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

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Editorial

A New Look for the Platinum Metals Review Website

The Platinum Metals Review website now has a new design, launched in October 2011.

The new website offers:
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• Improved navigation to the articles you want
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The website and all its features are available at: www.platinummetalsreview.com.

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2010 Impact Factor

Platinum Metals Review now has an Impact Factor for the first time in its history. This is a measure of the average number of citations for articles published in the Journal, and is reported annually by Thomson Reuters, one of the leading sources of information for businesses and professionals, as one of the evaluation tools provided by its Journal Citation Reports® service. Our Impact Factor for 2010 is 2.543, a respectable value for a multidisciplinary Journal with an emphasis on chemistry.

Congratulations to our authors, peer reviewers and readers who have helped make this achievement possible. By submitting your work to Platinum Metals Review you will help to ensure that we maintain the high quality of the journal and continue to enhance the visibility of your research.
High Temperature Strengthening Mechanisms in the Alloy Platinum-5% Rhodium DPH

Investigation of dispersion strengthened platinum alloy for high temperature applications

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To improve the high temperature properties, platinum can be hardened by solid solution and/or oxide particles. The investigated alloy, dispersion hardened platinum-5% rhodium (Pt-5%Rh DPH), was produced via melting and subsequent annealing of the semi-finished product in order to obtain an oxide particle dispersion. Despite the relatively large oxide particles formed in this process, the creep strength is much higher in comparison to conventional Pt-5%Rh. The aim of this paper is to study the strengthening mechanisms in the alloy Pt-5%Rh DPH by transmission and scanning electron microscopy. The size distribution of oxide particles shows a bimodal distribution, and the average oxide particle diameter is 315 nm for particles larger than 150 nm. For particles between 25 nm and 150 nm, the average diameter is 49 nm. The size ranges of oxide particles are not substantially affected by high temperature creep deformation, but particles of <25 nm evolve during high temperature creep. It was found that all particles of different size ranges interact with dislocations and hence contribute to the strengthening of Pt-5%Rh DPH. Dislocation forests are pinned on the surface of oxide particles larger than 150 nm in diameter. Dislocation pile ups form between particles with a size range of about 500 nm. Medium size and small particles of diameters between 50 nm and 10 nm act as obstacles to single dislocations through backside pinning.

Introduction
Platinum-rhodium alloys can be used under high chemical, mechanical and thermal loadings due to the high melting point of platinum (1770°C), and its exceptional corrosion and oxidation resistance up to high temperatures. The creep strength of platinum materials is improved by solid solution hardening and/or by oxide dispersions (1). For strengthening by solid solution the elements rhodium and iridium
are added. Besides the hardening effect, the melting point is also raised. A fine dispersion of oxide particles in the metallic matrix may also improve creep strength (2–5).

Most platinum fabricators offer oxide dispersion strengthened platinum alloys (ODS alloys). The production of ODS alloys is based on various principles. Several authors (4,6) describe the mechanical alloying of platinum powder with zirconia and/or yttria powders. A wet chemical coprecipitation of a platinum and zirconyl chloride powder can also produce a fine metal ceramic powder mixture (7). In both cases a subsequent powder metallurgical processing results in semi-finished products.

An alternative preparation route to disperse fine oxide particles is the internal oxidation of a platinum alloy containing elements with a high oxygen affinity (8). However, the complete internal oxidation of semi-finished platinum products was long considered to be unlikely because of the limited solubility and diffusivity of oxygen in platinum. Hence, the internal oxidation of semi-finished platinum products would require very long times for the heat treatment which would involve strong grain growth in the inner and not yet oxidised material as well as oxide formation at the grain boundaries. Both effects are considered to cause brittleness. To overcome these difficulties the volume of the oxidised material is reduced, and measures to accelerate the internal oxidation are taken. A possible manufacturing route is the internal oxidation of powder or turnings of Pt-Zr alloys in air and again a subsequent powder metallurgical processing to semi-finished products (9). Fine liquid drops of a platinum alloy with reactive constituents may already be internally oxidised during a spray process of the molten alloy in a cold mould in an oxidising atmosphere (10). The ingot is then worked down to products like wires or sheets. Thin foils of a Pt-Zr alloy can be internally oxidised reasonably quickly at higher temperatures in air. A stack of these thin internally oxidised foils can subsequently be welded together to form sheet material by hot rolling (11).

W. C. Heraeus GmbH developed a family of ODS platinum materials called DPH. In a first production step zirconium, yttrium and cerium are added to a platinum melt in elemental form and the molten alloy is cast to ingots. During a subsequent operation semi-finished products, like sheets, tubes and rods, are annealed in an oxidising atmosphere leading to the internal oxidation of the bulk platinum alloy. The internal oxidation leads to the formation of finely dispersed oxide particles of the elements with high affinity for oxygen, i.e. Zr, Y and Ce (12, 13). The fundamental differences to the internal oxidation processes described above are that large volumes of semi-finished platinum parts are internally oxidised in short times and no powder metallurgical processes are involved.

These DPH materials overcome the disadvantages of previously known ODS materials produced by powder metallurgy for example the difficulties in fabrication, especially in welding, and their limited ductility (14). Furthermore these materials show a great improvement of the creep properties in comparison to the solid solution hardened Pt-Rh and PtIr alloys (14). This is remarkable, since the mean particle size, as known so far, is bigger than that obtained via the powder metallurgical route and exceeds the value for optimal strengthening given by Bürgel (15). The mechanism of strengthening by oxide particle dispersion is the interaction between particles and dislocations as discussed in the present paper (1, 16–20). The Pt-5%Rh DPH alloy was developed as an alternative material to the widely used Pt-10%Rh DPH alloy mainly for applications in the glass industry as fibre bushings, plungers and stirrers with reduced Rh content, due to the steadily increasing Rh price (21).

In this work we focus on the investigation of creep deformed Pt-5%Rh DPH sheets using scanning electron microscopy (SEM) and transmission electron microscopy (TEM) to study the strengthening mechanisms.

**Experimental**

The material investigated was Pt-5%Rh DPH produced by Heraeus and containing up to 1 wt% Zr, Y and Ce (13). The creep specimens were wire cut from a 0.87 mm thick sheet which had undergone a standard thermomechanical finishing process. Creep tests were carried out at 1600ºC under a load of 5 MPa in air using a tensile creep test device developed in-house (22–24). To analyse the microstructure and especially the evolution of the dislocation structure, the creep tests were interrupted after different time periods. TEM samples were prepared from the crept specimens by mechanically grinding and successive electrochemical twin-jet polishing with a dilute aqueous potassium cyanide solution at 18ºC and 30 V until a hole appeared in the sample.
All SEM images were acquired using a ZEISS 1540EsB CrossBeam® workstation. The particle size distribution was determined from SEM images of the ground and polished TEM samples, where at least ten images with an average number of 170 particles per image were measured. The area fraction method was used.

All TEM investigations were carried out with a ZEISS Libra 200 FE equipped with an OMEGA energy filter. Measurements using energy filtered transmission electron microscopy (EFTEM) (25) were performed to investigate the local distribution of elements. This method is based on electron energy loss spectroscopy (EELS) in combination with imaging in the TEM using inelastic processes of inner-shell electron excitations. The advantage of EELS and EFTEM measurements is the high spatial resolution of below 1 nm and high energy resolution of about 1 eV (26, 27).

Results
Tensile Creep Testing
The first specimen ruptured after 17 h creep at 1600ºC under a load of 5 MPa in air (Figure 1). On the basis of this creep curve, it was decided to perform additional creep tests and interrupt these (fast cool down under load) after 1 h and 8 h respectively in order to investigate the change in the microstructure.

The observed decrease in strain after about 1 h during the 1 h and 17 h creep tests was thought to be due to poor temperature control. A change in the specimen surface caused a variation of its emissivity. Because a pyrometer was used, the actual temperature of the specimen was therefore higher than measured in the early creep stage, leading to thermal strains which add to the creep strains shown in Figure 1. The temperature control of the sample interrupted after 8 h creep deformation was more accurate, so that no thermal strains were added during the first creep stage. Specimens of the ruptured sample and the sample interrupted after 8 h high temperature creep were used for TEM analysis.

SEM Investigations of the Oxide Particle Distribution
The oxide particle distribution is important for the high temperature strength properties (16). This includes both the location and size distribution of the oxide particles. Due to the thermomechanical finishing process the microstructure consists of elongated, aligned grains with an average grain aspect ratio of 5 (Figure 2(a)). In Figure 2(b) the local distribution of the oxide particles is shown. Large oxide particles are primarily situated at the grain boundaries, whereas finely dispersed particles can be found inside the

Fig. 1. Creep curves of Pt-5%Rh DPH tested at \( T = 1600^\circ \text{C} \) under a load of \( \sigma = 5 \text{ MPa} \) in air
grains. This can be traced back to the production route of internal oxidation, as the oxygen solubility and the nucleation rate is higher at the grain boundaries than inside the grains (28).

**Figure 3** shows the size distribution of particles (particle count) inside the grains for Pt-5%Rh DPH in the as received condition. The oxide particles inside the grains show a bimodal size distribution. The maximum of 60% for the particles smaller than 150 nm falls in the range between 25–50 nm with an average diameter of 49 ± 22 nm. Particles with diameters smaller than 25 nm can hardly be resolved in the SEM and are therefore neglected in the description of the particle size distribution. For particles larger than 150 nm, 65% have diameters between 150–300 nm and the average diameter is 315 ± 34 nm. The average particle diameter increases to 342 ± 26 nm for the ruptured sample after 17 h creep deformation, but is within the scatter of the measurements. The initial average size of oxide particles is therefore smaller than for the Pt DPH alloy reported by Vorberg et al. (29).

Particles with diameters smaller than 25 nm could not be found either on SEM or on TEM micrographs of Pt-5%Rh DPH in the as received condition. However, particles with diameters of <25 nm are present in the ruptured sample and contribute to the strengthening of the Pt-5%Rh DPH alloy, as shown in the following section.

**Fig. 3.** Size distribution of oxide particles in Pt-5%Rh DPH as received; the small insert shows the size distribution of oxide particles from 25 to 150 nm

**Fig. 2(a).** Microstructure of the Pt-5%Rh DPH alloy after thermomechanical treatment; (b) location distribution of the oxide particles inside the grains and on the grain boundaries of the area indicated by the white rectangle of Figure 2(a)
TEM Investigations of Particle–Dislocation Interactions

After 8 h of creep deformation at 1600°C dislocation pile-ups are observed on oxide particles with diameters above about 500 nm in the Pt-5%Rh DPH sample (Figure 4). The Burgers vector was determined using the $\mathbf{g} \times \mathbf{b} = 0$ criterion ($\mathbf{g}$ = diffraction vector, $\mathbf{b}$ = Burgers vector) (30). Under two different two-beam conditions the Burgers vector in the pile-up was determined to be $\pm a/2[01\bar{1}]$ ($a$ = lattice parameter). All dislocations in a pile-up have the same Burgers vector, hence forming a low angle grain boundary.

Small particles are invisible under the two-beam bright-field (BF) condition, but can be resolved under weak-beam dark-field (WBDF) conditions (Figure 5). The reason is that under weak-beam conditions the thickness of dislocation lines is smaller and the contrast is higher, because only the part of a dislocation with the biggest strain field (the dislocation core) contributes to the contrast (31, 32). Thus the weak-beam method is a useful tool to investigate the interaction mechanisms between dislocations and particles (33).

Strong bowing of dislocations around oxide particles with diameters of less than 10 nm is observed in Pt-5%Rh DPH after 8 h high-temperature creep, indicating a pinning of dislocations at the incoherent interface between matrix and particles (positions A in Figure 6). Dislocations obviously do not shear these incoherent, medium sized particles but climb over them (Figure 7(a)), followed by backside pinning at the interface between matrix and particle (Figure 7(b)). According to Arzt and Rösler (34, 35), the detachment of the dislocation from the particle is the decisive step slowing down dislocation movement, hence increasing creep strength. Bypassing of the particles by the Orowan mechanism (15) is not seen.

The pinning of a dislocation on the backside of an oxide particle with a diameter of less than 10 nm immediately before being detached is clearly resolved in the WBDF image of Figure 6 at position B. This indicates that the dislocation is immobilised by an attractive force after completing the climb process over the particle. Additional energy is therefore required to detach the dislocation from the matrix/particle interface, contributing to the creep strength of Pt-5%Rh DPH (35). A particle of less than 10 nm in diameter, not connected with a dislocation, can be seen at position C in Figures 6(a) and 6(b). To prove that the bright areas in WBDF images and the corresponding dark areas in BF images with diameters in the range of 10–25 nm are particles, EFTEM measurements were carried out. The EEL spectra of Figure 8(b) were extracted from a series of 21 energy filtered images acquired in an energy loss window from 127–207 eV. The EEL spectrum extracted from point 1 in Figure 8(a) clearly shows the Y-M45 and Zr-M45 edges proving the presence of an
Y and Zr containing particle, most likely a Zr/Y mixed oxide. To exclude effects from dislocation contrast on the acquired energy filtered images, a second spectrum was extracted from point 2 in Figure 8(a). The corresponding EEL spectrum in Figure 8(b) shows no absorption edges.

The observed interaction mechanisms of dislocations with oxide particles are in agreement with observations made by Häussler et al. (18) and Bartsch et al. (36) for ODS nickel-base superalloys. Also a comparison with the ODS NiAl alloy investigated by Behr et al. (20) and the alloy Inconel MA 754...
investigated by Nardone et al. (37) confirm the strengthening mechanisms observed in the examined Pt-5%Rh DPH alloy.

Conclusions

The Pt-5%Rh DPH alloy shows an elongated grain structure after the thermomechanical finishing process. Scanning electron microscopy reveals oxide particles of diameters larger than 1 μm at grain boundaries. In the as received condition a bimodal particle size distribution is found inside the grains. The average particle diameter of the initial state is 315 nm and remains almost unchanged after high temperature creep deformation for 17 h. This observation is in contrast to measurements carried out by Vorberg et al. (29) in Pt DPH, where the average particle diameter increases from 400 nm to 550 nm after 10 h creep deformation at 1600°C. Particles with diameters of less than 25 nm could not be found in the alloy as received. However, imaging and electron spectroscopy analysis clearly demonstrates that oxide particles of less than 25 nm in diameter are present in the alloy after 8 h and 17 h creep at 1600°C. Hence, this very fine fraction of oxide particles evolves during creep and interacts with dislocations, hindering their movement through backside pinning.

Various mechanisms slowing down creep deformation of Pt-5%Rh DPH at 1600°C have been confirmed. It has been shown that dislocations interact with oxide particles of all sizes as follows:

- Dislocation pile-ups forming low angle grain boundaries are found at oxide particles with diameters above about 500 nm.
- Dislocations organised in forests are pinned at the surfaces of oxide particles in the range of 150–500 nm.
- Medium sized oxide particles around 50 nm force non-conservative dislocation climb followed by backside pinning.
- Kinked dislocations indicate that very small particles below 25 nm also pin dislocations.

The observed dislocation interactions with oxide particles of all size ranges are in general agreement with observations in Pt DPH (29). However, the stress to rupture of the Pt-5%Rh DPH alloy during creep testing at 1600°C is higher than values measured for Pt-10%Rh, Pt DPH and Pt-5%Au DPH (38). In comparison to Pt DPH, the higher creep strength is believed to originate from a larger fraction of oxide particles with diameters of less than 150 nm in Pt-5%Rh DPH than found in Pt DPH (29). In general, the observed strengthening mechanisms by the oxide particles of different size ranges lead to the deceleration of creep deformation of Pt-5%Rh DPH at 1600°C compared to pure Pt and solid solution strengthened Pt-5%Rh and Pt-10%Rh.

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“Proton Exchange Membrane Fuel Cells: Materials Properties and Performance”

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Introduction

This book is part of the series “Green Chemistry and Chemical Engineering” published by CRC Press. The series aims to meet the challenges of the 21st century in chemistry and chemical engineering by detailing the development of alternative sustainable technologies. The present volume focuses on providing updated, detailed background information on key developments in material properties and performance for proton exchange membrane fuel cells (PEMFCs). Although PEMFCs are currently at an early commercialisation stage, and moving into volume commercialisation, significant technical challenges still remain. These include reliability, durability, cost, operational flexibility, technology simplification and integration.

The book’s chapters are divided between the major components of the unit fuel cell, including: platinum group metal (pgm) catalysts, catalyst layers (CLs), membranes, diffusion layers, bipolar plates and materials modelling. This selective review covers the chapters on pgm electrocatalysts, CLs and diffusion layers.

