslemere, Surrey, UK) including:

- **Poisoning**: e.g. poisoning of Pt hydrogenation catalysts by species such as sulfur, selenium, tellurium, phosphorus, arsenic, zinc, mercury, lead, halides, ammonia and ethene; and poisoning of Pt/Pd automotive catalysts (for oxidation of CO and hydrocarbons) by lead, phosphorus and zinc.
- **Thermal degradation**: e.g. for Ni/Al2O3 catalysts which transform to non-catalytic nickel aluminate at high temperature, the addition of Rh or Ru enhances catalyst stability. Furthermore, sintering of a base metal catalyst may be prevented by the addition of a higher melting point noble metal (e.g. Rh or Ru).
- **Escape of vapours**: e.g. Ru may be lost from a catalyst on exposure to air at room temperature through the formation of ruthenium trioxide which is then converted to volatile ruthenium tetroxide.
- **Regeneration**: e.g. a sintered reforming catalyst (such as Pt/Al2O3) may be regenerated by oxychlorination which involves exposure to a chlorinating agent mixed with 5% O2 in N2 at 450–500°C for 1–4 hours. This results in the formation of AlCl3 and thereafter of PtCl2(AlCl3)2 which can be reduced to form monodispersed Pt clusters. The AlCl3 is transformed back into Al2O3 during this process.

Geoffrey White (BASF Catalysts, Beachwood, Ohio, USA) discussed the turnaround of industrial catalytic reactors. He described the special loading and activation procedures required by eggshell-type pgm catalysts, and the subsequent recycling of the spent catalyst.

Environmental Catalysis

James Lulizi Aluha, Gary Patrict and Elma van der Lingen (Mintek, Randburg, South Africa) presented a comparative study on the performance of Ni-Pd-Pt, Au-Pd-Pt and Au-Ni-Pd (supported on Al2O3 or TiO2) as potential sulfur-tolerant diesel oxidation catalysts that would operate under a cold start engine regime. The addition of nickel was found to inhibit sintering
of the precious metal, while in most cases deactivation was a result of poor alloy formation and the oxidation of Pd to PdO. It was found that Ni-Pd-Pt and Au-Ni-Pd performed better than Au-Pd-Pt for both low-temperature CO oxidation and total hydrocarbon oxidation (propane) below 350°C, even after ageing in SO₂ at 500°C for 24 hours (see Figure 1).

**Chemical Synthesis**

In an effort to explain the promotional effect of potassium on the rate of ammonia synthesis from H₂ and N₂ over ruthenium and rhodium catalysts supported on active carbon, Sanyasi Sitha and Linda J. Jewell (University of the Witwatersrand) carried out a density functional theory study in which the adsorption of nitrogen on Ru₁₀ and Rh₁₀ (neutral and anionic clusters, in order to account for the effect of promoter electron density) was presented. Ru catalysts are known to be active for ammonia synthesis, while Rh catalysts require potassium promotion to generate activity. In each case three types of interactions (super molecules) were identified (see Figure 2) with Ru showing only one super molecule as stable when neutral or anionic (potassium promoted). By contrast the neutral Rh cluster shows all three super molecules as stable, while an anionic Rh cluster only has one stable super molecule.

The synthesis of gold-polyaniline composite catalysts by the addition of H₄AuCl₄ to polyaniline, followed by reduction with sodium borohydride, was reported by Tlhabologo Kabomo and Mike Scurrell (University of the Witwatersrand). Characterisation of this material by transmission electron microscopy (TEM) showed a mean gold particle size of 3.2 ± 0.8 nm, and X-ray photoelectron spectroscopy (XPS) revealed that the majority of the gold is on the polyaniline surface in a metallic state. Shifts to low-energy operation revealed that gold interacts with the nitrogen atom of the polyaniline. Gold nanoparticle size was also found to decrease with increasing ratios of sodium borohydride to gold. The pH during synthesis was also found to affect gold particle size, with particles less than 5 nm in diameter being formed at pH values above 3. This was explained by the fact that polyaniline becomes protonated at pH values below 3, and is deprotonated at higher pH values. A test reaction using a gold-polyaniline composite catalyst for the reduction of 4-nitrophenol to...
4-aminophenol was performed, and this demonstrated that the rate of reaction increases with decreasing gold particle size.

Poster Presentations

The most interesting of the posters involving precious metals are summarised below:

‘High Dispersion Platinum Catalysts on Mesoporous Carbon Support for Fuel Cells’ by Hanna S. Abbo, Ivan R. Green and Salam J. J. Titinchi (University of the Western Cape) reported the development of a polyol process capable of generating well-dispersed 1–3 nm Pt nanoparticles deposited on different types of carbon supports for use as electrocatalysts for oxygen reduction in fuel cells. This method is claimed to have many advantages over others in that it gives high yield at low cost and is environmentally benign.

‘Gold Catalysed Glucose Oxidation Techno-Economic Assessment’ by Brendan Beeming and Gary Pattrick (Mintek, Randburg, South Africa) described a gold-catalysed glucose oxidation process which allows the more economic production of gluconic acid and sodium gluconate than the current enzymatic technology. 190,000 tons of gluconic acid and its salts are produced annually, with the main product being sodium gluconate for use as a cement setting retardant in the construction industry. The gold-catalysed process therefore offers producers with smaller plants an opportunity to compete in this aggressive market where economies of scale dominate in terms of the enzymatic process.

‘Platinum Nanowires Supported on Surface-Decorated Carbon Sphere and Their Electrochemical Performance’ by Feng Li, Gary Pattrick and Elma van der Lingen (Mintek, Randburg, South Africa) reported that Pt nanowires can be grown on Vulcan XC72R via the formic acid reduction method by employing a nitric acid pretreatment of the carbon. Results indicated that the surface pretreatment process introduces large amounts of oxygenated groups (such as carboxylic and hydroxyl), and high-resolution scanning electron microscopy (HRSEM) showed that these oxygenated groups favour the growth of Pt nanowires. Electrochemical characterisation showed higher oxygen reduction reaction (ORR) activity for Pt nanowires grown on surface-decorated carbon spheres when compared to nanowires on raw carbon black.

‘Microwave Polyol Synthesis of Ru/CNT Catalysts’ by L. F. Mabena, R. Suprakas and N. Coville (School of Chemistry University of the Witwatersrand) presented a simple method to prepare Ru nanoparticles on carbon nanotubes using sodium citrate stabiliser and ethylene glycol as a reducing agent to reduce RuCl₃ by microwave irradiation. The intention here was to prepare a material suitable for alkaline fuel cells.

‘Oxygen Chemisorption on Alumina Supported Gold Catalysts’ by Jennifer Case, Eric van Steen and David W. Gammon (Department of Chemical Engineering, University of Cape Town) discussed the use of oxygen chemisorption to determine the metal crystallite size for Au/Al₂O₃ catalysts. Unlike pgm catalysts, gold catalysts cannot be characterised using H₂ or CO adsorption, since they tend to oxidise these gas species at very low temperatures. By measuring oxygen uptake at 200°C over a pressure range of 0.1–700 mm Hg and using a dual isotherm model, the spherical crystallite sizes can be calculated. These calculated values were found to agree with those arrived at by TEM.

‘Formation of Supported Rhodium Nano Crystallites of Controlled Size and Their Application in CO Hydrogenation’ by Nothando Mungwe, Eric van Steen and Michael Claeys (Department of Chemical Engineering, University of Cape Town) described a method of preparing model catalysts with varied Rh crystallite sizes (2–14 nm) using a novel reverse micelle method.

‘Hydrogen Spillover in the Fischer-Tropsch Synthesis: the Role of Platinum and Gold as Promoters in Cobalt-Based Catalysts’ by Doreen Nabaho, Eric van Steen and Michael Claeys (Department of Chemical Engineering, University of Cape Town) demonstrated that gold is a likely candidate as a promoter for low-temperature Fischer Tropsch catalysts, given that platinum is more expensive and also results in increased methane selectivity which lowers the yield of desired higher hydrocarbons. Initial results show that gold, just like platinum, also increases the reducibility of cobalt oxides. It remains to be seen if the gold promoter will result in a lower affinity for carbon monoxide making it less ‘methanating’ than a platinum promoter.

Conclusions

South Africa is the leading source of pgms and there is a need for local beneficiation and to add value to this commodity within South Africa. Novel catalyst research offers a possibility in this regard, and with the establishment of HySA, c*change™ and other support initiatives South African pgm research will continue to grow in areas such as the hydrogen
economy (fuel cells, hydrogen storage etc.) and emissions control, and as promoters for base metal catalysts (e.g. cobalt-based low-temperature Fischer Tropsch catalysts).

The abstracts of the oral and poster presentations given at this conference are available by emailing the CATSA Media Officer, Cathrin Welker, at: cathrin.welker-nieuwoudt@sasol.com. The next meeting (CATSA 2010) is planned to be held from 7th–10th November 2010 on the Campus of the University of the Free State in Bloemfontein, South Africa (2).

References


The Reviewer
Jason McPherson completed his postgraduate studies in precious metal catalysis at the University of Cape Town, South Africa, in 2003. Currently he heads up the Scale-up and Commercialisation Unit of Project AuTEK’s Catalysis Programme (Mintek, South Africa) and as such is actively involved in the production, marketing and application of AuTEK’s AUROlite™ range of gold catalysts. He is highly active in application areas such as CO oxidation, preferential oxidation, liquid phase oxidations (e.g. glucose, glycerol) and selective hydrogenation. He is also a technology advisor to the World Gold Council (London, UK) and is currently the Chairman of the Catalyst Society of South Africa.
Challenges in Catalysis for Pharmaceuticals and Fine Chemicals II

Optimising processes catalysed by the platinum group metals

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Received by Fabrizio Nerozzi
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On 20th October 2009 around 100 delegates from the chemical industry and academia met in London, UK, for the second meeting on “Challenges in Catalysis for Pharmaceuticals and Fine Chemicals”. The event was organised jointly by the Society of Chemical Industry Fine Chemicals Group and the Royal Society of Chemistry Applied Catalysis Group. It followed the very successful first event that took place in 2007 and was reviewed in this Journal (1).

Topics covered included: the latest developments in coupling redox processes for carbon–carbon bond formation; cross-coupling reactions; nitrile hydrogenation; organocatalysis; amide bond formation by catalysis; and novel techniques for development of catalysed reactions. Like its predecessor, this meeting also focused on one of the principles of ‘green chemistry’: in this case, finding ways of minimising chemical waste by choosing those reagents and catalysts that produce the most atom-efficient processes. A series of seven oral presentations from speakers representing British and international academic institutions and the pharmaceutical industry was supported by a poster display during lunch. John Birtill (Consultant in Catalyst Technology, UK) of the RSC Applied Catalysis Group made the closing remarks.

The following is a brief review of the research work on platinum group metal (pgm)-catalysed reactions presented at the meeting.

Advances in Processes Catalysed by Platinum Group Metals

John Blacker (University of Leeds, UK) introduced the role of the Institute of Process Research and Development (iPRD) at the University of Leeds, a collaboration between academic and industrial chemists and engineers, which aims to advance process technologies in areas such as synthesis, catalysis, crystallisation, intensification and manufacture. Inspired by the great efficiency and complexity of biocatalytic pathways, chemists have tried for many years to develop catalysts able to emulate nature’s
Recent advances in the alkylation and arylation of nitrogen- and oxygen-containing functional groups, C–C bond formation, aromatic heterocycle formation, protection and de-protection, and reduction and resolution were described with a few examples. Catalysed by iridium complexes, amines can be alkylated with other amines (Scheme I) (2), or alcohols (3), and aldol condensations can occur between alcohols (4) via an in situ oxidation to carbonyl derivatives. Homogeneous rhodium-based catalysts such as [Rh(COD)Cl]₂−Bu-JOSIPHOS are effective in the reduction of unprotected β-keto-enamines to β-keto-amines (5). Nanocatalysts were also described as a new area of intense research. The size of the particles gives rise to novel physical properties (including modified diffusional behaviour and zeta potential, quantum photo and electronic effects, and quantum tunnelling) that can be exploited in catalysed processes. Examples using palladium and rhodium nanocatalysts were given, including a chiral diphosphite-modified rhodium(0) nanoparticle catalyst for use in styrene hydroformylation (6).

**Industrial Scale Catalysed Reactions**

Matthias Beller leads a research group at the Leibniz-Institut für Katalyse e.V. (Universität Rostock, Germany). In the last decade they have contributed to the industrial application of three catalyst systems. CataCXium® A, 1, is an electron-rich, non-pyrophoric phosphine ligand, useful in reactions involving aryl halide activation such as palladium-catalysed carbonylations (7), whereas a group of phosphine ligands named cataCXium® P, 2, (8) have found application in the palladium-catalysed hydroxylation (9) and amination (10) of aryl halides. The third system uses potassium hexacyanoferrate(II) (K₄[Fe(CN)₆]) in conjunction with Pd(OAc)₂ (11, 12) to prepare benzonitriles from aryl halides on an industrial scale (Scheme II). It has seldom been possible to achieve this, as cyanide sources are usually highly toxic, with the associated negative impact on the environment and implications for health and safety. Cyanides are also efficient catalyst poisons. Professor Beller described the advantages of K₄[Fe(CN)₆], a complex characterised by low toxicity and low manufacturing cost: properties that make it a convenient choice for palladium- and copper-catalysed processes even on an industrial scale.

Paul Murray (AstraZeneca, UK) described the use of principal component analysis (PCA) and experimental design to optimise palladium-catalysed coupling reactions, including a redox neutral coupling reaction, a Buchwald-Hartwig reaction and a Suzuki reaction. AstraZeneca is working in collaboration with the University of Bristol, UK, on a ‘predictive catalysis’ project with the aim of developing computational descriptors for ligand and catalyst attributes. The optimisation of a catalysed process is complicated by the number of variables at play (including, for the type of reactions being studied, the choice of catalyst precursor, phosphine complex, amines, solvent, and other reaction conditions). The descriptors are used in a PCA that is ultimately a variable reduction procedure. By reducing the redundancy in the data set, PCA can guide the chemist to the most efficient way to explore the chemical space.

**Improved Atom Economy**

Michael Krische (University of Texas at Austin, USA) focused his lecture on the formation of C–C bonds via hydrogenation and transfer hydrogenation, stressing the fact that these transformations provide more atom-economic processes than the classic C–C bond formation reactions such as aldol condensation. These hydrogenation and transfer hydrogenation reactions are catalysed by rhodium and iridium cationic complexes such as Rh(COD)OTf/(R)-Tol-BINAP or (R)-xylyl-WALPHOS (13) or [Ir(COD)Cl]₂/(R)-(R)-Cl,MeO-BIPHEP (14). For example, aldehydes can be prepared by reacting alkynes with carbon monoxide and hydrogen, while α,β-unsaturated
ketones in the presence of hydrogen and the catalyst can undergo aldol condensations with virtually no waste. Importantly, primary alcohols can be used in place of aldehydes in these condensations, by exploiting the fact that the iridium catalyst is able to convert them to the aldehyde in situ (14). This is an advantage considering that aldehydes are usually susceptible to oxidation and polymerisation.

Atom economy was also the main theme of the presentation by David Cole-Hamilton (University of St Andrews, Scotland, UK). Cole-Hamilton’s group has developed a bidentate phosphine ligand (bis-(di-tert-butylphosphinomethyl)benzene, 3) (15) which can be used with [Pd₂(dba)₃] in palladium-catalysed carbonylations.

Hydrogenation of a carbon–carbon double bond, Figure 1 (16). The chiral induction was obtained by linking chiral pyrrolidine-based sulfide ligands to the palladium nanoparticles.

