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Johnson Matthey Highlights
Welcome to the New Johnson Matthey Technology Review

Johnson Matthey and Sustainability

Johnson Matthey has a strong focus on sustainability, which underpins our commercial activities in manufacturing products which help to reduce the environmental impact of our daily lives and/or improve quality of life. Our products and services mitigate harmful emissions from vehicles, increase the efficiency of manufacturing chemicals, recycle precious metals to ensure resources go further, and make positive contributions to human health through manufacturing active pharmaceutical ingredients and specialised medical components, to name just a few.

In 2007 we launched a formal framework with targets to help achieve its aims – this is ‘Sustainability 2017’, our ten year programme to reduce our impact on the planet and improve the contribution we make for the benefit of all our stakeholders. It has two main drivers: to be more efficient with the resources we use as a business, and to design new products and services which help our customers to be more sustainable and competitive.

Johnson Matthey was also one of the first FTSE 100 companies to acknowledge the importance of this area by combining the reporting of sustainability performance with its annual financial results. We view sustainability as key to the future success of our business and are on course to meet our ‘Sustainability 2017’ targets of cutting our carbon emissions in half, halving our consumption of key resources, achieving zero waste and eliminating accidents and occupational illness cases while simultaneously doubling our underlying earnings per share.

Investment in Research and Development

Research and development (R&D) is vital to the long term sustainability of our business. Johnson Matthey is a technology company – we continue to invest significantly in R&D and many of our programmes are focused on bringing new sustainable products and technologies to the marketplace. Johnson Matthey has developed core competences in key areas of science that underpin our businesses: these include control at the atomic scale, materials characterisation and modelling. As well as internal programmes, the company also runs sponsored university programmes and collaborative external projects. There are thus many opportunities for academics and other researchers to collaborate with Johnson Matthey in a variety of areas in which the company is active.

Johnson Matthey will be celebrating its 200th anniversary in 2017 and R&D has been at the heart of the company since its foundation. One example of our ongoing R&D efforts is the development and design of emission control catalysts to meet tightening legislation around the world to reduce harmful emissions from vehicles and improve air quality. It is 40 years since Johnson Matthey manufactured its first emission control catalyst and the continued investment in R&D which has enabled the successful design and manufacturing of this technology over the years was recognised most recently in April 2014, when Johnson Matthey won a Queen’s Award for Enterprise in Sustainable Development.

Of course none of this would be possible without the hard work of our research teams around the world, as well as our interaction with academic collaborators. In the UK, Johnson Matthey is involved in many collaborative research projects, including the new £12.9 million (US$21.6 million) Engineering and Physical Sciences Research Council (EPSRC)-funded
UK Catalysis Hub, located at the Research Complex at Harwell, UK, which will co-ordinate multi-disciplinary scientists and chemical engineers from over 30 different universities and industry. Johnson Matthey is also a co-sponsor, along with Oxford Brookes University, for a new University Technical College to be situated in Swindon, UK, which will open in September 2014. Here we will contribute to the college curriculum and provide vocational experience to help train future engineers.

Johnson Matthey has also recently announced the establishment of a S$5.3 million (US$4.2 million) joint research laboratory in Singapore with Nanyang Technological University. This will be the company’s first research collaboration of this type in Asia and will investigate new materials and renewable energy solutions focussing on technologies for air and water purification and for energy storage.

So as you can see, the research and development of innovative new technology is engrained in the company and I am therefore very proud to introduce the new Johnson Matthey Technology Review. The broader scope of the journal will attract a huge variety of content from a wide range of researchers in all areas where Johnson Matthey is active. We are keen to continue our links to academia in all the technology areas where Johnson Matthey operates and this collaborative approach will continue to be reflected in this journal. I hope that you will enjoy reading it and find inspiration in its pages.

ROBERT MACLEOD, Chief Executive

A Collaborative Approach

The pages of Platinum Metals Review over recent years have highlighted several of Johnson Matthey’s academic collaborations involving platinum group metals (pgms). One collaboration between Johnson Matthey, the University of Aberdeen and Cranfield University in the UK generated a new palladium-based ethylene scavenger to control ethylene-induced ripening of fruit (1). Another study with University College London, UK, determined the species present in fresh and road aged light-duty diesel catalysts (2). The Controlling Access of Reactive Molecules to Active Centres (CARMAC) programme aimed to use chemical engineering and an understanding of reaction mechanisms to improve catalyst specificity and selectivity for the chemical manufacturing industry (3). Johnson Matthey’s flame spray pyrolysis and analytical facilities are acknowledged in a study on platinum-doped titania nanoparticles (4).

Editorial Policy

The Johnson Matthey Technology Review will continue to publish articles and reviews from Johnson Matthey’s many academic collaborators. The journal is not exclusive to those who have an existing relationship with the company. Our new Editorial Policy (5) has more details of the expanded range of topics that the Johnson Matthey Technology Review will cover, from the traditional precious metals science and technology that were the focus of Platinum Metals Review for its 58 year history, to new areas in membrane technology, base metal catalysis, battery technology and much more.

We invite and welcome submissions or proposals for articles and reviews from anyone working in fields covered in our Editorial Policy. All are welcome to contribute to the journal which is provided free as a service to the global scientific community – please get in touch if you wish to contribute. We look forward to hearing from you.

SARA COLES, Assistant Editor

References

Comparative Investigations on Platinum Cluster Salts

Experimental characterisation of platinum carbonyl cluster salts for applications in molecular electronics

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To evaluate future applications of metallic clusters in nanoscience and nanotechnology, the electronic properties of the high-nuclearity carbonyl anionic platinum cluster \([\text{Pt}_{19}(\text{CO})_{22}]^{4-}\) were investigated using two different organic cations. In particular, \(N,N'\)-diethyl viologen dication (\(\text{Vio}^{2+}\)) and \(N,N'\)-dimethyl-\(9,9'\)-bis-acridinium dication (\(\text{Acr}^{2+}\)) were employed as counterions, oxidising agents and characterisation probes. The reactions of \([\text{Pt}_{19}(\text{CO})_{22}]^{4-}\) tetra-n-butylammonium salt, \((\text{TBA}^+)_4([\text{Pt}_{19}(\text{CO})_{22}]^{4-})\), with both \((\text{Vio}^{2+})_2([\text{Pt}_{19}(\text{CO})_{22}]^{4-})\), ‘PtVio’, which was structurally characterised by single crystal X-ray diffraction (XRD) analysis. However, when using \((\text{Acr}^{2+})_2([\text{Pt}_{19}(\text{CO})_{22}]^{3-})\) stoichiometry for the precipitated solid, ‘PtAcr’, was inferred from the experimental evidence, leading to an interesting ‘doubly-radicalic salt’. This new type of salt, consisting of a radical anionic Pt cluster and a radical cation, is characterised by extremely simple synthesis and isolation processes and by the lowest solid-state resistivity found in high-nuclearity cluster salts with redox-active cations (1).

Introduction

Large metal carbonyl clusters are well-known compounds resembling fragments of metal aggregates stabilised by surrounding carbon monoxide ligands and free negative charges. A recent review reports the synthesis and characterisation of nanosized homo- and heterometallic Pt carbonyl clusters up to 38 and 165 metal atoms respectively (2). Carbonyl clusters are excellent models for the metallic state because their molecular structures mimic very well either bulk metal packings (i.e. cubic close-packed (ccp), hexagonal close-packed (hcp)) or quasicrystalline phases in amorphous metals (i.e. Bagley’s pentagonal packing (3)) and can be considered as useful tools to study metallic physical properties, such as electrical conductivity and magnetic behaviour. Electron-transfer processes
involving high-nuclearity metal carbonyl clusters have been investigated (4) as they have a number of potential applications in nanoscience and nanotechnology (5). Electrochemical research is particularly focusing on high-nuclearity Pt carbonyl clusters, such as \([\text{Pt}_{19}(\text{CO})_{22}]^{4-}\) and \([\text{Pt}_{24}(\text{CO})_{30}]^{2-}\), which behave as molecular charge capacitors, showing several redox waves with features of electrochemical reversibility (4). This multivalence in redox activity could be exploited to obtain electron-transfer materials based on salts of redox-active anionic clusters and redox-active organic counterions. So far, the only reported examples encompass heterometallic low-nuclearity carbonyl clusters, which are characterised by less developed electrochemical properties and multivalence than high-nuclearity clusters (1). Interestingly, in those cases, an order-of-magnitude decrease was observed in the solid-state cluster salts’ resistivity when passing from non redox-active cations to the redox-active \(N,N'-\text{diethyl viologen}\). In order to better understand the chemistry of such compounds and explore their potential exploitations, the present article reports a comparative study on new cluster salts: a simple exchange-salt and an electron-transfer salt. The latter, in particular, is characterised by the lowest solid-state resistivity found in previously reported electron-transfer cluster salts (1).

**Experimental**

The compounds were obtained through the spontaneous reaction of the homo-metallic high-nuclearity Pt carbonyl cluster salt \((\text{TBA}^+)_4([\text{Pt}_{19}(\text{CO})_{22}]^{4-})\) with either \(N,N'-\text{dimethyl-9,9'-bis-acridinium dication (Acr}^{2+}\) tetraphenylborate salt, \((\text{Acr})^+\text{(BPh}_4^-)\), or \(N,N'-\text{diethyl viologen dication (Vio}^{2+}\) tetraphenyloborate salt, \((\text{Vio})^+\text{(BPh}_4^-)\). These particular organic dications were chosen not only for their redox activity, which played a key role in the synthetic stage, but also for their well-known and widely applied fluorescence, (6–10), in order to have probe molecules through which the nature of the final compounds could be investigated. In particular, Vio is characterised in its dicationic state by a twisted XRD structure (7) and, as density functional theory calculations indicate, it turns planar when the radicalic state is reached (11). In cyclic voltammetry, this dication shows two chemically and electrochemically reversible monoelectronic reduction steps (see the Supplementary Information section available on the web version of this article). On the other hand, the Acr structure evolves from twisted to semi-planar when going from its dicationic to its neutral state (6, 8) and its cyclic voltammetry, even if it is affected by such conformational changes, indicates a higher oxidising power than \(\text{Vio}^{2+}\) (see Supplementary Information).

**Materials and Reagents**

All products and solvents were handled and kept under inert (\( \text{N}_2 \)) atmosphere using Schlenk glassware in order to avoid the possible presence of atmospheric oxygen, which could oxidise and decompose the Pt cluster framework. The classic literature synthesis (12, 13) was performed for the cluster, which can be briefly summarised as follows. Beginning with a Pt wire, a three-step synthesis was carried out, involving:

(a) The dissolution of metallic Pt in \(\text{aqua regia}\), initially forming hexachloroplatinic acid (\(\text{H}_2\text{PtCl}_6\)) and then sodium hexachloroplatinate (\(\text{Na}_2\text{PtCl}_6\)) by addition of sodium chloride

(b) Reductive carbonylation of \(\text{Na}_2\text{PtCl}_6\), which was treated with sodium hydroxide under CO atmosphere in methanol solution:

\[
9\text{Na}_2\text{PtCl}_6 + 76\text{NaOH} + 37\text{CO} \rightarrow (\text{Na}^+)_2([\text{Pt}_9(\text{CO})_{18}]^{2-}) + 54\text{NaCl} + 19\text{Na}_2\text{CO}_3 + 38\text{H}_2\text{O}
\]

(c) Thermal decomposition – thermal CO evolution in refluxing acetonitrile was used to promote new metal-metal bonds and enlarge the metal nuclearity of the cluster to obtain the final carbonyl cluster \([\text{Pt}_{19}(\text{CO})_{22}]^{4-}\):

\[
3[\text{Pt}_9(\text{CO})_{18}]^{2-} \rightarrow [\text{Pt}_{19}(\text{CO})_{22}]^{4-} + [\text{Pt}_8(\text{CO})_{x}]^{2-} + (32-x)\text{CO}.
\]

The synthetic reactions of \((\text{Vio}^{2+})_2([\text{Pt}_{19}(\text{CO})_{22}]^{4-})\), \(\text{PtVio}\), and \((\text{Acr}^+)\text{(TBA}^+)_2([\text{Pt}_{19}(\text{CO})_{22}]^{4-})\), \(\text{PtAcr}\), were performed in acetonitrile (\(\text{CH}_3\text{CN}\)) at room temperature starting from \((\text{TBA}^+)_4([\text{Pt}_{19}(\text{CO})_{22}]^{4-})\) and either \((\text{Vio})\text{(BPh}_4^-)\), obtained from the commercial bromide salt, or \((\text{Acr}^{2+})\text{(BPh}_4^-)\), obtained from the commercial nitrate salt. In the former case, a 1:2 molar ratio is stoichiometrically required to obtain PtVio precipitation; in the latter case, a 1:1 molar ratio is stoichiometrically required but experimentally a 1:2 molar ratio proved helpful in shifting to the right the precipitation equilibrium of PtAcr.

**Instrumentation**

IR solution spectra were collected with a Bruker Vector 22 instrument in a calcium fluoride (\(\text{CaF}_2\)) cell, which was loaded under a constant nitrogen flux.
ESR analyses were performed with a Bruker ELEXSYS E500 instrument both at room temperature, i.e. \( T = 298 \, \text{K} \), and at low temperature, i.e. \( T = 77 \, \text{K} \). The microwave frequency used was 9.7999 GHz for spectra recorded at room temperature and 9.4756 GHz for spectra recorded at low temperature. The power of the microwaves used was 6.3 mW and, when dealing with low temperature analyses, two different types of gain were used: 40 dB and 60 dB.

Direct current (DC) magnetic susceptibility and magnetisation measurements were performed on powder samples with a Magnetic Property Measurement System (MPMS®) XL-5 SQUID magnetometer. Temperature dependent susceptibility was measured in the range of 2 K–300 K in a field exceeding the saturation magnetisation of ferromagnetic impurities. Field dependent magnetisation was measured within the field range \( \mu_0H = \pm 5 \, \text{T} \). The samples, always handled in inert atmosphere, were sealed in a pre-calibrated quartz vial whose contribution was cancelled by using the instrument’s automatic background subtraction mode. A residual helium pressure of 1 mbar guaranteed a good thermal contact.

Electrical resistivity measurements were carried out under nitrogen in a glove bag with a Keithley 2400 SourceMeter on polycrystalline materials pressed into pellets (with a diameter of 8 mm or 13 mm, thickness ca. 1 mm) using a four-point probe.