Chapter 1: ‘Recent Developments in Electrocatalyst Activity and Stability’

This chapter, by David Thompsett (Johnson Matthey Technology Centre, Sonning Common, UK), is successful in providing an overview of the wide range of electrocatalyst topics associated with hydrogen, reformate and direct methanol fuelled-PEMFCs. The chapter highlights the key aspects by means of examples, rather than attempting a comprehensive study of all areas. The chapter is subdivided into sections on pgm electrocatalyst discovery (combinatorial and computational approaches), preparation (conventional and more novel approaches) and testing (Figure 1), followed by...
detailed sections on the activity and stability of cathode oxygen reduction catalysts based on pgms. Finally there is a section on anode catalysts for hydrogen oxidation, reformate and direct methanol applications. Different types of non-carbon and carbon supports and the modification of carbon supports are also described, along with an overview of the mechanisms of support degradation and materials-based mitigation strategies.

There is a strong focus on materials composition and preparation aspects and how these are linked to performance and stability. Although less detail is provided on mechanistic aspects in some sections, clear references are made to recent reviews elsewhere. A wide range of catalyst preparation strategies are described, defined as conventional, colloidal, molecular precursor and surface modification.

Chapter 2: ‘Catalyst Layers and Fabrication’

This chapter by Zhong Xie et al. (National Research Council of Canada Institute for Fuel Cell Innovation, Vancouver, British Columbia, Canada) provides an overview of the main types of CL used in PEMFCs. It is mainly directed at hydrogen-fuelled systems, rather than direct methanol fuel cell (DMFC) or other variants. After a general introduction, the chapter is organised into a description of the components of the CL and their functions; a description of the main types of CL; fabrication methods for the CLs and finally a section on their optimisation. Only platinum-based catalysts are considered, but several forms are covered, for example, unsupported (Pt black), carbon-supported and various directly deposited types (sputtered, electrodeposited, etc.) (Figure 2). In

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**Fig. 1(a).** Restored high-resolution transmission electron micrograph of a 6 nm Pt particle supported on carbon; (b) the best-fitted simulation; and (c) the three-dimensional atomic model used to calculate (b) are also shown (Copyright 2010. Reproduced by permission of Taylor and Francis Group, LLC, a division of Informa plc)
terms of ionomers, Nafion is dominant, with a short section on non-perfluorosulfonic acid (non-PFSA) ionomers, but there is little reference to other fluoro-polymer ionomers.

The writing is mostly clear, although there are several typographic errors, and sufficient references are included for those wanting more information. The chapter is not intended to be comprehensive and will suit those looking for a short introduction to this technology area. It is very similar in scope to Litster and McLean’s chapter ‘PEM Fuel Cell Electrodes’ in “Fuel Cells Compendium” (1), and contains a number of the same examples. Quite a wide range of different fabrication techniques are covered from well established ink-based methods to more recent vacuum and laser deposition techniques.

Little analysis is provided on how the CLs function in practice or what the mechanistic effects are of changes in structure and composition. For a detailed analysis of PEM CLs, the chapter ‘Principles of MEA Preparation’ by Shyam Kocha in the “Handbook of Fuel Cells” (2) is recommended, or the book “PEM Fuel Cell Electrocatalysts and Catalyst Layers” edited by Zhang (3).

**Chapter 4: ‘Diffusion Layers’**

Chapter 4 is a contribution from Mauricio Blanco and David Wilkinson (National Research Council of Canada Institute for Fuel Cell Innovation, Vancouver, British Columbia, Canada) and it covers the design, manufacture and fuel cell performance of the diffusion layers in hydrogen- and methanol-fuelled PEMFCs.

After a brief introduction to the purpose of the diffusion layer and the driving forces for improvement, the structures of the various types of diffusion layer are discussed. The conventional carbon-based materials are covered, but more interestingly there are significant sections covering less common approaches, namely metal layers and the use of semiconductor fabrication techniques. As the authors admit, there is frustratingly little comparison between the fuel cell performance of the more exotic layers with the conventional carbon-based technology, but this not an omission; merely an accurate reflection of the state of the literature. There is more comparison of the relative merits of carbon papers and cloths during which, presumably due to the requirement for brevity, there is a tendency for generalisations to be made, based on limited and sometimes quite old literature. This might not reflect the current practice in the industry, but as the references are all provided the more sceptical reader can follow up the points of interest. The lengthy section on microporous layers is a good survey of this often neglected feature of the diffusion layer. The concluding section on characterisation techniques is

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**Fig. 2. Schematic of the hydrogen fuel cell architecture using an ultra-low platinum loading thin-film Pt/MWNT (carbon multiwalled nanotube) catalyst layer (Copyright 2010. Reproduced by permission of Taylor and Francis Group, LLC, a division of Informa plc)**
a useful compilation of the relevant properties of the layers and ways of evaluating them.

This chapter is well written and is extensively referenced with 279 citations. It is a useful introduction to those interested in starting work in this field as well as an extensive literature review for the more experienced practitioner.

Conclusions
Overall, these chapters of the book provide a useful short introduction suitable for new workers entering the field, together with extensive literature reviews for those looking for more detail on the topics under discussion. The developments that have taken place in the area of fuel cell catalyst materials and properties will provide the background to increase the competitiveness of PEMFCs as one of the long term solutions to reduce reliance on fossil fuels and improve energy sustainability, security and efficiency. New materials, improvements in pgm-based catalysts and the associated engineering design and modelling are closing the technical gaps which will enable this to happen.

References

Sarah Ball, who reviewed Chapter 1, is a Principal Scientist in the Fuel Cell Research Group at the Johnson Matthey Technology Centre (JMTC), Sonning Common, UK. She is interested in anode catalysis for reformate-tolerant materials and pgm-containing alloys for PEMFCs.

Jonathan Sharman, who reviewed Chapter 2, is Fuel Cell Research Manager at JMTC and leads a group carrying out research into membrane electrode assemblies (MEAs) for PEMFC, DMFC and phosphoric acid fuel cell (PAFC) systems. With a background in materials science and electrochemistry, he has been active in fuel cell research for over nine years and is coauthor of a number of patents and papers on PEMFC MEAs.

Ian Harkness, who reviewed Chapter 4, is a Principal Scientist in the Fuel Cell Research Group at JMTC, where he has worked for more than ten years on the development of MEAs for both hydrogen- and methanol-fuelled PEMFCs.
“Medicinal Organometallic Chemistry”

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Introduction
The Topics in Organometallic Chemistry series from Springer presents critical overviews of research results in organometallic chemistry, covering a broad range of topics in pure and applied organometallic chemistry. The theme of Volume 32 in this series, “Medicinal Organometallic Chemistry”, is the potential medical applications of organometallic compounds. Edited by Gérard Jaouen and Nils Metzler-Nolte, this book describes recent advances in the design, synthesis, mechanistic understanding and medical application of organometallic compounds.

Medicinal Organometallic Chemistry
This volume encompasses the medicinal organometallic complexes of iron, titanium, technetium and gold among other metals; however this review will focus on those chapters featuring the platinum group metals (pgms). The discovery of the anticancer properties of cisplatin was arguably one of the major discoveries for anticancer chemotherapy in the twentieth century and now platinum anticancer drugs feature in multiple chemotherapy regimens (1). Though cisplatin is a simple inorganic complex (cis-PtCl$_2$(NH$_3$)$_2$), it has had a major impact on all aspects of inorganic medicinal chemistry including organometallic medicinal chemistry. The mechanism of action of cisplatin is believed to be the formation of DNA intrastrand crosslinks. Much of the early work on metal-based compounds focused on their interaction with DNA. However, it is now increasingly apparent that many metal complexes with potential antitumour activity do not behave like cisplatin, and it has been proposed that we should move away from the ‘platinum paradigm’ by developing drugs based on other metals such as ruthenium which have a different mechanism of action (2, 3) (Figure 1). Another apparent misconception is that organometallic compounds are too unstable to be useful as drugs, but
many organometallic compounds are now being developed that are stable under physiological conditions. These concepts are exemplified by many of the contributions in this book.

Ana Pizarro et al. (University of Warwick, UK) take up these themes in the second chapter by reviewing the activation mechanisms of organometallic complexes with potential anticancer activity. The hypothesis is that their cytotoxic activity towards cancer cells is based upon the substitution of one or more of the metal ligands by the biological target molecule. The first step in this substitution reaction is hydrolysis to form an aqua complex, followed by a second substitution with the target biomolecule. However, it is essential to control the aqueous reactivity to prevent potential complex hydrolysis reactions. A series of ruthenium- and osmium-arene complexes have been designed to interact differently to the platinum drugs with DNA. These compounds consist of an arene ligand, a neutral chelating ligand and a monoanionic ligand, forming a ‘piano-stool’ structure (Figure 2). The arene ligand and the chelate ligand provide stability to the structure, while the monoanionic ligand provides potential for substitution reactions with biomolecules. The choice of suitable ligands can control the thermodynamic and kinetic stability of the molecules, and hence their biological activity. These compounds are designed to interact with DNA in a bifunctional manner by both intercalation and direct metallation.

Various ruthenium complexes have demonstrated antitumour activity in preclinical studies and it is apparent that for many of these the primary biological target is not DNA. Angela Casini et al. (École Polytechnique Fédérale de Lausanne, Switzerland) describe in the third chapter the biological target of Ru-arene compounds with the formula \([\text{Ru(η}^6\text{-arene})\text{Cl}_2\text{(pta)}]\) (pta = 1,3,5-triaza-7-phosphatricyclo[3.3.1.1]decane), named RAPTA compounds. Interestingly, in mouse cancer models these compounds are able to inhibit tumour metastasis without affecting the growth of the primary tumour. This has led to a search for alternative biological targets, with a focus on two enzymes: thioredoxin reductase and cathepsin B, both of which contain cysteine in their active site. Though in general RAPTA compounds were found to be weak inhibitors of thioredoxin reductase, they were able to inhibit cathepsin B by coordination of the Ru(II) to the cysteine in the active site.

Protein phosphorylation by kinase enzymes is a major regulatory mechanism for protein activity and transmission of intracellular signals. There is a growing trend towards targeted therapy in which cancer drugs are aimed at specific molecular targets such as kinases. An excellent example is the drug imatinib which is targeted at the gene fusion protein breakpoint cluster region-Abelson (bcr-abl) tyrosine kinase and has changed the landscape for chronic myeloid leukemia therapy. Seann Mulcahy and Eric Meggers (Philipps-Universität Marburg, Germany) describe in the sixth chapter the ability of metal-containing compounds to form rigid 3D structures which can then be used as structurally diverse, unique scaffolds for the
design of specific enzyme inhibitors. Staurosporine, an indolocarbazole alkaloid, is a relatively non-selective protein kinase inhibitor. By using cyclopentadienyl half-sandwich Ru complexes as a structural scaffold for staurosporine mimetics, and combining features of the indolocarbazole within the half-sandwich complex, highly potent and specific protein kinase inhibitors have been identified for the protein kinases Pim1, MSK1 and glycogen synthase kinase (GSK3α). These kinases are all potential targets for anticancer drugs (Figure 3).

Biopolymers such as DNA and proteins are seen as the conventional biomolecular targets. However, O₂ⁿ, NO and CO are alternative biomolecular targets amenable to interaction with metal complexes. The essential physiological roles of both O₂ⁿ and NO are well understood, whereas the role of CO is an emerging field of study. Like NO, CO may be an important signaling molecule. Brian Mann (University of Sheffield, UK) in the tenth chapter describes the development of Ru carbonyl CO-releasing molecules (CO-RMs) as potential drugs. Much of the work on the biological activity of CO-RMs has focused on two molecules: [Ru(CO)₂Cl₂]₂ (CORM-2) and [Ru(CO)₂Cl(glycinate)] (CORM-3). Both of these molecules have shown activity in a variety of biological and disease models. It is unclear what the clinical development path is for these molecules.

The pgms get a brief mention in other chapters. Elizabeth Hillard et al. (École Nationale Supérieur de Chimie de Paris, France) in the fourth chapter discuss development of the ferrocene functionalised modulators known as hydroxyferrocifens as anticancer agents. The hydroxyferrocifens consist of ferrocene linked to the active metabolite of tamoxifen, a breast cancer drug which targets the oestrogen receptor (‘ER’), the aim being to combine the anti-oestrogen effect of tamoxifen with the cytotoxic properties of metal complexes. Ruthenium analogues termed hydroxyruthencifens were prepared but only showed activity against an ER⁺ cell line, suggesting that the organometallic moiety gave no additional advantage over tamoxifen itself. Lastly for the pgms, Christophe Biot (Université de Lille 1, France) and Daniel Dive (Université Lille Nord de France) in the seventh chapter describe the antimalarial properties of ferrocene complexes and briefly mention studies on the coordination of chloroquine (CQ) to Rh(COD)Cl.

Conclusions
Overall this is an informative book and will be welcomed by those working in the field of inorganic medicinal chemistry. The main areas of interest from a pgm perspective are the two chapters describing work on the Ru-arene complexes and their potential antitumour activity, and the chapter on metal complexes as scaffolds for novel kinase inhibitors. The chapter on CO-RMs is of interest but is disappointing with a writing style consisting of multiple bullet points with brief supporting text.

One of the appealing aspects of this book is its historical perspective. The introduction by the book’s two editors, Gérard Jaouen and Stéphane Gibaud, traces the history of bioorganometallic chemistry from the elucidation of the crystal structure of cyanocobalamin to the discovery of the arsenical drug salvarsan by Erlich, to the antitumour activity of the titanocene complexes and the more recent Ru-arene complexes, set within the context of the discovery of cisplatin. This historical perspective is encapsulated in the chapter on arsenic drugs which have progressed from Fowler’s solution for malaria (first proposed for use in 1786) to arsenic trioxide which is currently being evaluated as a drug for acute promyelocytic leukemia. The main disappointment in this book is the lack of translation of the chemistry to a clinical perspective. Ultimately it will be the clinical translation of medicinal organometallic chemistry which will be the true measure of its success.

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“Medicinal Organometallic Chemistry”

The Reviewer
The species present in a variety of fresh and road aged light-duty diesel catalysts were determined by platinum L₃ edge X-ray absorption spectroscopy (XAS). It was found that it is not sufficient to use the analysis of X-ray absorption near edge structure (XANES) alone to determine the nature of species present in fresh and road aged catalysts. Detailed analysis of the extended X-ray absorption fine structure (EXAFS) revealed the presence of a mixture of oxidic and metallic species in the fresh catalysts. Metallic components were predominantly found in the road aged catalysts. The present study did not find any chloroplatinate species in the systems investigated.

Introduction
Platinum group metals (pgms) play a crucial role in a variety of applications and in particular for a host of catalytic applications (1–3). Supported pgm catalysts are used widely for industrial bulk and fine chemical synthesis. However the largest application is currently in vehicle emission control (VEC) catalysts to efficiently reduce particulate matter (PM), carbon monoxide (CO), oxides of nitrogen (NOx) and hydrocarbons (4, 5). In most modern VEC catalyst formulations, the use of palladium (with rhodium) predominates for gasoline engines whilst platinum is required for most diesel systems. VEC catalysts have been studied extensively and have continued to develop to keep pace with ever more stringent emission control regulations (4, 6). VEC systems are diverse and complex but generally contain amounts of pgm in the range of 0.1–1 wt% with a mixed oxide catalytic functional support and a thermally stable structural support (4, 5, 7, 8). Several studies have been carried out to determine the chemical species
present in VEC catalysts before, during and after use (4–6), although the nature of the species present in the system are still not completely understood. More recently, there have been concerns that chloroplatinate species, seen in some pgm processing applications, can exist in used catalysts in specific environments (9). Thus it is our aim to determine the types of species present in VEC catalysts, and in particular any minor components within the overall Pt atomic environments, using XAS.

Characterisation of automotive exhaust catalysts has been carried out using a variety of analytical techniques. In particular, electron microscopy has been used to determine the particle size and shape of supported catalysts; Fourier transform infrared (FTIR) spectroscopy studies to investigate the adsorption of gaseous molecules such as CO; X-ray photoelectron spectroscopy (XPS) to determine the oxidation states of outer layer atoms; X-ray diffraction (XRD) to examine the crystallinity and particle size of phases; and XAS to determine the electronic and geometric structure of the active species (7, 10–17). Among these techniques XAS is particularly useful (18), since measurements can be conducted directly (without high vacuum), representatively (all atoms are reflected in the signal and not those just at the surface or within crystalline domains) and with a high degree of sensitivity to determine the nature of Pt species in the catalyst. The main drawback of this technique is that it provides averaged information. For example, if more than one type of particle is present, with different shapes and sizes, the technique will provide only an average structure for all particles.

Here we report the use of XAS techniques, in particular XANES and EXAFS, to determine the types of species present in fresh and road aged diesel VEC catalysts that contain platinum as a major active constituent. Other elements, for example palladium and rhodium, may also be present in the catalyst formulation; however, the aim of this study is to understand speciation with respect to platinum in the catalyst.