Barbara Villa-Marcos (University of Liverpool, UK) presented work on direct asymmetric reductive amination of ketones and amines to chiral amines, Scheme III (17). The reaction uses a catalytic system formed by a combination of an iridium(III)-diamine complex and a chiral phosphate counteranion and proceeds via a metal-Bronsted acid cooperative mechanism.

Concluding Remarks

The fine chemical and pharmaceutical industries’ need for robust, environmentally friendly and safe processes has proven to be an invaluable driving force in catalyst research. Researchers both in academic institutions and in industry have made significant progress in recent years and today many examples of platinum group metal catalysts matching enzyme efficiency are a reality. This pace of continuous innovation in the field of catalysis is sure to provide new and exciting material for future “Challenges in Catalysis” meetings.

The next meeting will be held during the second half of 2011, at a time and location to be arranged.
Fig. 1. Schematic representation of enantioselective hydrogenation of carbon–carbon double bonds over a chirally modified palladium surface (Image courtesy of the American Chemical Society (16))

Scheme III (17)

References


The Reviewer

Fabrizio Nerozzi is a Team Leader at Johnson Matthey Catalysis and Chiral Technologies based in Royston, UK, since 2009. Previously he worked at GlaxoSmithKline (later GlaxoWellcome) in Stevenage, UK, as a Medicinal Chemist, and later as a Team Leader. He graduated in Chemistry at the University of Bologna, Italy, in 1998.

REACH Regulation and the Platinum Group Metals

Preparation of the pgm sector for REACH and the likely impact of the legislation on the pgm market in Europe

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Introduction
The European Regulation on Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH; Regulation (EC) No 1907/2006) (1) is a framework for the assessment of chemicals which aims to improve the European Union (EU) market in terms of innovation and competitiveness while also protecting human health and the environment. REACH requires chemical manufacturers and importers to register a technical dossier of information on substances which are used, produced or imported into the EU in quantities of one or more tonnes per year. The definition of ‘chemicals’ as used under this legislation includes metals and metal compounds, therefore the REACH regulation affects the platinum group metal (pgm) sector of the metals industry.

REACH was adopted in June 2007, with a series of deadlines for registration of phase-in substances beginning in June 2008 and continuing in step-wise fashion until May 2018, corresponding to the different tonnage ranges (see Figure 1) (2). Three years after its adoption, several industry sectors have now fully structured their response to comply with the various information requirements of the regulation.

A Collaborative Approach
Starting in 2006, leading companies including Heraeus, Johnson Matthey, Metalor, Norddeutsche Affinerie (now Aurubis), Umicore and many others recognised the importance and complexity of the REACH regulation and organised the sector into the Precious Metals and Rhenium Consortium (PMC). This dedicated consortium was formed on 15th September 2007 under the umbrella of the European Precious Metals Federation (EPMF), a member of Eurométaux. The PMC aims to prepare the technical dossiers for chemical substances on behalf of its member companies, as required by REACH. The International Platinum Group Metals Association (IPA) is a sister association of the EPMF from a cooperation point of view and as such, topics of relevance
to the pgms are shared between the two associations. Work on REACH is led by the EPMF and is fully supported by the IPA, especially as regards communicating updates to the pgm industry.

Setting up a joint structure for REACH involved many steps, including the drafting of a legal agreement defining the working scope, membership conditions and a cost-sharing formula in accordance with REACH’s principles of fairness, transparency and non-discrimination. The design of a technical programme for all materials in the scope of the regulation was also carried out.

It is extremely difficult to accurately predict the total budget that is required to accomplish the various tasks and activities involved in the technical work, administration, testing and registration of substances. However it is far from negligible. On a more positive note, the data sharing and joint submission obligations imposed by the REACH regulation have encouraged the sector to work in a collaborative manner towards the common goal of successful REACH registrations, in the process generating an improved data set to help protect human health and the environment. Across its activities, the PMC makes every effort possible to operate in a manner which is not only cost-efficient, but also fair and transparent to all.

The membership of the PMC has steadily grown from 25 Members in 2007 to 48 in 2010. Today, alternatives to consortia membership are being developed and proposed, such as ‘Letters of Access’ which would allow a more passive participation in the preparation of the registration dossier, while still fulfilling REACH’s requirement for joint submission.

The PMC is working very closely with other non-ferrous metals consortia (under the umbrella of Eurométaux) to ensure that the approach taken by the PMC to fulfil the information requirements of REACH is consistent with the approach taken by other metals registrants, while still meeting the needs specific to precious metals and the pgms in particular. REACH has so far had a very positive impact on
the research, development and recognition of metal-specific testing, risk assessment and classification techniques. Most of the existing techniques were tailored to address the properties of organic compounds, and the need to respond to an equivalent set of information requirements for inorganic materials has boosted the development of appropriate testing protocols, exposure prediction models and tools to derive sound classifications for complex mixtures such as refining streams. Most of the guidance on risk assessments is detailed in the "Health Risk Assessment Guidance for Metals" (HERAG) (3) and "Metals Environmental Risk Assessment Guidance" (MERAG) (4) documents, which have been recognised by the European Chemicals Agency (ECHA) and included in REACH guidance where relevant. The overall exchange of experiences and views across the non-ferrous metals industry has also benefited from REACH, and all of the data thus gathered are being used in the preparation of the pgm registration dossiers.

Although the first official registration deadline on most of these pgm compounds is 31st May 2018, the PMC is putting accelerated effort into finalising dossiers earlier, with a target of progressing pgm registrations by 2013. The core work programme is handled by a Secretariat consisting of three full-time equivalent Officers, and by the PMC member company experts. External consultant research organisations and specialised testing laboratories are also involved.

### Registration of PGM Compounds

The pgms and over sixty of their compounds are being prepared for REACH registration by the PMC. More than three quarters of these compounds require registration as substances which will be placed directly on the market, while the rest will be registered as intermediates (substances used in a manufacturing process but not present in the final product) which will be handled under strictly controlled conditions. The platinum and palladium families are the two largest, with fifteen and twenty materials covered, respectively. Osmium and osmium compounds are out of the scope of work of the PMC since these are currently below the tonnage thresholds in the REACH regulation. Some of the pgm substances affected by REACH at the time of writing this article are listed in Table I. The complete and updated substance

<table>
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<tr>
<th>Substance name</th>
<th>Formula</th>
<th>CAS</th>
<th>EINECS</th>
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<td>215-218-3</td>
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<td>231-125-0</td>
</tr>
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<td>231-095-9</td>
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<td>12036-10-1</td>
<td>234-840-6</td>
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</table>

*Osmium and osmium compounds are covered by the REACH regulation but are outside the scope of the Precious Metals and Rhenium Consortium as they are currently below the annual tonnage thresholds
A variety of substances (pure and impure forms of the pgms, plus chlorides, hydroxides, oxides, tetraamines and other pgm salts) need to be prepared for registration in such a way as to minimise unnecessary or duplicate testing. To that end, so-called 'integrated testing strategies' are being applied, including grouping and 'read across' techniques. Grouping means that several materials are included in a common cluster based on the oxidation state of the metal, its known solubility, and other similar parameters in order to assess the (eco-)toxicity of the materials, on the assumption that they will behave similarly to each other in human cells, tissues or organs and/or in the environment. Read across is a technique for using the (eco-)toxicological information relating to one or several materials to describe another material of the same cluster or group. This is done as recommended by REACH to avoid unnecessary testing. In some cases, information on the metallic ion is sufficient to predict the overall behaviour of a given compound.

In common with the situation for other metals, REACH risk assessments and the revised CLP/GHS classifications will have an influence on the European Economic Area (EEA) pgm supply chain. For example, it will most likely trigger adjustment of the existing risk management measures which are applied during the manufacture, transport, handling and elsewhere in the overall life cycle of pgms. This will be reflected in the need to update Material Safety Data Sheets which, in some cases, will be extended to include the new REACH exposure scenario information, aimed at better guiding users to protect health as well as the environment. After the final REACH deadline in 2018, legal entities wishing to manufacture or import pgm substances onto the EEA market at or above quantities of one tonne per year will effectively require a licence to do so, in the form of a company-specific ‘REACH registration number’ (unless this has already been addressed via their upstream supply chain). This number will provide legal evidence of REACH compliance, and will be of particular importance during imports and exports of pgm materials (and subject to checks by customs authorities). Obtaining this licence through REACH registration procedures involves a number of human resource and financial commitments that not all companies may be able to make. Those companies who do not have enough capacity to follow REACH in detail can partially rely on the Consortium, its staff and Members. However, REACH is a continuous exercise that requires a minimum investment by each company; therefore relying on the Consortium is only a short-term solution.

It should be noted that some exemptions under REACH exist, for example in relation to articles not deemed to be chemical substances. In addition, certain naturally occurring substances are exempt from registration as long as they have not been chemically modified, and this includes some minerals, ores and ore concentrates. The REACH regulation is also not intended to apply to waste, since this is addressed via
a separate set of legislation. However, if waste is recovered back into substances that are then placed on the market for further commercial use, then, with some exemptions, REACH applies as it does to any other substance placed on the market from the point at which the recovered substance ceases to be waste (and therefore waste management controls no longer apply). One of the useful exemptions applies if the recovered substance is the same as its virgin equivalent that has been previously registered, and this could potentially be the case for pgm recovery from spent catalysts (provided that they are not imported from outside the EEA).

Conclusions

The above represents a very abridged summary of REACH and CLP/GHS requirements. The precise influence of these regulatory changes will be more apparent after the first registrations of the pgms and pgm compounds in 2013, and will continue to occupy the pgm sector until at least 2018 (the last registration deadline under the REACH regulation). Although to date REACH remains a piece of EU legislation, there are also signs that it is heavily influencing the thinking of other regulators around the world in relation to their local chemical control regimes. Clones of REACH – or at least revised regulations which incorporate some of its facets – are predicted to be introduced elsewhere in the world.

References

1 Regulation on Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH), Regulation (EC) No 1907/2006, 18th December, 2006; Official Journal of the European Union, L 396/1, 30th December, 2006

Further Reading

More information for the EU and international metals industry on the REACH regulation can be found through the following websites:

The Author

Caroline Braibant is the Secretary-General of the European Precious Metals Federation (EPMF). She is the principal contact within the EPMF for further information about REACH as it applies to the platinum group metals. Prior to this, she was REACH Manager of EPMF from 2007 to mid-2008. She obtained a Master’s degree in Environmental Sciences and Management from the Université Catholique de Louvain (Louvain-la-Neuve, Belgium) in 2006; a Postgraduate Diploma in Human Ecology at the Vrije Universiteit Brussel (Brussels, Belgium) in 2005; and became a Biotechnology Engineer at the Instituto Tecnológico de Costa Rica (ITCR) Cartago, Costa Rica in 2004.
Catalyst Preparation for the 21st Century

Controlled catalyst synthesis to match form to function


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Catalysis accounts for around three billion dollars per annum in the US chemical industry alone (1), and it can be estimated that each US dollar spent on catalysis creates around 155 dollars’ worth of products (see box below) (1–3). All these catalysts have to be prepared, and the majority of large-volume chemical processes utilise heterogeneous catalysts. 

Catalysts are synthesised by a variety of means, and over the last century there has been a consistent trend towards smarter preparation methods leading to higher-quality catalysts. In the light of this is it is perhaps prudent to consider how these catalytic materials are made and how they will be made in the future. With this in mind, the one-day symposium, Catalyst Preparation for the 21st Century, was jointly organised by the Applied Catalysis Group of the Royal Society of Chemistry (RSC) and the Catalysis Subject Group of the Institution of Chemical Engineers (IChemE) and took place on 18th March 2010 at Burlington House in London, UK, home of the RSC (4).

The event was a great success and there was a good atmosphere as the audience listened to seven excellent talks from leading academic and industrial researchers. These varied in content from methods of catalyst manufacture, to understanding the current place of catalysis in the world’s economy, to the challenges that must be faced by the scientific community over the next twenty years to allow us to maintain our current lifestyle.

A series of insightful talks demonstrated how catalysts and materials can be synthesised in a controlled and predictable fashion to achieve higher activities and selectivities, and why heterogeneous catalyst synthesis should no longer be considered a ‘black art’. These talks covered a range of applications, organic reactions and synthetic methods: from fuel cells (energy production) to Fischer-Tropsch synthesis and the selective hydrogenation of unsaturated multifunctional molecules. The catalyst synthesis methodologies discussed ranged from impregnation, alloying and laser sputtering, to direct reduction and precipitation of stabilised colloids onto surfaces – the latter having been considered an academic curiosity until...
Investment in Catalysis in the Chemical Industry

North America was the largest single region in terms of catalyst use in 2005, with 34% of global demand, and the US accounted for 90% of this (1). The US chemical industry shipped US$611 billion worth of products in 2005 (2). It has been estimated that 80% of chemical processes involve catalysis at some point (3), which means that US$489 billion worth of shipments were derived from catalysed chemical processes in the US in 2005. North American demand for catalysts in 2005 amounted to US$3.5 billion, of which 90% was within the US (1), leading to a total expenditure of US$3.15 billion on catalysts in the US in 2005. Therefore it can be calculated that each US$1 spent on catalysts generated US$155 worth of products shipped by the US chemical industry in 2005.

Insight into Catalyst Materials

Krijn de Jong (Utrecht University, The Netherlands) gave the Plenary Lecture in which he demonstrated how images of catalysts created using three-dimensional transmission electron microscopy (TEM) tomography can be used to reveal structural information including pore structure and connectivity. TEM only samples around 10–13 g of material at a time. However, in combination with porosity information from bulk techniques such as mercury intrusion porosimetry or X-ray diffraction (XRD) it proves to be a very powerful tool (5, 6). De Jong showed that careful control and a proper understanding of the catalyst synthesis could lead to materials with significantly enhanced activity.

Dave Thompsett (Johnson Matthey Technology Centre, Sonning Common, UK) provided an overview of the demanding requirements placed on catalysts for fuel cells. These include:

- stability in the highly acidic oxidising environment found within a fuel cell;
- the ability to form porous layers to allow transportation of fuel (hydrogen) in and water out;
- good conductivity;
- high activity at low temperature; and
- low cost.

Of all the commercial materials available, only Pt and Pt-transition metal alloys supported on carbon are currently able to meet these requirements. Increasing the Pt loading increases the activity. However, doubling the Pt metal content does not double the activity, as particle size increases with Pt loading leading to a decrease in the electrochemically active surface area per unit mass of Pt (Figure 1). This suboptimal response to increased loading creates challenges for catalyst synthesis.

The use of alloying metals such as ruthenium can create a greater tolerance of impurities such as carbon monoxide, while addition of base metals such as cobalt, titanium, nickel or iron allows the amount of platinum present to be reduced without losing activity, and consequently lowers the cost of the unit.

One interesting approach to catalyst synthesis described by Thompsett was a ‘carbothermal’ method in which the carbon support acts as a reductant for the catalytic metals. In the case of platinum-titanium bimetallic nanoparticles, it was shown that the Pt is reduced first, followed by the Ti. The temperature of the Ti reduction was lower than anticipated and this is believed to be due to the Pt in the sample catalysing the process.

Frank Daly (Oxford Catalysts Group PLC, UK/ Velocrys, Inc, USA) described the Fischer-Tropsch catalyst produced by Oxford Catalysts and used by Velocrys in their microchannel reactor. The catalyst used is Ru-promoted Co/SiO2 with loadings of 0.27% Ru and 50% Co. The support has an unusually large particle size of 250 μm, and is surface-modified to prevent formation of significant amounts of cobalt silicate. Performance data were presented in terms of residence time for a syngas mixture of 2:1 H2:CO with selectivities for CH4 of 8.7–10% and C5+ of 84–85% at CO conversions of 50–70% depending on the gas flow used.