For PtVio, the XRD analysis was performed on crystals obtained by slow diffusion of isopropyl alcohol into a dimethylformamide (DMF) cluster salt solution. The final structure obtained for PtVio was deposited at the Cambridge Crystallographic Data Centre (CCDC), Cambridge, UK, with deposition number CCDC 951529.

Results and Discussion

Infrared Characterisation

The IR spectrum of PtVio in DMF, Figure 1(a), mainly shows the terminal and bridging carbonyl absorption features of the starting \([\text{Pt}_{19}(\text{CO})_{22}]^{4–}\) tetraanion (4) at 2002 cm\(^{-1}\)(s), 1930 cm\(^{-1}\)(w) and 1801 cm\(^{-1}\)(m) with a tiny fraction of oxidised cluster at 2024 cm\(^{-1}\) and 1820 cm\(^{-1}\), suggesting that a part of PtVio (hereinafter indicated as PtVio*) underwent an internal redox reaction, thus containing \([\text{Pt}_{19}(\text{CO})_{22}]^{3–}\) and Vio*.

The IR spectrum of PtAcr in DMF, Figure 1(b), shows the terminal and bridging carbonyl absorption features of the never before isolated \([\text{Pt}_{19}(\text{CO})_{22}]^{3–}\) trianion at 2020 cm\(^{-1}\) (s), 1953 cm\(^{-1}\)(w) and 1821 cm\(^{-1}\)(m) with an expected 20 cm\(^{-1}\) shift from \([\text{Pt}_{19}(\text{CO})_{22}]^{4–}\) absorption features (4).

Electron Spin Resonance Spectrum of PtVio Sample

The ESR spectrum of PtVio sample is composed of a single V line at \( g \approx 2.002 \) characterised by a peak-to-peak width \( \Delta H_{pp} = 11.47 \, \text{G} \) nearly independent of temperature, at least down to 77 K. At room temperature, this line is Lorentzian, Figure 2(a), whereas it becomes slightly asymmetric at 77 K. (The 77 K spectrum is not shown because of its low signal to noise ratio.)
Electron Spin Resonance Spectrum of PtAcr Sample

The ESR spectrum (not shown here) of the PtAcr sample consists at room temperature of a Lorentzian-shaped A line at g ≈ 2.001 with ΔHpp ≈ 13.50 G. This feature changes somewhat at lower temperature, Figure 2(b), becoming 35% Gaussian- and 65% Lorentzian-shaped and assuming a line width ΔHpp ≈ 13.20 G at 77 K, whereas a second overlapping ESR pattern B appears, characterised by g_x ≈ g_y ≈ 2.03; g_z ≈ 2.38 <g> = 2.15 as represented by the calculated red line in Figure 2(b).

Only one paramagnetic species was detected at room temperature with both the PtVio and PtAcr samples, generating in both cases a single ESR line, although this was a bit narrower with the former (V line) than with the latter (A line). The former can be attributed to a Vio⁺ monocationic radical, i.e. the organic component of PtVio⁺. This is similar to that reported in (14) for the cation radical [Vio⁺]₅[Ag₁₃Fe₈(CO)₃₂]⁻·₄ DMF. Analogously, the A line, rather similar to V, can be attributed to an Acr⁺ monocationic radical. The partially Gaussian shape of A at low temperature can be accounted for by the constrained mobility of the radical species. The partially Gaussian shape of A at low temperature can be accounted for by the constrained mobility of the radical species. The B spectrum which is added to the A line of PtAcr at low temperature is attributable to the trianionic odd-electron [Pt₁₉(CO)₂₂]⁻•. This broad signal is comparable to that reported for the electrogenerated monoanion [Pt₂₄(CO)₃₀]⁻ at liquid nitrogen temperature (4). That signal was unresolved and displayed a significant spectral anisotropy, attributed to three different g parameters, with a mean g value <g> = 2.117, which is only just lower than that of B measured in the present study. Furthermore, the ESR spectrum reported in (4) was rapidly collapsing with increasing temperature, as observed with B, which disappeared at room temperature, though residual traces of it overlapping A cannot be completely excluded in this case.

A rather similar situation is reported in (1), in which [Fe₃Pt₃(CO)₁₅]⁻ and [Vio⁺] in THF solution showed an ESR pattern composed of two overlapping lines with different widths. The g values of B are compatible with the g values of [Fe₃Pt₃(CO)₁₅]⁻, but the g value of B is lower than previously reported (15). As a consequence, the <g> = 2.15 mean value found for B in the present study is lower than the <g> = 2.21 reported previously (15). Furthermore, the hyperfine parameter due to the coupling with three Pt atoms was resolved in the previous study, differently from the present case.

Fluorometric Characterisation

Having established (see Supplementary Information) that no fluorometric interference could result from the starting cluster, solid-state fluorometric analysis, at a constant excitation wavelength of 366 nm, was carried out on both final compounds, exploiting the known (6–10) fluorescence properties of the two cations used. Unfortunately, this analysis was not helpful for Vio, since its fluorescence properties (7) proved too weak to allow fluorometric characterisation.

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Fig. 2. Solid-state ESR spectra of: (a) PtVio at room temperature, V line: g ≈ 2.002; ΔHpp = 11.47 G; and (b) PtAcr at 77 K, A line: ca. 35% Gaussian and 65% Lorentzian; ΔHpp ≈ 13.20 G. Experimental B line: blue; calculated B track: red; <g> = 2.15
The fluorometric emission of Acr was not only much more intense than that of Vio, but was also dependent on the oxidation state of the molecule. Having recorded reference spectra for both its reduced and dicationic oxidised state, it was possible to observe that the fluorometric profile of PtAcr shows the absence of Acr$^{2+}$ fluorometric emission, thus indicating that the final stoichiometry of PtAcr should not include the organic molecule dicationic state (Acr$^{2+}$).

For a thorough description of the experimental set-up and a more complete report on the final results, see Supplementary Information.

**Magnetic Analysis**

The DC SQUID high-field susceptibility measurements of the PtAcr and PtVio samples in solid-state are shown in Figure 3.

The PtAcr susceptibility highlights its paramagnetic nature, as shown by its Curie-like temperature dependence, Figure 3. On the one hand, magnetisation curves, $M(H)$, recorded at low temperature clearly indicate that paramagnetism arises from half integer spin states, since the experimental data fit the standard $J = \frac{1}{2}$ Brillouin function (not shown). On the other hand, the temperature dependence of the PtAcr susceptibility allows the microscopic origin of the observed signal to be identified. The least-square analysis, displayed by the blue line in Figure 3, was performed according to the Curie-Weiss law (Equation (i)):

$$\chi(T) = \frac{N\mu_B^2g^2S(S + 1)}{3k_B(T - T_{CW})} + \chi_0$$  

(where $\mu_B$ is the Bohr magneton and $k_B$ is the Boltzmann constant). ESR measurements have shown a significant contribution to paramagnetism coming from the orbital angular momentum and for this reason the average Landé $g$-factor $g = 2.15$ was introduced. The least square analysis, following Equation (i), of the observed susceptibility then gives (assuming $S = \frac{1}{2}$) $N = 1.22(2) \times 10^{24}$ spin mol$^{-1}$. This result is fully consistent with the presence of two spin centres per formula unit ($N \sim 2N_{AV}$), namely a spin $\frac{1}{2}$ contribution arises from the odd electron trianionic $[\text{Pt}_{19}(\text{CO})_{22}]^{3-}$, while an equivalent spin $\frac{1}{2}$ contribution is given by the organic radical cation.

The room temperature magnetisation curve of bulk PtVio (not shown) displays a weak diamagnetic behaviour ($\chi_{dia} = -14 \pm 1$ mm$^3$ mol$^{-1}$). Nevertheless, the temperature dependence of its high-field susceptibility exhibits a sizeable paramagnetic fraction, as shown.

![Fig. 3. Temperature dependence of the high field molar susceptibility of PtAcr (blue line, square markers) and PtVio (black line, round markers) samples. A relatively high field (3 T for PtAcr and 0.35 T for PtVio) was applied, in order to saturate the contribution of ferromagnetic impurities. The constant value of $\chi_0$ was subtracted to $\chi$. Inset: zoom of the AFM peak of PtVio, due to the presence of PtVio$^*$](image-url)
by the black line in Figure 3. Such a signal can be mainly attributed to the spin $\frac{1}{2}$, $[\text{Pt}_{19}(\text{CO})_{22}]^{3–}$ and Vio$^+$, contributions of PtVio$^*$. This agrees with the detection of partly oxidised clusters by IR spectroscopy and partially reduced cations by ESR spectroscopy. At higher temperatures PtVio susceptibility departs from that of a classical paramagnet: the residual slope of the susceptibility curve is usually a signature of triplet-singlet spin gap thermal excitation.

The data in the range from 9 K to 300 K were fitted to the Bleaney-Bowers equation (Equation (ii)) (16):

$$\chi(T) = A \left[ \rho \frac{e^{-\Delta/k_B T}}{1 + 3e^{-\Delta/k_B T}} \right] + (1 - \rho)(T - T_{CW})^3 + \chi_0$$

where $\rho A = C = N_{\mu B} g^2 S_a(S_a + 1)/3k_B$ is the Curie-Weiss constant of the paramagnet, $\rho A = 2N_{\mu B} g^2 S_a(S_a + 1)/3k_B$ is the spin gap fraction and $\Delta$ is the exchange integral of the triplet-singlet spin gap. The least square analysis of the data with Equation (ii) reveals that the majority of the sample, i.e. bulk PtVio, is diamagnetic and does not contribute to the magnetic susceptibility ($\rho = 0.262(7)$, $N_{\mu B} = 0.44$ $N_{\mu B}$ and $N_0 \sim 0.06$ $N_{\mu B}$). As anticipated, the main contribution in Equation (ii) (73.8% of the amplitude) is due to the paramagnetic fraction arising from PtVio$^*$. Similarly to the case of PtAcr, PtVio$^*$ contributes with two spin $S_a = \frac{1}{2}$ per formula unit, one from $[\text{Pt}_{19}(\text{CO})_{22}]^{3–}$ and one from the Vio$^+$ counter ion. Hence, from the amplitude of this paramagnetic signal it can be estimated that PtVio$^*$ is 22% of the sample. An additional fraction, corresponding to 6% of PtVio$^*$, consists of three $\text{Vio}^2$($[\text{Pt}_{19}(\text{CO})_{22}]^{4–}$) elemental cell, see Figure 4(a), contains four cluster units and eight cation molecules, confirming the anion-to-cation stoichiometric ratio. Small differences in the dihedral angles formed by viologen organic rings can be attributed to solid-state packing steric factors rather than intrinsic electronic ones (11). The $[\text{Pt}_{19}(\text{CO})_{22}]^{4–}$ structure has an idealised $D_5h$ symmetry, consisting of three five-membered rings stacked in an eclipsed conformation with the other four Pt atoms lying on the fivefold axis, two internally sandwiched between the rings and two externally capping the outer pentagonal units. The metal core is surrounded by only 12 terminal COs and 10 edge-bridging COs between the stacked rings, a very small number of protecting carbonyl ligands per surfacial metal atom (CO-to-metal ratio of 1.29) (13).

It was not possible to obtain a crystal structure for PtAcr, notwithstanding several experimental attempts made using a wide variety of crystallisation solvents. However, the combined characterisation results converge to one most plausible stoichiometry that can be formulated as $(\text{Vio}^{2–})_2([\text{Pt}_{19}(\text{CO})_{22}]^{4–})$. Moreover, the XRD structure of this compound, Figure 4(a), was determined using crystals obtained by slow diffusion of isopropanol into a PtVio DMF solution. The $(\text{Vio}^{2–})_2([\text{Pt}_{19}(\text{CO})_{22}]^{4–})$ structure has an idealised $D_5h$ symmetry, consisting of three five-membered rings stacked in an eclipsed conformation with the other four Pt atoms lying on the fivefold axis, two internally sandwiched between the rings and two externally capping the outer pentagonal units. The metal core is surrounded by only 12 terminal COs and 10 edge-bridging COs between the stacked rings, a very small number of protecting carbonyl ligands per surfacial metal atom (CO-to-metal ratio of 1.29) (13).

It was not possible to obtain a crystal structure for PtAcr, notwithstanding several experimental attempts made using a wide variety of crystallisation solvents. However, the combined characterisation results converge to one most plausible stoichiometry that can be formulated as $(\text{Acr}^+)_2(\text{TBA}^+)_2([\text{Pt}_{19}(\text{CO})_{22}]^{3–})$, a salt consisting of a radicalic organic molecule and an odd-electron cluster, resulting from an electron-transfer synthetic path, Figure 4(b). Indeed, this is the only stoichiometry compatible with the composition of the reaction mixture, considering that the trianionic state of the starting cluster is clearly evident from the IR spectra reported, that the absence of Acr$^{2+}$ can be inferred from fluorescent data and that the presence and identity of two radicalic species was shown in ESR spectra and quantified on the basis of SQUID results.
Resistivity Measurements

The PtAcr data show a perfect linear correlation in a wide current range with a final resistivity value $\rho = 2.3 \times 10^3 \Omega \text{cm}$, Figure 5(b). On the other hand, Figure 5(a) shows that PtVio data keep a linear correlation in a narrower current range, as a result of the higher resistivity of PtVio, $\rho = 1.47 \times 10^6 \Omega \text{cm}$, compared to that of PtAcr.

The three-order-of-magnitude difference in the solid-state resistivity values of the PtAcr and PtVio compounds observed in this present study is currently under investigation. It is thought to be related to the presence of radicalic redox-active centres in the PtAcr sample, in contrast to the closed-shell redox-active centres found in the PtVio sample. The possible influence of structural powder factors, as suggested by scanning electron microscope (SEM) images (see the Supplementary Information), should also be considered, since electrical measurements have been performed on pressed polycrystalline pellets.