Experimental

Data Collection

The Pt L_{3} edge XAS experiments were carried out at beamline B18 at the Diamond Light Source, UK (Figure 1), which operates at ca. 3 GeV electron energy. Pt foil of thickness 25 μm was used to
calibrate the monochromator and was used as one of the reference materials, using data collected after calibration. Three additional reference compounds were also measured: platinum(IV) oxide (PtO_2), potassium tetrachloroplatinate(II) (K_2PtCl_4) and platinum(II) chloride (PtCl_2). All the reference compounds were obtained from Alfa Aesar and were mixed with alumina in such a way that the overall concentration of Pt was ca. 5 wt%. In a typical experiment, 150 mg of the powder sample was pressed into a 13 mm diameter disc (approximately 1.5 tons of pressure was applied to get a good pellet) and used for XAS measurements. XAS data for all the reference materials were collected using transmission mode in which two ion-chambers (filled with argon or helium to a required amount) were employed for measuring the incident intensity (I_0) and intensity after transmission (I).

Experiments were also performed on a Johnson Matthey prepared standard model alumina supported platinum catalyst, 1% Pt/Al_2O_3, which is here denoted as RM1. The data derived from this model catalyst were used to establish analysis procedures to determine the types of species present in diesel VEC monolith catalysts.

Road aged diesel saloon car VEC catalyst samples were obtained from UK registered car dealerships in selected geographic regions to represent coastal and non-coastal environments. The exact source of manufacture of the catalysts was not identified, to maintain anonymity. Two replacement original equipment manufacturer (OEM) parts were ordered for the respective vehicles. One was fitted to the vehicle, the other was utilised as a control sample for this characterisation study and is referred to as ‘fresh’. Attempts were made to collect data with spatially resolved information by cutting the monolith samples to a flat plate and measuring the attached washcoat in fluorescence mode, but the quality of the data was not satisfactory. Subsequent measurements were therefore made using pellets made from scraped washcoat powder from the monolith, since the Pt concentration is fairly low for fluorescence mode (a nine element Canberra detector was employed for this purpose).

In general very good quality data were obtained and data up to ca. 18 Å⁻¹ could be analysed; however a few data sets, in particular PtO_2 and the fresh catalyst samples, were not satisfactory above ca. 14.5 Å⁻¹. The XANES part of the data was found to be very reliable in all cases.

Data Analysis Methods
Initial processing of the data was carried out using the ATHENA software package (19, 20) for normalisation and background subtraction. In addition this software package was used to calculate linear combinations of two or more possible species which may be present in the XANES data. This was used to estimate the concentration of different oxidation state species present in the catalysts. To determine the structure of various phases present in the system, detailed analysis of the EXAFS data was performed. This allowed the possible first neighbour atoms, X, in Pt-X (X = Pt, O or Cl) species to be determined up to ca. 3 Å using the EXCURV (21) software package. Raw data without Fourier filtering was used for detailed analysis by curve fitting procedures. Since only the first neighbours were analysed, a single-scattering approximation was used.

Results and Discussion
Using both XANES and EXAFS data, the reference and model materials are first discussed in order to better understand the types of platinum species present in fresh and road aged diesel VEC catalysts.

Reference Materials
Figure 2(a) shows the Pt L_3 edge XANES data for the reference materials Pt foil, PtO_2 and K_2PtCl_4, representing the three different types of neighbours one would expect in a real catalyst. The main absorption peak (usually called the ‘white line intensity’) is related to the 2p_3/2 to 5d transition (which is the dipole allowed transition). The intensity of the XANES signal depends on the transition probability and the density of unoccupied states (18). In this case, all the transition states are the same and so the white line intensity corresponds closely to the density of unoccupied states. In this case, Pt^{IV} (α-PtO_2) shows the highest and Pt^0 (Pt foil) the lowest intensity.

Other factors such as the near neighbour distances (level of bonding contribution), solid state effects, any bimetallic species that are present and importantly particle size effects (nano and bulk) can also affect the white line intensity or perturb the width (shape) and other features (22). Oxidic compounds typically show a higher intensity than chlorinated compounds. This particular area is not completely understood and hence it is difficult to quantify these aspects. The majority of studies based on analysis of XANES data rely on crystalline reference materials, although
catalysts containing highly dispersed species do not possess long-range order; solid state effects can therefore alter the spectral features and mean that analysis of the XANES data may not yield accurate results. Despite these issues, qualitative information can be gained by analysing the XANES data (23).

More recently, several features in XANES spectra, in particular just above the white line, have been interpreted based on both theory and comparison with experimental data, and used for suggesting possible Pt-X species present in a given system. For example, feature B (see Figure 2) has been identified as representative of Cl neighbours in the system (24–27). However, this feature was also found to be present, although at a different energy, in pure metallic platinum (Pt foil, Figure 2(a)) although it was absent in the reference oxidic compound (PtO2, Figure 2(a)). In addition, a similar feature B in two different Pt-Cl containing compounds (PtCl2 and K2PtCl4, Figure 2(b)) appear to be present at different energies.

In order to determine whether such differences in the energy position of feature B are related to the Pt-Cl distance, a curve fitting analysis of the EXAFS data of the Pt-Cl containing reference compounds was carried out. To extract non-structural parameters associated with curve fitting analysis, in particular the amplitude reduction factor (AFAC), Pt foil data for which the crystal structure is precisely known was analysed. The best fit between experimental and calculated EXAFS spectra and the associated Fourier transform (FT) for Pt foil is shown in Figure 3. Once the AFAC was obtained, a further test was carried out using EXAFS data for PtO2. The best fit between experimental and calculated data is shown in Figure 3. Only the first Pt-O shell was considered here, and the phase was assumed to be α-PtO2. Although PtO2 exists in two forms, α-PtO2 and β-PtO2, the latter is a high pressure phase and unlikely to be present. This system has been characterised by Graham and co-workers (28, 29).

Subsequently, EXAFS data of the two Pt-Cl containing reference compounds, PtCl2 and K2PtCl4, were analysed in detail. The best fit between the experimental and calculated EXAFS data, and the associated FTs, are shown in Figure 4. All the coordination numbers (N), bond distances (R) and Debye-Waller factors (σ²) derived from the analysis are given in Table I. From Table I, it is clear that the Pt-Cl distances are closely similar and well within the typical error limits of ca. ±0.02 for determining bond distances from EXAFS data. This suggests that the differences in feature B seen for various Pt-Cl containing platinum species may not be related to Pt-Cl distances; further detailed studies are required to substantiate this finding.

Model Catalyst

Figure 5 shows the XANES spectra of the model catalyst RM1 heated in air at different temperatures. The white line intensity is higher for the systems processed at low temperatures which indicates that there is more than one component present in these low temperature systems.
Fig. 3. Best fit between experimental Pt L3 edge EXAFS data and calculated data for Pt foil (top) and PtO₂ (bottom). On the right are shown the corresponding Fourier transforms of the experimental and calculated data. Note that in the analysis of the Pt foil data, crystal structure data is used to maintain a coordination number of 12 for the first shell. The amplitude reduction factor was 0.94. For PtO₂, the obtained amplitude reduction factor of 0.94 was kept constant and the coordination number (N) was varied. In all cases the interatomic distances (R) were refined along with the threshold energy (E₀) and Debye-Waller factor (σ²) to obtain the best fit.

Table I
Structural Parameters of Reference Materials Determined from the Analysis of EXAFS Data

<table>
<thead>
<tr>
<th>System</th>
<th>Atom pair</th>
<th>Coordination number, N</th>
<th>Interatomic distance, R, Å</th>
<th>Debye-Waller factor, σ², Å²</th>
<th>Fit index</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt foil</td>
<td>Pt-Pt</td>
<td>12</td>
<td>2.77</td>
<td>0.005</td>
<td>36</td>
</tr>
<tr>
<td>PtO₂</td>
<td>Pt-O</td>
<td>5.6</td>
<td>2.00</td>
<td>0.0034</td>
<td>39</td>
</tr>
<tr>
<td>PtCl₂</td>
<td>Pt-Cl</td>
<td>4</td>
<td>2.32</td>
<td>0.0034</td>
<td>31</td>
</tr>
<tr>
<td>K₂PtCl₄</td>
<td>Pt-Cl</td>
<td>4.3</td>
<td>2.32</td>
<td>0.0041</td>
<td>32</td>
</tr>
</tbody>
</table>
In order to establish the species present in the RM1 catalyst after processing at different temperatures, the EXAFS data were analysed. Figure 6 shows the best fit between experimental and calculated data for all the RM1 catalyst samples along with their respective FTs. The results of the analysis are given in Table II. It is clear from the analysis that the as received RM1 sample contains a significant oxidic component. The inclusion of other species in the fitting procedure, in particular Cl neighbours, did not yield a better fit to the experimental data or produce physically meaningful results. RM1 heated at 600ºC for 18 hours shows predominantly metallic Pt. However, adding a Pt-O contribution resulted in a better fit and a 10% improvement in the fit index (goodness of fit). This suggests that the oxidic platinum species present in the as received RM1 catalyst are not completely converted

![Fig. 4. Best fit between experimental Pt L3 edge EXAFS data and calculated data for PtCl2 (top) and K2PtCl4 (bottom). On the right are shown the corresponding FTs of the experimental and calculated data. In both cases the coordination number, interatomic distances and Debye-Waller factor (σ2) were refined to obtain the best fit](image)

![Fig. 5. Comparison of the Pt L3 edge XANES data of model Pt/Al2O3 catalysts (RM1) heated in air at different temperatures](image)
Fig. 6. Best fit between experimental and calculated EXAFS data and the respective Fourier transforms of RM1 model catalysts heated in air at different temperatures.
Table II

Structural Parameters Obtained from the Analysis of EXAFS Data of Model RM1 Catalysts as Received and Calcined at Various Temperatures

<table>
<thead>
<tr>
<th>System</th>
<th>Atom pair</th>
<th>Coordination number, N</th>
<th>Interatomic distance, R, Å</th>
<th>Debye-Waller factor, σ², Å²</th>
<th>Fit index</th>
</tr>
</thead>
<tbody>
<tr>
<td>RM1 as received</td>
<td>Pt-O</td>
<td>2.3</td>
<td>2.01</td>
<td>0.0055</td>
<td>36</td>
</tr>
<tr>
<td></td>
<td>Pt-Pt</td>
<td>3.0</td>
<td>2.75</td>
<td>0.008</td>
<td></td>
</tr>
<tr>
<td>RM1 600ºC</td>
<td>Pt-O</td>
<td>1.0</td>
<td>1.98</td>
<td>0.011</td>
<td>37</td>
</tr>
<tr>
<td></td>
<td>Pt-Pt</td>
<td>9.2</td>
<td>2.76</td>
<td>0.005</td>
<td></td>
</tr>
<tr>
<td>RM1 900ºC</td>
<td>Pt-Pt</td>
<td>11.6</td>
<td>2.76</td>
<td>0.0045</td>
<td>39</td>
</tr>
</tbody>
</table>

to metallic platinum when heated at 600ºC. Samples heated at 900ºC could be modelled based only on bulk platinum and there was no need to include additional species to fit this data. The coordination number of these samples was found to be ca. 11.8, which is very close to bulk Pt metal. This suggests that sintering has taken place, leading to the formation of bulk-like species (30).

Diesel VEC Monolith Catalysts

XANES Data Analysis

Pt L₂ edge XANES data of fresh and road aged catalysts, both obtained from a non-coastal environment, along with Pt foil, PtO₂ and K₂PtCl₄ are compared in Figure 7. The white line intensity is slightly higher for the fresh catalyst than for the road aged catalyst, and the XANES spectrum of the road aged catalyst is closer to that of bulk Pt metal. A tiny peak above the white line intensity at around 11,585 eV is present in Pt foil and is more pronounced in aged catalyst than in fresh catalyst (Figure 7(a)). This feature is also present in K₂PtCl₄ and PtCl₂, but seems to appear at different energies.

In order to obtain more quantitative information, a linear combination fit analysis was carried out on the fresh and road aged catalysts using the ATHENA software. Typical best fits obtained using a linear combination of Pt foil, PtO₂ and K₂PtCl₄ data are shown in Figures 7(b) and 7(c). For the fresh catalyst, the analysis suggests that the majority of the species are Pt⁰. A minor component can be due to either PtCl or Pt-O species or a combination of both. It is important to note that although the calculated linear combination data matches the white line area, features at higher energies could not be matched precisely using this combination. Attempts were made to use other types of Pt-Cl compounds but the best fits were again not completely satisfactory. This may be due to the use of crystalline bulk materials data as the reference while the XANES features may have been affected by the high ppm dispersion in the VEC catalysts, as well as a Pt/Pd alloying effect due to the presence of Pd in the catalyst washcoat formulation. Chemical analysis found the chlorine content in the fresh catalyst sample to be ca. 33 ppm, well below what would be stoichiometrically required if Pt-Cl species were present in the XANES data of the fresh or road aged catalysts. (See Supplementary Data available on the web version of this article.)

EXAFS Data Analysis

The analysis of the EXAFS data was found to be much more reliable for determining Pt speciation, since the Pt-O, Pt-Cl and Pt-Pt distances are significantly different (2.02 Å, 2.31 Å and 2.74 Å, respectively). The results of the best fit between calculated and experimental data for the fresh and road aged catalysts derived from non-coastal and coastal environments are shown in Figures 8 and 9, along with their respective FTs. The results of the analysis are given in Table III.

The active components present in the coastal and non-coastal catalyst samples were found to be different. In the non-coastal samples, palladium was found to be present as well as platinum. Inductively coupled plasma (ICP) analysis also confirmed its presence in this catalyst. (See Supplementary Data.) However, in the coastal samples, only platinum was present.
It is clear from the structural parameters listed in Table III that the major components in all the catalysts were metallic species. The fresh catalysts from both non-coastal and coastal environments contained small amounts of platinum in an oxidic environment. The amount of Pt-O species appears to be higher for the non-coastal samples compared to the coastal samples, but was still lower than for the model RM1 catalyst described earlier. Furthermore, analysis of the EXAFS data of the fresh non-coastal catalyst showed the presence of a bimetallic Pt-Pd component, in addition to monometallic Pt-Pt. This is easily distinguishable in the analysis of the EXAFS data, despite the fact that Pt-Pt and Pd-Pd distances are comparable in magnitude. When an attempt was made to include a Pt-Cl component in the analysis it always yielded both unrealistic Pt-Cl distances (much shorter than expected) and also unrealistic Debye-Waller factors.

The structural data reported in Table III for the road aged catalysts showed the presence of predominantly metallic species with a high proportion of monometallic Pt-Pt. There was no significant increase in the Pt-Pd contribution compared to the fresh non-coastal catalyst. It is difficult to conclude whether the monometallic component is similar to bulk species, due to sintering, since both the mono- and bimetallic components contribute to the coordination number. Coastal samples, which did not contain any palladium, also showed an increase in the Pt-Pt coordination number upon ageing. The oxide component decreased upon ageing in both catalysts. The increase in the Pt-Pt coordination number in the road aged catalyst

Fig. 7(a). Comparison of Pt L3 edge XANES spectra of fresh and road aged non-coastal catalysts with selected reference materials. Linear combination fits obtained from the best fit for: (b) the fresh catalysts; and (c) the road aged catalysts are also shown. The estimated concentration of individual components determined by linear combination fit analysis is given in parentheses on the charts.
suggests that some sintering may have taken place, although the coordination number remains below the value seen for the model RM1 catalyst heated at 900ºC. It is well known that prolonged use of VEC catalysts leads to sintering and deterioration in their performance (4, 5, 30). However, it is difficult to correlate such effects in this case, since the age, usage and history of the road aged catalysts studied is not known. The main important finding from this study is that, based on a detailed analysis of the EXAFS data, it can be inferred that chloroplatinate species were not detected in either fresh or road aged diesel VEC catalysts.