Shik Chi (Edman) Tsang (Oxford University, UK) described how Pt nanoparticles between 4 nm and 14.4 nm in size could be synthesised by using stabilisers to prevent aggregation. Particles within this size range had differing numbers of edge and face sites present. Further refinements could be made by capping specific (corner) sites of the Pt nanoparticles with cobalt (Figure 2) (7) to probe where reactions...
take place on solid surfaces; this was demonstrated by using the Co-capped Pt nanocatalyst for the reduction of $\alpha,\beta$-unsaturated aldehydes to the corresponding alcohols, which resulted in a selectivity of almost 100% (8).

Peter Witte (Process Catalysis Research, BASF, The Netherlands) demonstrated how Pt, Pd and mixed Pd-Pt catalysts on titanium silicate can be synthesised by an intriguing route. The metal particles were created by reduction using hexadecyl(2-hydroxyethyl)dimethylammonium dihydrogen phosphate, which also acted as a stabilising agent. During the reduction process the hydroxyl group of the quaternary ammonium salt becomes oxidised to an aldehyde (9).

Fig. 1. Plot showing the increase in platinum crystallite size (as measured by X-ray diffraction (XRD)) and the corresponding decrease in electrochemically active surface area (ECA) per unit mass of platinum with increased platinum loading in a conventionally prepared fuel cell catalyst (Image courtesy of Dave Thompsett, Johnson Matthey Technology Centre, Sonning Common, UK)

Fig. 2. Cobalt atoms (blue) are applied to ‘cap’ corner sites of a platinum nanocrystal (red) to create an ultraselective nanocatalyst for the hydrogenation of $\alpha,\beta$-unsaturated aldehydes to corresponding alcohols (7) (Image courtesy of Edman Tsang, University of Oxford, UK)
These particles can then be deposited onto a support such as titanium silicate and, with the stabiliser still present, used to catalyse reactions such as the selective reduction of alkynes to dienes with high cis-trans selectivity. During repeated reduction cycles the stabiliser is slowly lost to the solution.

**Poster Session**

In support of these presentations was a series of twenty-five high quality posters. Once again these covered a range of topics related to catalyst synthesis. Prizes were awarded for the best student and post-doctoral posters. The winners included Jonathan Blaine (University of Southampton, UK), who presented a poster on heterogeneous, single-site multimetallic nanoparticle catalysts from molecular precursors, and Francisco Rafael Garcia Garcia (Imperial College London, UK), with a poster on a novel inorganic hollow fibre microreactor for H₂ production by the water-gas shift reaction.

**Concluding Remarks**

Significant improvements in catalysis have been made over the last fifty years. Despite this, innovation continues to occur as new applications are developed and more stringent demands are placed on catalysts, including environmental legislation for emissions abatement. With each new demand those who prepare catalysts have risen to the challenge and improved the properties of their materials. This steady advance in properties is still seen in some of the oldest catalytic materials such as platinum, which has been in use since the early 1800s. Improvements continue to be made and will be for some time to come.

**References**


**The Reviewers**

Simon Crabtree is the Manufacturing Science Research Manager at Johnson Matthey Catalysts’ Billingham site in North East England. He obtained his degree and PhD from the University of Durham, UK. During his PhD he was supervised by Dr Mel Kilner and worked on homogeneous rhodium catalysis. He graduated in 1996 and joined Davy Process Technology as part of their petrochemical process development group, working across their portfolio of products including syngas products (methanol), dehydrogenations and carbonylations. Davy Process Technology was acquired by Johnson Matthey in 2006.

Peter Ellis is a Principal Scientist at Johnson Matthey Technology Centre, Sonning Common, UK. He obtained his degree and PhD from the University of Durham, where he was supervised by Dr Mel Kilner and worked on homogeneous and heterogeneous catalysis projects. He worked at a postdoctoral researcher with Professor Robbie Burch at Reading University, UK, and Queen’s University Belfast, UK, on the direct synthesis of hydrogen peroxide from hydrogen and oxygen. He joined Johnson Matthey in 2002 and has worked on the synthesis of nanoparticles, catalysts for the Fischer-Tropsch reaction and gold-copper alloy catalysts.
Analysis of the non-patent scientific literature can be used to reveal trends in platinum group metals (pgms) research. In this article, a study was carried out using the Chemical Abstracts database on key terms related to the pgms for the years 1998 and 2008, revealing an increase in research during this time period across most of the pgms both globally and especially in China. Platinum and ruthenium showed the most growth with areas such as nanotechnology and magnetic memory becoming particularly significant for ruthenium. In China, the fields of electrochemistry and energy conversion technologies including fuel cells, were among those showing growth.

This article follows on from a previous article in this Journal, which detailed how the technique of patent mapping can be used to gain an understanding of patenting trends and identify emerging technologies from the study of intellectual property (1). Non-patent literature is more abundant and is also a rich source of information – allowing not only detailed studies on topics of interest, but also analysis of global research trends in a particular field. In general it may also indicate areas of research that are further from commercial application than those appearing in the patent literature. This article demonstrates how analysis of the published literature can reveal trends in pgm research including, for example, which of the pgms are the focus of most research interest, in which parts of the world, and how this is changing over time. More detailed examination can then reveal upcoming technology areas and their possible application.

The Chemical Abstracts database from the Chemical Abstracts Service (CAS) (2) provides abstracts from an extremely wide-ranging selection of scientific publications, including journals, conference proceedings, books, dissertations and other types of publication, and so lends itself well to this type of study. It provides access to publications from a wide geographical area whose abstracts have been translated.
into English. In addition, one of its outstanding benefits is the quality of indexing attached to each abstract. During the indexing process key substances used in the research, and controlled terms relating to the research, are assigned to each publication. Therefore, a paper in which platinum is a key substance will have the CAS registry number of platinum as an indexed, and hence searchable, feature. Accessing the Chemical Abstracts database through the STN® online service also enables large amounts of data to be sorted to allow meaningful analysis.

Global Publishing Trends in PGM Research

Searches were carried out of non-patent literature published during 1998 and 2008, using the CAS registry number for each pgm. The results were compared in order to yield an understanding of the relative interest in each metal and the waxing or waning of that interest over time. 2003 figures were also determined in order to confirm the trends seen.

Writing this paper required the analysis of publications from all over the world and additionally the use of indexing terms that are added manually by the CAS. Although the main publishers supply details quickly to CAS, it may take some time for publications from certain countries to be forwarded and also translated and indexed. So, in order to avoid some countries being prejudiced in the analysis, 2008 was considered to provide the most recent, and virtually complete, data set at the time of writing. Nevertheless, a small number of 2008 publications from some countries are still being uploaded at the time of this article going to press.

Table I shows that published pgm research increased by 73% over the ten-year timeframe of the study. Publications concerning platinum were the largest contributor to this growth, while papers relating to ruthenium and to some extent palladium also saw a large increase in number. However, the same cannot be said for rhodium and osmium. The reasons for this are not clear, but a possible contributory factor for rhodium may be its volatile price in recent years (3).

Table 1

<table>
<thead>
<tr>
<th>Platinum group metal</th>
<th>Number of publications in 1998</th>
<th>Number of publications in 2003</th>
<th>Number of publications in 2008</th>
<th>Change from 1998 to 2008, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Platinum</td>
<td>3061</td>
<td>3287</td>
<td>5779</td>
<td>89</td>
</tr>
<tr>
<td>Palladium</td>
<td>1733</td>
<td>2203</td>
<td>2610</td>
<td>51</td>
</tr>
<tr>
<td>Rhodium</td>
<td>654</td>
<td>620</td>
<td>628</td>
<td>-4</td>
</tr>
<tr>
<td>Iridium</td>
<td>355</td>
<td>448</td>
<td>459</td>
<td>29</td>
</tr>
<tr>
<td>Osmium</td>
<td>136</td>
<td>142</td>
<td>134</td>
<td>-1</td>
</tr>
<tr>
<td>Ruthenium</td>
<td>565</td>
<td>813</td>
<td>975</td>
<td>73</td>
</tr>
<tr>
<td>Total number of papers (all pgms)a</td>
<td>5155</td>
<td>6406</td>
<td>8920</td>
<td>73</td>
</tr>
</tbody>
</table>

The total number of papers is less than the arithmetic sum of the number of references for each pgm. This is a result of index terms for more than one metal being used in a single paper.
Table II details the most common areas of study for papers published in 2008 where ruthenium was a key material. It can be seen that both magnetic phenomena and energy conversion devices ranked highly.

Further insight into the details of these topics can be gleaned by examination of the top 10 controlled terms (a set of terms from a defined lexicon) that have been applied to these publications. For example, the most commonly used controlled index terms for the ruthenium papers in 2008 included nanotechnology, fuel cells and magnetic tunnel junctions for magnetoresistive random access memory (MRAM) – none of which featured in the 1998 top research topics. In comparison, catalysts both for oxidation and hydrogenation were popular topics of research both in 2008 and 1998.

**Geographical Trend Analysis**

Another useful indexing feature within Chemical Abstracts is the ability to search each document to find the country in which the primary researcher is located. Hence an analysis of the countries most involved in research using pgms can be carried out. The results are produced in the form of a list of publishing countries ranked by the number of publications from each country. Analysis of the collated results by continent is shown in Figure 1.

It is apparent that over the ten years studied there was a 13% drop in the proportion of research papers emanating from Europe, with a commensurate increase in the relative proportion of research coming from Asian countries. Further analysis indicates which countries within each region are responsible for the changes. The top ten publishing countries and how their positions altered over the ten years are shown in Table III.

The most notable change is the rise of China to the top of the league table resulting from a 3.7 fold increase in the number of publications over this timeframe. This pushed the USA and Japan into second and third place despite a large increase in their research output. Other Asian countries such as South

<table>
<thead>
<tr>
<th>Section Code – Subsection Code</th>
<th>Number of documents</th>
</tr>
</thead>
<tbody>
<tr>
<td>Magnetic Phenomena – Magnetic Properties</td>
<td>95</td>
</tr>
<tr>
<td>Electrochemical, Radiational and Thermal Energy Technology –</td>
<td>82</td>
</tr>
<tr>
<td>Energy Conversion Devices and Components</td>
<td></td>
</tr>
<tr>
<td>(including Batteries, Fuel Cells, Solar Cells etc.)</td>
<td></td>
</tr>
<tr>
<td>Surface Chemistry and Colloids – Solid/Gas Systems</td>
<td>71</td>
</tr>
<tr>
<td>Magnetic Phenomena – Other</td>
<td>45</td>
</tr>
<tr>
<td>Electric Phenomena – Semiconductor Junctions and Devices</td>
<td>43</td>
</tr>
<tr>
<td>Fossil Fuels, Derivatives and Related Products – Special Products</td>
<td>34</td>
</tr>
<tr>
<td>from Petroleum</td>
<td></td>
</tr>
<tr>
<td>Electrochemical, Radiational and Thermal Energy Technology –</td>
<td>32</td>
</tr>
<tr>
<td>Energy Sources e.g. Solar, Thermal, Hydrogen, Biofuels etc.</td>
<td></td>
</tr>
<tr>
<td>Electrochemistry – Electrodes, Electrode Reactions, Electrode Potentials</td>
<td>30</td>
</tr>
<tr>
<td>Industrial Organic Chemicals, Leather, Fats, Waxes – Manufacture</td>
<td>27</td>
</tr>
<tr>
<td>of Industrial Organic Chemicals</td>
<td></td>
</tr>
<tr>
<td>Electric Phenomena – Conductors, Semiconductors, Resistors and Contacts</td>
<td>17</td>
</tr>
</tbody>
</table>
Fig. 1. Comparison of the relative geographical distribution of papers on platinum group metals research published in 1998 and in 2008

### Table III

**Top Ten Countries Publishing Platinum Group Metals Research in 1998 and 2008**

<table>
<thead>
<tr>
<th>Country</th>
<th>1998 Proportion of publications, %</th>
<th>1998 Number of publications</th>
<th>2008 Proportion of publications, %</th>
<th>2008 Number of publications</th>
</tr>
</thead>
<tbody>
<tr>
<td>USA</td>
<td>17.6</td>
<td>906</td>
<td>China</td>
<td>19.8</td>
</tr>
<tr>
<td>Japan</td>
<td>15.0</td>
<td>772</td>
<td>USA</td>
<td>16.4</td>
</tr>
<tr>
<td>China</td>
<td>9.2</td>
<td>474</td>
<td>Japan</td>
<td>12.9</td>
</tr>
<tr>
<td>Germany</td>
<td>8.4</td>
<td>433</td>
<td>Germany</td>
<td>5.5</td>
</tr>
<tr>
<td>Russia</td>
<td>5.7</td>
<td>293</td>
<td>South Korea</td>
<td>5.4</td>
</tr>
<tr>
<td>France</td>
<td>4.7</td>
<td>244</td>
<td>France</td>
<td>3.2</td>
</tr>
<tr>
<td>UK</td>
<td>3.8</td>
<td>198</td>
<td>Taiwan</td>
<td>3.1</td>
</tr>
<tr>
<td>South Korea</td>
<td>3.7</td>
<td>193</td>
<td>UK</td>
<td>2.9</td>
</tr>
<tr>
<td>India</td>
<td>2.8</td>
<td>144</td>
<td>India</td>
<td>2.9</td>
</tr>
<tr>
<td>Italy</td>
<td>2.8</td>
<td>142</td>
<td>Russia</td>
<td>2.7</td>
</tr>
<tr>
<td>Total pgm publications</td>
<td>73.7</td>
<td>5155</td>
<td>Total pgm publications</td>
<td>74.8</td>
</tr>
</tbody>
</table>
Korea and Taiwan also moved up the rankings. European countries such as Germany, France and the UK saw growth in the numbers of publications although little change to their ranked positions. The apparent decline in the number of publications for Russia in 2008 vs. 1998 is most likely to be an artefact of the delay in publishers forwarding their information to CAS. Therefore it is not possible to draw any conclusions from this data at the time of writing.

Growth of Research in China
The data in Table III show that published pgm-related research grew by a substantial amount in China over the ten years from 1998 to 2008. While this is an impressive growth trend, it should be noted that publications from China in every technology area also increased, sometimes at an even higher rate than that reported here for the pgms.

By looking more closely at the CAS registry numbers for the pgm papers we can determine whether research in China showed the same trends as the rest of the world for each metal. Table IV shows that research activity in China for all the pgms increased very significantly during this time, with platinum, palladium and ruthenium showing the highest growth.

A comparison of Table I (data for the whole world) and Table IV (China only) shows that growth was consistently higher in China than the rest of the world for each pgm.

Table V details the top ten Chemical Abstracts Section and Sub-Section Codes for the Chinese pgm literature published in 2008, showing that the most popular research area concerned energy conversion devices such as fuel cells. A comparison of the top ten Section Codes in 2008 with those from 1998 shows that some subjects such as electrochemistry and inorganic analytical chemistry have remained popular. Other subjects, such as energy conversion devices have moved significantly upwards within the top 10 ranking, and subjects including radiation chemistry, photochemistry, ferroelectricity and semiconductors have now appeared in the top 10 whereas they were of considerably less interest in 1998.