Fig. 4. (a) (Vio$^{2+}$)$_2$([Pt$_{19}$(VO)$_{22}$]$_4^{-}$) CCDC 951529 elemental cell; for a three-dimensional visualisation of the structure, see the quick response (QR) code on the right; (b) schematic mono-electronic transfer representation showing [Pt$_{19}$(CO)$_{22}$]$^{4-}$ on the left side and Acr$^{2+}$ on the right side. For this compound no crystal structure was obtained probably because of the instability due to its intrinsic doubly-radicalic nature

Fig. 5. (a) PtVio V/Volt vs. I/$\mu$A plot; (b) PtAcr V/Volt vs. I/$\mu$A plot. In both cases, the final resistivity values were obtained from the slopes of the linear fits to the experimental points.
Furthermore, interestingly, the extremely low resistivity value obtained for PtAcr can be compared to the reported values of intrinsic semiconductors such as silicon or germanium and has been previously reached, in the case of Pt carbonyl clusters, only when Pt frameworks self-assemble into infinite wires upon crystallisation (18, 19).

**Conclusions**

In conclusion, it has been shown that high-nuclearity Pt cluster salts, in combination with organic redox-active cations, should be considered as promising materials for future applications in molecular electronics. In particular, when using Vio$^{2+}$, the final compound, $(\text{Vio}^{2+})_2[(\text{Pt}_{19}(\text{CO})_{22})^{4-}]$, exhibited an exchange-salt stoichiometry. In such a doubly-closed-shell salt, the incipient redox activity of both the cluster and the cation, as indicated by the experimental results obtained in this study, together with the stability of the starting system, could be exploited to prepare doubly-radicalic species, such as $(\text{Vio}^{+})(\text{Vio}^{2+})([\text{Pt}_{19}(\text{CO})_{22}]^{3-})$, via controlled photochemical, chemical or thermal post-synthesis inductions.

On the other hand, when using Acr$^{2+}$, as a result of its higher oxidising power, a spontaneous redox reaction occurred and a reasonable $(\text{Acr}^{+})(\text{TBA}^+)_2([\text{Pt}_{19}(\text{CO})_{22}]^{3-})$ stoichiometry for the precipitated solid was inferred from the available evidence, leading to an interesting fluorescent ‘doubly-radicalic salt’. This type of salt, isolated and fully characterised here for the first time and consisting of a radical anionic Pt cluster and a fluorescent radical cation, was obtained by an extremely simple synthetic process and shows the lowest solid-state resistivity compared to previously reported cases (1), reaching semiconductor-like values. Therefore, it is possible to conclude that the future development of the new Pt cluster salts described above could break the boundaries of synthetic Pt cluster chemistry, eventually entering the field of materials chemistry.

**Acknowledgements**

The authors would like to thank Piero Macchi (University of Bern, Switzerland) for the PtVio crystallographic structure determination. Moreover, we would like to thank Monica Panigati, Stefania Righetto and Serena Cappelli (University of Milan, Italy) for their help in acquiring the cyclic voltammetry, fluorometry and electron spin resonance experimental data, respectively.

**References**

11. P. Macchi, Department of Chemistry and Biochemistry, University of Bern, personal communication, 2013
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This review briefly describes the vacuum electrostatic levitation furnace developed by JAXA and the associated non-contact techniques used to measure the density, the surface tension and the viscosity of materials. The paper then presents a summary of the data taken with this facility in the equilibrium liquid and non-equilibrium liquid phases for the six platinum group metals (pgms): platinum, palladium, rhodium, iridium, ruthenium and osmium over wide temperature ranges that include undercooled and superheated phases. The presented data (density, surface tension and viscosity of Pt, Rh, Ir, Ru and Os and density of Pd) are compared with literature values.

1. Introduction

Due to their unique characteristics such as inertness, corrosion and oxidation-resistance, biocompatibility, catalytic behaviour, high melting temperatures and good conductivity, the pgms are used in a host of applications (for example, automotive, aerospace, electronics, industrial heating, medical and jewellery) (1). To design high-performance alloys and to optimise industrial processes (for example, refining, casting and welding), knowledge of the density, surface tension and viscosity and their temperature dependences is often required. This understanding is required not only for the equilibrium liquid phase but also for the non-equilibrium, undercooled phases, because alloys with new microscopic structures can be synthesised from such phases. However, the high melting temperature of pgms (Pd: 1828 K; Pt: 2041 K; Rh: 2236 K; Ru: 2607 K; Ir: 2720 K; Os: 3306 K) (1) and the risk of contamination at elevated temperatures make measurements of their thermophysical properties of their equilibrium and non-equilibrium liquid phases very challenging using traditional methods.

The electrostatic levitation furnace and the associated non-contact diagnostics techniques developed by JAXA over the years (2, 3) have circumvented the difficulties associated with high-temperature processing and allowed an accurate determination of several properties of the pgms (4–13). High-temperature processing was achieved in vacuum using laser heating, thus isolating the sample from contaminating walls as well as surrounding gases. The containerless processing conditions also permit a deep undercooling of the material samples because of minimised heterogeneous nucleation and because sample heating and levitation were independent.

This paper first briefly describes the facility and the property measurement methods and then summarises
the experimental data for the density, surface tension and viscosity for the liquid phase of the pgms.

2. Experimental

2.1 Electrostatic Levitator

Properties were measured using an improved electrostatic levitator (Figure 1) (2, 3) in a vacuum environment (~10^{-5} Pa) originally based on a design by Rhim et al. (14). With this instrument, ca. 2 mm diameter samples charged by electronic emission were levitated one at a time between electrodes. A feedback loop between the applied electric fields and the position information obtained from the shadow of the sample illuminated with helium-neon lasers and detected by sensors ensured stable levitation. The sample was heated with up to four focused laser beams: three carbon dioxide laser beams (10.6 µm, total power 200 W) separated by 120° in a horizontal plane and one neodymium-doped yttrium aluminium garnet (Nd:YAG) laser beam (1.064 µm, 500 W) from the top. A complete description of the facility and the levitation initiation procedures can be found elsewhere (2, 3, 10, 12). This configuration provided temperature homogeneity and sample position stability and allowed control of sample rotation. The radiance temperature was measured with a single-colour pyrometer (0.90 µm, 120 Hz acquisition rate). The sample was observed by black and white high-resolution charged-coupled-device cameras. The cameras were located at right angles from each other and were equipped with telephoto lenses in conjunction with background illumination lamps. This provided magnified views of the sample and helped to monitor the sample position and to align the heating laser beams.

2.2 Property Measurements

This levitation furnace was particularly suitable to measure the density, surface tension and viscosity of pgms in their equilibrium and undercooled liquid phases. Since sample heating and levitation were independent, a precise laser heating control allowed undercooled melts to be maintained for time scales much longer than those required for the measurements.

2.2.1 Density

Density measurements were carried out using an imaging technique described elsewhere (3, 15). Once a levitated sample was melted, it took a spherical shape due to surface tension and the distribution of surface charge and images from a high-resolution camera (30 frames per second) and temperature data were simultaneously recorded with time (Figure 2). The laser beams were then blocked with mechanical shutters allowing the sample to cool radiatively. After the experiment, each image was matched with the
thermal history of the sample (Figure 3), digitised and the sample radius was extracted by software. Since the sample was axi-symmetric and because its mass was known, the density was found as a function of temperature. Calibration was done by levitating a sphere with a precisely known radius under identical experimental conditions.

2.2.2 Surface Tension and Viscosity

The surface tension was determined by the oscillation drop technique, a method in which the frequency of the oscillation of a levitated molten sample about its equilibrium shape is measured (16). This technique was explained earlier (17) and is summarised below for completeness. In this method, a sample was first heated, melted and brought to a selected temperature, while ensuring excellent position stability, low sample rotation and sample sphericity. Then, a \( P_2 \cos(\theta) \)-mode drop oscillation was induced to the sample by superimposing a small sinusoidal electric field on the levitation field. Following the termination of the excitation field, the transient signal generated by the change in diameter of the oscillating drop was detected and analysed using a custom made program. This was done many times for a given temperature and repeated for numerous temperatures. Using the characteristic oscillation frequency \( \omega_c \) of this signal, which was calculated by a fast Fourier transform and then corrected for nonuniform surface charge distribution (18), the surface tension \( \sigma \) could be found from Equation (i) (17, 19):

\[
\omega_c^2 = \left( \frac{8\sigma r_0^3}{\rho} \right) \left[ 1 - \left( \frac{Q^2}{64\pi r_0^3 \varepsilon_0} \sigma \right) \right] [1 - F(\sigma, q, e)]
\]

where

\[
F(\sigma, q, e) = \left[ \frac{243.31 \sigma^2 - 63.14 q^2 \sigma + 1.54 q^4 e^2}{176 \sigma^3 - 120 q^2 \sigma^2 + 27 \sigma q^4 - 2 q^6} \right] (ii)
\]

and \( r_0 \) is the radius of the sample when it assumed a spherical shape, \( \rho \) is the liquid density, \( Q \) is the drop charge, \( \varepsilon_0 \) is the permittivity of vacuum and \( q \) and \( e \) are respectively defined by Equations (iii) and (iv):

\[
q^2 = \frac{Q^2}{16 \pi^2 r_0^3 \varepsilon_0} (iii)
\]

and

\[
e^2 = \frac{E^2 r_0 \varepsilon_0}{(iv)}
\]

with \( E \) being the applied electric field (levitation and excitation). Similarly (17, 20), using the decay time \( \tau \) given by the same signal, the viscosity \( \eta \) was found by Equation (v):

\[
\eta = \rho \omega_c^2 (5\tau) (v)
\]

In Equations (i) and (v), the value of the density \( \rho \) at the corresponding temperature and the real-time value of the radius \( r_0 \), obtained by the imaging technique, were used so that sample evaporation does not distort the surface tension and the viscosity data.

3. Experimental Results

3.1 Density

All pgm samples were successfully levitated, melted, undercooled and solidified with the electrostatic levitator (4–8, 10, 11) and the processing data specific for each metal are listed in Table I. During these experiments, the density of equilibrium and non-equilibrium liquid phases was measured over large temperature ranges that cover the superheated and undercooled regions. Figure 4 presents typical plots for all pgms. The data measured by electrostatic levitation (4–6, 8, 10, 11) together with the literature values (21–36) are summarised in Table II. To our knowledge, these levitation measurements are the only ones that explore the undercooled region to date. The density of the pgms, like that of other pure metals, exhibited a linear behaviour as a function of temperature. In the density measurements, the uncertainty was estimated to be less than 2% from the resolution of the video grabbing
Fig. 3. Representative thermal history obtained for millimetre size pgm samples showing heating above the melting temperature, radiative cooling, undercooling, recalescence and solidification: (a) Pd (6); (b) Pt (11); (c) Rh (4); (d) Ru (5); (e) Ir (8); and (f) Os (10). (T_m = melting temperature)
capability (640 × 480 pixels) and from the uncertainty in mass (±0.0001 g).

At the melting point, the values obtained by levitation agree generally very well with those measured by other techniques (for example, the drop weight technique, isobaric expansion, pendant drop and sessile drop) when respective experimental uncertainties are taken into account (Table II) (21–36). The discrepancies observed in the temperature coefficients could be attributed to the difference in processing techniques and the extent to which evaporation losses have been considered. The containerless approach presented in this report operates under high vacuum, isolating the reactive molten samples from container walls and gases and can process samples in such a short time (<3 s for Pt and Rh; <2 s for Pd, Ru and Ir, and <1 s for Os) that evaporation is not an issue. This is supported by measurements of the sample mass before and after the experiment that lead to values within the uncertainties of the balance (0.1 mg). Evaporation rates were not measured in these experiments but could be obtained by levitating a sample for a long time (for example, 15 minutes) as explained elsewhere (37). The conventional methods often imply chemical reactions between the melt and a crucible, a support or residual gases. This can alter the final density values.

Other possible sources of error could arise from the imaging technique (for example, optical focusing or image digitisation) and the measurements of sample mass. Material purity, oxygen solubility in the samples and gasification could also, to some extent, explain the discrepancies. Temperature measurements too are subject to errors and are complicated by the fact that emissivity data are scarce for metals above their melting temperature and, to our knowledge, have not been reported for undercooled materials (38). The interested reader can find a detailed analysis for each of the pgms elsewhere (4–6, 8, 10, 11) together with a complete comparison with the literature data, when available, obtained with conventional methods (21–36).

### 3.2 Surface Tension

The surface tension was measured over large temperature ranges, well above the melting temperature and down into the undercooled region as shown in Figure 5 for all pgms except Pd (4, 5, 8, 10, 11). Although the density as a function of temperature was known and the radius could be tracked in real time, severe evaporation for Pd samples hindered these measurements because of the time needed to perform the experiments (one hour) and because the window of the vacuum chamber as well as the electrodes of the levitator became coated which made the sample unstable.