**Conclusion**

A detailed XANES and EXAFS analysis of fresh and road aged diesel VEC catalysts, obtained from registered UK car dealers in both non-coastal and coastal regions, was carried out to determine the species present in both fresh and road aged light-duty diesel catalysts. Although a linear combination fit of the XANES data has been widely used in many studies to determine the speciation, the present studies suggest that both XANES and EXAFS data are required to clearly show the nature of the species present in a catalyst. The results from the VEC catalysts studied here show that it is unlikely that there are Pt species associated with chlorine present in the system whether used in a coastal or a non-coastal environment. If species other than metallic (or bimetallic) components are present in the system, they are associated with oxygen atoms and may be present as a discrete oxidic phase or as a result of the metal particles interacting with the oxidic support.
Fig. 9. Best fit between experimental and calculated EXAFS data (left) and the respective Fourier transforms (right) of fresh coastal catalyst (top) and road aged coastal catalyst (bottom)

Table III
Structural Parameters Obtained from Analysis of Pt L3 edge EXAFS Data of Fresh and Road Aged Diesel VEC Catalysts

<table>
<thead>
<tr>
<th>VEC catalyst system</th>
<th>Atom pair</th>
<th>Coordination number, N</th>
<th>Interatomic distance, R, Å</th>
<th>Debye-Waller factor, σ², Å²</th>
<th>Fit index</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fresh non-coastal</td>
<td>Pt-O</td>
<td>1.71</td>
<td>2.01</td>
<td>0.009</td>
<td>42</td>
</tr>
<tr>
<td></td>
<td>Pt-Pt</td>
<td>3.63</td>
<td>2.74</td>
<td>0.0055</td>
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<tr>
<td></td>
<td>Pt-Pd</td>
<td>1.53</td>
<td>2.74</td>
<td>0.0055</td>
<td></td>
</tr>
<tr>
<td>Road aged non-coastal</td>
<td>Pt-Pt</td>
<td>7.44</td>
<td>2.71</td>
<td>0.0045</td>
<td>35</td>
</tr>
<tr>
<td></td>
<td>Pt-Pd</td>
<td>2.71</td>
<td>2.74</td>
<td>0.0045</td>
<td></td>
</tr>
<tr>
<td>Fresh coastal</td>
<td>Pt-O</td>
<td>0.7</td>
<td>2.0</td>
<td>0.005</td>
<td>47</td>
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<tr>
<td></td>
<td>Pt-Pt</td>
<td>7.11</td>
<td>2.76</td>
<td>0.006</td>
<td></td>
</tr>
<tr>
<td>Road aged coastal</td>
<td>Pt-O</td>
<td>0.38</td>
<td>1.98</td>
<td>0.004</td>
<td>37</td>
</tr>
<tr>
<td></td>
<td>Pt-Pt</td>
<td>10.8</td>
<td>2.76</td>
<td>0.0045</td>
<td></td>
</tr>
</tbody>
</table>
Acknowledgements
We would like to express our thanks to the members of the International Platinum Group Metals Association for funding this project. Gopinathan Sankar thanks the Royal Society, London, UK, for an Industry Fellowship. We also thank the Diamond Light Source beamline staff (Anna Krone-Nizolek, Giannantoni Cibin and Andy Dent) for their help with the setup and collection of the platinum data.

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Dr Klaus Rothenbacher is the Scientific Manager for the European Precious Metals Federation in Brussels since 2009. He is responsible for technical aspects of regulatory evaluations under REACH and CLP of, among other metals, platinum and platinum compounds.

Professor Gopinathan Sankar obtained his PhD at the Indian Institute of Science (IISc), Bangalore, India, afterwards he moved to the Royal Institution of Great Britain in 1990. In 2007, he moved to the Department of Chemistry, University College London where he pursues catalytic science. He held a Royal Society Industry Fellowship at Johnson Matthey in 2007, for four years.
The 25th Santa Fe Symposium on Jewelry Manufacturing Technology

Further research on platinum casting by the industry reinforces previous findings.

Reviewed by Christopher W. Corti
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The 25th annual Santa Fe Symposium attracted a record attendance of 165, with delegates from 11 countries worldwide, confirming the more optimistic outlook by the US jewellery industry noted last year. Held in Albuquerque, New Mexico, USA, from 15th–18th May 2011, the Symposium had a very strong programme of presentations covering a wide range of topics (1). Platinum featured and, as usual, attracted much interest. The major sponsors were given the opportunity to have a display table in the lobby area, as last year, and thus both Johnson Matthey New York and Platinum Guild International USA had a strong presence.

Platinum Alloys

The soldering of platinum received attention this year with Jurgen Maerz (Platinum Guild International, USA) reviewing the topic in his presentation, 'Platinum Solders: Proper Use and Application of Platinum Solders in Jewelry Making'. Maerz first addressed the types of solder used in soldering platinum jewellery: this categorised platinum solders into those containing up to 95% platinum and those which contained no platinum, perhaps better classed as plumb and traditional solders respectively. Traditional solders contain no or very little platinum and come in a range of soldering or flow temperatures in grades from extra easy 1000 to extra hard 1400 with additional grades of platinum welding 1500, platinum special welding 1600, platinum seamless 1700 and platinum weld 1773, where the number refers to the approximate flow temperature in °C.

In contrast, plumb platinum solders have a high platinum content and flow temperatures in the range 1300°C for the easy flow grade (contains 90% platinum) to 1500°C for the hard flow grade that contains 95% platinum. Maerz makes the point that these solders enable soldering without fear of under-carating of the platinum jewellery in the USA where there is a zero tolerance on assay. To ensure compliance with this standard, he noted, platinum alloys are often 'sweetened' to 952 fineness to allow use of non-plat-
Maerz then addressed the techniques of soldering platinum, with many practical tips. For example, use of a flux is not necessary with the higher melting solders. The lower melting solders tend to be based on palladium-silver alloys and do need flux to prevent oxidation. Solder flow is often poor over distance, so Maerz recommends placing many small pieces of solder along a seam close together and following the seam with the soldering flame. Joint gaps should be a close fit too. For soldering prongs to a ring, he recommends pre-melting the solder onto the prong wire and then allowing the heat of the torch to make the connection to the ring (Figure 1). Because of the lower thermal conductivity of platinum compared to gold and silver, Maerz advises that preheating the work piece with the torch, as done for gold and silver, is not necessary with platinum. He also advises the use of welding goggles with a number 5 rating to prevent eye damage; UV radiation is released on soldering platinum because of the high temperatures involved.

Maerz ended his presentation, in his own inimitable style, with a series of examples of platinum soldering, using video clips to show how it is done.

Soldering of 950 platinum-ruthenium alloy was also covered briefly by Stewart Grice (Hoover & Strong, Inc, USA) in his presentation, ‘Characterization of Jewelry Solders and their Applications in the Manufacturing Process’. Grice discussed the principles of soldering, properties of solders and strengths of joint geometries. He also covered welding. To test the theory that any alloy with a liquidus temperature lower than the solidus temperature of the alloys being joined should give a good soldered joint, provided it wets well, he used normal carat gold alloys rather than solder alloys to solder both gold and platinum alloys. The series included 950 PtRu alloy soldered with a standard 18 carat palladium white gold which had a relatively wide melting range. This gave a good quality joint, which, he considered, proved his point.

Following last year’s report on research into investment casting of platinum, conducted in an EU-funded project (see (2)), a further presentation by a major US caster of platinum jewellery was the subject of much discussion this year. Teresa Fryé (TechForm Advanced Casting Technology, USA) reported on a study carried out with Jörg Fischer-Bühner (Legor Group Srl, Italy) to examine the casting behaviour of a number of platinum alloys in popular use in the USA and to determine which performs best from a consumer standpoint. In her presentation, ‘Platinum Casting Alloys in the 21st Century: A Comparative Study’, she studied Pt-5 wt% Ru, Pt-5 wt% Co and Pt-10 wt% Ir as well as several 950 platinum alloys that had additions to increase hardness, some of which are age-hardenable. Characteristics that were assessed included shrinkage porosity, form-filling, hardness and the effects of post-casting thermal treatments.

Fryé commenced her presentation with a review of previously published work that included the early (1995) work of James Huckle (Johnson Matthey New York, USA) (3, 4) on the comparative behaviour of various platinum casting alloys. This showed 950 PtCo to have the best casting behaviour, Pt-10 wt% Ir and Pt-15 wt% Pd to have good behaviour and 950 PtCu and 950 PtRu as having poor casting characteristics. Subsequent work by other US manufacturers has confirmed the preference for 950 PtCo alloy and this alloy is the preferred choice today.

Casting trials in collaboration with Legor Group Srl, Italy, showed that 950 PtRu still results in large amounts of scattered shrinkage porosity, even with a double top sprue (Figure 2). It was observed that approximately 1% additions of a metal such as gallium to 950 PtCo can increase hardness to above HV 170 and such an alloy (‘950 Pt-Co+’) was examined. The metallographic analysis of castings gave hope that porosity levels nearly as low as those for 950 PtCo.
(Figure 3(a)) alloy can be consistently obtained in alloys based on the significantly harder 950 Pt-Co+ alloy (Figure 3(b)).

Fryé also reported on a survey of platinum designers, custom jewellers and retailers carried out by TechForm Advanced Casting Technologies in 2007 which highlighted that the most frequent defect is subsurface porosity that only emerges on polishing. The overall conclusion was that a harder casting alloy that could better hold a high lustre would be desirable.

Following on from his paper at the 2010 Symposium on the metallography of platinum alloys (see (2)), Paolo Battaini (8853 SpA, Italy) extended his work to discuss ‘Dynamic Recrystallization and the Hot Working of Precious Metal Alloys’. This covered several precious metals: sterling silver, 18 carat white gold and two platinum alloys – 950 PtRu and 950 PtCu. The beneficial effects of hot working on microstructure and properties were discussed and Battaini demonstrated how hot working leads to more uniform and finer recrystallised grain structures, compared to cold working and static recrystallisation, and tends to close up and seal internal porosity from casting. This latter was well demonstrated for hot worked bars of 950 PtCu alloy (Figure 4 and Figure 5).

Other Precious Metal Alloys

In his presentation, ‘New Metals & Alloys of Interest in the Jewelry Industry’, Ajit Menon (United Precious Metal Refining, Inc, USA) looked at jewellery materials that are cheaper than precious metals and attracting industry interest at a time of record precious metal prices. This embraced coloured brass alloys, coloured (low fineness) silver alloys, low carat golds, stainless steel, titanium and low fineness platinum group metal (pgm) alloys. He noted the marketing of platinum- or palladium-containing sterling silver alloys but observed that these do not have good hardness values, although improved tarnish resistance is claimed over conventional sterling silvers. He also discussed 420 and 585 fineness palladium alloys and noted that these have better hardness, lustre and scratch resistance compared to 950 fineness palladium alloys. Market demand for such alloys is noticeably low, however.

John Wright (Wilson-Wright Associates, UK) gave a presentation entitled, ‘Buy by Weight: Think Volume’, in which he emphasised that the size of a piece of jewellery is what attracts customers but the precious metals are sold on a weight basis. Thus, alloying precious metals may improve their properties and can also help to create more volume through lowering of the density (most base metals have lower density).
One example he cited was the development of a 505 fineness platinum-palladium alloy in which nearly 2/3 of the atoms are palladium by volume, although only 49.5% by weight.

Manufacturing Processes
One of the highlights of this Symposium was the paper presented by Paul Nordt III (John C. Nordt Co, Inc, USA). His presentation, ‘Modern Manufacture of Seamless Wrought Wedding Bands – An Engineering Approach’, examined how modern engineering and metallurgy have been applied to the manufacture of products in response to current market conditions. His company produces wrought seamless wedding bands by hot extrusion in platinum, palladium, gold and silver. The key aspects of the work he reported include vacuum melting and hot working to achieve a fine grained microstructure, near netshape processes to maximise precious metal yield, customer-accessible computer aided design (CAD) code generation integrated with ‘on the fly’ computer numerically controlled (CNC) code generation for precision machining, the application of ‘lean manufacture’ principles for one-piece flow, maximised inventory turnover and loss control and quality systems consistent with the International Organization for Standardization (ISO 9001:2008).

The basis of Nordt’s work was the need to build a better business model for his company. He described the fabrication options for ring manufacturing and their pros and cons, then discussed the whole production process in detail. For example, he noted that platinum and palladium billet casting is done under vacuum with a special pour cycle to inhibit pipe formation during solidification. His discussion included observations on product yields and how this has led to improved technologies (for example, minimising numbers of basic extruded tube sizes, cutting tubes with no metal loss or upsetting of basic tube blanks to give a range of ring blank sizes), how to service customer delivery requirements and quality management.

Professor Wolfgang Böhm (University of Pforzheim, Germany) gave an interesting presentation on ‘Where to Direct Development Money? Some Examples of Successful and Not-So-Successful Projects’. He described a number of projects on innovative materials and manufacturing processes that his university has undertaken for the jewellery industry in recent years. Some have been successfully exploited but others have foundered. One project he described was the use of powder metallurgy to fabricate jewellery with colour contrasts. In particular, he gave an example of mixing platinum wire studs and nuggets with a red gold powder using a ‘press and sinter’ approach to give a material with high colour contrast (Figure 6). The structure is random, making each piece unique, and the product is akin to traditional mokume gane materials.

Other Presentations
As usual, there were a number of other presentations, some of which were focused on gold and silver. The
Symposium commenced with the return of ‘Basic Metallurgy of the Precious Metals – Part I’ by Chris Corti (COReGOLD Technology Consultancy, UK). The link between the jeweller and jewellery design was discussed by Chuck Hunner (Golden Spirit, USA). Investment (lost wax) casting was discussed by Marco Actis Grande (Politecnico di Torino, Alessandria Campus, Italy) with respect to direct casting of rapid prototyping resin models and a similar paper was presented by Alan Andrews (Best Cast Inc, USA) from a production standpoint. The application of glass and epoxy enamels was reviewed by Rick Greinke (Award Concepts, Inc, USA), and Nora Isomäki (Beneq Oy, Finland) gave new wear results on her company’s anti-tarnish nano-coatings on silver.

Frank Cooper (Birmingham City University, UK) gave an interesting report on the production of a gold-plated silver copy of a medieval gold cross found in the Staffordshire hoard in 2009 in his presentation, ‘A Gift Fit for a Pope, 1500 Years after Its First Creation’. The manufacturers’ approach to refining precious metal scraps was discussed by Brett Gober (Freedom Design & Contracting, USA), showing that it pays to be analytical. The properties of carat golds were discussed in two presentations by Greg Raykhtsaum (Sigmund Cohn Corp, USA) and by Daniele Maggian (Progold SpA, Italy). A novel powder metallurgy approach to manufacture of mokume gane materials that gives higher yields of useable material was discussed by Chris Ploof (Chris Ploof Studio, USA) and Joe Strauss (HJE Company, Inc, USA). Lastly, new analysis technology was discussed by Andreas Zielonka (The Research Institute for Precious Metals and Metals Chemistry (FEM), Germany) in his presentation, ‘X-Ray Computed Tomography – A Powerful Tool for Non-Destructive Materials Analysis’. This allows high resolution analysis of structure and defects in large objects in either 2D or 3D.

Concluding remarks
This was another excellent international symposium for jewellers, and was particularly special as it celebrated the 25th anniversary of the Santa Fe Symposia. Speakers past and present marked the occasion with the presentation of a gift (a photograph album of speakers throughout the 25 years) to one of the co-founders, Eddie Bell.

As noted, platinum featured strongly at this symposium and interesting new results have emerged that should lead to better platinum jewellery.

References
1 The Santa Fe Symposium: http://www.santafesymposium.org/ (Accessed on 18th August 2011)

The Reviewer
Christopher Corti holds a PhD in Metallurgy from the University of Surrey (UK) and has recently retired from the World Gold Council after thirteen years, the last five as a consultant. During this period, he served as Editor of Gold Technology magazine, Gold Bulletin journal and the Goldsmith’s Company Technical Bulletin. He continues to consult in the field of jewellery technology and as a recipient of the Santa Fe Symposium® Research, Technology and Ambassador Awards, he is a frequent presenter at the Santa Fe Symposium. From 1978–1988 he was a Research Manager at the Johnson Matthey Technology Centre, Sonning Common, UK, and from 1988–1992 he was Technical Director at Johnson Matthey’s Colour and Print Division.
The Discoverers of the Ruthenium Isotopes

Updated information on the discoveries of the six platinum group metals to 2010

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This review looks at the discovery and the discoverers of the thirty-eight known ruthenium isotopes with mass numbers from 87 to 124 found between 1931 and 2010. This is the sixth and final review on the circumstances surrounding the discoveries of the isotopes of the six platinum group elements. The first review on platinum isotopes was published in this Journal in October 2000 (1), the second on iridium isotopes in October 2003 (2), the third on osmium isotopes in October 2004 (3), the fourth on palladium isotopes in April 2006 (4) and the fifth on rhodium isotopes in April 2011 (5). An update on the new isotopes of palladium, osmium, iridium and platinum discovered since the previous reviews in this series is also included.

Naturally Occurring Ruthenium

Of the thirty-eight known isotopes of ruthenium, seven occur naturally with the authorised isotopic abundances (6) shown in Table I.

The isotopes were first detected in 1931 by Aston (7, 8) using a mass spectograph at the Cavendish Laboratory, Cambridge University, UK. Because of difficult experimental conditions due to the use of poor quality samples, Aston actually only detected six of the isotopes and obtained very approximate

<table>
<thead>
<tr>
<th>Mass number</th>
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<tr>
<td>$^{96}\text{Ru}$</td>
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<td>1.87</td>
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<td>$^{101}\text{Ru}$</td>
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<td>$^{102}\text{Ru}$</td>
<td>31.55</td>
</tr>
<tr>
<td>$^{104}\text{Ru}$</td>
<td>18.62</td>
</tr>
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</table>
percentage abundances. However, he did speculate on the existence of a seventh isotope with mass number 98. In 1943 Ewald (9) of the Aus dem Kaiser Wilhelm-Institut für Chemie, Berlin-Dahlem, Germany, carried out a more refined spectrographic analysis and obtained precision values for the isotopic abundances, including confirming the isotope of mass number 98.