Conclusions
This short paper has shown how the Chemical Abstracts database can be used to obtain meaningful analysis of trends in both the use of individual pgms and the geographical distribution of the research. It has been shown that the ten years between 1998 and 2008

**Table IV**

<table>
<thead>
<tr>
<th>Platinum group metal</th>
<th>Number of publications in 1998</th>
<th>Number of publications in 2008</th>
<th>Increase, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Platinum</td>
<td>280</td>
<td>1162</td>
<td>315</td>
</tr>
<tr>
<td>Palladium</td>
<td>181</td>
<td>538</td>
<td>197</td>
</tr>
<tr>
<td>Rhodium</td>
<td>67</td>
<td>102</td>
<td>52</td>
</tr>
<tr>
<td>Iridium</td>
<td>35</td>
<td>76</td>
<td>117</td>
</tr>
<tr>
<td>Osmium</td>
<td>14</td>
<td>16</td>
<td>14</td>
</tr>
<tr>
<td>Ruthenium</td>
<td>62</td>
<td>166</td>
<td>167</td>
</tr>
<tr>
<td><strong>Total number of papers (all pgms)</strong></td>
<td><strong>474</strong></td>
<td><strong>1771</strong></td>
<td><strong>274</strong></td>
</tr>
</tbody>
</table>

*a* The total number of papers is less than the arithmetic sum of the number of references for each pgm. This is a result of index terms for more than one metal being used in a single paper.
2008 saw overall growth in research involving platinum, ruthenium and to a lesser extent palladium and iridium, while research using rhodium and osmium remained flat or even declined slightly. Analysis has also indicated that there was a change in the relative geographical distribution of research, with a large rise in the number of publications from China pushing the USA, Japan and European countries down in the rankings despite growth in all of these regions. Research activity in China for all the pgms increased very significantly with platinum, palladium and ruthenium exhibiting the highest growth.

The paper has also illustrated how some of the indexing features of the Chemical Abstracts Service are used at Johnson Matthey to provide an overview of research trends in a subject area, or to provide an analysis of research over a wide or more specific geographical area. This type of analysis can also be carried out on patent data sets and so complement the mapping technique. However, examination of non-patent literature provides information on technology areas that are generally further from commercial exploitation and may allow emerging markets to be identified at an earlier stage.

### References


### The Author

Helen Gavin is an Information Scientist working in the Technology Forecasting and Information department at Johnson Matthey Technology Centre, Sonning Common, UK. She is particularly interested in the use of publicly available information for competitive advantage.
Effect of Platinum Addition to Coinage Metals on Their Ultrasonic Properties

Determination of second- and third-order elastic constants, sound velocity and ultrasonic attenuation

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http://www.platinummetalsreview.com/

By Devraj Singh* and Pramod K. Yadawa

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*E-mail: dsingh1@aset.amity.edu

Ultrasonic attenuation for the longitudinal and shear waves due to phonon-phonon interaction and due to thermoelastic relaxation mechanisms have been evaluated in bimetallic alloys of the coinage metals (copper, silver or gold) with 1, 2, 3 or 4 at% platinum. The evaluations were carried out along the $\langle 100 \rangle$, $\langle 111 \rangle$ and $\langle 110 \rangle$ crystallographic directions at room temperature. Second- and third-order elastic constants, ultrasonic velocities and thermal relaxation times have also been computed for these alloys. In each case, the addition of platinum to the coinage metal reduces the attenuation, which indicates that bimetallic alloys with a higher platinum content are more ductile and stable and contain fewer defects in their crystal structure than those with a lower platinum content. The predominant mechanism of attenuation of ultrasonic waves is phonon-phonon interaction rather than thermoelastic loss. The results are compared with available theoretical data and experimental measurements for the pure coinage metals. These results, in combination with other well-known physical properties, can be applied to the non-destructive testing of materials for various industrial applications.

Introduction

Ultrasonic non-destructive testing (NDT) is a useful technique that can be applied to a range of materials for the characterisation of their microstructures, the appraisal of defects and the determination of physical properties such as density, thermal conductivity and electrical resistivity. Ultrasonic measurements taken during the fabrication and heat treatment of materials can be used to ensure that the preferred microstructure is obtained and to prevent the formation of defects, including defects in welds between two different alloys. Insight into the interaction of ultrasound with microstructure is also important for resolving many material problems. However, attenuation and backscattering reduce the detectability of
defects, especially in platinum alloys with coarse grains or complex microstructures. Therefore it is desirable to minimise attenuation in order to maximise the usefulness of ultrasonic testing.

Information about the microstructure can also be used in material description studies, such as non-destructive determination of grain size. Wave propagation velocity is another key parameter in ultrasonic characterisation and can provide information about crystallographic texture. The ultrasonic velocity, $V$, is directly related to the elastic constants by the relationship shown in Equation (i):

$$V = \sqrt{\frac{C}{\rho}}$$

where $C$ is the relevant elastic constant and $\rho$ is the density of that particular material. The elastic constants, in particular, provide valuable information on the stability and stiffness of materials (1, 2).

**Physical Properties of Different Alloys**

The temperature and magnetic field dependence of the ultrasonic attenuation in rare earth alloys and compounds with crystal-field split energy levels were studied by Becker et al. (3). The elastic constants of copper-aluminium alloys were calculated by Soma using a pseudo-alloy-atom model (4). The effects of platinum addition to gold and of indium addition to a gold-platinum alloy on their optical properties were investigated using a computer-controlled spectrophotometer by Shiraishi et al. (5). Banhart et al. studied the Fermi surface geometry and electrical resistivity of copper-platinum alloys (6). These alloys are particularly interesting because a face centred cubic (fcc) phase exists over the whole range of alloy compositions. Characterisation of gold-silver and gold-copper alloy nanoparticles prepared in chloroform has been done by Kim et al. (7).

Gold-platinum alloys (containing ~10% platinum) are of particular interest for their use in dentistry. The biocompatibility and tensile strength of gold-platinum alloys were studied by Hironobu (8). A proposal for the classification of precious metal dental alloys according to their resistance to corrosion based on the ISO 10271 Standard “Dental Metallic Materials – Corrosion Test Methods”, 2001, was given by Manaranche and Hornberger (9). Gold and platinum-based ceramo-metallic alloys were studied by Susz et al. to correlate their physical properties to their tendency to release cations (10). Rudolf et al. developed the mechanical property and microstructure characterisation of gold-platinum dental alloys (11). These alloys are used in dentistry because of their extremely high chemical stability in the mouth, in addition to desirable mechanical properties such as high strength, ductility and elasticity. Au-Pt-Zn-based alloys have had the advantage of being around for some considerable time. They are part of clinical experience and are extremely successful. The bond between the ceramic and the metal, in particular, is very strong and highly reliable. When considering formulations of Au-Pt-Zn-based alloys for porcelain bonding, high gold contents are required to ensure biocompatibility and large platinum concentrations are necessary to sufficiently raise the melting range above the porcelain firing temperature, to prevent distortion during porcelain application (12, 13).

**Ultrasonic Attenuation Studies**

Ultrasonic properties have received less attention than other physical properties (14), but progress in materials science means that the study of ultrasonic attenuation now has greater possibilities. Ultrasonic attenuation is related to the thermal conductivity through the thermal relaxation time (15, 16). Investigators have aimed their efforts at explaining the temperature dependence of attenuation in terms of a model in which an ultrasonic phonon interacts with a thermal phonon in the lattice (17–19). All of these studies indicate that the major portion of attenuation is caused by direct conversion of acoustic energy into heat via phonon-phonon interaction and through thermal relaxation phenomena. In metals at low temperatures the most important factor contributing to ultrasonic attenuation is electron-phonon interaction. At these temperatures, the electron mean free path increases to the same magnitude as the mean free path of acoustic phonons at high frequency. Hence, the probability of interaction (20) between conducting electrons and phonons increases, as explained by Pippard (21).

The present paper is focused on the ultrasonic study of bimetallic alloys. To the best knowledge of the authors, such studies in the selected alloys have not yet been reported. The selected alloys are (in at%): copper-platinum (Cu<sub>100−x</sub>Pt<sub>x</sub>), silver-platinum (Ag<sub>100−x</sub>Pt<sub>x</sub>) and gold-platinum (Au<sub>100−x</sub>Pt<sub>x</sub>), where in each case $x = 1, 2, 3$ or 4. These alloys all have an fcc structure. Ultrasonic velocities, attenuation and thermal relaxation time are evaluated in these compounds along the crystallographic directions (100),
(110) and (111) at room temperature. The second-order elastic constants (SOEC) and third-order elastic constants (TOEC) are also calculated using the Born-Mayer model (22, 23).

**Second- and Third-Order Elastic Constants**

The Coulomb and Born-Mayer potentials are applied to evaluate the SOEC and TOEC (22). The elastic constants are then used to compute ultrasonic parameters such as ultrasonic velocity, thermal relaxation time and the acoustic coupling constants. These parameters are used in turn to evaluate ultrasonic attenuation. All the equations used to compute the SOEC and TOEC of these alloys are presented in our previous paper (23).

The SOEC and TOEC are calculated from the nearest neighbour distance, $r_{00}$, (24). These are given in Table I. The hardness parameter, $b$, (25) for each alloy is 0.315 Å. The SOEC and TOEC of the (Cu, Ag or Au)-Pt alloys as obtained from the Coulomb and Born-Mayer potentials up to the second nearest neighbour are presented in Table II.

Published experimental data on the elastic constants for the chosen alloys are not available for comparison. Comparison of the present values to

<table>
<thead>
<tr>
<th>Alloy composition, at%</th>
<th>Nearest neighbour distance, $r_{00}$, Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu$_{99}$Pt$_1$</td>
<td>2.5621</td>
</tr>
<tr>
<td>Cu$_{98}$Pt$_2$</td>
<td>2.5442</td>
</tr>
<tr>
<td>Cu$_{97}$Pt$_3$</td>
<td>2.5663</td>
</tr>
<tr>
<td>Cu$_{96}$Pt$_4$</td>
<td>2.5684</td>
</tr>
<tr>
<td>Ag$_{99}$Pt$_1$</td>
<td>2.889</td>
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<td>Ag$_{97}$Pt$_3$</td>
<td>2.885</td>
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<tr>
<td>Ag$_{96}$Pt$_4$</td>
<td>2.888</td>
</tr>
<tr>
<td>Au$_{99}$Pt$_1$</td>
<td>2.887</td>
</tr>
<tr>
<td>Au$_{98}$Pt$_2$</td>
<td>2.886</td>
</tr>
<tr>
<td>Au$_{97}$Pt$_3$</td>
<td>2.885</td>
</tr>
<tr>
<td>Au$_{96}$Pt$_4$</td>
<td>2.888</td>
</tr>
</tbody>
</table>

Table I

**Values of the Nearest Neighbour Distance, $r_{00}$, for Bimetallic Alloys of the Coinage Metals with Platinum**

Table II

**Second- and Third-Order Elastic Constants of Bimetallic Alloys of the Coinage Metals with Platinum at 300 K**

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Second-order elastic constants, $10^{10}$ N m$^{-2}$</th>
<th>Third-order elastic constants, $10^{10}$ N m$^{-2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$C_{11}$</td>
<td>$C_{12}$</td>
</tr>
<tr>
<td>Cu$_{99}$Pt$_1$</td>
<td>6.957</td>
<td>2.002</td>
</tr>
<tr>
<td>Ag$_{99}$Pt$_1$</td>
<td>5.821</td>
<td>1.081</td>
</tr>
<tr>
<td>Ag$_{98}$Pt$_2$</td>
<td>5.694</td>
<td>1.078</td>
</tr>
<tr>
<td>Ag$_{97}$Pt$_3$</td>
<td>5.652</td>
<td>1.083</td>
</tr>
<tr>
<td>Ag$_{96}$Pt$_4$</td>
<td>5.632</td>
<td>1.085</td>
</tr>
<tr>
<td>Au$_{99}$Pt$_1$</td>
<td>5.250</td>
<td>1.131</td>
</tr>
<tr>
<td>Au$_{98}$Pt$_2$</td>
<td>5.140</td>
<td>1.132</td>
</tr>
<tr>
<td>Au$_{97}$Pt$_3$</td>
<td>5.104</td>
<td>1.134</td>
</tr>
<tr>
<td>Au$_{96}$Pt$_4$</td>
<td>5.551</td>
<td>1.126</td>
</tr>
</tbody>
</table>
Theoretical and experimental studies of pure metals, as shown in Table III, demonstrates that results obtained from the present investigation are lower than those of the pure metals as reported by other investigators (26, 27). The values of the elastic constants show that the crystals are elastically stable, since the stability conditions: \(C_{44} > 0, C_{11} > 0, \text{and } C_{11} > C_{12}\) are satisfied. The elastic constants also indicate that thermal softening occurs as the platinum content in each alloy is increased. The obtained values of the SOEC and TOEC are of the same order as previous experimental and theoretical studies of metallic alloys and metals (14, 27). Therefore we conclude that our theoretical approach to evaluate the SOEC and TOEC is valid for the selected bimetallic alloys.

### Ultrasonic Attenuation and Related Parameters

The most important causes of ultrasonic attenuation in metallic alloys are phonon-phonon interaction and the thermoelastic mechanisms at room temperature. Expressions for calculating ultrasonic attenuation and related parameters are given in our previous papers (16, 28).

Ultrasonic velocities for the longitudinal wave, \(V_L\), and the shear wave, \(V_S\), together with the Debye average velocity, \(V_D\), of the chosen alloys are plotted in Figure 1. The thermal conductivity of the alloys is taken from previously published values (29). Total attenuation, \((\alpha f^2)_{\text{Total}}\), is given by (Equation (ii)):

\[
(\alpha f^2)_{\text{Total}} = (\alpha f^2)_{\text{Th}} + (\alpha f^2)_{L} + (\alpha f^2)_{S}
\]

where \((\alpha f^2)_{L}\) is the ultrasonic attenuation due to phonon-phonon interaction for the longitudinal wave; \((\alpha f^2)_{S}\) is that for the shear wave; \((\alpha f^2)_{Th}\) is that due to thermal relaxation; \(\alpha\) is the ultrasonic attenuation coefficient and \(f\) is the frequency. Thermal conductivity, \(k\), thermal relaxation time, \(\tau\), and total attenuation along the \(\langle 100 \rangle\), \(\langle 110 \rangle\) and \(\langle 111 \rangle\) orientations are presented in Figures 2 and 3 for the copper, silver and gold alloys. It can be seen from Figure 1 that, as we increase the platinum content of the alloys, the ultrasonic velocities change slightly due to a change in the elastic constants. Wave velocities are highest for the Cu-Pt alloys and lowest for the Au-Pt alloys. Based on wave velocity, Cu-Pt alloys may prove to be more workable than the other alloys in this study, and therefore more suitable for further investigation into potential industrial applications than the Ag-Pt or Au-Pt alloys. The wave velocity of these compounds is useful for finding their anisotropic properties. The order of velocities in the present case is

<table>
<thead>
<tr>
<th>Material</th>
<th>Second-order elastic constants, (10^{10} \text{ N m}^{-2})</th>
<th>Bulk modulus, (10^{10} \text{ N m}^{-2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{Cu}_99\text{Pt}_1)</td>
<td>6.96 2.00 2.30</td>
<td>5.38</td>
</tr>
<tr>
<td>Cu (experimental)</td>
<td>17.62 12.49 8.17</td>
<td>13.70</td>
</tr>
<tr>
<td>Cu (27)</td>
<td>13.61 11.98 6.65</td>
<td>12.53</td>
</tr>
<tr>
<td>(\text{Ag}_99\text{Pt}_1)</td>
<td>5.82 1.08 1.35</td>
<td>3.74</td>
</tr>
<tr>
<td>Ag (experimental)</td>
<td>13.15 5.73 5.11</td>
<td>10.07</td>
</tr>
<tr>
<td>Ag (27)</td>
<td>8.82 7.91 4.42</td>
<td>8.20</td>
</tr>
<tr>
<td>(\text{Au}_99\text{Pt}_1)</td>
<td>5.25 1.13 1.37</td>
<td>3.58</td>
</tr>
<tr>
<td>Au (experimental)</td>
<td>20.16 16.97 4.54</td>
<td>17.32</td>
</tr>
<tr>
<td>Au (27)</td>
<td>15.00 12.86 7.03</td>
<td>13.57</td>
</tr>
</tbody>
</table>
Fig. 1. Ultrasonic velocity for bimetallic alloys of the coinage metals copper, silver or gold with platinum. $V_L =$ ultrasonic velocity for the longitudinal wave, $V_S =$ ultrasonic velocity for the shear wave, $V_D =$ Debye average velocity

Fig. 2. Thermal conductivity, $k,$ (in $\text{W m}^{-1} \text{K}^{-1}$) and thermal relaxation time, $\tau,$ (in $10^{-13}$ s) for bimetallic alloys of the coinage metals copper, silver or gold with platinum
found in the same way as for an earlier study (15). The thermal relaxation time of these alloys is of the order of $10^{-11}$ s, which is as expected for pure metals and alloys (14, 30).