The uncertainty of the measurements was estimated to be better than 5% from the response of the oscillation detector and from the uncertainty in density measurements. In all measurements, the surface tension exhibited a linear behaviour as a function of temperature. The data, including those reported in the literature, are listed in Table III. At the melting point, the values obtained by electrostatic levitation (4, 5, 8, 10–12) show very good agreement with most published values when the respective experimental uncertainties are considered (22, 28, 32, 34, 36, 39–41) and the

---

### Table I: Processing Data for Platinum Group Metals (4–6, 8, 10, 11)

<table>
<thead>
<tr>
<th>Metal</th>
<th>Melting temperature, K</th>
<th>Purity, wt%</th>
<th>Undercooling, K</th>
<th>Superheating, K</th>
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<td>2236</td>
<td>99.9</td>
<td>416</td>
<td>14</td>
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<td>575</td>
<td>35</td>
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Fig. 4. Representative density data of equilibrium and non-equilibrium liquid pgms measured with an electrostatic levitator and compared with literature values as a function of temperature: (a) Pd (6, 21–25); (b) Pt (11, 22, 26, 27); (c) Rh (4, 23, 28–31); (d) Ru (5, 23, 32); (e) Ir (8, 23, 33–35); and (f) Os (10, 23, 36)
Table II  Summary of the Density Data for Platinum Group Metals Measured by Electrostatic Levitation (4–8, 10, 11) Compared with Literature Values (21–36)

<table>
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<th>Metal</th>
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<th>Density, $\rho$</th>
<th>Temperature range, K</th>
<th>Reference</th>
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<td>$d\rho/dT$, kg m$^{-3}$ K$^{-1}$</td>
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<td>12.2</td>
<td>−0.50</td>
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Fig. 5. Representative surface tension data of equilibrium and non-equilibrium liquid pgms measured with an electrostatic levitator and compared with literature values as a function of temperature: (a) Pt (11, 22, 23, 39, 40); (b) Rh (4, 23, 28, 41); (c) Ru (5, 23, 32); (d) Ir (12, 23, 34, 40); (e) Os (10, 23, 36)
Table III  Summary of the Platinum Group Metals Surface Tension Data Measured by Electrostatic Levitation (4, 5, 8, 10–12) Compared with the Literature Values (22, 23, 28, 32, 34, 36, 39–41)

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<td>Os</td>
<td>3306</td>
<td>2480</td>
<td>−0.34</td>
<td>3230–3605</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2500</td>
<td>3306</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>2400</td>
<td>3306</td>
<td></td>
</tr>
</tbody>
</table>
Fig. 6. Representative viscosity data of equilibrium and non-equilibrium liquid pgms measured with an electrostatic levitator and compared with literature values as a function of temperature: (a) Pt (11, 12, 42); (b) Rh (4, 12, 43); (c) Ru (5, 12); (d) Ir (8, 12); (e) Os (10, 13).
Table IV  Summary of the Platinum Group Metals Viscosity Data Measured by Electrostatic Levitation (4, 5, 8, 10–13) Compared with the Literature Values (42, 43)

<table>
<thead>
<tr>
<th>Metal</th>
<th>Tm, K</th>
<th>Viscosity, η</th>
<th>Temperature range, K</th>
<th>Reference</th>
<th>Note</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>η(Tm), 10⁻³ Pa s</td>
<td>η₀ exp(E/RT)</td>
<td>η₀, 10⁻³ Pa s</td>
<td>E, 10³ J mol⁻¹</td>
</tr>
<tr>
<td>Pt</td>
<td>2041</td>
<td>4.82</td>
<td>0.25</td>
<td>49.9</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>7.1</td>
<td>1.72</td>
<td>22.8</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>6.74</td>
<td>1.53</td>
<td>25.263</td>
<td></td>
</tr>
<tr>
<td>Rh</td>
<td>2237</td>
<td>2.9</td>
<td>0.09</td>
<td>64.3</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>4.9</td>
<td>1.31</td>
<td>24.7</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>5</td>
<td>2236</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ru</td>
<td>2607</td>
<td>6.1</td>
<td>0.60</td>
<td>49.8</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>5.0</td>
<td>0.47</td>
<td>51.2</td>
<td></td>
</tr>
<tr>
<td>Ir</td>
<td>2719</td>
<td>7.0</td>
<td>1.85</td>
<td>30.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>6.0</td>
<td>0.59</td>
<td>52.2</td>
<td></td>
</tr>
<tr>
<td>Os</td>
<td>3306</td>
<td>4.2</td>
<td>0.0017</td>
<td>220</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>7.0</td>
<td>0.098</td>
<td>117.5</td>
<td></td>
</tr>
</tbody>
</table>

(a) Denotes the improved measurement procedure (20)

temperature coefficients compare generally well with those calculated by Allen (23).

Here again, the discrepancy observed between the results (values at the melting temperature as well as temperature coefficients) obtained with electrostatic levitation and other methods could be understood due to the fact that the containerless approach in high vacuum isolated the samples from container walls and gases, whereas the other methods imply possible chemical reactions between the reactive melts and a crucible, a support or residual gases. Melt contamination is possible and can drastically impact the surface tension. Sources of discrepancy or contamination include material purity, oxygen solubility in the samples, gasification and surface oxidation or nitridation from residual gases. Temperature measurements can also affect the end results. A full comparison with the data reported in the literature, when available, as well as a complete analysis could be found in prior papers (4, 5, 8, 10–12).

3.3 Viscosity

The viscosity could also be measured over large temperature ranges, well above the melting temperature and down into the undercooled region as shown in Figure 6 for all pgms except Pd (4, 5, 8, 10–13). Although the density as a function of temperature was known and the radius could be tracked in real time, severe evaporation for Pd samples again hindered these measurements because of the time needed to perform the experiments (one hour) and because the window of the vacuum chamber as well as the electrodes of the levitator became coated and made the sample unstable. The data shown in Figure 6 were taken using a new procedure that consisted of measuring the viscosity on small samples and using a...
lower feedback control frequency to minimise the effect on the damping oscillation (20). Data from the literature (Zhuchenko et al. (42) and Demidovich et al. (43)) are also superimposed in Figure 6. The temperature dependence of the viscosity exhibited an Arrhenius behaviour for all measured metals. The uncertainty of the measurements was estimated to be better than 15% from the response of the oscillation detector. The values of the levitation measurements (4, 5, 8, 10–13) and the very scarce literature data (42, 43) are summarised in Table IV for completeness.

4. Conclusions

The density, the surface tension and the viscosity of pgms in their equilibrium and non-equilibrium liquid phases were measured using the unique capabilities of an electrostatic levitation facility. The data obtained with electrostatic levitation were compared with those reported in the literature. The density and surface tension data summarised in this report highlight that measurements were taken over wide temperature ranges and that electrostatic levitation alone can offer values in the undercooled region. Furthermore, for refractory pgms (Ru, Ir, Os), electrostatic levitation is the only technique that can provide density and surface tension data over a temperature span covering even the undercooled region. Furthermore, for refractory pgms (Ru, Ir, Os), electrostatic levitation is the only technique that can provide density and surface tension data over a temperature span covering even the undercooled region. Ongoing efforts focus on measurements of surface tension and viscosity of Pd to complete the series of property measurements of the pgms.

Acknowledgments

The authors would like to thank the Japan Society for the Promotion of Science for a Grant-in-Aid for Scientific Research (B). The authors are also grateful to Y. Watanabe and H. Tomioka (AES Co Ltd) for technical help in several experiments and post-levitation microstructure analysis.

References

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Junpei Tamura-Okada is an assistant professor of the Institute of Space and Astronautical Science of JAXA. His interests are the measurement of the physical properties of undercooled liquids and the development of new materials from undercooled liquids.
Is Osmium Always the Densest Metal?

A comparison of the densities of iridium and osmium

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Having established that osmium is the densest metal at room temperature the question arises as to whether it is always the densest metal. It is shown here that at ambient pressure osmium is the densest metal at all temperatures, although there is an ambiguity below 150 K. At room temperature iridium becomes the densest metal above a pressure of 2.98 GPa, at which point the densities of the two metals are equal at 22,750 kg m⁻³.

Introduction

Reviews by Crabtree (1) and the present author (2–5) established that at 293.15 K (20°C) osmium is the densest metal at 22,589 ± 5 kg m⁻³ compared to 22,562 ± 11 kg m⁻³ for iridium, the difference of 27 ± 12 kg m⁻³ considered as confirming this. The question then arises as to whether osmium is always the densest metal. Although it would have been desirable to consider this in terms of a full pressure-temperature-volume evaluation, limited high pressure data for iridium confines the evaluation to just two aspects – the effect of temperature at ambient pressure and the effect of pressure at room temperature.

The Effect of Temperature at Ambient Pressure

The thermal expansion of iridium is known with precision below room temperature, satisfactory up to 2000 K and estimated above this temperature (4) whilst the thermal expansion of osmium is known only between room temperature and 1300 K and is estimated below room temperature (5). Because the room temperature thermal expansion coefficient of iridium at 6.47 × 10⁻⁶ K⁻¹ is higher than the average value for osmium at 4.99 × 10⁻⁶ K⁻¹, it would be expected that with the greater contraction below room temperature iridium would be the densest metal at low temperatures. However this proves not to be the case with the density of osmium at 0 K being 22,661 ± 11 kg m⁻³ compared to a value of 22,652 ± 11 kg m⁻³ for iridium. The difference of 9 ± 16 kg m⁻³ indicates an ambiguity and the possibility that iridium could be the densest metal statistically. Assuming that the assigned accuracy for osmium increases linearly from ±5 kg m⁻³ at 293.15 K to ±11 kg m⁻³ at 0 K then the density ambiguity exists below 150 K where the density difference becomes equal at 14 ± 14 kg m⁻³. The variation of the density of both elements over the range from 0 to 300 K is shown in Figure 1. In the high temperature region there is no ambiguity with the density difference increasing to 147 ± 12 kg m⁻³ at 1300 K, the experimental limit for osmium, whilst comparison with neighbouring elements rhodium (6) and ruthenium (7) suggests that the average thermal expansion coefficient for osmium will continue to be lower than that of iridium so that osmium will remain the densest metal in the high temperature region.

The Effect of Pressure at Room Temperature

The effect of pressure (P) on volume (V) is given in terms of a third order Birch–Murnaghan equation of state:

\[
P = 1.5B_0(Y^{7/3} - Y^{5/3})[1 + 0.75(B'_0 - 4)(Y^{2/3} - 1)]
\]

where \( Y = V/V_0 \) and \( V_0 \) is the volume at zero pressure, \( B_0 \) is the bulk modulus and \( B'_0 \) is the pressure derivative of the bulk modulus. When \( B'_0 = 4 \) the equation is said to be second order.

The equation indicates that the higher the value of \( B_0 \) then the less compressible would be the material and
therefore it was a complete surprise when Cynn et al. (8) determined the value of $B_0$ for osmium to be 462 GPa compared to 443 GPa for diamond which appeared to overturn a long held belief that diamond was the least compressible element. This resulted in further measurements for osmium as indicated in Table I which suggest that the value determined by Cynn et al. appears to have been too high and subject to a systematic error which Liang and Fang (9) suggested was due to different quasi-hydrostatic conditions which were better determined in the later experiments. Distinction is made between determining the bulk modulus by elastic constant measurements (EC) and volume compression (VC).

The selected values are simple averages with the assigned accuracies encompassing all of the accepted values. The selected value of $B_0$ for osmium is now less than that of diamond and therefore the latter regains its status as the least compressible element. Pantea et al. (14) showed that low temperature had little effect on the value of $B_0$ for osmium with the value at 0 K being only 5 GPa greater than that at 300 K. However at high temperature Voronin et al. (13) showed a decrease of 58 GPa between 300 K and 1273 K.

Room temperature volume compression values for iridium are given in Table II with the cross-over pressures calculated from Equation (i) using selected values of $V_0$ as 8.5195 ± 0.0042 cm$^3$ mol$^{-1}$ for iridium (4) and 8.4214 ± 0.0013 cm$^3$ mol$^{-1}$ for osmium (5).

Since the measurements of Cynn et al. (8) for osmium appear to be subject to a systematic error it is considered that the same error may apply to their measurements on iridium and that these values should not be considered further. The third order and second order equations determined from the measurements of Cerenius and Dubrovinsky (18) lead to pressure values which do not agree with each other or with the selected curve in the graphical representation. However values of $B_0$ calculated from elastic constants measurements at 355 GPa for MacFarlane and Rayne (19) and 361 GPa for Adamesku et al. (20) show excellent agreement with the second order value of Cerenius and Dubrovinsky and it is considered possible that systematic errors in measurements which may have influenced the third order fit were restrained by the second order fit. The third order fit is therefore rejected. However the calculated cross-over pressure for the second order fit is well below the experimental limit of measurements at 10 GPa and therefore must initially be considered with some suspicion. The selected compressibility curve is therefore the interpretation by Gschneidner Jr. (21) of the pressure measurements of Bridgman (22) which up to 3 GPa can be represented by the equation:

$$V/V_0 = 1 - 2.775 \times 10^{-3} P - 2.64 \times 10^{-10} P^2$$  \hspace{1cm} (ii)

where $P$ is the pressure in GPa.
Table I. Determination of the Bulk Modulus of Osmium

<table>
<thead>
<tr>
<th>Authors</th>
<th>Reference</th>
<th>Method</th>
<th>(B_0), GPa</th>
<th>(B'_0), GPa</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cynn et al.</td>
<td>(8)</td>
<td>VC</td>
<td>462 ± 12</td>
<td>2.4 ± 0.5</td>
<td>(a)</td>
</tr>
<tr>
<td>Joshi et al.</td>
<td>(10)</td>
<td>VC</td>
<td>434</td>
<td>(4.0)</td>
<td>(b)</td>
</tr>
<tr>
<td>Kenichi</td>
<td>(11)</td>
<td>VC</td>
<td>395 ± 15</td>
<td>4.5 ± 0.5</td>
<td></td>
</tr>
<tr>
<td>Occelli et al.</td>
<td>(12)</td>
<td>VC</td>
<td>411 ± 6</td>
<td>4.0</td>
<td></td>
</tr>
<tr>
<td>Voronin et al.</td>
<td>(13)</td>
<td>VC</td>
<td>435 ± 19</td>
<td>3.5 ± 0.8</td>
<td></td>
</tr>
<tr>
<td>Pantea et al.</td>
<td>(14)</td>
<td>EC</td>
<td>405 ± 5</td>
<td>–</td>
<td></td>
</tr>
<tr>
<td>Pandey et al.</td>
<td>(15)</td>
<td>EC</td>
<td>411.9</td>
<td>–</td>
<td></td>
</tr>
<tr>
<td>Armentrout and Kavner</td>
<td>(16)</td>
<td>VC</td>
<td>421 ± 3</td>
<td>(4.0)</td>
<td></td>
</tr>
<tr>
<td>Chen et al.</td>
<td>(17)</td>
<td>VC</td>
<td>390 ± 6</td>
<td>(4.0)</td>
<td></td>
</tr>
</tbody>
</table>

Selected 413 ± 25 4.0 ± 0.5

Notes to Table I

(a) Not included in the average
(b) Revision of the measurements of Cynn et al. (8)

Table II. Determination of the Bulk Modulus of Iridium

<table>
<thead>
<tr>
<th>Authors</th>
<th>Reference</th>
<th>(B_0), GPa</th>
<th>(B'_0), GPa</th>
<th>Cross-over Pressure, GPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cynn et al.</td>
<td>(8)</td>
<td>383 ± 14</td>
<td>3.1 ± 0.8</td>
<td>–</td>
</tr>
<tr>
<td>Cerenius and Dubrovinsky</td>
<td>(18)</td>
<td>306 ± 23</td>
<td>6.8 ± 1.5</td>
<td>1.47</td>
</tr>
<tr>
<td></td>
<td></td>
<td>354 ± 6</td>
<td>(4.0)</td>
<td>3.04</td>
</tr>
</tbody>
</table>

The cross-over pressure using Equations (i) and (ii) is 2.98 GPa at a density of 22,750 kg m\(^{-3}\) in excellent agreement with the second order value of Cerenius and Dubrovinsky. In fact the agreement of the extrapolated values of the latter agree so closely with Equation (ii) at 3 GPa that they can be considered as being representative of the volume compression values for iridium from this pressure up to the experimental limit at 65 GPa.