Artificial Ruthenium Isotopes
Early investigations of activities associated with ruthenium tended to lead to half-life values which initially did not appear to be connected to each other. For example, in 1935 Kurchatov, Nemenov and Selinov (10) used slow neutron bombardment to obtain half-lives of 40 seconds, 100 seconds, 11 hours and 75 hours, and in 1936 Livingood (11) used deuteron bombardment to obtain different half-lives of 4 hours, 39 hours, 11 days and 46 days. In 1937, Pool, Cork and Thornton (12) used fast neutron bombardment and obtained activities with half-lives of 24 minutes and 3.6 hours and in 1940 Nishina et al. (13) also used fast neutron bombardment to obtain ruthenium activities of 4 hours and 60 hours and a rhodium activity of 34 hours. However, Nishina et al. (14) later speculated that the 60 hour activity was in reality a mixture of the 4 hour ruthenium and 34 hour rhodium activities plus a further long lived ruthenium activity which had not been identified. They also pointed out that in 1940 Segrè and Seaborg (15) had found a 4 hour half-life ruthenium activity in fission products. In 1938, De Vries and Veldkamp (16) used the different technique of slow neutron bombardment and had identified three activities: a 4 hour activity which they suggested was $^{103}$Ru, a 20 hour activity which they suggested was $^{105}$Ru and a 45 day half-life activity which they suggested was $^{105}$Rh. All of these suggestions were incorrect but it would appear that all of the activities observed with an approximate 4 hour ruthenium activity in fission products. In 1938, De Vries and Veldkamp (16) used the different technique of slow neutron bombardment and had identified three activities: a 4 hour activity which they suggested was $^{103}$Ru, a 20 hour activity which they suggested was $^{105}$Ru and a 45 day half-life activity which they suggested was $^{105}$Rh. All of these suggestions were incorrect but it would appear that all of the activities observed with an approximate 4 hour half-life were probably $^{105}$Ru and the 46 day activity identified by Livingood and the equal 45 day activity identified by De Vries and Veldkamp were probably $^{105}$Ru. None of these observations could be seriously considered as being contenders to the discovery of any isotopes since the discovery criterion of an accurate determination of the atomic mass number had not been met.

Discovery Date
As discussed in previous articles in the present series (1–5), the actual year of discovery is generally considered to be that when the details of the discovery were placed in the public domain such as manuscript dates or conference report dates. However, once again complications arise with the case of internal reports which may not be placed in the public domain until several years later. As with rhodium (5), several ruthenium isotopes were first identified during the highly secretive Plutonium Project of the Second World War which was not actually published until 1951 (17), although much of the information had become available in 1946 in the tables of Siegel (18, 19) or in the 1948 edition of the “Table of Isotopes” (20).

Discovery Acceptance
The discovery criteria used in this series of papers relate to the identification of the ground state and those isomers in which the half-life exceeds one millisecond, except in the very special circumstances where the ground state half-life is itself very short and the half-lives of corresponding isomers are of a similar order. This procedure was adopted to keep the tables succinct by avoiding the inclusion of the exceedingly large number of isomers with half-lives of less than one millisecond which are known for the isotopes of the platinum group elements and which would have greatly complicated the text.

Half-Lives
Selected half-lives used in Table II were generally those accepted in the revised NUBASE database (21) although literature values were used when either these were not available or had been superseded by later determinations.

An Update on the Discovery and Discoverers of the Platinum Group of Elements
Since the publication of the first four reviews in this series (1–4) a number of new isotopes have been discovered for palladium, osmium, iridium and platinum and the discovery circumstances for these isotopes are listed in Table III. The total number of isotopes for each element and their mass number ranges are now as shown in Table IV.

In addition the half-life of $^{199}$Ir was unknown until determined to be 6 seconds by Kurtukian-Nieto (77).

The Number of Nuclides
If a nuclide is defined as being a unique combination of protons and neutrons, then the platinum group elements currently include 235 known nuclides out of a total for all elements of about 3200. Of these, 286 are primordial, that is they were present when the Earth was formed and are still present now. The
Table II
The Discoverers of the Ruthenium Isotopes

<table>
<thead>
<tr>
<th>Mass number</th>
<th>Half-life</th>
<th>Decay modes</th>
<th>Year of discovery</th>
<th>Discoverers</th>
<th>References</th>
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<tr>
<td>87</td>
<td>ps</td>
<td>EC + β⁺</td>
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<td>1992</td>
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<td>25, 26</td>
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<td>90</td>
<td>12 s</td>
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<td>1991</td>
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<td>De Lange et al.</td>
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<td>94</td>
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<td>95</td>
<td>1.643 h</td>
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<td>1948</td>
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<td>37</td>
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<td>96</td>
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<td>Aston</td>
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<td>97</td>
<td>2.9 d</td>
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<td>1944</td>
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<td>38, 39</td>
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<td>98</td>
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(Continued)
Table II (Continued)

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<td>49, 50</td>
<td>K</td>
</tr>
<tr>
<td>110</td>
<td>11.6 s</td>
<td>β&lt;sup&gt;-&lt;/sup&gt;</td>
<td>1969</td>
<td>Wilhelmy et al.</td>
<td>51, 52</td>
<td></td>
</tr>
<tr>
<td>111</td>
<td>2.12 s</td>
<td>β&lt;sup&gt;-&lt;/sup&gt;</td>
<td>1975</td>
<td>Fettweis and del Marmol</td>
<td>53</td>
<td>L</td>
</tr>
<tr>
<td>112</td>
<td>1.7 s</td>
<td>β&lt;sup&gt;-&lt;/sup&gt;</td>
<td>1969</td>
<td>Wilhelmy et al.</td>
<td>51, 52</td>
<td></td>
</tr>
<tr>
<td>113</td>
<td>800 ms</td>
<td>β&lt;sup&gt;-&lt;/sup&gt;</td>
<td>1988</td>
<td>Pentilä et al.</td>
<td>54</td>
<td>M</td>
</tr>
<tr>
<td>113m</td>
<td>510 ms</td>
<td>iT ?, β&lt;sup&gt;-&lt;/sup&gt;?</td>
<td>1998</td>
<td>Kurpeta et al.</td>
<td>55</td>
<td></td>
</tr>
<tr>
<td>114</td>
<td>540 ms</td>
<td>β&lt;sup&gt;-&lt;/sup&gt;</td>
<td>1991</td>
<td>Leino et al.</td>
<td>56</td>
<td></td>
</tr>
<tr>
<td>115</td>
<td>318 ms</td>
<td>β&lt;sup&gt;-&lt;/sup&gt;</td>
<td>1992</td>
<td>Äystö et al.</td>
<td>57, 58</td>
<td></td>
</tr>
<tr>
<td>115m</td>
<td>76 ms</td>
<td>iT</td>
<td>2010</td>
<td>Kurpeta et al.</td>
<td>59</td>
<td></td>
</tr>
<tr>
<td>116</td>
<td>204 ms</td>
<td>β&lt;sup&gt;-&lt;/sup&gt;</td>
<td>1994</td>
<td>Bernas et al.</td>
<td>60</td>
<td>N</td>
</tr>
<tr>
<td>117</td>
<td>142 ms</td>
<td>β&lt;sup&gt;-&lt;/sup&gt;</td>
<td>1994</td>
<td>Bernas et al.</td>
<td>60</td>
<td>N</td>
</tr>
<tr>
<td>118</td>
<td>123 ms</td>
<td>β&lt;sup&gt;-&lt;/sup&gt;</td>
<td>1994</td>
<td>Bernas et al.</td>
<td>60</td>
<td>N</td>
</tr>
<tr>
<td>119</td>
<td>ps&lt;sup&gt;b&lt;/sup&gt;</td>
<td>β&lt;sup&gt;-&lt;/sup&gt;?</td>
<td>1995</td>
<td>Czajkowski et al.</td>
<td>61, 62</td>
<td></td>
</tr>
<tr>
<td>120</td>
<td>ps&lt;sup&gt;b&lt;/sup&gt;</td>
<td>β&lt;sup&gt;-&lt;/sup&gt;?</td>
<td>2010</td>
<td>Ohnishi et al.</td>
<td>63</td>
<td>P</td>
</tr>
<tr>
<td>121</td>
<td>ps&lt;sup&gt;b&lt;/sup&gt;</td>
<td>β&lt;sup&gt;-&lt;/sup&gt;?</td>
<td>2010</td>
<td>Ohnishi et al.</td>
<td>63</td>
<td></td>
</tr>
<tr>
<td>122</td>
<td>ps&lt;sup&gt;b&lt;/sup&gt;</td>
<td>β&lt;sup&gt;-&lt;/sup&gt;?</td>
<td>2010</td>
<td>Ohnishi et al.</td>
<td>63</td>
<td></td>
</tr>
<tr>
<td>123</td>
<td>ps&lt;sup&gt;b&lt;/sup&gt;</td>
<td>β&lt;sup&gt;-&lt;/sup&gt;?</td>
<td>2010</td>
<td>Ohnishi et al.</td>
<td>63</td>
<td></td>
</tr>
<tr>
<td>124</td>
<td>ps&lt;sup&gt;b&lt;/sup&gt;</td>
<td>β&lt;sup&gt;-&lt;/sup&gt;?</td>
<td>2010</td>
<td>Ohnishi et al.</td>
<td>63</td>
<td></td>
</tr>
</tbody>
</table>

<sup>a</sup>m = isomeric state

<sup>b</sup>ps = particle stable (resistant to proton and neutron decay)

Notes to Table II

A ⁸⁸Ru Hencheck et al. (24) only proved that the isotope was particle stable. The half-life was first determined by Wefers et al. in 1999 (64).

B ⁸⁹Ru Mohar et al. (25, 26) only proved that the isotope was particle stable. The half-life was first determined by Li Zhankui et al. in 1999 (65).

C ⁹⁰Ru Mohar et al. (25, 26) also claimed the discovery of this isotope in 1992 and appeared to be unaware of the prior discovery by Zhou et al. (27, 28). However they only determined that the isotope was particle stable whereas Zhou et al. had already determined the half-life.
Notes to Table II  (Continued)

D  $^{93}\text{Ru}$ The discovery by Aten Jr. and De Vries-Hamerling (34) is considered to be tentative but was confirmed by Doron and Lanford (66) in 1971.

E  $^{93\text{m}}\text{Ru}$ Doron and Lanford (66) also claimed to have discovered this isomer in 1971 but de Lange et al. (35) could not confirm their half-life of 45 s.

F  $^{95}\text{Ru}$ Mock et al. (67) appeared to independently claim the discovery even though their manuscript date was October 1948; the discovery claim by Eggen and Pool (37) had already been published in July 1948.

G  $^{97}\text{Ru}$ The 1944 discovery by Sullivan, Sleight and Gladrow (38) was not made public for this isotope until included in the 1946 public report (39).

H  $^{103}\text{Ru}$ and $^{105}\text{Ru}$ The 1944 discovery for these isotopes by Sullivan, Sleight and Gladrow (38) was not made public until included in the 1946 table of Siegel (18, 19).

I  $^{106}\text{Ru}$ Although produced in 1946, the results of Glendenin (44) were only made public at this time by including in the 1946 table of Siegel (18, 19).

J  $^{107}\text{Ru}$ A preliminary identification of this isotope by Glendenin (68, 69) in 1944 was made public in the 1946 table of Siegel (18, 19).

K  $^{109}\text{Ru}$ Franz and Herrmann (70) proposed the existence of a 12.9 s half-life isomer but this could not be found by Kaffrell et al. (71).

L  $^{111}\text{Ru}$ Franz and Herrmann (70) also tentatively identified this isotope in 1975.

M  $^{113}\text{Ru}$Franz and Herrmann (70) tentatively claimed to have discovered this isotope in 1975 but Penttilä et al. (54) consider that the isotope observed was probably $^{113}\text{Rh}$.

N  $^{116}\text{Ru}$ to $^{118}\text{Ru}$ Bernas et al. (60) only determined that these isotopes were particle stable. The half-lives were first measured by Montes et al. (72) in 2005.

P  $^{120}\text{Ru}$ A 1995 claim by Czajkowski et al. (61) to have discovered this isotope was highly preliminary and was not included in the later 1997 report by Bernas et al. (62). Ohnishi et al. (63) detected this isotope in 2010 but did not claim the discovery possibly under the impression that the isotope had already been found but they can be considered to be the actual discoverers.

Table III
New Discoveries

<table>
<thead>
<tr>
<th>Element</th>
<th>Mass numbera</th>
<th>Half-life</th>
<th>Decay mode</th>
<th>Year of discovery</th>
<th>Discoverers</th>
<th>References</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd</td>
<td>125</td>
<td>psb</td>
<td>$\beta^-$ ?</td>
<td>2008</td>
<td>Ohnishi et al.</td>
<td>73</td>
<td></td>
</tr>
<tr>
<td></td>
<td>126</td>
<td>psb</td>
<td>$\beta^-$ ?</td>
<td>2008</td>
<td>Ohnishi et al.</td>
<td>73</td>
<td></td>
</tr>
<tr>
<td></td>
<td>127</td>
<td>psb</td>
<td>$\beta^-$ ?</td>
<td>2010</td>
<td>Ohnishi et al.</td>
<td>63</td>
<td></td>
</tr>
<tr>
<td></td>
<td>128</td>
<td>psb</td>
<td>$\beta^-$ ?</td>
<td>2010</td>
<td>Ohnishi et al.</td>
<td>63</td>
<td></td>
</tr>
</tbody>
</table>

(Continued)
### Table III (Continued)

<table>
<thead>
<tr>
<th>Element</th>
<th>Mass number&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Half-life</th>
<th>Decay mode</th>
<th>Year of discovery</th>
<th>Discoverers</th>
<th>References</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Os</td>
<td>161</td>
<td>570 μs</td>
<td>α</td>
<td>2008</td>
<td>Page et al.</td>
<td>74</td>
<td></td>
</tr>
<tr>
<td></td>
<td>195m</td>
<td>26 ns</td>
<td>IT</td>
<td>2002</td>
<td>Podolyák et al.</td>
<td>75</td>
<td>A1</td>
</tr>
<tr>
<td></td>
<td>197</td>
<td>2.8 min</td>
<td>β⁻</td>
<td>2003</td>
<td>Xu et al.</td>
<td>76</td>
<td></td>
</tr>
<tr>
<td></td>
<td>198</td>
<td>ps&lt;sup&gt;b&lt;/sup&gt;</td>
<td>β⁻ ?</td>
<td>2006</td>
<td>Kurtukian-Nieto et al.</td>
<td>77, 78</td>
<td>B1</td>
</tr>
<tr>
<td></td>
<td>199</td>
<td>5 s</td>
<td>β⁻</td>
<td>2005</td>
<td>Kurtukian-Nieto et al.</td>
<td>79</td>
<td></td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>6 s</td>
<td>β⁻</td>
<td>2005</td>
<td>Kurtukian-Nieto et al.</td>
<td>79</td>
<td></td>
</tr>
<tr>
<td></td>
<td>201</td>
<td>ps&lt;sup&gt;b&lt;/sup&gt;</td>
<td>β⁻ ?</td>
<td>2007</td>
<td>Kurtukian-Nieto</td>
<td>78</td>
<td></td>
</tr>
<tr>
<td>Ir</td>
<td>200</td>
<td>ps&lt;sup&gt;b&lt;/sup&gt;</td>
<td>β⁻ ?</td>
<td>2006</td>
<td>Kurtukian-Nieto et al.</td>
<td>77, 78</td>
<td>B1</td>
</tr>
<tr>
<td></td>
<td>201</td>
<td>ps&lt;sup&gt;b&lt;/sup&gt;</td>
<td>β⁻ ?</td>
<td>2006</td>
<td>Kurtukian-Nieto et al.</td>
<td>77, 78</td>
<td>B1</td>
</tr>
<tr>
<td></td>
<td>202</td>
<td>11 s</td>
<td>β⁻</td>
<td>2006</td>
<td>Kurtukian-Nieto et al.</td>
<td>77, 78</td>
<td>B1</td>
</tr>
<tr>
<td></td>
<td>203</td>
<td>ps&lt;sup&gt;b&lt;/sup&gt;</td>
<td>β⁻ ?</td>
<td>2006</td>
<td>Kurtukian-Nieto et al.</td>
<td>77, 78</td>
<td>B1</td>
</tr>
<tr>
<td>Pt</td>
<td>203</td>
<td>10.1 s</td>
<td>β⁻</td>
<td>2005</td>
<td>Kurtukian-Nieto et al.</td>
<td>79</td>
<td></td>
</tr>
<tr>
<td></td>
<td>204</td>
<td>10.3 s</td>
<td>β⁻</td>
<td>2006</td>
<td>Kurtukian-Nieto et al.</td>
<td>77, 78</td>
<td>B1, C1</td>
</tr>
<tr>
<td></td>
<td>205</td>
<td>ps&lt;sup&gt;b&lt;/sup&gt;</td>
<td>β⁻ ?</td>
<td>2010</td>
<td>Alvarez-Pol et al.</td>
<td>80</td>
<td>D1</td>
</tr>
</tbody>
</table>

<sup>a</sup>m = isomeric state  
<sup>b</sup>ps = particle stable (resistant to proton and neutron decay)

### Notes to Table III

A1  Although the ground state of <sup>195</sup>Os has not been discovered information on the very high level isomer is included to indicate that the isotope has been observed.