Figures 2 and 3 show that ultrasonic attenuation follows the decreasing trends in thermal conductivity and thermal relaxation time with increasing platinum content in these alloys. This is expected since the ultrasonic attenuation, $\alpha/f^2$, is proportional to the thermal relaxation time, $\tau$, and the acoustic coupling constant, $D$; and $\tau$ is proportional to the thermal conductivity, $k$. Although a large number of physical parameters are involved in calculating ultrasonic attenuation, Figures 2 and 3 show that total attenuation along each orientation follows the same trend as the thermal relaxation time and the thermal conductivity along the same orientation. The thermal relaxation time gives the collective effect of thermal conductivity, specific heat per unit volume, $C_v$, and Debye average velocity, $V_D$.

It can also be seen from Figure 3 that the total attenuation in the Cu-Pt alloys is low in comparison to that in the Ag-Pt and Au-Pt alloys. The Cu-Pt alloys have the fewest defects in their crystal structure at room temperature, while the Ag-Pt and Au-Pt alloys may have more defects at room temperature and have greater attenuation. In all of the alloys, ultrasonic attenuation due to the thermoelastic relaxation process is negligible, at approximately 0.2% to 0.5% of the total attenuation, while attenuation due to the phonon-phonon interaction mechanism is greater than 99% of the total. Hence, ultrasonic attenuation due to phonon-phonon interaction is the predominant component of attenuation in these materials.

From Figure 3, it is very clear that as platinum content is increased in these alloys, attenuation decreases. Hence the platinum is playing a critical role in these compounds. Because no experimental data for the chosen alloys are available for comparison, we have compared our results with data for pure copper, silver and gold. The calculated value of ultrasonic attenuation for the longitudinal wave along the $(100)$ direction is $59 \times 10^{-15}$ Np s$^2$ m$^{-1}$ for Cu$_{99}$Pt$_1$, while the experimental value of attenuation in pure Cu is $97 \times 10^{-15}$ Np s$^2$ m$^{-1}$ along the $(100)$ direction (30), and attenuation in pure Pt along this orientation is much lower at about $6.25 \times 10^{-16}$ Np s$^2$ m$^{-1}$ (31). So it is clear that Pt has advantages in comparison to Cu for aspects like ductility and stability. The selected Cu-Pt alloys have lower attenuation than the Ag-Pt and

![Fig. 3. Total ultrasonic attenuation over frequency (in $10^{-15}$ Np s$^2$ m$^{-1}$) for bimetallic alloys of the coinage metals copper, silver or gold with platinum](image-url)
Au-Pt alloys. Hence the Cu-Pt alloys are expected to be more ductile, stable and contain fewer defects in their crystal structure. This type of ultrasonic attenuation behaviour is in accordance with the fact that ultrasonic attenuation is inversely proportional to ultrasonic velocity to the power of 3/5, and this explains the calculated attenuation behaviour presented here. This is also a confirmation of the present theoretical approach.

**Conclusions and Scope for Future Work**

This paper compares calculated values of the second-order elastic constants for the selected bimetallic alloys with experimental values for the pure coinage metals. The ultrasonic velocities for the longitudinal and shear waves increase with increasing magnitude of the elastic constants, and in this study are higher in the copper-platinum alloys than in the silver-platinum or gold-platinum alloys. The thermal relaxation time, $\tau$, decreases with increasing platinum content in the alloys studied. The ultrasonic attenuation is also shown to decrease with increasing platinum content in these bimetallic alloys. Based on these results, Cu$_{96}$Pt$_4$ is expected to be more ductile and stable and contain fewer defects in its crystal structure than the other alloys included in this study. On the basis of our results, Cu$_{96}$Pt$_4$ may prove to be more workable than the other alloys in this study and is therefore recommended as a suitable material for further investigation into potential industrial applications. The preliminary results obtained in this work can be used for further experimental investigation with the pulse echo overlap (PEO) technique for ultrasonic measurements, and with conventional analytical techniques such as polarising microscopy, X-ray diffraction (XRD), surface tension analysis, solid state nuclear magnetic resonance (NMR), scanning electron microscopy (SEM) and transmission electron microscopy (TEM).

**References**


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The Authors

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Pramod K. Yadawa is a Lecturer in the Department of Applied Physics, AMITY School of Engineering and Technology, New Delhi. His major field of interest is the ultrasonic characterisation of structured materials.
Introduction

Thirty-five years ago the use of catalytic systems for controlling tailpipe pollutants from vehicles was virtually non-existent, yet now every new car in the major countries of the world is equipped with one or more emissions control catalysts. Over this time the autocatalyst industry has grown to become a multi-billion dollar worldwide business, and underpinning this success is the extremely high catalytic activity of the platinum group metals (pgms), especially rhodium and palladium as well as platinum itself.

On a vehicle, operating conditions are not smooth and steady as they are on a large single-stream methanol or ammonia plant (1). Low-temperature catalyst activity is vital during ‘cold-starts’ and very high temperatures (1000°C) can result from occasional engine misfires so very good catalyst thermal durability is a prerequisite. Conditions are highly transient – the gas flow rate changes often and it pulsates as exhaust gas is discharged from each cylinder in turn. The exhaust gas flow can be very high and the corresponding space velocity much higher than in a chemical plant, and there can be detrimental catalyst poisons such as sulfur and phosphorus species in the exhaust gas, as well as continuous physical vibration etc.

The primary pollutants from combustion of petrol, diesel and other hydrocarbon fuels such as liquefied petroleum gas (LPG) and compressed natural gas (CNG) are unburnt or partially oxidised hydrocarbons (HCs) and carbon monoxide (CO). Nitric oxide (NO) is also present, being formed from oxygen and nitrogen combining at the high-temperature flame front during combustion. Once in the air HCs and NO can undergo a series of photochemical reactions that lead to even more noxious secondary oxidising pollutants such as ozone (O₃) and organic compounds like peroxyacetyl nitrate (PAN) that are powerful and
very unpleasant lachrymators. So while cars and other vehicles with internal combustion engines have given society previously undreamt of mobility, they have also contributed to major undesirable environmental consequences (2, 3). The approach for solving this problem has been to deal with the primary pollutants at their source and prevent them from entering the environment by catalytically oxidising HCs and CO, and catalytically reducing NO to small amounts of water (H₂O), carbon dioxide (CO₂) and nitrogen (N₂). And in the case of three-way catalysts (TWCs) these three reactions are done simultaneously.

Catalytic Air Pollution Control
Since their introduction the importance of catalytic control technologies has grown, and the first edition of the book “Catalytic Air Pollution Control” by Ronald Heck and Robert Farrauto (then with Engelhard Corporation), published in 1995 as a relatively slim volume with a little more than 200 pages, was a particularly significant contribution (4). Its appearance was timely and it provided a valuable easy-to-read reference for those working in the area of environmental control, and especially the catalytic control of tailpipe emissions from passenger cars. Seven years later there followed an enlarged second edition (5) with almost twice the number of pages. Suresh Gulti, formerly with Corning Incorporated, joined the two original authors and his contributions provided additional coverage of the ’chemical engineering’ aspects of conventional flow-through monolithic catalysts, the design and sizing of ceramic diesel particulate filters and other related substrate details. The latest, third edition has 522 pages, and is again an enlargement and update over the previous edition and covers the recent developments.

The Third Edition
The present book is divided into four main sections: the first deals with ’Fundamentals’ and is followed by sections entitled ’Mobile Sources’, ’Stationary Sources’, and ’New and Emerging Technologies’. The ’Fundamentals’ section has been expanded to give more detailed background on kinetics of catalytic reactions, characterisation of catalysts and their modes of deactivation. In this section there are chapters on catalyst fundamentals, preparation of the components of monolithic-based catalysts, catalyst characterisation, the chemical engineering of catalysts, including the chemical kinetics of catalytic reactions, heat and mass transfer considerations, and pressure drop characteristics. The last chapter in this section deals with the various modes of catalyst deactivation including thermally induced modes such as sintering; poisoning by, for example, sulfur species and lubrication additives such as calcium, zinc and phosphorus; and washcoat loss. Importantly it also covers the diagnostics used to identify the mode of deactivation in practical situations.

The second section deals with ’Mobile Sources’ and forms the heart of the book, with some 270 pages and more than 500 cited references concerned with automotive catalysts and the substrates used to produce them (see Figure 1). The introduction of emissions control catalysts on cars is classified chronologically into different generations, and the most important

Fig. 1. Metal foil-based substrates (left) as well as extruded cordierite substrates (right) are used to manufacture three-way catalysts for gasoline engines and oxidation catalysts for diesel engines. NOx-trapping and selective catalytic reduction catalyst formulations for lean-NOx control are also coated onto flow-through substrates.
areas of TWCs for controlling emissions from stoichiometric gasoline engines and oxidation catalysts and particulate filters for diesel engines (see Figure 2) are well covered. The control of NOx emissions under the lean conditions of a diesel engine is not straightforward and the technologies being implemented are NOx-trapping with a basic catalyst component such as an alkaline earth with periodic exhaust gas enrichments to convert stored nitrate to nitrogen, and selective catalytic reduction (SCR) with ammonia derived from an aqueous urea solution. Both approaches are now in series production. Some of the legislative emissions requirements are touched on in this chapter, and details of the test cycles used in different regions of the world are provided. However, the focus is mainly on chemical and catalytic technical aspects such as the stabilisation of alumina surface area, and details of engine-based cycles used to accelerate the ageing of catalysts during development work – an aspect that often has slight attention paid to it in academic studies, but is vital when developing practical catalysts that have to maintain high performance over 120,000 (or more) miles of use! Another technology that is often overlooked is the retaining of ceramic monolithic catalyst in a stainless steel can – here it is covered in considerable detail. The section concludes with a relatively short (17 pages) chapter on the catalytic decomposition of ozone in high-flying aircraft.

The next section deals with the control of pollutants from ‘Stationary Sources’, and is a third of the size of the previous one on mobile sources. It has four chapters concerned with Volatile Organic Compounds (VOCs), Reduction of NOx, Carbon Monoxide and Hydrocarbon Abatement from Gas Turbines and Small Engines. The first chapter here includes emissions from sources such as catalytic incineration and wood burning stoves. Interestingly this is one of the few areas where deactivated catalysts are regenerated routinely. With modern pgm-based VOC oxidation catalysts sintering is not a problem and deactivation usually takes place through fouling or masking of the surface by material present in the flue gas. The most commonly used regeneration technique is to chemically wash the catalyst to dissolve the offending material without disrupting the structure of the underlying catalyst. Treatments often make use of mild acids and chelating agents, and if properly done catalyst lives may be extended to between five and ten years. However, in general the overall economics of catalyst regeneration mean that in some situations it might be more appropriate to replace old catalyst with new, depending on the time it takes to carry

![Fig. 2. Cutaway view of a catalysed soot filter (CSF) mounted directly on the turbocharger of a passenger car diesel engine. This cost-effective technology efficiently controls hydrocarbon, carbon monoxide and particulate emissions into the environment (Image copyright Martyn V. Twigg)](image-url)
out the regeneration procedure and the economic penalty of not having the catalyst operating.

The final section on ‘New and Emerging Technologies’ is relatively small (49 pages) and includes on-vehicle ambient ozone decomposition by catalytic coatings on radiators. At first a platinum catalyst was suggested and later a particular form of manganese dioxide containing the complex anion called cryptomelane, (Mn(V)6Mn(II)2O16)−, which is more cost effective than platinum, went into series production on some cars. However, this technology has not been as widely adopted as was thought would be the case. A larger chapter then considers fuel cells and the generation of on-board hydrogen for mobile applications such as fuel cells. First, types of fuel cells are discussed, and the authors concentrate on the low-temperature proton exchange membrane (PEM) fuel cells that use pgms as electrocatalysts. Then routes to hydrogen are detailed. In the chemical industry this is done via steam reforming of hydrocarbons, especially natural gas, to form a mixture of hydrogen and carbon oxides (mainly CO) called synthesis gas, or syngas, that is used in large single-stream plants to manufacture ammonia and methanol (1). For mobile on-vehicle use methanol is a very convenient ‘fuel’ for hydrogen production via low-temperature steam reforming over copper-based catalysts (6). It will be interesting to see if these electrically-based power systems will have sufficient advantages to replace the highly refined ultra low emission internal combustion engines in the future.

Commercial Catalytic Systems

This book is unlike most textbooks on catalysis. The authors are industrial researchers who have been deeply involved in the development and application of innovative commercial catalytic emissions control systems for vehicles. They were responsible for many successful innovations that have benefited society, and in some ways their book gives a hint of the excitement of doing this. Throughout the book the emphasis is on the applied aspects and what is actually done industrially. Catalytic systems are included for both stationary and mobile sources and because the authors are from industry the topics are considered from a very practical point of view that is not found in standard textbooks. However, there are questions at the end of each chapter, rather in the form of a college textbook, and these would be of value to instructors using the book for specialist graduate courses. The cited references are collected together at the end of each chapter, and since there is no author index, tracking the work of a particular research group in different areas can be difficult. However, the titles of papers referred to are provided and this is helpful in identifying papers a reader might wish to pursue further. There is a subject index that usefully could be more exhaustive; it occupies only five pages.

Concluding Remarks

Overall this is a very good book that provides real technical insight into an important area of catalysis. Although there are occasionally some inaccuracies, for instance the mechanism of filtration with diesel particulate filters, this book will be of benefit to those working in the immediate area of catalytic pollution control, as well as those concerned with broader aspects of environmental chemistry both at the professional and student levels. Librarians are encouraged to ensure this volume is on their shelves.

References


The Reviewer

Martyn Twigg is the Chief Scientist of Johnson Matthey PLC and was previously Technical Director for the Environmental Catalysts and Technologies Division. Following work at the University of Toronto, Canada, and a fellowship at the University of Cambridge, UK, he joined ICI where he aided the development and production of heterogeneous catalysts used in the production of hydrogen, ammonia and methanol. Martyn has authored or co-authored many research papers, written numerous chapters in encyclopedic works, and edited and contributed to several books. He edits a book series on fundamental and applied catalysis.
Monographs on precious metal compounds and complexes published in China in recent years have been relatively scattered rather than systematic and comprehensive. This book, “A Handbook of Synthesis of Precious Metals Compounds and Complexes”, published in Chinese and edited by Jianmin Yu, aims to present the most complete collection of information on precious metals compounds and complexes from a large number of sources from both within China and abroad. Some of the information is available in the book for the first time in Chinese.

Compounds and Complexes of Precious Metals

This handbook provides detailed data obtained from both theoretical and practical studies on the synthesis of precious metals compounds and complexes. The book has eleven chapters, covering the synthesis and properties of gold, silver and platinum group metal (pgm) compounds and complexes.