The average value of \(B_0\) from Equation (ii) at 355 GPa (21) is in such excellent agreement with the values obtained from the elastic constant measurements of MacFarlane and Rayne (19) and Adamesku et al. (20) and the second order value of Cerenius and Dubrovinsky (18) that 355 ± 10 GPa can be considered as representing the value of \(B_0\) for iridium in the room temperature region. A further room temperature value of 371 GPa (actually 37,800 kgf mm\(^{-2}\)) selected by Darling (23) is almost certainly due to a different interpretation of the measurements of Bridgman.

Taking into account the assigned accuracies of the selected \(B_0\) value for osmium and iridium the cross-over pressure is considered to be accurate to 5% (±0.15 GPa). Based on this value and the density values for the individual elements then the density at the cross-over point can be considered to be accurate to ±20 kg m\(^{-3}\). The behaviour of the density values with pressure in the relevant region 2.5 GPa to 3.5 GPa are shown in Figure 2 where the value for iridium at 3.5 GPa is the second order value of Cerenius and Dubrovinsky.
Conclusions

At ambient pressure it is shown that osmium appears to be the densest metal at all temperatures although there is an ambiguity below 150 K which will not be resolved until new measurements are carried out on the low temperature thermal expansion of osmium. At room temperature iridium appears to become the densest metal above a pressure of 2.98 ± 0.15 GPa and a density of 22,750 ± 20 kg m−3, although it is considered that further experimental determinations are definitely required. With the presently available data it is considered that representative room temperature \( B_0 \) values are 413 ± 25 GPa for osmium and 355 ± 10 GPa for iridium.

References


Fig. 2. Density in the cross-over region
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.
Dennis Dowden and the Development of Catalytic Science

Celebrating a twentieth century pioneer in the scientific understanding of catalysis

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In the twentieth century Dennis Albert Dowden, affectionately referred to as DAD by friends and colleagues, was an important figure in the development of an understanding of the structure of industrial heterogeneous catalysts, the species present and the processes taking place on them. He was born in Bristol, UK, and following education at the University of Bristol and a short period at Amherst College in the USA, in 1938 he joined Imperial Chemical Industries (ICI) at Billingham in the North East of England. He worked there on catalysis, catalyst manufacture and catalytic processes for the next thirty-seven years. His major contribution was to bring a wide range of sciences and a rational approach into what had been until then regarded as “black art”, capable of only empirical analysis. His influence extended across ICI, which at that time operated many industrial catalytic processes, and academically he was influential worldwide and especially in the USA.

1. Dowden’s Early Career and Domestic Life

1.1 Early Family Life

Dowden was born in Bristol, UK, on 15th August 1914, just a few days after the start of the First World War. His family was far from wealthy. His father, Charles Henry Dowden, worked at the Wills Tobacco Company, and the family situation was made very much more difficult when he, a pacifist, a committed socialist and a local political labour leader, spent two years in Dartmoor Prison as a conscientious objector. His mother, Ada, left alone with young Dennis, worked as a seamstress and somehow managed to support them both. At that time not “going to war” was seen as unpatriotic and very much looked down upon, and this made life even more difficult as they were shunned by shop keepers and many townsfolk. However, they survived and when his father returned home he eventually got a job in a warehouse through church contacts. Later, in 1920, the family was enlarged by the birth of a daughter, Joan. Dowden’s parents thought that everything could be achieved through education and they encouraged their children to do well at school. When he was eleven or twelve Dowden was taken by his mother to the opening of the new University of Bristol (previously it was University College) by King George V. He said he looked up at the great tower and thought, “I will go there one day”; and he did!

1.2 Academic Studies

Dowden excelled academically and he won a scholarship both to Merrywood Secondary School and subsequently to the University of Bristol where he studied Chemistry from 1932 to 1937 and his record card shows he had a “very satisfactory first year”. In fact he later graduated with first class honours. Chemistry at Bristol was particularly strong in the area of interfacial chemistry, and as early as 1913 Professor James W. McBain postulated the existence of ‘colloidal ions’, now known as micelles, to explain the electrolytic conductivity of sodium palmitate solutions (1), while in the Physics Department, where Dowden studied for two years, there were eminent researchers like Nott,
Jones, Lennard Jones, Gurney, Frolich, Heitler, the two Londons and Sucksmith.

In the Chemistry Department Professor William E. Garner worked on the gas solid interface developing adsorption calorimetry (2). During his time at the University of Bristol Dowden did postgraduate research (Figure 1) with Professor Garner on the heats of adsorption of gases on high surface area solids that at the time was a research frontier. Indeed, the now familiar BET method for estimating surface areas of catalysts was published (3) about the time Dowden left the University of Bristol. Although he had done good careful topical research, like many others at that time at the University of Bristol he did not submit a thesis for a PhD, something in later life he said he regretted. Notwithstanding this it was an exceptional achievement then for a child from his working class, anti-establishment background to go to university and do so well.

In the USA Professor Beebe at Amherst College had become involved with the measurement of heats of chemisorptions (4). He had spent several sabbatical years at Bristol where he developed a long-standing friendship with Professor Garner, so when he obtained research funds he perpetuated the connection through having visiting Bristol postdoctoral students, of whom Dowden was the first. Dowden went to Amherst College in 1937 and continued research on heats of adsorption of gases on chromia. He measured the heats of adsorption of argon, hydrogen, deuterium, carbon monoxide, nitrogen, and oxygen on reduced chromia by calorimetry at low temperatures. The results were interpreted in terms of an initial ‘van der Waals adsorption’ followed, in some situations, by a slow exothermic change leading to ‘activated adsorption’. But his time in the USA was not all devoted to work, for Dowden found time to drive across the USA to California with a friend calling at some universities on the way and returning by Greyhound bus, at the height of the Great Depression! The research Dowden did at Amherst and Bristol resulted in two substantial publications, the first in the Journal of the American Chemical Society (5) and the second in the Journal of the Chemical Society (6). The latter paper was received on 29th March 1939 and the authors expressed their thanks for grants for the purchase of apparatus to ICI Ltd, and to the Colston Research Society. This Society was founded in Bristol in 1899 as the ‘University College Colston Society’, by Bristol citizens who wanted to assist the University College. From 1908 to 1948 it gave grants to specific research projects in various departments. Since 1948 the Society has supported symposia.

1.3 Return to the UK and Start of Industrial Career

Dowden returned to the UK in 1938, probably in part because of the impending Second World War, and he joined the Billingham Division of ICI in the North East of England (Figure 2). ICI there at the time had a general policy for recruiting preferentially graduates with DPhils or PhDs from Oxford, Cambridge or Imperial College London. It is therefore quite remarkable that in the late 1930s ICI employed Dowden who came from the University of Bristol without a PhD. Professor Garner may have influenced the situation since he had contacts at ICI and their financial support was acknowledged in Dowden’s paper (6). However, it is clear Dowden’s exceptional abilities were recognised early in his career. At first at Billingham he was a Safety Officer in the Research Department, and a little later he moved to the catalyst manufacturing factory at Clitheroe in Lancashire, as a plant manager. Here catalyst for the production of high octane fuel for fighter planes and other catalysts were

Fig. 1. Dennis Dowden when a postgraduate research student at The University of Bristol, UK, in 1935/36. His supervisor was Professor William E. Garner and his research involved measurement of the heats of adsorption of gases on chromic oxide, work he continued with Professor Beebe at Amherst College in the USA
produced. During this time Dowden learnt about large-scale catalyst manufacture and the underlying inorganic chemistries involved before getting deeply involved in industrial catalyst research and development. He once said that the real impact of catalysis was not revealed to him until after he had joined ICI.

### 1.4 Research at Billingham and Domestic Life

Still during the war Dowden returned to do research at the main site at Billingham, where he worked on catalysts and catalytic processes for almost four decades. He was confronted with a broad spectrum of exploratory catalytic chemistry involving hydrogenation and oxidation as well as related pilot plant and full scale plant problems, and he said he did his first ‘plant training’ on coal liquefaction, though it is not clear if this was before or after going to the Clitheroe catalyst works. At Billingham Dowden got to know Iris Coxall who worked in a Drawing Office and they were married on 11th October 1947 at the Stockton Register Office. He was 33 and gave his profession as ‘Research Chemist at Chemical Factory’, she was 23 and a ‘shorthand typist’. Their fathers’ occupations were given as Warehouseman (Charles H. Dowden) and Boilersmith (Thomas Coxall), and the witnesses were Charles H. Dowden and Lavinia M. Coxall.

At first they lived in a company flat in Norton, a village only a short distance from Billingham, and later they bought a house in Eaglescliffe close to Yarm-on-Tees a few miles south of Billingham. They had two children, Diana born in 1952 and Simon born in 1956. In 1965 a property in Javea in Spain was purchased and this provided the family with many unforgettable happy summer holidays. Dowden liked to think of himself as something of a thespian, and for many years he had acting roles in Middlesbrough amateur dramatic society productions at The Little Theatre and he appeared in Norton Hall Club ‘Smoker’ productions. The company name Synthetic Ammonia and Nitrates Ltd at Billingham was the origin of the name of the Synthonia Club that provided a range of social amenities for workers that included bars and a large theatre area. Each year a Research Department Christmas musical revue took place there that mocked and made fun of the management, only occasionally...
was there a guest appearance by more senior people such as Dowden. Norton Hall Managers Club located some distance away in Norton Village was limited to senior staff while the Cross Roads Club at Hartburn Village was open to all ICI staff. Each year there was an evening entertainment known as the ‘Smoker’ at Norton Hall in which Dowden sometimes appeared. His liking for good wine and good food was legendary, and he especially enjoyed champagne that he would give as gifts to friends and colleagues. It is therefore not surprising that for many years Dowden was a member of the important Norton Hall Club Wine and Food Committee responsible for stocking the Club’s extensive wine cellars.

2. Scientific and Technical Context

The Nobel Prize for Chemistry in the year Dowden was born was awarded for “the exact determinations of the atomic weights of a large number of the chemical elements”. This award to Professor T. W. Richards of Harvard University was the first Nobel Prize in Chemistry awarded to an American. It was announced on 11th November 1915 and in many ways illustrates the stage to which chemistry had progressed (7). It was a very different world compared to that of today; now we have a fundamental understanding in many scientific and technical areas, whereas then many phenomena, such as catalysis, were known but far from understood. The life of Dowden ran parallel to the rapid development of the chemical sciences, the growth of industrial catalysis and in particular the gradual growth of the scientific understanding of catalysis in which he was so very much involved.

When Dowden was born catalysts were used commercially, in fact the origins of catalysis can be traced back to the researches of Humphry Davy at The Royal Institution in London who discovered the catalytic properties of platinum in 1817 (8). Several catalytic inventions followed and particularly notable was a patent for the oxidation of sulfur dioxide over platinum catalysts granted as early as 1831 for sulfuric acid manufacture (9, 10). (Like Dennis Dowden, Peregrine Phillips lived in Bristol. Phillips was a manufacturer of vinegar, and surprisingly little is known about him (see, for example, Cook (10)). However, the era of large scale industrial catalysis only really started with the operation of the first Haber-Bosch plant for ammonia synthesis at Oppau, Germany, in September 1913 that produced 7200 tons of ammonia annually (11).

The invention of many other catalytic processes followed, for example, in 1923 methanol from synthesis gas which was at the time derived from coal (12). Key to the successful development of the ammonia process was the catalysis work by a team led by A. Mittasch, who around 1910 obtained a more satisfactory ammonia synthesis catalyst than the original osmium Haber catalyst (13). This was obtained by an empirical scatter-gun approach involving the testing of some twenty thousand catalyst formulations (14). (Jennings’ book has a foreword by Dennis Dowden in which he refers to “hydrogenolysis of atmospheric nitrogen” as an “epoch making advance”). This approach led to a widespread belief that this was the only way to obtain new or improved catalysts. Many workers did not believe a rational approach was possible and they described, often with some glee, the process of catalyst development as a ‘black art’. While it now seems bizarre that this should have been so, the view persisted for a long time (15).

The enormous improvement in understanding catalytic reactions and catalyst manufacture resulted in part from the general advance in experimental methods over the past century. Nevertheless our understanding was very much pushed forward by Dowden’s rational scientific approach.

3. Contributions to Scientific Understanding

When Dowden began working at ICI he was surrounded by processes for the manufacture of industrial catalysts, their continual improvement and the many reactions they catalysed. His previous research at Amherst College (5) and the University of Bristol (6) on adsorption of gases on chromia was leading-edge and gave him insights into the nature of reacting adsorbed species on catalysts, and gradually he began to consider the ways in which these species might be bound to the catalyst surfaces. That is, the intimate bonding patterns involved during catalytic processes.

But this was to come later for starting a new job had many demands and there must have been little time to pursue such ideas. Indeed Dowden appears not to have published scientific papers for a decade after his university papers appeared. In fact he published surprisingly little during his career at ICI. In the 1950s he had been commissioned to write an introductory Methuen Monograph on catalysis but this was not
completed. After retirement, in the 1970s he started work on turning his lecture series into a book on rational catalyst design but progress was difficult, and only a few chapters were completed when unknown to Dowden a book on this topic by D. L. Trimm appeared largely based on Dowden’s lecture notes but with scant acknowledgement (16).

It is a great regret Dowden did not produce anywhere near as many scientific papers as might have been expected, and there seem to have been two broad reasons for this. First, as a highly sociable man he much preferred to talk about catalysis rather than sit down alone to write about it. Second, there was something of the perfectionist about him: he was never really satisfied with what he had written and he was a compulsive rewriter, going through many versions of every paper. Indeed those of us who read these drafts often felt the earlier versions were more satisfactory, before the various elaborations, qualifications and so on had been incorporated. It follows that it is not surprising that many of his papers were conference contributions, where time limits forced him to produce completed papers. Dowden enjoyed the intellectual stimulation and social aspects of participating in international catalysis conferences, and he attended all the important ones he could and made long lasting friendships with many eminent academics.