B1  Kurtukian-Nieto et al. (77) only showed results in the form of a chart with actual mass numbers being given by Kurtukian-Nieto (78) in 2007.

C1  Kurtukian-Nieto et al. (77) only determined the isotope to be particle stable. The half-life was first determined by Morales et al. (81) in 2008.

D1  Evidence for this isotope was also given by Benlliure et al. (82).

### Table IV

**Total Number of Isotopes and Mass Ranges Known for Each Platinum Group Element to 2010**

<table>
<thead>
<tr>
<th>Element</th>
<th>Number of known isotopes</th>
<th>Known mass number ranges</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru</td>
<td>38</td>
<td>87–124</td>
</tr>
<tr>
<td>Rh</td>
<td>38</td>
<td>89–126</td>
</tr>
<tr>
<td>Pd</td>
<td>38</td>
<td>91–128</td>
</tr>
<tr>
<td>Os</td>
<td>41</td>
<td>161–201</td>
</tr>
<tr>
<td>Ir</td>
<td>40</td>
<td>164–203</td>
</tr>
<tr>
<td>Pt</td>
<td>40</td>
<td>166–205</td>
</tr>
</tbody>
</table>
Some of the Terms Used for This Review

<table>
<thead>
<tr>
<th>Term</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atomic number</td>
<td>The number of protons in the nucleus.</td>
</tr>
<tr>
<td>Mass number</td>
<td>The combined number of protons and neutrons in the nucleus.</td>
</tr>
<tr>
<td>Nuclide and isotope</td>
<td>A nuclide is an entity containing a unique number of protons and neutrons in the nucleus. For nuclides of the same element the number of protons remains the same but the number of neutrons may vary. Such nuclides are known collectively as the isotopes of the element. Although the term isotope implies plurality it is sometimes used loosely in place of nuclide.</td>
</tr>
<tr>
<td>Isomer/isomeric state</td>
<td>An isomer or isomeric state is a high energy state of a nuclide which may decay by isomeric transition (IT) as described in the table below, although certain low-lying states may decay independently to other nuclides rather than the ground state.</td>
</tr>
<tr>
<td>Half-life</td>
<td>The time taken for the activity of a radioactive nuclide to fall to half of its previous value.</td>
</tr>
<tr>
<td>Electron volt (eV)</td>
<td>The energy acquired by any charged particle carrying a unit (electronic) charge when it falls through a potential of one volt, equivalent to $1.602 \times 10^{-19}$ J. The more useful unit is the mega (million) electron volt (MeV).</td>
</tr>
</tbody>
</table>

Decay Modes

α  Alpha decay is the emission of alpha particles which are $^4$He nuclei. Thus the atomic number of the daughter nuclide is two lower and the mass number is four lower.

β⁻ Beta or electron decay for neutron-rich nuclides is the emission of an electron (and an anti-neutrino) as a neutron in the nucleus decays to a proton. The mass number of the daughter nuclide remains the same but the atomic number increases by one.

β⁺ Beta or positron decay for neutron-deficient nuclides is the emission of a positron (and a neutrino) as a proton in the nucleus decays to a neutron. The mass number of the daughter nuclide remains the same but the atomic number decreases by one. However this decay mode cannot occur unless the decay energy exceeds 1.022 MeV (twice the electron mass in energy units). Positron decay is always associated with orbital electron capture (EC).

EC Orbital electron capture in which the nucleus captures an extranuclear (orbital) electron which reacts with a proton to form a neutron and a neutrino, so that, as with positron decay, the mass number of the daughter nuclide remains the same but the atomic number decreases by one.

IT Isomeric transition in which a high energy state of a nuclide (isomeric state or isomer) usually decays by cascade emissions of γ (gamma) rays (the highest energy form of electromagnetic radiation) to lower energy levels until the ground state is reached.

p  Proton decay in which a proton is emitted from the nucleus so both the atomic number and mass number decrease by one. Such a nuclide is said to be ‘particle unstable’.

n  Neutron decay in which a neutron is emitted from the nucleus so the atomic number remains the same but the atomic mass is decreased by one. Such a nuclide is said to be ‘particle unstable’.
Professor Michael Thoennessen

Michael Thoennessen (Figure 1) is a Professor in the Department of Physics & Astronomy at Michigan State University (MSU), USA, and Associate Director at the National Superconducting Cyclotron Laboratory (NSCL) located on the campus of MSU. His main research interest is the study of exotic nuclei far from stability, concentrating on neutron-unbound nuclei beyond the neutron dripline. He performs most of his experiments at NSCL with the Modular Neutron Array (MoNA) – a large-area high efficiency neutron detector (Figure 2). He recently initiated a project to document the discovery of all isotopes. These reviews are currently being published in the journal *Atomic Data and Nuclear Data Tables*. The detailed description for each isotope has been carried out for about 70% and will be finished next year. Whilst some of the discovery criteria differ from these adopted here, there is generally good agreement as to assigning credit to the discoverers.
remaining ~2900 are described for these purposes as being ‘artificial’ radioactive nuclides, since a number of the primordial nuclides are also radioactive but with very long half-lives. There exist in nature a significant number of nuclides other than those of primordial origin due to various radioactive decay modes of naturally occurring thorium and uranium isotopes. The limits on the stability of the nuclides are defined by the proton and neutron drip lines beyond which the nuclides lose particle stability, become unbound and emit protons in the case of the proton drip line and neutrons in the case of the neutron drip line. Nuclides do exist beyond the drip lines but in the case of the light elements both the proton and neutron drip lines have been approached throughout the Periodic Table. For the medium to heavy elements, a large number of nuclides remain to be discovered before the neutron drip line is reached. Thoennessen and Sherrill (84) predict that up to the presently known limits of the Periodic Table the number of nuclides remaining to be discovered is likely to be at least equal to the number already known. There is optimism that at least 1000 of these will be discovered in the next ten years.

References

17. J. M. Siegel, Rev. Mod. Phys., 1946, 18, (4), 513


The Author

John W. Arblaster is interested in the history of science and the evaluation of the thermodynamic and crystallographic properties of the elements. Now retired, he previously worked as a metallurgical chemist in a number of commercial laboratories and was involved in the analysis of a wide range of ferrous and non-ferrous alloys.
“Catalysis in the Refining of Fischer–Tropsch Syncrude”

By Arno de Klerk (University of Alberta, Edmonton, Alberta, Canada) and Edward Furimsky (IMAF Group, Ontario, Ottawa, Canada), RSC Catalysis Series, No. 4, Royal Society of Chemistry, Cambridge, UK, 2010, 294 pages, ISBN: 978-1-84973-080-8, £121.99, US$205.00, €139.95 (Print version); e-ISBN: 978-1-84973-201-7 (Online version)

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Email: stewart.brown@matthey.com

Introduction
“Catalysis in the Refining of Fischer-Tropsch Syncrude” is the fourth book in the Royal Society of Chemistry’s Catalysis Series. Written by Arno de Klerk and Edward Furimsky from the University of Alberta and the IMAF group in Ontario, Canada, respectively, this book provides a review of the somewhat neglected area of refining and upgrading catalysts, rather than the more widely published area of Fischer-Tropsch synthesis itself (1). This book provides an excellent and comprehensive evaluation of the catalytic processes for syncrude conversion to useful products such as fuel and oils.

The book consists of eleven chapters, which are well presented and divided into easily manageable segments. The writing style is very clear and explains the processes concisely and simply. The first two short chapters put syncrude refining into context within the Fischer-Tropsch process as a whole and allow non-specialists to quickly grasp the technology. The remaining chapters take the reader on a logical and well thought out journey through the Fischer-Tropsch production of syncrude; the upgrading of waxes, oxygenates and crude; the catalysis of the refining process; the commercial products obtained during the process; and finally a review of the current patent literature and future perspectives.

Fischer-Tropsch Processes
Fischer-Tropsch is the process whereby synthesis gas (hydrogen and carbon monoxide) is converted into a mixture of hydrocarbons, oxygenates, water and carbon dioxide. The hydrocarbons thus produced can be refined and used in place of more conventional liquid fuels derived from crude oil. Synthetic fuel can be produced by a variety of methods, with gas-to-liquid (GTL), coal-to-liquid (CTL) and biomass-to-liquid (BTL) being the most widespread. An outline of a Fischer-Tropsch facility is summarised in Figure 1.

Fischer-Tropsch synthesis has been carried out predominantly using iron- and cobalt-based catalysts...
since the 1930s, having been commercialised in Germany in 1936 to provide transport fuel for the coal rich, oil poor nation. South Africa has since become the largest user of Fischer-Tropsch technology, developed in response to international sanctions that prevented the import of crude oil, and nearly the entire country’s diesel is currently produced from coal by this method (2).

In the present book, Chapters 3 and 4 provide a good technical overview of and background to the chemistry of Fischer-Tropsch reactions. These chapters concentrate on how different reaction and catalyst conditions affect the composition of the syncrude (Figure 2). Chapter 3 concludes with an examination of current industrial Fischer-Tropsch processes. The message is that this area of chemistry is not just an academic pursuit, but rather a key technology for future energy security and fuel production. The table of production facilities provides a timeline from the first facilities employed by Germany during the Second World War right up to the gigantic Shell ‘Pearl GTL’ plant in Qatar. This plant began shipments of its GTL Gasoil product in 2011 with full production scheduled for 2012. In Chapter 4, the reader is taken in more detail through the initial processing steps of Fischer-Tropsch synthesis and how the syncrude produced differs from that obtained from conventional crude oil. The differences in chemical composition are vital in understanding which downstream refining and upgrading processes are required to produce useful commercial products.

**Platinum Group Metals in the Upgrading of Fischer-Tropsch Syncrude**

Chapter 5 is where the main topic of the book really gets going, it is by far the largest chapter in the whole book with over 120 pages devoted to it. Here the reader is provided with a review of the technical detail behind the catalysis of upgrading Fischer-Tropsch syncrude. The chapter is split into four main sections corresponding to the most widely utilised conversion technologies. These are:

(a) oligomerisation,
(b) isomerisation and hydroisomerisation,
(c) cracking and hydrocracking,
(d) hydrotreating.

Although this chapter contains the most significant amount of information, it only concerns the upgrading of syncrude rather than the refining. Catalytic reforming, which is an important platinum group metal (pgm) utilising process in refineries, is mentioned in a later chapter.

In terms of pgm usage, all but the oligomerisation section contain numerous references to pgm-catalysed processes. The subsections proceed in a logical fash-
ion, describing first the background and mechanism of each process, then the various catalysts used. The use of platinum and palladium as promoters in various zeolite, silica-alumina, phosphate and sulfonated zirconia catalysts is given considerable coverage, well illustrated by graphs and tables detailing conversion, yield and selectivity relationships with various feedstocks. The catalytic mechanisms detailed throughout this book are very clear, giving the reader an understanding of the chemistry behind the refining and upgrading processes. The vast range of different temperatures, pressures, feeds, catalysts and other factors are emphasised, giving a good feel for the complexity of syncrude upgrading. The authors compare and contrast these different factors and clearly show the effect of each on the final products.

Each section gives a solid introduction and mechanistic outline to each process, followed by an examination of the commercial aspects and a comprehensive review of the current literature regarding catalyst developments. They conclude with a comparison of the various modes of deactivation for different catalysts and conditions. This is an area often neglected when concentrating on activity, yields and selectivity.

**Refining Catalysts**

Chapter 8, despite being somewhat shorter than Chapter 5, nevertheless contains an excellent review of refining catalysts, such as those employed in reforming, a significant area of pgm demand. The first part of the chapter demonstrates the differences between conventional oil refineries and those employing Fischer-Tropsch technology. The generic plant designs illustrated at the beginning of the chapter highlight the major differences in how the various refined fractions are produced and again drives home the message that to produce high quality fuels and oils using Fischer-Tropsch synthesis requires specialised equipment, processes and catalysts to deal with the different chemistries of syncrude and conventional crude oil. The first table in Chapter 8 highlights this further by examining the current conventional conversion processes and their compatibility with Fischer-Tropsch refineries.

There are two subsections dedicated to the use of platinum on acidic alumina and on non-acidic zeolite respectively, highlighting the importance of platinum for the production of synthetic fuels. The higher amounts of oxygenates in Fischer-Tropsch feed have been shown to deactivate the acidic support, although it is very compatible with the non-acidic Lzeolite catalyst (Figure 3). The
much lower sulfur content of the feed is a distinct advantage over conventional crude feedstocks.

The final chapters examine the commercial products obtained from Fischer-Tropsch syncrude, the current patent literature and future perspectives in this technology. The authors do a very good job of putting the catalysis reviewed in the preceding chapters into a commercial context, whilst showing what the future may hold for this exciting area. The final chapter makes the interesting point that Fischer-Tropsch plants have historically been built to deal with issues of energy security. Going forward it appears that investment will be driven by both the requirement to produce fuels from alternative carbon sources and the price differential between conventional crude and that produced by Fischer-Tropsch technology.

Conclusions

The authors state that a review of catalysis in the refining of Fischer-Tropsch syncrude is the main objective of the book. This objective has been achieved admirably, providing an accessible and comprehensive review of Fischer-Tropsch refining catalysis from the fundamental chemistry to the commercial aspects and applications. The reader is required to have a general understanding of chemistry and catalysis, and the book will appeal both to those looking to gain initial exposure to this topic, and to readers with greater knowledge of the subject. The use of the pgms features strongly throughout the book, dominating the chapters on upgrading and refining syncrude.

Overall, this book will be of interest to a wide audience, from those involved in the academic pursuit of improving the catalysis to those involved with the commercial development of Fischer-Tropsch refining. It is clearly an exciting area to be involved with and the potential to provide an alternative to conventional fuel sources is something that the authors convey particularly well.

References

Dr Stewart Brown graduated with an MChem (Hons) and a PhD in Chemistry from the University of Liverpool, UK. He joined Johnson Matthey in 2004 and spent 5 years as a Process Development Chemist, involved in the scale-up of new catalysts and processes for the Emission Control Technologies business unit. In 2009 he transferred to Precious Metals Marketing and is currently a Market Analyst within the Market Research team, focusing on platinum group metal demand from the chemical, electronics, automotive and petroleum refining sectors.
The latest annual Industry Review by Fuel Cell Today was officially launched on 14th September 2011 at the 4th World Hydrogen Technologies Convention in Glasgow, Scotland. This Review provides an introduction to fuel cell technology as well as a brief history of key developments and a timeline (see Figure 1). The developments in fuel cell unit shipments and megawatts shipped during the period 2007–2010 are covered in the 'State of the Industry' chapter and supported by data tables and a forecast for the full year of 2011.

Fuel cells are one of the most versatile energy solutions ever created as they allow clean, efficient, reliable power generation for almost any device requiring electrical power. As such, fuel cells compete as a substitute for a range of power supplies in numerous portable, stationary and transport applications. This report analyses the fuel cell industry in terms of developments by application, region and electrolyte.

2011 Shipments Expected to Grow by 25% Compared to 2010

There has been a twenty-fold increase in shipments of fuel cells with year-on-year growth in both units and megawatts shipped in the last five years. Overall shipments of fuel cells increased by 40% in 2010 compared with the previous year, reaching a new high of 230,000 units. Portable fuel cells represented 95% of this total. In 2010, over 97% of the fuel cells sold globally used proton exchange membrane fuel cell (PEMFC) technology and most were fuelled by hydrogen. Annual fuel cell shipments are expected to grow by 25% between 2010 and 2011, exceeding 285,000 units. Since 2009, Europe has been the leading region of adoption of fuel cells, followed by North America and Asia (including Japan), with all regions globally seeing considerable increases in shipments over that time.

Overview of the Market Sectors

As fuel cells are increasingly adopted for various applications, it is important to view the industry as an assembly of sectors at varying stages of development.