The physical and chemical properties of the main compounds and complexes of the precious metals are reviewed in Chapter 1. The chemical formulae, English names, relative molecular weights and methods of synthesis of the compounds and complexes of gold (a total of 43), silver (48), palladium (103), platinum (226), rhodium (143), iridium (137), osmium (74) and ruthenium (148) comprise the most important part of the book and occupy Chapters 2 to 9. The synthesis of five pharmaceutical intermediate compounds and seven precious metal anticancer drugs is discussed in Chapter 10, and the synthesis of seven acetylacetonate complexes of precious metals which are used for making chemical vapour deposition (CVD) materials are detailed in Chapter 11.

An Industrial Perspective

The editor of the book, Jianmin Yu, is a Professor at Kunming Sino-Platinum Metals Catalyst Co, Ltd, in
Yunnan Province, China. He is interested in the extraction, separation, recovery and refining of precious metals. He is also the legal representative of Kunming Yu Jin Technology Development Co, Ltd, which was established in April 2008 to develop key technologies in precious metals mining and resources. In addition to editing the book, he is the author of Chapters 4 to 8. Chapters 1 and 9 are written by Jun Lu, Senior Engineer at Kunming Yu Jin Technology Development Co, Ltd, and Chapters 2 and 3 are written by Yunkun Zhao, a researcher at the same company. Production of the book was commissioned and supported by the Yunnan Provincial Science and Technology Bureau Fund.

This book is aimed at three groups of people:
(a) Scientists engaged in research and development of precious metal-based materials, pharmaceuticals and fine chemicals;
(b) Researchers and technical personnel in the areas of separation, purification, refining and analysis of precious metals;
(c) Teachers and students in metallurgy, materials science, chemistry, chemical engineering or pharmaceutical science in universities and specialised secondary schools.

The text is clear, the examples and illustrations are easy to understand, and many references are listed for further information, which makes the book suitable for people of different levels of expertise to use and refer to. It might have been helpful to give the cited references after each method instead of listing them together at the back of the book, to help the reader to more easily find detailed information on a particular method of interest.

The English index of all substance names and the English abbreviations used in the book are given in an appendix. This list of substances covers a variety of precious metal complexes with ligands ranging from amines, halogens and phosphines to arsines, cyclopentadiene, dimethylglyoxime, oxalic acid and thioethers, reflecting the broad range of applications that are discussed in the book. Another appendix lists the technology services that the Kunming Yu Jin Technology Development Co, Ltd, provides. It would perhaps have been helpful for readers if a list of companies who can supply pgm sponge and basic raw materials in China and worldwide had also been included here and this could be considered for future editions.

Concluding Remarks
Covering a total of 941 compounds and complexes of precious metals in a systematic way, this is a useful book for anybody involved in synthesis and applications of these compounds or complexes and is one of the most complete texts on the subject published in China to date.

The Reviewer
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Platinum Group Metals in Glass Making
An overview of the role of the pgms in the glass industry

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http://www.platinummetalsreview.com/

The platinum group metals (pgms) are characterised by their high melting points and resistance to corrosion. The glass industry most commonly uses platinum, platinum-rhodium alloys and, recently, iridium. These protect a variety of components and ceramic substrates used in glass manufacture from erosion by molten glass, including thermocouples, furnace and forehearth parts. This protection takes the form of a fabricated part or a coating applied to a substrate. Glass manufacturers use these pgm products to get financial benefits, such as increased output, reduced downtime, extended equipment life, shape retention of ceramic parts and fewer defects in the end product. Another important advantage is that pgms are recyclable: as with glass, precious metals can be recycled, melted and reused indefinitely. In addition to these advantages, a choice of pgm-based technologies is available to the industry and this flexibility ensures that both protection and metal use can be optimised.

Introduction
The platinum group metals (pgms) have been used for many years in the glass industry (1, 2). Due to their high melting points and superior resistance to corrosion, they are invaluable for protecting manufacturing equipment from attack by molten glass and corrosive vapours (1, 3). Although the initial cost of pgms may be high, they are fully recyclable and, depending on the product, 95% to 98% of the metal can usually be recovered and converted into revenue once the useful life of the component is over (4).

While there are many established products available to glass manufacturers, newer options with their own unique characteristics are being introduced to complement these. This article provides a brief overview of the use of pgms for glass manufacture, including typical materials, where they find application and the benefits they offer. It will also consider how pgm products are positioned to respond to more challenging requirements as the glass market evolves.
Common Alloys and Forms

Platinum-Rhodium Fabrications

Fabrications are self-supporting parts or linings that are usually made of welded sheets of platinum-rhodium alloys. Typically, between 5 wt% and 20 wt% rhodium is added to platinum to provide strength (3, 4), although alloys with 30 wt% rhodium are also available (5). Sheet metal, tubes and more complex assemblies such as stirrers (Figure 1(a)), leeder chambers, refiners or spout bowls constitute what are known as pgm fabrications. Fabrications or linings can withstand repeated thermal cycling, cracking of the ceramic substrate and exchange of contacting parts.

For the most demanding applications, platinum-rhodium alloys with dispersed zirconia particles can give fabrications increased mechanical strength and durability. Although only small quantities are necessary, the zirconia particles stabilise the grain structure of the alloy and improve its resistance to contamination (6). The general term used for these special alloys is ‘doped’ alloys, and they are also referred to as grain stabilised or dispersion hardened materials (3, 7).

Platinum and Platinum-Rhodium Coatings

The deposition of a thin layer of platinum or platinum with 10 wt% rhodium can be used for ceramic protection in the manufacture of all glass types, including soda lime, crystal, borosilicate, opal, solar and speciality glass, and is ideal for long runs with limited thermal cycling (8). Coatings range from 200 µm to 500 µm in thickness and rely strongly on the integrity of the ceramic substrate. The coating is applied using a low-temperature process that does not affect the substrate; hence, a minimal risk of damage to the component is involved. This makes coatings suitable for fused cast material which is sensitive to thermal shock. The coating process, usually carried out by plasma or flame deposition, is flexible and accommodates complex shapes (Figure 1(b) (4, 9)). Direct heating, where an electric current is passed through the pgm layer to heat the glass, is also compatible with this technology.

Platinum-Gold Fabrications and Coatings

Alloys of platinum with 5 wt% gold are used both in the form of fabrications and as coatings on ceramic substrates (10). They offer advantageous glass non-wettability characteristics, meaning that the surface tension of the molten glass in contact with the alloy surface is high and the glass will ‘roll off’ the surface rather than spread across it, but they are only suitable for lower-temperature applications (11). They can be doped with zirconia to increase strength (12), and in the form of fabrications are particularly relevant to platinum laboratory apparatus (PLA) and nozzle tips for glass fibre bushings. As a coating, platinum-gold protects orifice rings used in the container manufacturing industry, preventing the glass from sticking to, and solidifying on, the coated surface and so facilitating the removal of the ceramic part when it needs to be replaced.

Fig. 1. (a) Fabricated stirrer for molten glass, made of platinum-rhodium sheet (design from Fuller Glastechnologie Vertriebs-GmbH); (b) A plunger, which oscillates vertically to repeatedly force precisely measured amounts of glass through an orifice ring (9), is ACT® coated with platinum-rhodium. ACT® is Johnson Matthey Noble Metals’ advanced coating technology (4)
Advantages Offered by PGM Products
Suitable Technology for Each Application

In the 1990s, fabrications made with grain stabilised pgm alloys became less popular due to their higher cost of manufacture, but the early 2000s saw a revival in demand for these doped alloys as rhodium prices increased (13), making the conventional platinum-rhodium alloys comparatively more expensive to use. Due to their superior mechanical strength, doped alloys are now used extensively to replace traditional platinum-rhodium alloys with lower-rhodium equivalents, thereby reducing the investment in precious metal required (4, 14).

Also in the 1990s, the use of platinum coatings led to further benefits in terms of reduced pgm use. As they rely on the mechanical strength of the substrate (10), coatings use less metal overall and do not require the addition of rhodium for strength. However, fabrications continue to play an important role as their environmental resistance and robustness cannot always be matched by a coated ceramic substrate.

As an example, thermocouple assemblies can be protected from glass erosion or chemical attack using precious metal, either in the form of a drawn tube with one end closed or applied as a coating on an alumina sheath. Both types of thermocouple protection are proven to be durable and to withstand high-temperatures such as those found in the crown of the furnace. A coated protection (Figure 2(a)) minimises the amount of pgm required to protect the assembly against glass erosion and is a more cost-effective choice for less demanding applications, but a fabricated sheath (Figure 2(b)) will better withstand thermal cycling and in general be a more robust option under severe conditions. As every glass plant has its own unique characteristics, trials of various forms of protection can be undertaken to establish which technology is most suitable in each case.

Improved Glass Product Quality

It is possible to use unprotected, consumable ceramic parts in the forehearth section of a glass furnace. However, while their performance has improved progressively, problems which can affect end product quality may still be experienced (15). For example, dimensional stability and durability are two of the key requirements placed upon the feeder consumable set used in an automated feeding process for mass production of glass tableware and glass containers such as bottles (9, 16). Over time, corrosion of the ceramic leads to altered dimensions in the feeder parts (9,16), causing variability in the finished product. However, the use of a protective pgm coating on the ceramic will ensure complete resistance against attack by molten glass, providing protection at the glass line and against corrosive vapour condensates, thus stabilising the forming process and allowing the formed shape to be more controlled and of consistent quality. In one case it has been found that the number of dishwashing cycles that glass tableware can withstand is more than doubled by using pgm in critical areas.

Fig. 2. (a) Thermocouple sheaths of different diameter, ACT® coated with a platinum-rhodium alloy; (b) Fabricated thermocouple sheaths made from grain stabilised platinum-rhodium alloy
areas of the forehearth, because the occurrence of cords (visible streaks caused by differences in glass viscosity (17)) is minimised.

This could find particularly interesting application in supporting the glass container and tableware industries in their effort to move towards more sustainable products. Properly protected components could help reduce the final weight of glass bottles by allowing tighter tolerances and should help minimise the rejection rate, thus optimising the energy cost per unit produced.

Another problem encountered when using unprotected ceramic parts is contamination of the glass melt by dissolution of the ceramic (15, 16). This may also cause defects in the glass product (15, 16) and can be prevented by using pgm protection in the stirrer cell and on ceramic surfaces in the critical zone prior to forming (16). Protection on stirring components, in the form of a fabricated part or coating, further ensures that stirring efficiency is maintained and inhomogeneities in the batch are minimised.

For these reasons, the use of pgm coated or fabricated components is particularly beneficial in the manufacture of glass for specialist applications where quality is paramount, including solar glass, optical glass, vitroceramic (a glass-ceramic material used in many modern hobs or stove tops) and glass components for pharmaceutical containment (Figure 3).

Examples of components which benefit from pgm protection are mandrels in the tubing industry, tweels and lipstones for speciality flat glass, and chambers and refiners for crystal and optical glass.

Extended Furnace Life
Any measure taken to extend the life of a glass furnace potentially offers considerable return on investment. This objective is often achieved by protecting the furnace throat. Some glass manufacturers use bare fused cast ceramics, including chromium oxide blocks, to construct the throat, but further dimensional stability and durability may be required. These unprotected blocks could also be a source of contamination of the glass melt by dissolution of the ceramic (15). For other types of glass, such as borosilicate and opal glass, the throat can be protected with platinum-rhodium linings or molybdenum shields, although more cost-effective solutions are sought.

A platinum-rhodium coated throat can be more cost-effective than installing platinum-rhodium linings or fabricated parts (Figure 4). The technology is applicable to furnaces for all types of glass, including soda lime, crystal, borosilicate, opal and specialty glass. The average coating thickness varies between 400 µm and 500 µm, and a medium-sized throat requires between 15 kg and 20 kg of platinum or platinum-rhodium alloy which can be recovered at the end of the campaign (4).

Iridium in the Glass Industry
Iridium has been available in the form of sheet for many years. However, before the mid 1980s, production was difficult and quality was variable. Since then, it has become possible to supply high-quality, uniform sheet iridium, typically in thicknesses between 0.7 mm and 4 mm. This has been facilitated by improved melting equipment and processing techniques. These product developments were driven by the increasing global demand for iridium crucibles, which are used in the electronics industry in the temperature range from 1500°C to over 2200°C. Glass processing equipment tends to be more complex in shape than a simple crucible, however manufacturing capabilities have continued to develop and iridium can now be formed to meet these needs. There are still limitations but these can usually be overcome by design adaptations.

Like platinum and rhodium, iridium is recyclable; but, with a substantially lower metal price (13), it is
more affordable upfront. Iridium has higher mechanical strength than grain stabilised platinum-rhodium alloys and excellent creep resistance (6). However the real advantage it offers is that it can be used under mildly reducing conditions, where platinum and its alloys may be subject to contamination and subsequent failure (18). Iridium can also be used at temperatures up to 2000°C in air but, unlike platinum-rhodium, it may require some oxidation protection, as above 1000°C it begins to show an appreciable degree of oxidation (6, 19). Iridium fabrications and linings therefore complement existing platinum-rhodium technology, and pgm solutions are now available for use in both oxidising and reducing environments. More information on iridium for glass manufacture can be obtained by contacting the author by email at: christophe.couderc@matthey.com.

Outlook
The globalisation of the glass industry continues to reduce end-product prices, even while higher technical specifications are demanded of manufacturers. Key characteristics that will increasingly be required of pgm technologies for the glass industry will include high-temperature strength and excellent glass contact corrosion resistance, with lower upfront capital investment. Many technologies that have been used for decades in the glass industry are still well suited to present needs. Others have responded less well to current economical conditions and technical requirements, but may still play a role in the future of the glass industry. These established products will be complemented by the new discoveries that continue to be made in the application of the platinum group metals to high-temperature and corrosive environments, ensuring the continued importance of these metals to industries such as glass manufacture.

References
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Christophe Couderc is the Business Development Manager, Glass, at Johnson Matthey Noble Metals in Royston, UK. He has a Masters in Chemistry and Physics from Université Toulouse III, is an Ingénieur Grandes Écoles (Mines d’Albi, France) and has an MBA from Tanaka Business School at Imperial College London. He launched iridium fabrications in the glass market sector and ACT® coating for furnace blocks. He is particularly interested in the applicability of pgm products to the manufacture of glass for highly specialised or niche applications.
Johnson Matthey's latest market survey of the platinum group metals (pgms), "Platinum 2010", was published on 17th May 2010. It covers supply and demand for the calendar year 2009, together with a short-term outlook on the status of the pgm market and pgm prices into 2010.

Platinum Market in Surplus in 2009
The platinum market was in surplus by 285,000 oz in 2009. Gross demand for platinum fell by 11.9 per cent to 7.04 million oz. Demand for platinum net of recycling fell by 8.5 per cent to 5.635 million oz, and supplies of platinum from current mining operations fell by 0.3 per cent to 5.92 million oz.

Supplies in 2009 Marginally Below 2008 Level
South African supplies of platinum rose by 0.3 per cent to 4.53 million oz. Increased output from newer mines and the sale of metal from stocks accumulated in 2008 offset losses from the closing of some uneconomic shafts and pits. North American supplies, hit by industrial action, fell to 260,000 oz and Russian supplies fell slightly to 785,000 oz. Expansion at Zimbabwean platinum mines led to output increasing by 27.8 per cent to 230,000 oz.

Autocatalyst Demand for Platinum Down
Gross demand for platinum in autocatalysts dropped by 39.0 per cent to 2.23 million oz in 2009 as global vehicle production fell heavily in nearly all regions. European gross demand was worst hit and dropped by over half to 970,000 oz due to a sharp, short-term decline in the market share of diesel cars. Meanwhile the proportion of diesel vehicles in the European region that were fitted with a platinum-catalysed diesel particulate filter (DPF) rose with the introduction of the light-duty Euro 5 emissions rules, that applied to vehicles from the final quarter of 2009.

Recovery of platinum from spent autocatalysts was also sharply down in 2009, falling by 26.5 per cent to 830,000 oz globally due to a decline in the number of vehicles scrapped.