3.1 Fundamentals of Catalysis

Those working in industrial organisations often find it difficult to publish work in the scientific literature because in addition to finding the time required to prepare papers there are always commercial concerns that are raised. So it is not surprising that from the start and throughout his career in ICI most of Dowden’s scientific publications dealt with general aspects of catalysis. His papers published over the period 1948–1950, were concerned with broad questions of relations between catalysis and the electronic structure of solids (17) and other theoretical aspects of catalysis (18), as well as contributions to an understanding of reactions on alloy catalysts (19) rather than a detailed study of a particular commercial catalyst. In particular Dowden wanted to relate catalyst performance, in terms of activity, selectivity and life, to electronic and physical structure properties, and it is characteristic that his first paper from ICI examined the relation between the performance of catalysts and their electronic structure. This was a different approach from most other workers, who were then more concerned with the mechanisms of the reactions taking place rather than why it took place on a certain solid. In contrast Dowden was following the early steps taken by Rideal and Taylor (20).

Dowden’s other papers in the 1950s were concerned with the activity of nickel catalysts (21), and a long one with Professor Garner at the University of Bristol on the electrical conductivity of zinc oxide/chromia type catalysts for high pressure methanol synthesis, perhaps reflecting some of Dowden’s original university research interests (22). Other papers during this time were concerned with properties of dehydration and dehydrogenation catalysts (23) and pioneering work on hydrogen-deuterium exchange on oxides rather than on metal catalysts (24), and a short review of work in this area was published (25). The role of chemisorption in catalysis was an ongoing theme with Dowden (26, 27). There was also a writing collaboration with George Bridger that resulted in a significant review on the scientific basis of catalyst testing that many researchers today would benefit from reading (28).

3.2 Academic Collaborations

At the time there was some opposition to trying to identify the places where the reactions took place on catalyst surfaces because many academics were happy to leave the description of the ‘active site’ as simply an asterisk on a straight line that only vaguely represented the catalyst surface (see for example (29)). Dowden wanted to go further and describe the surface and the molecular reaction mechanisms. He took a comparable approach to the reactions during catalyst manufacture. As a result he became concerned with these fundamental aspects while pursuing industrial research projects targeting very specific goals, and because of his acceptance by a wide circle of those in academia one of his roles in ICI was liaison with universities. As a result he brought many academics into ICI as consultants or ‘visiting workers’. For example, in 1957 Professor Geoffrey Bond (University of Hull, UK) was a ‘Summer Guest Worker’ at ICI in Billingham working on the selective hydrogenation of acetylene to ethylene over palladium/silver catalyst that appears particularly topical when read today (30), and another ‘Summer Worker’ at about the same time was Professor B. M. W Trapnell (University of Liverpool, UK) who worked on hydrogen/deuterium exchange on oxides with Dr N. Mackenzie, a member of Dowden’s team (24, 25).
3.3 Application of Crystal and Ligand Field Theory

One of Dowden’s most significant papers, at the height of his career, was ‘Crystal and Ligand Field Models of Solid Catalysts’. He delivered this at the Fourth International Congress on Catalysis, Moscow, Russia, in 1968. It was published in Russian in the Proceedings of the Congress and later in 1971 an English version appeared in *Catalysis Reviews* (31). His opening paragraph was: “Quantum chemistry is now some 40 years old, but the problem of calculating the rates of complex reactions, in a useful approximation, from fundamental atomic constants, remains intractable. Along with the rest of chemistry, heterogeneous catalysis has continued, in the main, to be descriptive and empirical although its study has mirrored changing attitudes in the cognate sciences, and there has been an uninterrupted search for unifying concepts.”

He continued: “Just as the simple band theory and its nomenclature ultimately failed to describe the properties of conductors so also it is an inadequate classification of catalysts and only a superficial interpretation of descriptive catalytic chemistry.” He then considered the energy states of a number of perfect ionic lattices, and continued to attempt to deal with charged defects in solids (mostly oxides) with imperfect lattices, taking the chemisorptions of hydrogen, oxygen and water as examples. Progression from insulators to semiconductors brought him closer to useful catalysts: “… it was necessary to investigate the hydrogen-deuterium exchange reaction over some stable oxide of the first long period; the hoped-for twin peaked pattern was found and a consolidated theory outlined”.

Dowden went on to show that a similar twin peaked pattern could be found in several hydrocarbon hydrogenation and dehydrogenation reactions. He then incorporated both crystal and ligand field effects in chemisorptions, and extended this approach to catalysis of some important reactions such as hydrogenation and dehydrogenation; polymerisation and depolymerisation; oxidation and deoxidation. He concluded that the qualitative aspects of the models he considered “…serve as guides in the investigation of chemisorption and catalysis. The potential power of these models for the prediction of catalyst activity and the design of catalysts has yet to be realised.”

There were several other related publications around this time (32–35) and the immense advances in computational chemistry which have taken place now make much of this seem elementary, almost naïve, but at the time it clearly pointed the way forward.

3.4 Influence in ICI and Beyond

During Dowden’s career at ICI his research group consisted of only a few people, in marked contrast to the large research groups prevalent today. Other groups at Billingham were directly working very successfully, on new processes, for example naphtha steam reforming and low pressure methanol synthesis (Figure 3). The remit of Dowden’s group was to examine the fundamentals of existing processes and to look for new processes that could be used by ICI. In effect he was given the freedom to examine almost any aspect of catalysis that took his interest. The atmosphere within his group approached the academic and it was very different to later industrial research, tightly constrained to limited targets. The wide range is shown by examples of the subjects worked on by members of his group: methane/steam reforming over platinum group metals, the kinetics of the catalytic oxidation of sulfur dioxide, homogeneous catalytic hydrogenation of olefins and acetylene by cobalt and nickel complexes, nitrogen fixation over reduced molybdenum oxides, and the selective oxidation of methane to methanol and formaldehyde. Sometimes he went beyond catalysis into other process areas, for example, examining crystal agglomeration (‘caking’), of importance in fertiliser manufacture. Not surprisingly, little of this work found its way directly into industrial practice but almost always there was an increase in the understanding of the underlying fundamental science. Certainly of equal importance and possibly of greater influence was Dowden’s readily available and penetrating advice to ICI research groups, not just those at Billingham but to many others across ICI. His advice always started from a detailed understanding of the process being considered and then incorporated his wide knowledge of the basic catalytic science. He was never an advocate of the empiricism of a Mittasch or a Ziegler. When Dowden retired he became more directly involved with research in universities and wrote several review papers, but he was still often at Billingham keeping up with the latest advances and offering advice on what should be done next. The
scientific papers published during this period are covered in the Retirement Section below.

4. Contributions to Technical Progress

While Dowden was well known in academic circles for his ideas about the structure of heterogeneous catalysts and the reactions taking place on their surfaces, his industrial work was of course more applied, and here his ‘ICI work’ is traced through published patents in which he is named as an inventor. There are as many of these patent families as publications in the open literature suggesting, understandably, that more time was devoted to the industrial work than to the more academic side. Here a representative number of Dowden’s patents are discussed that provide insight into the kinds of industrial research he carried out.

4.1 Research During the Second World War

Amongst his first patents was one on producing 1,5-pentanediol by hydrogenation of δ-hydroxyvaleric aldehyde (5-hydroxypentanaldehyde), Equation (i), using a nickel on Kieselguhr catalyst and the beneficial presence of water on the reaction, so presumably the reaction goes via the hydrated gem-diol.

\[
\text{HOCH}_2\text{CH}_2\text{CH}_2\text{CHO} + \text{H}_2 \rightarrow \text{HOCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH} \quad (i)
\]

This patent was filed during the war (23rd April 1943) (36) and might have been associated with possible explosive applications of 1,5-dinitratopentane, although there is no direct evidence for this. However it might be pertinent that Dowden’s university supervisor, Professor Garner, was said by Dowden to be an explosives expert and to have worked with the Ministry of Supply.

A patent (37) filed on 11th June 1945, just after the end of the Second World War in Europe, must also have been based on work done during the war, and was concerned with the effect of ammonia (or amine) on the hydrogenation of vinylfuran catalysed by nickel on kieselguhr. In the absence of ammonia complete hydrogenation to ethyl tetrahydrofuran took place, whereas with added ammonia only the external double

Fig. 3. Construction during early 1962 of the original naphtha steam reformers at Billingham that provided synthesis gas for the ICI Low Pressure Methanol Process. Both the naphtha steam reforming and methanol processes were commercially very successful with several hundred plants being licensed around the world.
Bond was hydrogenated to form ethylfuran in high yield, Equations (ii) and (iii).

Addition of amines produced a similar effect. Such selectivity effects was a theme Dowden often returned to.

4.2 Post-War Patents

A patent filed on 10th February 1949 concerned Raney-type catalysts made by alkali extraction of nickel/copper/aluminium alloys (38). This costly research must have taken a considerable amount of time and effort since it required specialised equipment for making alloys in addition to that for catalyst testing (the example given was hydrogenation of benzene to cyclohexane), and it was undertaken in the search for further ways of obtaining selective catalysed hydrogenations. This was followed by a patent (39) on the formation of diacetone alcohol (4-hydroxy-4-methyl-pentan-2-one) from the condensation of two molecules of acetone, Equation (iv), classically achieved using barium hydroxide, with a catalyst made by impregnating a lithium-stabilised alumina with molten calcium nitrate.

\[ 2(CH_3)\text{CO} \rightarrow \text{CH}_3\text{CH(OH)CH}_3\text{CO} \]  

An important feature was catalyst reactivation when necessary by calcinations at 750°C in air.

The next patent (40) disclosed an interesting method for producing a skeleton silica/alumina catalyst by heating a silica/alumina/alkaline earth glass to cause phase separation of the alkaline earth oxide followed by its dissolution in dilute hydrochloric acid. Applications mentioned for the catalyst so formed included hydrocarbon dealkylation and isomerisation as well as alcohol dehydration. An olefin hydration patent had been previously filed that claimed catalysts comprising a titania support with or without tungsten oxide and components such as antimony pentoxide and iron oxides (41).

4.3 Patents Concerning Key Processes

The ICI Billingham site was a major producer of nitrogen fertilisers, methanol and other commodity chemicals based on coal feedstock, and towards the end of the 1950s attention turned to the possibility of using straight-run naphtha that was increasingly available from European refineries as a more economic feedstock. Of the processes considered catalytic steam reforming was the most attractive, and while George Bridger was responsible for much of the catalysis work done in this area Dowden made a number of contributions especially in collaboration with Phin Davies on the use of platinum group metal catalysts with or without alkali (42), and addition of, for example, copper or silver to steam reforming catalyst (43). The effects of adding rhodium and other platinum group metals to alkali-stabilised unalkalised nickel steam reforming catalysts was explored for operation at relatively low temperatures to produce methane rich gas for use as ‘town gas’ (44). With ‘poison free’ synthesis gas available from hydrocarbon steam reforming the use of downstream copper-based catalysts became possible and Dowden made contributions to copper-based low-temperature shift catalysts having a variety of compositions including standard copper/zinc oxide/alumina and those containing magnesia (45).

4.4 Selective Oxidation and Hydrogenation Reactions

There was a period when Dowden’s patents featured oxidation reactions and various metal vanadates were explored as oxidation catalysts for partial oxidation of short chain alkenes using catalysts prepared by fusing thallium, potassium or silver compounds with vanadium pentoxide, and by careful selection of reactant, catalyst and space velocity reaction conditions were obtained that gave encouraging conversions to oxygenated compounds, although the selectivity was not particularly high (46). Other oxidation processes that were worked on included the oxidation of aromatic compounds with the target of good selectivity and activity that included products such as phthalic anhydride from ortho-xylene, Equation (v), and naphthalene (47, 48).
The oxidation of iso-butene to various oxygenates was also explored (49).

The use of platinum group metal homogeneous catalysts was found to enable a number of useful low-temperature oxidations such as the selective oxidation of cyclo-hexene to 2-cyclo-hexenone, Equation (vi), (50).

\[ \text{Cyclo-hexene} + \text{O}_2 \rightarrow \text{2-cyclo-hexenone} \]

Other homogeneous catalysts, specifically cobalt cyano complexes, were also used in the selective hydrogenation of dienes, for example the formation of 1-butene from butadiene (51).

4.5 Carbon Formation in Steam Reforming

By the late 1950s it had been decided that the time of coal as a feedstock for synthesis gas production at Billingham was over, and much research had been done investigating the possibility of pressure steam reforming naphtha to provide relatively cheap synthesis gas. The main practical problem was preventing formation of carbon from the hydrocarbon feed, and two approaches were investigated. Dowden was involved in both. The first was through the use of platinum group metal catalysts that catalyse carbon formation much less than does nickel (42, 52, 53). In practice however it proved better commercially to use nickel steam reforming catalysts incorporating potassium to catalyse gasification of carbon with steam more quickly than it is formed, and Dowden examined the effect of additions of other metal components including about 5% copper (43).

4.6 Speculative Process Patents

In the decade before retirement Dowden worked on a wide variety of projects that included the selective oxidation of methane to methanol with some interesting results (54), the use of copper, cobalt and manganese catalyst formulations incorporated into self cleaning cooking oven surfaces (55), exploratory work on the formation of 2,2'-bipyridyl from pyridine (56), and the hydrogenation of adiponitrile to hexamethylenediamine catalysed by fused magnetite reduced with hydrogen containing a small amount of ammonia that enhanced the surface area of the active catalyst (57). Work on hydrocarbon reactions over stabilised zirconia formulations was initiated by a belief that doping zirconia would generate suitable acidic sites to catalyse hydrocarbon carbonium reactions facilitated by the presence of platinum (58, 59). It became understood that the actual active acidic component was sulfated zirconia and work in Billingham was halted mainly because of rapid progress elsewhere in zeolitic acid catalysis. However, much later the catalytic properties of sulfated zirconia were intensively studied (60).

5. Retirement and Beyond

In 1973 Dowden's wife Iris died after a long illness, leaving him alone just as his retirement was approaching and his children were leaving home for life abroad (daughter Diana) and university studies (son Simon). During this time Dowden's influential work was recognised by prestigious awards: The Chemical Society Industrial Medal in 1973 and a Frank G. Ciappeta National Lecturer of the American Catalysis Society in 1974. Later in 1996 Dowden was awarded the International Congress on Catalysis Diploma in recognition of a lifetime's service to the community of catalytic scientists.