Portable Sector

The portable sector leads the way in terms of shipments, it has increased by 75% each year since 2007. This has been dominated by fuel cell educational devices and toys. There have been some notable developments in the use of fuel cells in external battery chargers, although this application has not yet reached commercialisation. Problems with miniaturisation and system integration have prevented the direct integration of fuel cells into portable consumer electronics. However, external fuel cell charging products are being offered, Horizon Fuel Cell Technologies presented the MiniPAK in June 2010, a pocket-sized fuel cell charger which can deliver up to 2 W of constant power using a standard USB port and uses refillable fuel cartridges capable of storing up to 12 Wh of net energy.

Stationary Sector

There was growth of 10% in stationary fuel cell shipments in 2010 compared to 2009. North America and Asia dominate the stationary markets which can be subdivided into three categories: megawatt-scale units used for prime power, uninterruptible power supply (UPS) units for backup power and micro-combined heat and power (micro-CHP) units for residential use. In the large stationary sector, UTC Power continues to ship its PureCell 400 kW phosphoric acid fuel cell (PAFC) systems to customers throughout the USA. These have been installed in supermarkets, office buildings, residential properties and recently six units were installed in the new buildings on the site of the World Trade Center. In Asia, specifically Japan, cumulative shipments of the Ene-Farm fuel cell system for residential use had reached 13,500, all of which are PEMFC, by the end of 2010.

Transport Sector

In 2010, shipments in the transport sector increased by 20% to reach a new high of 2400 units. The transport sector covers a huge range of end-uses, from cars and buses, to more niche uses such as ferries, unmanned aerial vehicles (UAV) and underwater vehicles for the military Government
Humphry Davy demonstrates the principle of what became fuel cells.

1839
William Grove invents the ‘gas battery’, the first fuel cell.

Charles Langer and Ludwig Mond develop Grove’s invention and name the fuel cell.

1889

1950s
General Electric invents the proton exchange membrane fuel cell.

1891
Francis Bacon demonstrates a 5 kW alkaline fuel cell.

1959

1960s
NASA first uses fuel cells in space missions.

1889
Charles Langer and Ludwig Mond develop Grove’s invention and name the fuel cell.

1959

1960s
US Navy uses fuel cells in submarines.

1889
Charles Langer and Ludwig Mond develop Grove’s invention and name the fuel cell.

1959

1960s
US Navy uses fuel cells in submarines.

1889
Charles Langer and Ludwig Mond develop Grove’s invention and name the fuel cell.

1959

1960s
US Navy uses fuel cells in submarines.

1970s
The oil crisis prompts the development of alternative energy technologies including PAFCs.

1990s
Large stationary fuel cells are developed for commercial and industrial locations.

2007
Fuel cells begin to be sold commercially as auxiliary power units and for stationary backup power.

2008
Honda begins leasing the FCX Clarity fuel cell electric vehicle.

2007
Fuel cells begin to be sold commercially as auxiliary power units and for stationary backup power.

2008
Honda begins leasing the FCX Clarity fuel cell electric vehicle.

2009
Residential fuel cell micro-CHP units become commercially available in Japan. Also thousands of portable fuel cell battery chargers are sold.

Fig. 1. Timeline showing key points in the development of fuel cells (Source: Fuel Cell Today)
assistance in the USA has helped fuel cells attain a commercial position in the electric forklift market. This trend is expected to continue as the technology is exported to other regions. Eight of the world’s leading automakers aim to introduce fuel cell electric vehicles (FCEVs) by 2015. In 2010, the London black taxi was remodelled to integrate a hydrogen fuel cell by a group of companies including Intelligent Energy and Lotus Engineering. A fleet of twenty vehicles is to be produced in time for the 2012 London Olympic Games. Intelligent Energy has also announced its Suzuki Burgman fuel cell scooter had been given European Commission Whole Vehicle Type-Approval (WVTA), this enables vehicles or components of the same type to be accepted for production and sale within Europe without further testing, paving the way for full commercialisation of fuel cell motorcycles.

Prospects for Fuel Cells
In the last few years, the prospects for fuel cells have considerably improved. In the last four years, more than 400,000 fuel cells were sold cumulatively. The various applications (portable, stationary and transport) are all boasting growth, with different electrolytes establishing their roles in particular sectors, and platinum-catalysed fuel cells seeing the most commercial traction to date.

Availability of the Industry Review
Electronic copies of the review are available for the first time as a free download. Free printed copies are available upon request. For more information or to download a copy, please visit http://www.fuelcelltoday.com/analysis/industry-review or email: info@fuelcelltoday.com.
Publications in Brief

BOOKS

“Concepts in Syngas Manufacture”

Syngas (synthesis gas) is playing a growing role in the energy sector, because it can be converted into a number of energy carriers and fuels. The steam reforming process is the main technology for the manufacture of syngas in use today. “Concepts in Syngas Manufacture” aims to give an analysis of the catalyst and process problems involved, and illustrates how basic principles can be applied to solve design and operational issues. Pt, Pd, Rh, Ir and Ru as catalytic materials are heavily featured in the book.

“Handbook of Industrial Catalysts”

The commercial importance of catalysis and the diverse intellectual challenges of catalytic phenomena have stimulated study by a broad range of scientists from a variety of disciplines. Increasing research activity has brought deeper levels of understanding, and these have been associated with a continually growing amount of published material. This book provides reviews and references to guide those working on industrial catalysts. Relevant chapters for pgm use include: ‘Hydrogenation Catalysts’, ‘Oxidation Catalysts’, ‘Refinery Catalysts’ and ‘Environmental Catalysts’. The book is aimed at catalysis researchers in industry and academia, and will also benefit students.

“The OLED Handbook”

“The OLED Handbook” is a comprehensive guide to organic light-emitting diode (OLED) technology, industry and market. Topics covered include:
(a) OLED technology and materials;
(b) How an OLED panel is produced;
(c) How OLEDs compare to LCD displays;
(d) What kind of OLED displays are available on the market today;
(e) OLED lighting technology, currently available panels and lamps (complete with technical specifications and prices);
(f) The future of OLED displays and lighting and the challenges ahead.

Edited by L. Zhang (Missouri University of Science and Technology, USA) and G. K. Krumdick (Argonne National Laboratory, USA), John Wiley & Sons, Hoboken, New Jersey, USA, 2011, 130 pages, ISBN: 978-0-470-76884-6, £60.50, €72.60, US$89.95; e-ISBN: 9781118086391

This book is the proceedings of a symposium held during the 2011 TMS Annual Meeting & Exhibition, San Diego, California, USA, 27th February–3rd March 2011. Recycling of e-waste involves the following steps:
(a) Disassembly: targeting hazardous or valuable components for special treatment;
(b) Upgrading: using mechanical processing and/or metallurgical processing to upgrade the content of desired materials, i.e. preparing materials for the refining process, such as grinding plastics into powders;
(c) Refining: recovered materials are retreated or purified using metallurgical processing. There is a proceedings paper dedicated to the recovery of Au, Ag and pgms from electronic waste.

“Thermochemical Conversion of Biomass to Liquid Fuels and Chemicals”
This book is an up-to-date overview of the thermochemical methods available for biomass conversion to liquid fuels and chemicals. In addition to traditional conversion technologies such as fast pyrolysis, new developments are covered, including catalytic routes for the production of liquid fuels from carbohydrates and the use of ionic liquids for lignocellulose utilisation. The chapters provide an introduction to each topic, as well as describing recent research.

JOURNALS

Applied Nanoscience

Editors: F. Stoddart (Northwestern University, USA) and M. M. Hussain (King Abdullah University of Science and Technology, Saudi Arabia); Springer; ISSN: 2190-5509; e-ISSN: 2190-5517

Applied Nanoscience is an open access journal (supported by the King Abdulaziz City for Science and Technology (KACST), Saudi Arabia) published under the brand SpringerOpen. It publishes original articles about nanoscience and the application of emerging nanotechnologies in areas as diverse as water science, advanced materials, energy, electronics, environmental science and medicine.

Nano Energy

Editor-in-Chief: Z. L. Wang (Georgia Institute of Technology, USA); Elsevier; ISSN: 2211-2855

Nano Energy, launching in 2012, will cover the science and engineering of nanomaterials and nanodevices relevant to energy harvesting, conversion, storage, utilisation and policy. Types of content will include review articles, rapid communications, full-length articles, and news and opinions. Nano Energy invites contributions on:
(a) Batteries;
(b) Fuel cells;
(c) Hydrogen generation and storage;
(d) Light-emitting diodes;
(e) Optoelectronic devices for efficient energy usage;
(f) Photovoltaics;
(g) Piezoelectric nanogenerators;
(h) Policy and perspectives in energy;
(i) Self-powered nanodevices/nanosystems;
(j) Supercapacitors;
(k) Thermoelectrics.

Special Issue: Catalysis for New Energy Technologies


With guest editors De Chen (Norwegian University of Science and Technology, Norway) and Chang-Jun Liu (Tianjin University, China), this special issue of ChemCatChem about catalysis for new energy technologies is based on the Symposium on New Energy Technologies as part of the 240th National Meeting of the American Chemical Society held in Boston, USA on 22nd–26th August 2010. It contains papers on photocatalysis, catalysis for biomass conversion, hydrogen production from both fossil fuels and biomass, and the conversion of hydrogen in fuel cells.

Special Issue: 7th Symposium on Fuel Cell Modelling and Experimental Validation (MODVAL7)


This symposium was held in Morges (Lausanne), Switzerland from 23rd–24th March 2010. Advances in modelling were presented, mainly on SOFCs and PEMFCs, as well as experimental work for model validation. This special issue of Fuel Cells has eleven original research papers from the symposium, including 'Experimental Investigations into Phosphoric Acid Adsorption on Platinum Catalysts in a High Temperature PEM Fuel Cell' and 'The Role of Reactive Reaction Intermediates in Two-Step Heterogeneous Electrocatalytic Reactions: A Model Study'.
ON THE WEB
Fuel Cell Today

Fuel Cell Today launched its new website on 12th September 2011, which comprises a number of new and updated features. These include:
(a) Improved navigation;
(b) Filtered topic pages allowing users to view content by technology or application;
(c) A new educational page with updated sections on fuel cell history (with a history timeline), technologies and applications;
(d) Analyst views – every two weeks a Fuel Cell Today analyst discusses a prominent topic in fuel cells;
(e) Additional downloadable content including event reports;
(f) An improved Industry Directory with filtering.
Find this at: http://www.fuelcelltoday.com/
Abstracts

CATALYSIS – APPLIED AND PHYSICAL ASPECTS

Continuous Flow Hydrogenation Using Polysilane-Supported Palladium/Alumina Hybrid Catalysts

Continuous flow systems for hydrogenation using Pd/(PSi–Al2O3) (PSi = polysilane) hybrid catalysts were developed. The original Pd/(PSi–Al2O3) catalysts were used in these systems for the hydrogenation of unsaturated C–C bonds and a nitro group, deprotection of a carbobenzyloxy group, and a dehalogenation reaction. High catalytic activity was retained for at least 8 h under neat conditions. No Pd leaching was detected. The hydrogenation reactions could also be carried out successfully in water.

CATALYSIS – REACTIONS

Direct Synthesis of Hydrogen Peroxide from Hydrogen and Oxygen over a Pd Core-Silica Shell Catalyst

Pd core-silica shell particles (Pd@SiO2) were obtained by encapsulating Pd colloidal NPs with a SiO2 shell via the Stöber method. The Pd core NPs were well dispersed and had uniform size (4 nm) and shape inside the porous SiO2 shell. Pd@SiO2 showed high performance for the direct synthesis of H2O2, which was better than those of impregnated Pd/SiO2 and Pd/Al2O3.

Catalytic Oxidative Cleavage of Olefins Promoted by Osmium Tetroxide and Hydrogen Peroxide

H2O2 was employed as the terminal oxidant in the OsO4-mediated oxidative cleavage of olefins, producing aldehyde and ketone products. Aryl olefins were cleaved in good to excellent yield. Alkyl olefins cleaved in moderate to good yield for di- and tri-substituted alkenes. The use of the more environmentally benign H2O2 as the terminal oxidant in lieu of Ozone addresses concerns about the salt stream associated with the original protocol.

EMISSIONS CONTROL

A Review of NOx Storage/Reduction Catalysts: Mechanism, Materials and Degradation Studies

NSR is employed for lean-burn gasoline and diesel vehicles. This Minireview covers reaction mechanisms, degradation mechanisms and catalyst developments. The NSR reaction and degradation mechanisms are discussed based on a typical NSR catalyst Pt/BaO/Al2O3, along with NSR catalyst developments for enhancing performance and alleviating their S poisoning and thermal degradation. (Contains 137 references.)

Modeling the Effects of Pt Loading on NOx Storage on Pt/BaO/Al2O3 Catalysts

A microkinetic model was developed for NOx storage on a series of Pt/BaO/Al2O3 catalysts with Pt loadings from 0–3.7 wt%. Ba sites were classified into two storage site populations: proximal and non-proximal (bulk). A simple model for estimating the capacities of the two Ba site populations using the Pt loading was used to explain trends in the storage of NO/O2 and NO2/O2 and integrates existing literature models for NO2 storage on BaO/Al2O3, Pt-catalysed NO oxidation to NO2, and spillover chemistry involving NO2. The model shows reasonable agreement with the measured storage of NO and NO2 in O2 at 340°C for a range of storage times and Pt loadings.

FUEL CELLS

Platinum Catalyst Degradation in Phosphoric Acid Fuel Cells for Stationary Applications

The fundamental decay mechanism of Pt alloy cathode
catalysts for PAFCs was studied with a surface area loss model and experimental electrochemical surface area measurements after real-world operation. The rate of change in electrochemical surface area was found to be affected by both time and temperature. The results suggest that Pt particle migration and coalescence on the C support surface is the dominant mechanism for surface area change in these PAFC catalysts.

Recent Advances in Catalysts for Direct Methanol Fuel Cells


This Perspective reviews potential pathways for increasing the cost-effectiveness and efficiency of low Pt alloys and coreshell-like catalysts, Pd-Me ((Me = Co, Fe, etc.), Ru-Se and heat-treated MeN<sub>x</sub>C<sub>y</sub>-based catalysts for DMFCs (see the Figure). Fundamental understanding of the composition–activity and structure–activity relationships, innovative synthesis and promising development directions are highlighted. The main degradation mechanism of the catalysts and the corresponding mitigating strategies are presented. (Contains 262 references.)

**Platinum Monolayer on IrFe Core–Shell Nanoparticle Electrocatalysts for the Oxygen Reduction Reaction**


Highly active and stable Pt monolayers were deposited on the IrFe core-shell NPs by galvanic replacement of underpotentially deposited Cu adatoms on the Ir shell surfaces. The specific and Pt mass activities for the ORR on the Pt<sub>ML</sub>/IrFe/C electrocatalyst were 0.46 mA cm<sup>–2</sup> and 1.1 A mg<sub>Pt</sub>–1, respectively. The catalysts were shown to have high durability.

**The Study on the Dynamic Response Performance of PEMFC with Electrodeposited RuO<sub>2</sub> • xH<sub>2</sub>O-Pt/C Electrode**


Electrodeposited RuO<sub>2</sub>•xH<sub>2</sub>O-Pt/C was characterised by SEM-EDS, which confirmed that RuO<sub>2</sub>•xH<sub>2</sub>O was electrodeposited on the surface of Pt/C. The performance of single cells with and without RuO<sub>2</sub>•xH<sub>2</sub>O-Pt/C at the cathode was studied using CV, electrochemical impedance spectra and polarisation curve techniques. When the PEMFC modified with RuO<sub>2</sub>•xH<sub>2</sub>O-Pt/C was operated at lower pressure, a faster and more stable dynamic response was found. Modifying with RuO<sub>2</sub>•xH<sub>2</sub>O-Pt/C not only slightly increases the single cell performance but also dramatically improves the dynamic response performance.

**METALLURGY AND MATERIALS**

**Gold-Platinum Nanoparticles: Alloying and Phase Segregation**


The phase and surface properties of supported AuPt NPs have been shown to range from single-phase alloy, partial alloy, to phase-segregated structures depending on the preparation conditions, bimetallic composition and supporting materials. This conclusion was also supported by DFT computation for small AuPt clusters and molecular dynamics simulations for AuPt NPs of various sizes. For AuPt NPs supported on C materials, the nanoscale alloying or phase segregation was demonstrated to be controllable by thermal treatment temperatures.

**APPARATUS AND TECHNIQUE**

**Novel PdAgCu Ternary Alloy: Hydrogen Permeation and Surface Properties**

Dense PdAgCu composite membranes were prepared by the sequential electroless plating of Pd, Ag and Cu on top of both disk and tubular porous stainless steel substrates. The H₂ permeation performance was investigated over 350–450ºC and a trans-membrane pressure up to 100 kPa. After annealing at 500ºC in a H₂ stream followed by permeation experiments, the alloy layer had a fcc crystalline phase with a bulk concentration (by EDS) of: 68% Pd; 7% Ag; and 25% Cu. The PdAgCu tubular membrane was stable for more than 300 h in a H₂ stream. The permeabilities of the PdAgCu samples were higher than the permeabilities of PdCu membranes with a fcc phase. The cosegregation of Ag and Cu to the membrane surface was observed after H₂ permeation experiments at high temperature.