Industrial Demand for Platinum Reduced
The economic downturn hit industrial demand for platinum in almost all applications as industrial plants operated well below capacity, product inventories were reduced and capital investment was delayed. A large amount of platinum was sold from the glass industry after redundant cathode ray tube glass factories were closed in China, and the fall in platinum demand was further affected by the fibre glass industry's move towards more durable higher-rhodium, lower-platinum alloys, particularly in North America and Europe. Although medical and biomedical demand for platinum was flat at 250,000 oz, total industrial purchases of platinum were 33.7 per cent lower than in 2008 at 1.14 million oz.

Rising Platinum Demand for Jewellery Manufacture
Gross purchases of platinum for jewellery manufacture climbed by 46.1 per cent in 2009 to 3.01 million oz worldwide. The reduced value of platinum led to a fall in recycling of scrap jewellery by 18.7 per cent to 565,000 oz, resulting in net global demand of 2.445 million oz, a rise of 79.1 per cent. In China, the booming economy and a lower average platinum price than in 2008 boosted gross demand to a record 2.08 million oz. The rebuilding of stocks of metal and finished jewellery throughout the trade contributed to the increase.

Within China, plain platinum and gold jewellery is typically priced per gram, with the price displayed on boards such as this (Image copyright David Jollie/Johnson Matthey PLC)
Palladium

Palladium Market Surplus in 2009
The palladium market was in surplus by 760,000 oz in 2009. Net demand declined by 5.0 per cent to 6.34 million oz, while supplies of palladium fell by 2.9 per cent to 7.10 million oz. Production from current Russian mining slipped marginally to 2.68 million oz and sales of material from Russian state stocks are estimated to have contributed another 960,000 oz of palladium to supplies, tipping the palladium market into surplus. South African supplies dropped by 60,000 oz to 2.37 million oz.

Incentives Support Autocatalyst Demand
Gross purchases of palladium for use in autocatalysts decreased by 9.3 per cent to 4.05 million oz in 2009, largely due to the fall in global vehicle output. However, European auto demand for palladium was almost flat compared to 2008, as various scrappage schemes supported the sale of gasoline-fuelled vehicles and palladium continued to gain ground at the expense of platinum in diesel engine catalysts. Demand for palladium for the rapidly expanding vehicle market in China grew to 685,000 oz, up by 76.0 per cent on 2008.

Weaker Palladium Jewellery Demand
In the jewellery sector, global gross demand for palladium decreased by 17.3 per cent in 2009 to 815,000 oz. Gross demand in China slipped from 740,000 oz to 560,000 oz as manufacturers devoted resources to making platinum jewellery. North American demand was flat but European demand was driven marginally higher by the introduction of a palladium hallmark in the UK. Net global demand fell by 12.9 per cent to 745,000 oz.

Industrial and Investment Demand for Palladium
Industrial gross demand for palladium (including dental demand) decreased by 5.8 per cent to 2.28 million oz in 2009 as the effects of recession lingered. Electrical gross demand fell by 100,000 oz to 1.27 million oz due to lower output of automotive electronics and heavy destocking of components in early 2009. Recycling of electronic scrap increased by 50,000 oz, leaving net electrical demand down 14.6 per cent at 875,000 oz.

Identifiable physical investment demand for palladium climbed by 48.8 per cent to 625,000 oz in 2009. Once again, there was strong buying interest in palladium through the European Exchange Traded Funds (ETFs), encouraged by the rising metal price.

Recycling of Platinum Group Metals
There is a new chapter in “Platinum 2010” on recycling, which describes the drivers and incentives behind recycling of pgm-containing post-consumer scrap. It defines “open loop” recycling, where control and ownership of the metal change hands, as opposed to “closed loop” recycling where the precious metal is reclaimed and recycled on behalf of the same organisation which initially purchased it. Open loop recycling figures for platinum, palladium and rhodium are reported for the automotive, electronics and jewellery sectors, with the metal recovered allocated to the region where the scrapped material had been in use.

Special Features
A special feature on ‘The Zimbabwean Mining Industry’ includes a schematic map showing the four major platinum deposits located along Zimbabwe’s Great Dyke, and describes progress towards the development of Zimbabwe’s mining potential. A feature on ‘The Chinese Platinum Jewellery Market’ discusses the various factors involved in this complex market, including “consumer pull”, “manufacturer push” and changes in stock levels of both finished jewellery and unprocessed metal.

Availability of “Platinum 2010”
The book can be downloaded, free of charge, as a PDF file in English, Chinese or Russian by visiting the Platinum Today website at: http://www.platinum.matthey.com/publications/pgm-market-reviews/archive/platinum-2010/. Alternatively the English version can be ordered in hard copy, by filling in the form at: http://www.platinum.matthey.com/publications/pgm-market-reviews/request-a-copy/, by emailing a request to: ptbook@matthey.com, or by writing to: Johnson Matthey, Precious Metals Marketing, Orchard Road, Royston, Hertfordshire SG8 5HE, UK.
CATALYSIS – APPLIED AND PHYSICAL ASPECTS

Pausing a Stir: Heterogeneous Catalysis in Dry Water

Dry water (DW) is a H2O-in-air inverse foam, formed by mixing H2O with hydrophobic silica particles (H18, Wacker Chemie) in a blender. This produces a free-flowing powder with ≤99% H2O, comprising H2O microdroplets where coalescence is prevented by a silica coating. Free-flowing DW-like powder was prepared by blending an aqueous solution of maleic acid with H18 (5 wt% based on water) and 5 wt% Ru/Al2O3 catalyst. Hydrogenation to succinic acid was carried out by pressurising I with H2 (20.7 bar) in a stainless steel autoclave. No stirring was used. The reaction was heated to 70ºC prior to introduction of H2.

Separation of Different Metathesis Grubbs-Type Catalysts Using Organic Solvent Nanofiltration

A coupled reaction–separation process was used for the metathesis of 1-octene to 7-tetradecene and ethene. Grubbs-type Ru-based catalysts and the STARMEM™ series (active polyimide surfaces) of organic solvent nanofiltration (OSN) membranes were used. STARMEM™ 228 membrane separated the catalysts from their post-reaction mixtures to below 9 ppm of Ru. The coupled reaction–separation and recycling process increased the TON from 1400 for a single-pass reaction to 5500 for the overall consecutive reaction–separation steps of four cycles.

EMISSIONS CONTROL

Effect of Cobalt Oxide on Performance of Pd Catalysts for Lean-Burn Natural Gas Vehicles in the Presence and Absence of Water Vapor

Pd-based catalysts modified by Co were prepared by co-impregnation and sequential impregnation methods. The activity of the catalysts was tested in a simulated exhaust gas from lean-burn NGVs. The PdCo/LaAl2O3 catalyst prepared by co-impregnation exhibited the best water-resistant performance. XPS analysis indicated that both CoAl2O4 and Co3O4 were present. For the catalyst prepared by sequential impregnation, the ratio of CoAl2O4/Co3O4 was higher than that of the catalyst prepared by co-impregnation.

FUEL CELLS

Recycling of Membrane Electrode Assembly of PEMFC by Acid Processing

PEMFC catalyst coated membranes (CCMs) were dipped into H2SO4 until a transparent solution composed of Pt and Nafion perfluorosulfonic acid resin was formed. The membrane was dissolved, and the amorphous C catalyst support nanoparticles were oxidised. Subsequently, ~95% Pt and almost all the Nafion were recovered by centrifugal separation. The fuel cell performance of the recycled Nafion was close to that of virgin Nafion.

Experimental Validation of the “EasyTest Cell” Operational Principle for Autonomous MEA Characterization

The “EasyTest Cell” was validated by comparative electrochemical tests on MEAs in conventional PEMFC and PEM water electrolyser testing cells and the EasyTest Cell. The electrodes investigated were magnetron sputtered C/Ti/IrOx (IrOx 0.12–0.4 mg cm–2) and C/Ti/IrOx/Pt/IrOx (IrOx 0.08/Pt 0.06/IrOx 0.08 mg cm–2); C/Ti/Pt (0.15 and 0.25 mg cm–2) sputtered at various Ar pressures; and E-TEK ELAT® electrode (V21, Pt loading 0.5 mg cm–2). It is reported that the results demonstrate the reliability, simplicity and experimental possibilities of the EasyTest Cell.

Synthesis by Spray Pyrolysis of Mesoporous NbRu2O7 as Electrocatalyst Supports in Fuel Cells

Spray pyrolysis was used to produce mesoporous powders of niobium oxide and niobium oxide with
12% Ru (by wt of metals). The NbO$_y$ and NbRu$_x$O$_y$ powders exhibited spherical particle morphology with internal mesoporosity introduced by surfactant templating, providing surface areas of 183 and 167 m$^2$ g$^{-1}$, respectively, after post-processing that included an acid etch and calcination. The electrical resistance of NbRu$_x$O$_y$ was reduced by ~5 orders of magnitude relative to NbO$_y$. CV showed that NbRu$_x$O$_y$ has activity for MeOH oxidation in basic solutions.

**METALLURGY AND MATERIALS**

**Melt Growth of ZnO Bulk Crystals in Ir Crucibles**

The thermochemical properties of ZnO make the growing of crystals difficult as it has a high melting point ($T_m = 1975^\circ$C) and undergoes thermal decomposition upon heating. The use of Ir crucibles is necessary. A thermodynamic analysis of melt growth of ZnO bulk crystals showed that the O$_2$ partial pressure in the surrounding vapour phase should be as low as possible during the heating cycle at lower temperatures in order to avoid Ir oxidation. Approaching the ZnO melting point, however, higher O$_2$ pressure is required to suppress ZnO decomposition. The required increase in O$_2$ supply with increasing temperature can be accomplished by the addition of CO$_2$ to the gas atmosphere. Experimental results confirmed these predictions.

**APPARATUS AND TECHNIQUE**

**Surface Characterization of Palladium-Alumina Sorbents for High-Temperature Capture of Mercury and Arsenic from Fuel Gas**

The interactions leading to the capture of Hg and As from fuel gas by Pd/Al$_2$O$_3$ sorbents were investigated. The adsorption of Hg is favoured by lower temperatures while As adsorption is favoured at 204–371$^\circ$C. The relative adsorption of Hg is suppressed in the presence of an excess of As. H$_2$S in the fuel gas moderately inhibits the adsorption of As while enhancing the adsorption of Hg. These differences in adsorption affinity of the Pd/Al$_2$O$_3$ sorbent can be overcome by adjusting the length and temperature of the adsorption bed.

**ELECTRICAL AND ELECTRONICS**

**Time and Frequency Domain Analysis of Hydrogen Permeation across PdC$_x$ Metallic Membranes for Hydrogen Purification**

The kinetics of H permeation across 20 µm-thick Pd$_{y}$Cu$_{1-x}$ membranes have been investigated. The permeation mechanism was established to include surface chemisorption of molecular H$_2$ (upstream side of the membrane), H diffusion across bulk regions, H recombination (downstream side) and evolution of H$_2$. Diffusion-controlled transport of H across the membrane is rate-determining. However, the value of the H diffusion coefficient does not rise exponentially with operating temperature (40–400$^\circ$C). At temperatures as low as 300$^\circ$C, new rate limitations appear; they are attributed to recrystallisation and/or phase transformation processes induced by temperature and the presence of H$_2$.

**Sputtered Amorphous Co–Pt–P Thin Films for Soft Underlayer of Perpendicular Magnetic Recording**

Amorphous Co-Pt-P thin films fabricated by DC sputtering were investigated by XRD and vibrating sample magnetometry. The maximum permeability of the Co-12 at% Pt-P films sputtered at RT was quite low when the P content was < 5.2 at%, but a Co-12 at% Pt-7 at% P thin film 1 was amorphous and had a permeability of ~500. 1 had excellent soft magnetic properties with maximum permeability of 500, coercivity of 18 Oe and saturation magnetisation of 760 emu cm$^{-3}$. 1 was gradually crystallised with increasing substrate temperatures; the crystallisation temperature was ~200$^\circ$C.

**Pd-Doped Sn–Ag–Cu–In Solder Material for High Drop/Shock Reliability**

Pd was selected as a minor alloying element in a new Sn-1.2Ag-0.7Cu-0.4In solder alloy. Bar solder was made for the tensile test, and solder balls were made for the rod drop impact test. The tensile properties and drop/shock reliability of Sn-1.2Ag-0.7Cu-0.4In-0.03Pd, 1, were compared with those of Sn-1.0Ag-0.5Cu and Sn-3.0Ag-0.5Cu. The UTS, yield strength and elonga-
tion of 1 were superior to those of the other alloys tested. 1 exhibited outstanding drop/shock reliability.

**MEDICAL AND DENTAL**

**Electrochemical Immunoassay for Human Chorionic Gonadotrophin Based on Pt Hollow Nanospheres and Silver/Titanium Dioxide Nanocomposite Matrix**


An electrochemical immunosensor for human chorionic gonadotropin (hCG) assay has been developed. Ag nanoparticles were doped into TiO2 and chitosan colloids to form Ag–TiO2–chitosan nanocomposites. The free amino groups of chitosan were used to attach Pt hollow nanospheres for immobilisation of hCG. Optimal response of the immunosensor was achieved at pH 6.5 and 25ºC with an incubation time of 40 min. The immunosensor exhibited a linear range from 0.5 to 250 mIU ml−1 hCG with a detection limit of 0.26 mIU ml−1 at 3× background noise.

**PHOTOCONVERSION**

**Platinum-Nanoparticle-Loaded Bismuth Oxide: an Efficient Plasmonic Photocatalyst Active under Visible Light**


Bi2O3 loaded with Pt nanoparticles was prepared via a simple photoreduction method. Pt/Bi2O3 was shown to act as a photocatalyst for the decomposition of the pollutants acetalddehyde, formaldehyde and methanol under visible light. The positive conduction band level of Bi2O3, which is able to transfer plasmon-induced electrons from the Pt nanoparticles, plays an important role in the catalytic properties of Pt/Bi2O3.

**Artificial Inorganic Leaves for Efficient Photochemical Hydrogen Production Inspired by Natural Photosynthesis**


Artificial inorganic leaves were developed by organising light harvesting, photoinduced charge separation and catalysis modules (Pt/N-TiO2) into leaf-shaped hierarchical structures using natural leaves as biotemplates. The TiO2 catalyst is doped with nitrogen originating from the plant. Pt nanoparticles were grown on the surface of the artificial inorganic leaf (AIL)-TiO2 by irradiating AIL-TiO2 in 20% aqueous MeOH containing 2 wt% H2PtCl6·6H2O. The enhanced light-harvesting and photocatalytic watersplitting activities exhibited are due to the reproduction of the leaves’ complex structures and self-doping with N.

**SURFACE COATINGS**

**Electrochemical Preparation and Characterization of Thin Deposits of Pd-Noble Metal Alloys**


The electrochemical deposition of Pd-Au, Pd-Pt, Pd-Rh and Pd-Pt-Rh from chloride solutions is described. These deposits were characterised electrochemically in H2SO4 solutions by CV. The surface morphology of the alloys was examined by SEM and STM. The alloy surface composition was investigated in situ by an electrochemical method and ex situ by AES, while the bulk composition was determined by EDX analysis and AAS.
CATALYSIS – INDUSTRIAL PROCESS

Ruthenium Addition to Nickel Catalyst
Johnson Matthey Plc, World Appl. 2010/018,405

A catalyst for hydrogenation and dehydrogenation reactions containing Ru and Ni in a molar ratio of $\left(0.15 \times 10^{-3}\right) - 0.06 : 1$ exhibits superior resistance to deactivation by acidic components in a feedstream compared to standard Ni-only catalysts. A preferred composition is $10 - 40$ wt% Ni and $0.05 - 0.25$ wt% Ru, with the remainder a porous transition alumina support. It can specifically be applied to the hydrogenation of carbonyl compounds such as butan-2-one and $n$-butyraldehyde in a feedstream containing acidic compounds such as $\leq 1$ wt% of a carboxylic acid.