Dowden was notably busy during retirement and he continued to be academically active (Figure 4). He was already a visiting professor at Imperial College London, UK, where he gave a series of lectures on catalyst design and he became a Research Fellow at Edinburgh University, UK, in 1975 where he shared accommodation with his son who was a student there. He was also a consultant and expert witness in patent litigation, he attended conferences whenever he could, wrote review articles and still he found time to visit ICI at Billingham often to keep abreast with the latest advances. He had been involved in a specialised debate with eminent scientists on the activation of hydrocarbons (61), and he became involved in research projects at Edinburgh University on hydrogen spillover (62) and ammonia synthesis (63, 64). The Head of Department there, Professor Charles Kemball, was chairman of the Publications Board of The Chemical Society and he actively solicited contributions to their publications (and especially ones he edited). As a result Dowden made several major contributions to the Chemical Society's Specialist Periodical Report – Catalysis, three early volumes of which he edited with Kemball (65–67). The chapters he wrote in Catalysis were on reactions of hydrocarbons on multimetallic catalysts (68) and spillover of chemisorbed species...
He also prepared two long scholarly chapters on catalysis published in the Chemical Society’s Annual Reports on the Progress of Chemistry (70, 71). Among his last academic publications was one based on a presentation given at an international conference on catalyst deactivation in the Algarve, Portugal during 18th–29th May 1981 (72). Rather fittingly his last publication listed in Chemical Abstracts is entitled ‘The Catalysis of Synthesis Gas Production’ reflecting his career at ICI Billingham and which appeared in the proceedings of the Priestly Conference held in London in 1983 (73).

6. Conclusions

With the death of Dowden on 16th June 2012 we lost one of the principal figures in catalysis, and especially in industrial catalysis, of the twentieth century. His work covered a wide area of academic and industrial catalysis and as a result he had a very broad knowledge in all of its aspects that in later life he was always very happy to share with others in constructive conversations. Invariably he showed an almost old-fashioned politeness, geniality and charm to everyone he met, and when he encountered spite or envy he was surprised and dismissed it with just a shrug. After he was retired he still regularly attended annual ICI meetings of academic workers, lectured at international conferences giving review lectures, and wrote many scholarly articles. At the Durham meeting to commemorate his life and work (74) it was notable that many people who had interacted with Dowden remarked on the help they received from him irrespective of whether they were students or senior people. His life ran parallel to the growth of catalysis and he contributed much to its development and fundamental understanding. He received various medals and awards in the USA and UK. His legacy is perhaps best illustrated by a comment given to one of the present authors by Professor Enrique Iglesia at the EUROPACAT IX international catalysis conference held at Salamanca in 2009: that his opening address to the conference was essentially Dowden’s work brought up to date.

7. Acknowledgements

Thanks are due to the many people who provided information about the life, work and times of Dennis Dowden that vastly extended reminisces of the present authors’ time working with him at Billingham. Without their help writing this article would not have been possible, and we are particular grateful to his sister Joan Agocs (who lives in Bristol, UK), his daughter Mrs Diana Nicholls (in Venezuela) and son Dr Simon Dowden (in the USA) for details about his family life. Professor Burtron Davis (University of Kentucky, USA) kindly provided an interview he had had with Dowden, and George W. Bridger gave a firsthand account of working at ICI Billingham during and after the Second World War. Professor Frank S. Stone (University of Bath, UK), the late Professor Wyn Roberts (University of Cardiff, UK), Professor Geoffrey Bond (Brunel University, UK) and Professor Peter B. Wells (University of Hull, UK) all helped with putting into the academic context the research work Dowden did, while Professor Julian Ross (University of Limerick, Ireland), Professor Neil Connelly (University of Bristol, UK), Professor Brian Vincent (University of Bristol, UK) and Hanna Lowery (Information Management, University of Bristol, UK) helped with understanding the time Dowden spent at the University of Bristol. Dr Martin Fowles and Dr Martin Partridge (Johnson Matthey Catalysts, UK) provided access to Billingham ICI material, Dr Richard Seymour

Fig. 4. Dowden in 2005. He remained active for several years after retirement from ICI attending international conferences, lecturing and writing articles. He very much enjoyed his retirement with family and friends that was as long as his career in ICI, during this time he maintained contact with several former colleagues having regular lunch meetings with them.
Johnson Matthey, UK) did invaluable literature searches, and Julian Harrop provided images from the former ICI archives. Details of Dowden’s scientific papers were obtained from Chemical Abstracts and those for his patents from the European Patent Office. A shorter obituary by the present authors appeared in Applied Catalysis A (75).

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The Authors

Following Fellowships at the Universities of Toronto and Cambridge Martyn Twigg joined a polymer group at ICI's Corporate Laboratory in the North West of England, and after involvement in projects at Agricultural Division at Billingham moved there in 1977. He knew Dennis Dowden as a “Catalysis Sage” and discussions with him were important in understanding fundamental catalyst concepts. Martyn worked on catalysts and catalytic processes including synthesis gas production via naphtha and natural gas steam reforming, methanol and ammonia synthesis, and proprietary catalysts and processes for herbicide manufacture and environmental protection applications. He studied catalyst activation and built a much used off-site catalyst reduction unit. After managing an international polymerisation project he was head-hunted to work at Johnson Matthey as Technology Director in the autocatalyst area that he successfully led until being appointed Chief Scientist. This provided an opportunity for research diversity that included carbon nanotube manufacture and catalyst medical applications. He was associated with four Queen's Awards, and was awarded the Royal Society of Chemistry Applied Catalysis Prize. He has more than 200 papers, co-authored books on transition metal mediated organic syntheses and catalytic carbonylation. He produced the “Catalyst Handbook”, co-edits the Fundamental and Applied Catalysis series with Michael Spencer, and has 150 published patent families on catalysts and catalytic processes. He opened the symposium ‘Dennis Dowden Commemoration, Catalysis – From Fundamentals to Application’ held at the University of Durham in 2013 with a lecture ‘Dennis A Dowden – An Appreciation of a Life in Catalysis’. Martyn has on-going collaborations with universities and holds honorary academic positions, and runs an active consultancy and catalyst development business.

Michael Spencer graduated in Natural Sciences at Cambridge University and studied the kinetics of gas-phase chlorination reactions there with P. G. Ashmore gaining a PhD. In 1957 he moved to the Research Department of ICI Billingham Division, in the North East of England, initially working with Dennis Dowden and several patents resulted. He spent all his industrial career at ICI in research becoming an ICI Science Associate and until Dennis Dowden's death in 2012 he had a highly professional, hugely enjoyable and extremely rewarding relationship with him. He worked mostly on a wide variety of topics in catalysis and also on other industrial subjects relevant to ICI such as electrochemistry, nitrogen fixation in electric discharges and crystallisation processes. In
catalysis he made major contributions to existing processes, such as methane/steam reforming and methanol synthesis, and also to the assessment of novel catalytic reactions for industrial use. In 1987 he was appointed Professor in the School of Chemistry, Cardiff University, Wales, where he has been involved in both teaching and research. Recent research work has included studies on the origins and the control of catalyst deactivation. He has over 150 publications, covering scientific papers, patents, book contributions and various articles of general interest. With Martyn Twigg he is co-editor of the book series Fundamental and Applied Catalysis, and currently he is working on a book about Welsh scientists.
Platinum Group Metal Catalysed Hydrodeoxygenation Of Model Bio-oil Compounds

Investigating catalysts for upgrading bio-oils to fuels and chemicals

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Introduction

The use of biomass as a starting point for the manufacture of chemicals and fuels has been the subject of increasing research effort in recent years. A wide range of biomass sources are being investigated and reported in the literature, but with a particular focus on second generation biorenewables, which use non-food sources of biomass. Examples of such biomass sources include algae-derived products, agricultural residues, wood and residues from forestry plantations and municipal solid wastes. Waste products are of particular interest due to their low cost and availability in large volumes. Analyses carried out by the United States Department of Energy suggest that future potential resources of sustainable biomass in excess of 1 billion tonnes will exist in the USA alone, in the form of agriculture residues, forestry biomass and energy crops. Such resources could be made accessible with only modest changes in land use and agricultural practises (1).

A range of technologies are currently under investigation to convert these feedstocks through to useful chemicals and fuels. Examples of such technologies include gasification to syngas, followed by conventional conversion to higher molecular weight compounds (for example, via Fischer-Tropsch synthesis, or methanol synthesis followed by methanol conversion technology), fermentation and hydroprocessing. Two process routes that have attracted increased interest in recent years are fast pyrolysis and advanced biotechnology combined with thermochemical conversion. These offer very different approaches to the conversion of waste biomass sources to useful chemicals and fuels. However, realisation of the potential of either option as a route to bio-derived products will require developments in both catalyst and process technology.

Fast Pyrolysis

Fast pyrolysis involves rapidly heating biomass in the absence of oxygen to generate so-called ‘bio-oil’, essentially a depolymerised and partially deoxygenated product. This may be carried out either in the presence of a catalyst (catalytic fast pyrolysis) or using a non-catalytic medium (for example sand). For biomass containing high levels of complex organic polymers, such as lignin and cellulose, pyrolysis is a convenient method of converting a solid material, often with a high water content, into a liquid suitable for further processing. It is also cited as a versatile technology option, in principle suitable for use with a range of feed materials.

Economic analyses indicate that pyrolysis is a potentially attractive route to drop-in hydrocarbon fuels from biomass. Data published by the United States Department of Energy predicts that pyrolysis has the potential to offer a low capital and low operating cost route to hydrocarbon fuels when compared with other biomass-based technologies (2). The advent of low cost hydrogen from shale gas has also been predicted to advantage pyrolysis-based routes to fuels (3). However, as noted above, developments in catalyst technology are required to economically upgrade pyrolysis oils through to conventional hydrocarbon fuels.
Pyrolysis Oil Upgrading: Model Compound Studies

Pyrolysis oil is a complex mixture of many smaller organic compounds, a small selection of which is shown in Figure 1 (4). In addition to these organic species, pyrolysis oil is also characterised by high levels of water (very variable, but water levels of 20% and above are quite usual), a high organic acid content (usually measured by total acid number, which would typically be in excess of 100) as well as a variety of inorganic impurities that can act as catalyst poisons. Given the complexity of pyrolysis oil and the challenges involved in accurately analysing the composition of the oil, many catalyst development studies have used model compounds to develop the catalysis needed to successfully upgrade pyrolysis oil to fuels and chemicals.

The transformation of pyrolysis oil to the molecules found in drop-in hydrocarbon fuels (see Figure 2 for some examples of such molecules) requires a number of catalytic transformations, for example deoxygenation, carbon–carbon bond formation, isomerisation and aromatisation. Hydrodeoxygenation is a convenient route to use hydrogen to eliminate oxygen from the molecules present in pyrolysis oil and a range of catalysts have been shown to be effective for this conversion (5, 6). Some of our work in Johnson Matthey has investigated the potential of metal-supported systems for pyrolysis oil upgrading via hydrodeoxygenation and some representative results are shown in Figure 3. This shows data for the hydrodeoxygenation of the model compound m-cresol, carried out in a batch autoclave reactor using a selection of supported nickel, palladium and platinum catalysts. Tests were carried out over a period of 2 hours at a hydrogen pressure of 20 barg and using a fixed metal to m-cresol mass ratio of approximately 1:2500, the latter being used to account for differences in the metal loading in each of the catalysts. The products identified by gas chromatography (GC) were a combination of hydrocarbons, predominantly methylcyclohexane and toluene, and the oxygenates 3-methylcyclohexanol and 3-methylcyclohexanone.

As can be seen from these data, high conversion of m-cresol is readily achieved using all three catalysts at 275°C under these test conditions. Selectivity towards hydrocarbons varies over the three catalysts, with the supported platinum catalyst demonstrating the highest selectivity to hydrocarbons at 275°C. Repeating the experiment with the 0.3% platinum on alumina catalyst at 300°C results in a significant increase in the degree of deoxygenation and yield of hydrocarbon products.

Other catalysts are reported in the literature as also being effective for deoxygenation of such model compounds.
compounds, including hyd processing catalysts such as supported cobalt-molybdenum (CoMo) and nickel-molybdenum (NiMo) catalysts (7, 8). Such materials undergo a pre-sulfiding step to yield the active form of the catalyst, a sulfided CoMo or NiMo site. Compared to the sulfur-based active sites found in CoMo and NiMo catalysts, the supported metal systems described above offer the advantage of a sulfur-free active site, particularly suited to conversion of feeds low in sulfur and for the production of low-sulfur fuels.

**Bifunctional Catalysis**

The development of more complex, bifunctional catalysts has opened up alternative reaction pathways for deoxygenation. Figure 4 shows some more model compound data, again for the hydrodeoxygenation of m-cresol over a selection of platinum-based catalysts (9). At 150°C and a hydrogen pressure of 20 barg, a 1% platinum on alumina catalyst was shown to give 100% conversion of m-cresol, but with a high selectivity to methylcyclohexanol and only 2% yield of hydrocarbons (methylcyclohexane). In contrast, a 1% platinum on a beta zeolite catalyst, also operating at 150°C, gave 100% m-cresol conversion, but with 99% yield of methylcyclohexane. Use of the beta zeolite by itself in the presence of hydrogen gave no measurable m-cresol conversion in these studies at temperatures up to 200°C. These data are consistent with hydrogenation of the aromatic ring occurring over platinum sites on the catalyst, with deoxygenation being driven by acid sites on the zeolite component of the active surface, for example via dehydration, followed by subsequent hydrogenation of the C–C double bond generated by water elimination. A simplified reaction scheme is given in Figure 5. Supporting evidence for this reaction pathway comes from studies carried out on 3-methylcyclohexanol, the product from the ring hydrogenation of m-cresol. If this substrate is reacted with the beta zeolite at 150°C and at a hydrogen pressure of 20 barg, 100% conversion of the alcohol is achieved. The product distribution is more complex than that determined for the 1% platinum on beta zeolite catalyst, due to the presence of a number of unidentified products, but is dominated by methylcyclohexene (57% selectivity). The use of bifunctional catalysts offers lower temperature routes for deoxygenation when compared to the temperatures required to achieve hydrodeoxygenation using conventional metal-supported catalysts.

**Fatty Acid Conversion**

Metal-supported zeolite catalysts such as those described above have also been shown to be effective for the conversion of other compounds to hydrocarbon...
molecules suitable for use in fuels. Long chain fatty acids and methyl esters have been recognised as interesting starting points for the synthesis of linear hydrocarbons such as those found in diesel fuels. Current commercial sources of these molecules, for example palm oil, are not economically attractive starting points for fuel production. However, the development of advanced biotechnology offers the potential for the generation of these molecules from waste streams such as carbon oxides and methane.