**ELECTRICAL AND ELECTRONICS**

**Characterization of IrO₂/CNT Nanocomposites**


IrO₂ nanocrystals (NCs) were grown on vertically aligned CNT templates, forming IrO₂/CNT nanocomposites, by MOCVD using (C₆H₇)(C₈H₁₂)Ir. The nanocomposites were characterised using FESEM, TEM, XRD and Raman scattering. The IrO₂ varied from particle- to tube-like NCs as the deposition time increased (5–60 min). The particle-like IrO₂ NCs may be used as a protective layer on CNTs, providing stable and uniform FE properties. The tube-like structure may increase the surface-to-volume ratio which makes the IrO₂/CNT nanocomposites possible candidates for supercapacitor applications.

**MEDICAL AND DENTAL**

**Conjugated Polyelectrolyte–Cisplatin Complex Nanoparticles for Simultaneous in Vivo Imaging and Drug Tracking**


A molecular brush based on a conjugated polyelectrolyte (CPE) grafted with dense PEG chains was complexed with cisplatin to form cisplatin-loaded NPs (CPE–PEG–Pt). The obtained NPs have high far-red/near-infrared fluorescence and are able to release the drug in a continuous and slow manner. These NPs were used to visualise HepG₂ cancer cells. The NPs also served as an in vivo fluorescent imaging probe that simultaneously tracks the in vivo drug distribution in mice upon intravenous administration.

**PHOTOCONVERSION**

**Cyclometallated Platinum(II) Complexes of 1,3-Di(2-pyridyl)benzenes for Solution-Processable WOLEDs Exploiting Monomer and Excimer Phosphorescence**


\[
\text{MePtCl} \quad \text{MePtNCS} \quad \text{N}^\text{C}N^\text{N}5\text{-Fluoro-1,3-di(2-pyridyl)benzene platinum(II)covalently bonded to the polymer backbone.}
\]
chloride, “FPtCl”, and N^C^N-5-methyl-1,3-di(2-pyridyl)-benzene platinum(II) isothiocyanate, “MePtNCS”, were synthesised and then characterised. Both were found to be highly efficient phosphorescent green emitters and could also display excimer emission in the red region. They were studied as triplet emitters in solution-processed, multilayer OLEDs, and compared to the known complex of 5-methyl-1,3-di(2-pyridyl)-benzene, “MePtCl”. “FPtCl” was the most efficiently emitting complex and was used as the dopant in a solution-processed WOLED.

New Design Tactics in OLEDs Using Functionalized 2-Phenylpyridine-Type Cyclometalates of Iridium(III) and Platinum(II)


This Focus Review highlights recent design tactics to develop functional metallophosphors for future OLED devices. Functionalised phosphorescent Ir(III) and Pt(II) ppy-type cyclometallated complexes show better prospects than their unfunctionalised counterparts in terms of switchable emission wavelength, phosphorescent quantum yield and phosphorescent lifetime. The aims are to enhance device efficiency and suppress efficiency roll-off, to achieve versatile colour tuning and simple device manufacture, and to obtain high quality white light from WOLEDs. (Contains 39 references.)
Patents

CATALYSIS – APPLIED AND PHYSICAL ASPECTS

Ruthenium in Conversion of Synthesis Gas
Johnson Matthey Plc, World Appl. 2011/089,377

A method for the conversion of synthesis gas into HCs involves the following steps: (a) passing a mixture of H2 and CO over a Co catalyst at 210–225ºC under 5–60 bar abs to produce a reaction product mixture of HCs, steam, CO and H2; (b) condensing and separating the H2O to produce a dewatered product mixture; (c) passing the dewatered mixture over a supported Ru catalyst at 230–265ºC under 30–60 bar abs; and (d) recovering the HCs. The support for the Ru catalyst is selected from oxidic support, graphite or silicon carbide. The Ru content of the catalyst is in 0.1–10 wt%, preferably 2.5–7.5 wt%. The Ru catalyst is a powder with a volume median diameter in the range 1–200 μm.

CATALYSIS – REACTIONS

Hydrogenation of 1,1-Difluoro-2-nitroethane
Bayer CropScience AG, World Appl. 2011/042,376

A process for producing 2,2-difluoroethylamine by hydrogenating 1,1-difluoro-2-nitroethane uses a catalyst selected from Pt, Pd, Rh, Ir, Os, Ru, Fe, Co and/or Ni, preferably Pt or Pd. The catalytic hydrogenation step involves introducing gaseous H2 into the reaction vessel or generating H2 in situ. The preferred catalysts are PtO2, Pd(OH)2 on activated C or a Lindlar catalyst.

Palladium in Production of Glyceric Acid
Rigas Tehniska Univ., European Appl. 2,332,899; 2011

A Pd catalyst is prepared for the selective production of glyceric acid. H3PdCl4 in HCl is added to (C8H17)3N solution in C6H5CH3, this is shaken and separated by a liquid extraction method. A carrier, selected from a group of inorganic nanopowders synthesised in plasma, is added to the Pd catalyst organic precursor obtained. This mixture is then dried. Pd is pyrolytically reduced by heating the mixture up to 573 K at 10–11 K min⁻¹ and calcination at 573–673 K for 4–5 min at 1 atm. The ratio of glycerol and Pd is n(glycerol)/n(Pd) = 300–500 mol/mol.

EMISSIONS CONTROL

Multiphase Three-Way Catalysts
Catalytic Solutions, Inc, World Appl. 2011/068,509

A TWC for the simultaneous conversion of NOx, CO and HC can consist of a perovskite and non-perovskite phase. The catalyst comprises a substrate, a washcoat and a multiphase catalyst represented by the general formula CeₙLn₁₋ₓAₓMOₙ₋₁ (x < 1; y < 10; s < 10; z > 0, where s = 0 only when y > 0 and y = 0 only when s > 0), where A is selected from Mg, Ca, Sr, Ba, Li, Na, K, Cs, and Rb; Ln is one or more lanthanides; and M is selected from Pt, Pd, Rh, Ru, Fe, Mn, Cr, Ni, Co, Cu, V, Zr, Ag, Au, Al, Ga, Mo, W or Ti. This composition has an additional precious metal component selected from Pt, Pd, Rh, Ir, Os, Ru and Ag.

NOx Trap with Two Zones
Johnson Matthey Plc, British Appl. 2,476,573; 2011

A NOx trap consists of at least one pgm, preferably Pt and/or Pd, at least one NOx storage material and bulk CeO₂ or a bulk Ce-containing mixed oxide deposited uniformly in a first layer (which has a first upstream zone for oxidising HCs and CO) on a honeycombed substrate monolith. A second downstream zone consists of a dispersion of rare earth oxide and has increased heat generation during desulfation. The proportions of the first and second zones are from 20:80 to 80:20. The honeycombed substrate monolith of the first zone is coated, this is then dried and fired; the second zone is impregnated with an aqueous solution of a rare earth element, then this is also dried and fired.

Destruction of Volatile Organic Compounds
Süd-Chemie Inc, World Appl. 2011/066,009

An oxidation catalyst for the destruction of CO, VOCs and halogenated VOCs is prepared by making an aqueous mixture slurry consisting of a solid solution of CeO₂ and ZrO₂ plus either Sn oxide and SiO₂ or both blended with a binder selected from colloidal Al₂O₃, SiO₂, TiO₂, ZrO₂ and CeO₂. The mixture is blended and coated to the substrate, which is produced from cordierite, mullite, Fe-Cr alloy and stainless steel and has a honeycomb or monolithic structure. The coated substrate is then dried and calcined, at least one of Pt and Ru are deposited on the calcined coated substrate and this is then dried and calcined.
Pt is between 20:1 and 1:20 and the loading of Pt and Ru on the substrate is 0.35–7.1 g l⁻¹.

**FUEL CELLS**

**Platinum-Cobalt Nanocube Catalyst**
Hyundai Motor Co, *US Appl*. 2011/0,118,111

A Pt-Co nanocube catalyst can be prepared by dissolving a Pt precursor, a Co precursor, a surface stabiliser and a reducing agent then heating at 120–200°C at the rate of 0.5–10°C min⁻¹ and the temperature of 200°C is maintained for 60–90 min in an inert gas atmosphere. The Pt-Co nanocube is then adsorbed on a C support (selected from ketjen black, CNT and fullerene) and the surface stabiliser is removed to obtain the catalyst. This method for preparing the catalyst allows the preparation of nanocubes with uniform size and cubic shape for high efficiency fuel cell applications.

**Iridium Catalyst in Fuel Cells**

Ir supported on C is used as a catalyst for the anode in a fuel cell. The catalyst layer is ≤6 μm thick and the loading of Ir is 0.01–0.3 mg cm⁻². Corrosion of the anode C is prevented and fuel cell lifetime is prolonged.

**APPARATUS AND TECHNIQUE**

**Protective Coating of Crucibles**

A crucible for use at high temperature consists of a partial protective layer containing Ir, Os, Ru or Re, preferably Ir, and a base body of W. Ir content in the layer is 5–50 at%. The protective layer is prepared from a powder mixture containing W powder and the powder of the coating material and this is applied by flame spraying or plasma spraying the wall to be coated.

**Palladium Nanoparticles in Carbon Nanotubes**

A novel method for preparing CNTs simultaneously formed and filled with Pd NPs using arc discharge (see Figure) in solution is claimed. A PdCl₂ solution is prepared using PdCl₂ powder, deionised water and HCl, a graphite electrode assembly is immersed in the solution and then, connected to a DC power supply. The electrodes are then brought into contact to strike an arc, separated, and an arc-discharge is created at >3000°C. The PdCl₂ solution is vapourised to leave a residue of Pd NPs. Graphene layers are formed which roll away from the electrodes and simultaneously encapsulate the Pd NPs. These unique nanotube structures have potential as gas sensors or as means for hydrogen storage.

**Nitride-Based Light-Emitting Device**

A nitride-based light-emitting device is composed of a substrate with an n-cladding layer, an active layer, a p-cladding layer, a Zn-containing oxide ohmic contact layer with a p-type dopant and a reflective layer consisting of at least one element selected from Pt, Rh, Ru, Ag, Cu, Zn, Sc, Co, Li, Be, Ca, Re, Ti, Ta, Na and La. The first layer is inserted between the p-cladding layer and the ohmic contact layer and the second layer is inserted between the ohmic layer and the reflective layer.

**RECOVERING PRECIOUS METALS**

**Recovering Precious Metals**

A hydrometallurgical procedure for recovering Pt, Pd, Rh, Ir, Ru and Au involves separating the precious metals from the base metals in HCl and precipitating using substituted quaternary ammonium salt (SQAS)
of formula \( H_{0.3}R_{4-x}NX \), where \( H = \) hydrogen, \( R = \) organic group, \( N = \) nitrogen and \( X = \) halide, preferably tetramethylammonium chloride. Pd is separated by precipitating as Pd-SQAS, the precipitate is added to water or acid, this is then boiled to solubilise the precipitated Pd-SQAS and any remaining precipitate is then removed. Pt and Ir are separated by precipitating as Pt-SQAS and Ir-SQAS, the remaining Pt-SQAS and Ir-SQAS precipitates are slurried in water, \( \text{NaNO}_2 \) is added, Pt-SQAS precipitate is removed and Ir-SQAS is precipitated with HCl.

**Recovery of High Quality Rhodium Powder**


A process to obtain high quality Rh powder is described. This process involves the reduction roasting of the Rh-containing residue with Fe, followed by removal of Fe, carried out in the presence of \( \text{H}_2\text{SO}_4 \). The remaining solid is then dissolved in HCl and \( \text{H}_2\text{O}_2 \) solution, then Rh is refined. This Rh black is subjected to a pretreatment heating stage at 200–400°C, then a first heating stage is performed in an inert gas atmosphere of 600–800°C. The sample undergoes a wet grinding and cleaning process then a second heating stage at 900–1100°C in an inert gas atmosphere.

**SURFACE COATINGS**

**Platinum-Catalysed Coating in Adhesive Tapes**

Bostik, Inc, *US Appl.* 2011/0,159,225

A conformable, pressure sensitive foam adhesive tape consists of a closed cell polyolefin foam core, a pressure sensitive adhesive on one side of this polyolefin foam core (this has a polyacrylate backbone and modified silyl functionality) and a release liner which has a Pt-catalysed polymeric polysiloxane coating. There is no control release agent in the release coating. The foam has a density of 300–800 kg m\(^{-3}\) and a tensile strength in the range of 400–600 psi.
The Role of Inductively Coupled Plasma-Optical Emission Spectrometry in Determining the Fineness of Precious Metals

Accurate precious metal analysis is routinely carried out to determine the precious metal content in a wide variety of different materials. This is particularly important for fineness determination for the hallmarking of precious metals for jewellery use (see Figure 1). The precious metal concentration in different materials can vary from parts per million (ppm) or lower in car catalyst or powdered ore samples, to virtually 100% in jewellery alloys or bullion bars. This article considers the benefits of analysis by inductively coupled plasma-optical emission spectrometry (ICP-OES).

The wide range of sample types in which precious metals occur require that a variety of classical and instrumental methods, or combinations of the two, be used in precious metal testing. In the last six decades more than 400 methods have been published for the analysis of precious metals (1, 2). Even an experienced analytical chemist may hesitate to choose the most suitable procedure for separation and determination of precious metals in a material of unknown composition. There can be a temptation to accept the more recently published procedure as being superior to those which are well tried and tested.

Analysing Precious Metal Content
It is estimated that less than 10% of all precious metal determinations can be performed by strictly instrumental techniques. Probably no more than 30% of all determinations are carried out by strictly classical chemical methods. Hence a large portion of the analytical workload must be handled by a combination of chemical and instrumental approaches, which as a result become strongly interdependent. Fire assay and smelting based techniques (Figure 2) are the earliest analytical procedures recorded in human history, and remain essential pretreatment steps for a large variety of samples.

To determine whether an analytical method can achieve the required performance for fineness determination, the method must be tested by frequent repetition, ideally with the same sample.
The Birmingham Assay Office uses ICP-OES extensively. It is one of the best techniques available for the analysis of the platinum group metals (pgms): platinum, palladium, rhodium, iridium and ruthenium, as well as base metals such as copper, zinc and nickel, being accurate to 1 ppm. The technique is destructive but it does accurately determine both major and trace elements.

Using this technique, a small sample is accurately weighed and dissolved in an appropriate acidic matrix (Figure 3) then subjected to temperatures (plasma) high enough to cause excitation of the sample atoms. Once the atoms or ions are in their excited states, they

<table>
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Inductively Coupled Plasma-Optical Emission Spectrometry

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Fig. 3. Sample preparation for ICP-OES. The chemist is checking for the presence of undissolved sample in the volumetric flask, before subjecting the solution to instrumental analysis.
decay to lower stable states by releasing energy. Light is emitted at a specific wavelength by each element present and these emission lines are measured and used to determine the concentrations of the elements of interest.

The high precision of ICP methods is due to the stability of intensity quotients of emission lines, essentially of gold (267.6 nm), platinum (265.9 nm), palladium (340.5 nm) and the internal standard element yttrium (371.02 nm). If the precious metal and yttrium lines are measured simultaneously, a reproducibility in results of at least 0.01% can be achieved.

Comparison with Classical Methods
Classical methods such as gravimetry have maintained their importance and set the standard for the accuracy of instrumental methods. In order to be approved by the ISO as an alternative analytical technique for determining the fineness of precious metal alloys, ICP methods would be required to achieve at least the same level of repeatability as gravimetric methods. In addition it is especially crucial that interference-free direct measurement of the precious metal can be achieved. This is, of course, necessary for the optimisation of ICP-OES.

Over a period of time it has been recognised that ICP-OES can be applied for a wide variety of precious metal alloys. The method is more easily and economically carried out than gravimetry, and can also be faster, as it can be used for multiple element determinations at the same time. It gives results with acceptable precision and its chemical selectivity is higher than for gravimetry. Above all, it attains a reproducibility and accuracy comparable with those of gravimetry.

Conclusion
ICP-OES is now routinely employed by several commercial laboratories for the analysis of pgm-containing powder and ore samples, after fire assay with nickel sulfide as the collector. It is common practice for the analysis of some non-metallic materials, such as car catalyst samples, to use a combination of both chemical (gravimetric) and instrumental approaches. The precision and accuracy of ICP methods make them highly suitable for fineness determination of precious metals for hallarking.

Anybody interested in the analytical chemistry of precious metals would do well to study the excellent reference works by Beamish and Van Loon (1), Beamish (3), Bugbee (4) and Smith (5, 6).

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References

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