Iridium Catalyst for High-Yield Sertraline Production

A dynamic thermodynamic resolution process for therapeutically active chiral amines such as sertraline consists of: (a) racemising a mixture of amine isomers in solution using an Ir catalyst $\mathbf{1}$; (b) adding a chiral resolving agent such as mandelic acid to allow selective crystallisation and removal of the desired isomer; and (c) returning the unwanted isomers to step (a). The catalyst may be recovered and recycled through reaction of $\text{NH}_3(\text{g})$ with $\mathbf{1}$ to form a solid complex.

Rhodium-Catalysed Production of Formic Acid
Schlumberger Holdings Ltd, British Appl. 2,464,710 (2010)

Formic acid can be produced from $\text{CO}_2$ and $\text{H}_2$ at $\leq 80^\circ\text{C}$ using a Rh catalyst containing a nitrosyl ligand, a bidentate organophosphorus ligand, preferably 1,2-bis(dicyclohexylphosphino)ethane (dcpe), and a halogen, preferably Cl. The catalyst is preferably $[\text{Rh(NO})(\text{dcpe})]\text{Cl}_2$ and TON is typically $>100$. The process is carried out in the presence of an organonitrogen base, specifically 1,8-diazabicyclo[5,4,0]undec-7-ene (DBU), which may also act as solvent, or an additional solvent such as toluene or acetone can be used.

EMISSIONS CONTROL

NOx Storage and Reduction with Enhanced Sulfur Tolerance

A NOx treatment system suitable for low- to mid-temperature operation has a first layer with: $0.1 - 20$ g l$^{-1}$ Pt and optionally Rh; $1 - 100$ g l$^{-1}$ La and/or oxides of La, which impart increased resistance to S poisoning; Ce and/or oxides of Ce; and optionally a heat-resistant inorganic oxide. A second component containing a solid acid is either formed as a second layer or mixed with the first. During rich conditions, stored NOx is reduced by CO, HC or $\text{H}_2$, producing $\text{N}_2$, $\text{NH}_3$ and $\text{H}_2\text{O}$. The second layer then adsorbs the $\text{NH}_3$, releasing it as a NOx reductant under lean conditions.

Platinum-Palladium Catalyst for $\text{H}_2$ SCR of NOx
Linde AG, US Appl. 2010/0,092,360

A catalyst has $0.01 - 2.0$ wt% of each of Pt and Pd, preferably $0.1$ wt% Pt and $0.05$ wt% Pd, on a nanocrystalline support of $50$ wt% MgO and $50$ wt% CeO$_2$. It is formed by wet impregnation from suitable precursors to give highly-dispersed Pt and Pd particles <2 nm in size, and may also have Pt-Pd alloy and oxides of Pt and Pd formed during preparation, calcination or reaction. The catalyst is described to have high activity ($>70\%$ conversion of NO) and $>80\%$ selectivity to $\text{N}_2$ in the SCR of NOx using $\text{H}_2$ as reducing agent, at low temperatures ($100 - 400^\circ\text{C}$) and in the presence of $2 - 10$ vol% $\text{O}_2$, making it ideal for stationary industrial applications.
FUEL CELLS

Controlled Synthesis of Platinum-Cobalt Nanoparticles
Honda Motor Co, Ltd, World Appl. 2010/014,500
Pt-Co nanoparticles for cathode catalysts are prepared by heating a mixture of: (a) a Pt precursor such as Pt(acac)₂; (b) a Co precursor such as Co₂(CO)₈; (c) a capping component, preferably oleic acid and/or oleylamine; and optionally (d) a reducing agent such as 1,2-hexadecanediol. Particle size is controlled by varying the concentration of (c) relative to the total concentration of (a) + (b). Particles ~1–5 nm in diameter are formed in the presence of solvent and particles ~6–12 nm in size are formed in its absence.

APPARATUS AND TECHNIQUE

Durable Palladium Membrane
NGK Insulators Ltd, European Appl. 2,156,883 (2010)
A 0.1–10 µm-thick Pd membrane and its use in a selectively permeable membrane reactor for H₂ production is claimed. Membrane composition is 40–90 wt% Pd with added metals A and B, independently selected from: Rh, Ir, Ag, Au, Co, Ni, Cu such that: A and B each form a complete solid solution with Pd, the A-B phase diagram has a triple point, and A and B do not form an intermetallic compound.

Platinum-Catalysed Hydropyrolysis of Steroids for Facilitated Detection
Imperial Innovations Ltd, European Appl. 2,157,434 (2010)
A mass spectrometry method for reliably measuring the ratio of ¹³C to ¹²C, indicative of natural or synthetic origin of a compound present in a urine sample for example, involves first hydropyrolysis at <350ºC in the presence of a catalyst selected from Pt, Pd, Rh or Ir, preferably Pt. The catalyst may be metallic or deposited at 1–20 wt% on a support which also adsorbs the products of hydropyrolysis. These products are fully deconjugated and can be purified by gas chromatography without the need for further derivatization.

Iridium Vessel for Melting X-Ray Opaque Glass
A process for preparing a novel, high-melting glass composition is claimed, using a melting vessel of solid Ir or Ir alloy (preferably ≥95 wt% Ir) and heating by high-frequency electromagnetic radiation (50 kHz to 2 MHz) to achieve melting temperatures of ≥1500ºC (preferably ≥1600ºC). The glass, which can be used in dental restorations, contains 0.1–25 mol% Yb₂O₃, rendering it X-ray opaque and therefore suitable for use with imaging techniques.

ELECTRICAL AND ELECTRONICS

Reflective Mask with Ruthenium-Niobium Layer
Hoya Corp, US Appl. 2010/0,084,375
A reflective mask blank for use in extreme UV lithography (EUVL) contains a 0.8–5.0 nm-thick RuNb protective film between the multilayer reflective film and the buffer film. For optimal chemical resistance, the RuNb compound is preferably 70–85 at% Ru and 15–30 at% Nb. During patterning of the buffer film using an etching gas containing O₂ and optionally Cl₂, an oxidised layer containing predominantly Nb forms on the protective film and prevents etching damage to the reflective film.

Lead-Free Thick Film Resistor Paste
Sumitomo Metal Mining Co, Ltd, Japanese Appl. 2010-015,844
A BaIrO₃ conductive powder suitable for use in a resistive paste with Pb-free glass frit and an organic medium or vehicle is prepared by: (a) calcining a precursor such as (NH₄)₂IrCl₆ to yield IrO₂; (b) calcining the IrO₂ powder with BaCO₃, Ba(NO₃)₂ and/or BaO powder at 650–1000ºC in air to produce BaIrO₃; (c) grinding the BaIrO₃ to give particles with 20–100 nm mean diameter; and (d) calcining again at 400–650ºC in air to adjust mean diameter to 40–100 nm for ideal, low-noise resistivity characteristics.

ELECTROCHEMISTRY

Lithium-Ion Battery Anode Grown on Platinum Substrate
Toyota Motor Corp, Japanese Appl. 2009-295,514
An anode for a rechargeable Li-ion battery is formed by vertically orientating the (003) plane of a LiCoO₂ single crystal on the (110) plane of a single crystal metal substrate, either Pt or Au. The lattice spacing of the substrate is close enough to that of the LiCoO₂ to allow the film to be grown epitaxially by pulsed laser deposition. This formulation is described as facilitating migration of Li⁺ ions within the anode, potentially allowing easier recharging and higher power output.
MEDICAL AND DENTAL

Targeted Delivery of Platinum(IV) Anticancer Complex
A pharmaceutical composition has a Pt(IV) anticancer compound, 1, mixed with protective excipients such as saccharides or peptides and optionally a lubricant or disintegrant, contained in a tablet or capsule for oral administration. The capsule is coated with a biodegradable layer and/or a pH-sensitive layer formulated to dissolve in the colon, allowing effective delivery of 1 to the site of colorectal carcinoma in doses of 5–500 mg, preferably 50–350 mg.

PHOTOCONVERSION

Homoleptic Platinum Complex for WOLEDs
Univ. North Texas, World Appl. 2010/016,990
Square planar complexes M(N^N>N)2, where M is Pt, Pd or Ni and N^N>N is a bidentate anionic ligand, preferably a triazolate, are claimed for use in the emissive layers of OLEDs, particularly white OLEDs (WOLEDs), and as the n-type material in organic thin film transistors used in complementary metal-oxide-semiconductor (CMOS) devices. A preferred complex, 1, has excellent colour stability even at high luminance and superior photoluminescent properties, allowing improved efficiency in these devices.

Iridium-Doped Phosphor
Kuraray Luminas Co, Ltd, US Appl. 2010/0,032,628
A phosphor is produced by firing a Group 12–Group 16 compound semiconductor such as ZnS, ZnSe, CdS or CdSe with an Ir compound such as IrCl3, (NH4)2IrCl6 or (NH4)2IrBr6 and optionally S and a flux. Firing is preferably accomplished using a ≥0.1 GPa shock wave to rapidly heat the mixture to reaction temperature, with subsequent rapid cooling, to allow Ir to disperse uniformly in the phosphor for optimal efficiency. Ir content is preferably 10–8,000 ppm, with the amounts of Ir contained within the phosphor and on the surface not varying by more than 5% relative to each other.

REFINING AND RECOVERY

Reuse of Ruthenium from Manufacturing Waste
Air Liquide, World Appl. 2009/122,240
Recovery and purification of RuO4, used as a precursor in the manufacture of semiconductor devices, is accomplished by: (a) heating the gaseous waste stream in a vessel at 50–800°C and 0.01–1000 torr, optionally in the presence of a Ru or RuO2 catalyst, to convert the RuO4 to a lower oxide in solid form; (b) reducing this with H2 to Ru metal with a specific surface area of >1.0 m^2 g^(-1), preferably ~7.0 m^2 g^(-1); (c) oxidising the metallic Ru using at least one of NO, NO2, O2, O3 or plasmas thereof to give RuO4; and (d) purifying this secondary stream to ≥99.9% RuO4 through distillation for reuse.
The Use of Metal Scavengers for Recovery of Precious, Base and Heavy Metals from Waste Streams

Introduction
A recent Final Analysis article discussed the use of Smopex® metal scavengers for the removal of residual palladium from synthesised products in the fine chemical and pharmaceutical industries (1). However, the use of Smopex® is not limited to scavenging precious metals to purify final products; it can also be used to clean up base and heavy metals from waste streams, particularly in areas where legislation dictates limits on the metal content of effluent.

Smopex® (Figure 1) is a fibrous metal scavenger which can selectively recover metal dissolved in solution, down to extremely low levels (parts per billion) (Figure 2). The fibres can be used mid-process or in a final step to recover metals from process waste streams prior to discharge to effluent. The fibres can be used at temperatures up to 120°C, where metal recovery is often more effective, and are non-hazardous.

Recovering Metal Value
The waste stream from an industrial process is often forgotten in the focus on optimising the process itself. In many cases the bulk of a spent platinum group metal (pgm) heterogeneous catalyst material can simply be filtered off and sent for refining to recover the pgm. However, there may also be small amounts of pgm which remain in solution at levels which are not economic to refine, and are thus lost to effluent. Such losses can accumulate over time, to the point where kilogram amounts of pgm may be unaccounted for.

All metal used in industry has a value, and this is particularly true of precious metals including the pgms. The value of pgm lost over time can be considerable, and further costs are incurred when the metal catalyst or salt must be 'topped up' to replace the losses in order to maintain the efficiency of the process.

Once it has been established that metal needs to be recovered from the effluent, there are a number of options, usually involving processing off-site. For example pgms can be recovered by reduction using reagents such as sodium borohydride or hydrazine.
although hydrazine is becoming less acceptable for use in industry due to its hazardous properties and handling issues.

The cost of transporting large volumes of waste solution containing small amounts of pgm can negate the benefit that can be achieved from refining it. In some cases there may be hazards associated with transport of certain substances contained within the mixture. Therefore it is desirable to concentrate the pgms to a level at which recovery via standard refining becomes possible. This can be achieved using Smopex® fibres, as they can selectively recover the pgms into a form that is suitable for use with standard refining processes.

In this way worthwhile quantities of pgms which would otherwise be lost to effluent can be recovered, as the following example illustrates.

**Case Study 1: Recovery of PGMs from Refining Waste**

A large-volume corrosive waste stream containing <10 ppm total pgms was being generated from a metal refining process. The waste stream had a hydrochloric acid (HCl) matrix with a pH of 1, and the metal content predominately consisted of base metals (iron, nickel and zinc) plus silver, with a combined total of <10 parts per million (ppm) of platinum, palladium, rhodium, iridium and ruthenium. Due to the high-throughput nature of the process, Smopex® was installed as part of the continuous process flow rather than separately in a batch reactor, to allow for the high flow-rate while still maintaining sufficient contact time with the fibre for metal recovery to occur. Laboratory test results are shown in Figure 3.

Due to the nature of the process, there was continual variation in the metals that were present and their concentration in the effluent stream. In order to facilitate recovery, a Smopex® fibre mixture was specifically developed to allow for the inconsistent nature of the stream. Smopex® has successfully recovered more than $1.5 million (US$2.2 million) worth of pgms from this process in the last two years. This metal could not have been economically recovered in the past and would potentially have been lost to effluent.

**Environmental Benefits**

Where base or heavy metals such as arsenic, lead or manganese are involved, the driver behind metal recovery is environmental (2–4). Increasingly strict limits are being imposed by legislation in regions such as the USA (2) and Europe (3) regarding the levels of metal that can be present in effluent that is

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**Fig. 3. Laboratory test results showing the rates of recovery of various platinum group metals and silver from a mixed metal effluent stream based on an aqueous hydrochloric acid solution, using Smopex®-105 at 20°C**
discharged into the environment. This means that very dilute aqueous streams may have to be tankered away for disposal, which is both costly and potentially hazardous. In addition, the method of disposal of this ‘contaminated’ material is still an issue.

In such cases, Smopex® fibres can be used at the end of the process to remove the base or heavy metals, producing a cleaned up effluent that can potentially be released directly from the site. This approach has advantages in reducing the volume of waste material which must be transported, as well as allowing the heat generated by the process itself to aid recovery on site. If necessary, more than one metal species can be recovered by tailoring the Smopex® fibre mix accordingly.

Metals can also be selectively recovered from waste which would be hazardous to transport to a refining site, and this is particularly useful where precious metals are present, as illustrated in the example below.

**Case Study 2: Hazardous Material Not Suitable for Shipping**

As the result of an oxo-alcohol manufacturing process, a harmful organic sidestream was being produced that was hazardous for transport, but contained significant amounts of pgm (<500 ppm rhodium). After screening, the most selective Smopex® fibres were chosen. These showed great affinity for the rhodium complex to be recovered at an elevated temperature (~90°C), and were particularly suited to the organic nature of the material. Achieving pgm recovery on site meant that the remaining hazardous material was easily treated in situ, reducing the need for handling or transport. The Smopex® treatment resulted in a recovery of 99% of the residual rhodium present in the waste stream.

**Conclusions**

Effluent which contains low concentrations of metals presents a problem in terms of both metal cost, particularly in the case of pgms, and the environment, in the case of base or heavy metals. One way to solve both types of problem is by using metal scavengers such as Smopex®, which can be applied on site as part of a batch or continuous process to recover pgms for refining or to remove base and heavy metals, leaving a cleaned up effluent suitable for direct discharge or further treatment as required.

JOANNE FRANKHAM and PASI KAUPPINEN

**References**


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