The development of catalysts for the conversion of fatty acids and methyl esters to hydrocarbon molecules has also been examined in our labs, initially using model compound studies. In a typical study, a feed of palmitic acid (CH₃(CH₂)₁₄COOH) in a hydrocarbon solvent (dodecane) underwent reaction under a hydrogen atmosphere over a range of catalysts. Figure 6 shows the product distribution achievable for a selection of supported palladium and platinum catalysts (10). A 5% palladium on carbon catalyst, operating at 298°C and 10 barg, was shown to give 54% conversion of the palmitic acid feed, with high selectivity to the linear C₁₅ hydrocarbon n-pentadecane under these conditions. No other products were detected in this study. The use of a 5% platinum on zeolite catalyst (mordenite, with a silica to alumina ratio of 20) under the same process conditions resulted in 95% conversion of the acid feed and a markedly different product distribution, determined by GC analysis as comprising 41% linear C₁₅ hydrocarbon, 2% branched C₁₅ hydrocarbons,
55% linear C16 hydrocarbon and 2% branched C16 hydrocarbons. The degree of fatty acid conversion and the distribution of hydrocarbon molecules in the product have been shown to be influenced by both process conditions (for example, hydrogen partial pressure) and catalyst details (metal loading, zeolite type, silica to alumina ratio) (10). This allows different hydrocarbon molecules to be obtained from the fatty acid feed, including linear and branched alkanes and aromatic hydrocarbons, the latter of particular interest for aviation fuel applications.

In contrast to the supported metal systems described above, the use of bifunctional catalysts in biomass conversion offers the potential for lower temperature operation, with resultant advantages in catalyst deactivation rates. Control of the acid functionality in the catalyst also allows a different range of hydrocarbon products to be produced, in particular more branched and aromatic hydrocarbons, which positively influences the fuel properties of the resultant hydrocarbon mix.

**Beyond Model Compound Studies**

As noted above, many biomass feeds, and in particular pyrolysis oil, are a complex mixture of organic compounds, acids, water and inorganic species. The presence of these additional components has a significant effect on the catalysis. For example, the water and acid components of bio-oil are of great significance in the choice of an upgrading catalyst, causing significant restructuring and potentially physical destruction of the catalyst.

Model compound studies such as those described above can play an important role in the development of catalysts suitable for biomass upgrading and an understanding of reactivity patterns. However, they do not adequately address all of the key technical challenges associated with biomass upgrading, in particular catalyst deactivation and longevity. In order to progress these aspects of catalyst development, studies using real bio-derived feedstocks are essential.

**Conclusions**

The model compound studies presented here have demonstrated the feasibility of using catalysis in combination with fast pyrolysis and biotechnological routes to upgrade a variety of biomaterials to fuels. Both technologies open up the potential to use low cost feeds as precursors to drop-in hydrocarbon fuels. Fast pyrolysis is particularly well suited to deal with a wide range of bio-feeds and to break down the complex organic polymers to smaller oxygenated molecules suitable for catalytic upgrading. In the catalytic conversion of fatty acids and methyl esters to hydrocarbons, modification of the catalyst and process conditions has also been shown to give the ability to produce a variety of molecules and hence to tailor the final composition of the fuel. Further work remains to be done, in particular to optimise the catalysts to deal with the combination of high water content, organic acids and inorganic poisons and overcome the challenges inherent in this promising area.
References


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247th American Chemical Society National Meeting and Exposition: Part I

Biomass coverage from the ACS spring conference on ‘Chemistry and Materials for Energy’

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Introduction

American Chemical Society National Meetings and Expositions are held twice a year in spring and autumn and constitute the largest gathering of chemical scientists at any point in the conference calendar. This year the 247th meeting was held from 16th–20th March 2014, hosted at the Dallas Convention Center, Texas, USA, a hulking concrete monolith adjacent to downtown Dallas. The overarching theme of the conference was Chemistry and Materials for Energy which was reflected in the focus of the Plenary and Kavli Foundation sponsored Lectures.

In total almost 14,000 chemical scientists attended the meeting, of which approximately 5000 were either undergraduate or postgraduate students, many appearing undaunted by the scale of their first conference. Over 10,000 scientific papers were presented, either in one of the myriad meeting rooms or numerous poster sessions. In addition to the technical programme, the Exposition comprised over 900 exhibitors from all over the world as well as a career fair with 30 employers seeking to fill 90 vacancies, although there were almost 800 job seekers.

This selective review will focus on biomass, in which both platinum group metals (pgms) and to a lesser extent base metals feature as catalytic materials.

Kavli Foundation Lectures

John A. Rogers (University of Illinois at Urbana-Champagne) ‘Biodegradable Electronics’
Emily A. Weiss (Northwestern University) ‘The Behaviour of Electrons at Nanoscopic Organic/Inorganic Interfaces’

Plenary Lectures

Jens K. Norskov (Stanford University, USA) ‘Catalysis for Sustainable Energy’
Héctor D. Abreuña (Cornell University, USA) ‘Operando Methods for Characterization of Fuel Cell and Battery Materials’
Michael R. Wasielewski (Northwestern University, USA) ‘Molecular Approaches to Solar Energy Conversion’
Transformation of Biomass

There were a number of talks covering various aspects of the thermochemical transformation of biomass or derived sugars and chemicals to value-added compounds. Typically, these types of transformations involve treating a slurry or solution of the biomass feedstock in an autoclave at elevated temperatures and pressures using hydrogen gas or a hydrogen transfer agent. The most common catalysts used in these reactions are supported pgm heterogeneous catalysts, although base metal variants, or more rarely homogeneous catalysts, have been shown to be effective.

One common starting platform is the C6 sugars (hexoses), readily obtained by hydrolysis of cellulose, which can then be treated in a number of ways to easily obtain other derivative chemical feedstocks. One such is 5-hydroxymethylfurfural (5-HMF), which has been touted as a promising intermediate in many biorefinery concept models but has not been studied as extensively as others. It can be easily accessed by dehydration of hexoses and has been successfully converted to chemicals such as levulinic acid, 2,5-dimethylfuran and succinic acid, for example. Jaya Tuteja (Japan Advanced Institute of Science and Technology) gave a talk on her recent work developing a series of pgm bimetallic catalysts which were effective for the hydrogenolysis of lignin in water and under mild conditions. They began the study by synthesising a series of highly active, stable bimetallic nickel nanoparticle catalysts which were effective for the hydrogenolysis of lignin in water and under mild conditions. They began the study by synthesising a series of pgm (ruthenium, rhodium, palladium, platinum, iridium), precious metal (silver, gold, rhenium) and base metal (copper, iron, cobalt, nickel, tin) monometallic catalysts via reduction of the corresponding metal precursor salt with aqueous sodium borohydride in the presence of poly(vinylpyrrolidinone) (PVP) as a stabilising agent.

In the presence of formic acid (FA), a mixture of products were formed from the hydrogenation of HMF, including 5-methylfurfural, 2,5-hexanediol, HDO and furans. In contrast, a reaction using Pd/Al₂O₃ led to tetrahydrofuran-2,5-dimethanol as the major product (30.6% yield, >99% HMF conversion) due to significant ring hydrogenation over hydrogenolysis (ring cleavage). This highlights the importance of a high Brønsted:Lewis acid ratio in the support to promote efficient HMF ring opening, whereas the Pd metal sites dissociate FA, leading to hydrogenation. A number of parameters were investigated including Pd loading, FA concentration and reaction time and the best conditions were found to be 7 wt% Pd/ZrP catalyst (50 mg) which afforded 43% yield of HDO from HMF (1 mmol) in ethanol solvent (3 ml) using FA (22 mmol) at 413 K for 21 h. Following this, the Pd/ZrP catalyst was easily separated from the reaction mixture and reusable at least 5 times without any significant loss of activity and selectivity. The authors proposed a reaction mechanism (see Figure 1) consisting of adsorption of HMF onto the catalyst surface and interaction with both metal and acidic support sites (step 1), followed by ring opening and deoxygenation by the acidic support sites to form an intermediate such as the hexa-triene-diol shown in steps 2 and 3. Following FA dissociation by the Pd metal centres (step 4) and keto-enol tautomerisation of the intermediate diol (step 5), C=C bond hydrogenation occurs to yield the desired HDO product as the final step.

A more challenging target is the hydrolysis and selective depolymerisation of lignin, which makes up a considerable proportion of woody biomass and is notoriously recalcitrant to treatment. Lignin consists of complex polymer networks made up of numerous oxygenated aromatic subunits which are linked with different types of C–O ether linkage, the most common of these being the ß-O-4 linkage. The number of different monomer units and range of similar C–O ether groups present make the selective conversion of lignin very challenging, as often very complex product mixtures are formed, if the catalyst is even effective at all. Ning Yan (National University of Singapore) gave an interesting talk on her recent work developing a series of highly active, stable bimetallic nickel nanoparticle catalysts which were effective for the hydrogenolysis of lignin in water and under mild conditions. They began the study by synthesising a series of pgm (ruthenium, rhodium, palladium, platinum, iridium), precious metal (silver, gold, rhenium) and base metal (copper, iron, cobalt, nickel, tin) monometallic catalysts via reduction of the corresponding metal precursor salt with aqueous sodium borohydride in the presence of poly(vinylpyrrolidinone) (PVP) as a stabilising agent.
It was postulated that the resulting colloidal catalysts may be more accessible to insoluble lignin than typical heterogeneous catalysts and so they were screened immediately after synthesis for hydrogenolysis activity against 2-phenoxy-1-phenylethanol, a typical lignin model compound containing a single β-O-4 linkage (see Figure 2) (3). A total of 15 compounds were identified by gas chromatography mass spectrometry (GC-MS), high performance liquid chromatography (HPLC), and nuclear magnetic resonance (NMR) spectroscopy and categorised as dimers (compounds 1–7) and monomers (compounds 8–15) (see Figure 2) the yield of which gives an indication of β-O-4 hydrolysis activity. A blank reaction showed no conversion and of the 13 catalysts tested, Ni showed the highest selectivity towards monomers, indicating high selectivity for hydrolysis of the β-O-4 linkage.

Subsequently, a range of Ni based bimetallic catalysts containing 20% of the metals listed above were synthesised by a similar reduction route to the monometallic variants. The standout monomer yield of 72% was achieved with the NiAu catalyst which showed that addition of Au to Ni in this application promoted C–O bond hydrogenolysis of the model compound, which is in stark contrast to many other reactions where addition of Au to Ni typically reduces catalyst activity. The effect of the Ni: Au ratio was examined (Figure 2(c)) and an optimal ratio of 7:3 (Ni₇Au₃) was found to give 99% conversion of the model 2-phenoxy-1-phenylethanol compound with a monomer yield of 87% within 1 h. A physical mixture of monometallic Ni and Au catalysts in a 7:3 ratio gave only a 16% monomer yield, suggesting a significant cooperative metal effect in the bimetallic catalyst. Investigation of conversion and product distribution with respect to time showed that catalyst deactivation did not occur during the course of the reaction and that the observed dimers are reaction intermediates, with the Ni₇Au₃ catalyst showing an activity three times that of monometallic Ni. Numerous characterisation techniques were used to probe the composition and structure of the Ni₇Au₃ bimetallic catalyst. Transmission electron...
microscopy (TEM) shows spherical catalyst particles with diameter 4.1 ± 1.0 nm and consisted of metallic Ni and Au as determined by X-ray absorption near edge structure (XANES). Previous examples of NiAu catalysts consisted of a Ni core and Au surface, but the authors propose a significantly different structure here where they believe the catalyst consists of a crystalline Au core and Ni enriched shell. They support this with data from extended X-ray absorption fine structure (EXAFS) showing high Au–Au coordination numbers and low Ni–Ni coordination numbers, suggesting Ni is predominantly located at the surface; and X-ray photoelectron spectroscopy (XPS) determined an Ni:Au ratio of 3.8:1, which is higher than the stoichiometric ratio (2.3:1) and that found by inductively coupled plasma mass spectrometry (ICP-MS) of 2.8:1, suggesting the surface is Ni-enriched. UV-visible data additionally suggest that small Au⁰ clusters form and catalyse the reduction of Ni, acting as nuclei for the growth of a Ni-enriched shell. Finally the Ni₇Au₃ catalyst was assessed in the hydrogenolysis of organosolv lignin, a more realistic lignin feedstock, at 170°C under 10 bar H₂ in water.

(3) Figure 3. A mixture of monomers were produced directly and quantified by gas chromatography-mass spectrometry (GC-MS), with the best yields of ~14 wt% monomers being produced after running for 12 h. Although this yield is low, the authors stress that the direct production of aromatic monomers from lignin, particularly under relatively mild reaction conditions, is not well known and represents a promising starting point for future work.

Alternative Processes

An alternative process for the conversion of biomass into liquid chemicals is fast pyrolysis, involving heating a biomass feedstock to 400°C–600°C in the absence of air, which produces a product referred to as bio-oil. This substance is a complex mixture of over 400 different compounds derived from the thermal breakdown of the cellulose, hemicellulose and lignin present in biomass. In addition to this, bio-oil has a low energy density, due to the high oxygen content of the constituent parts, has high viscosity and is very corrosive. These factors render crude
bio-oil unstable, as further reactions take place after ageing, affecting the molecular weight and viscosity of the oil. This necessitates additional catalytic upgrading before it can be processed to produce drop-in fuels and chemicals. The best approach to ameliorate these effects is to upgrade the vapours prior to condensation and this requires careful tuning of the catalyst properties to convert the most unstable components of the oil without sacrificing valuable C–C bonds.

Steven Crossley (University of Oklahoma, USA) presented work on the effect of the support phase of ruthenium on titania catalysts on the upgrading of pyrolysis vapour (4). Although more expensive than Ni or Fe, Ru has been shown to be active under conditions containing mixtures of oxygenates and water. However, the use of Ru on a large scale has been hampered due to its high mobility under high-temperature oxidative conditions and sintering during catalyst preparation, reaction or regeneration. For this study a model compound, guaiacol, has been used to represent some of the species present in bio-oil. Initial work concentrated on the effect of calcination temperature and TiO$_2$ phase on the activity and selectivity of the Ru/TiO$_2$ catalyst, studied at 400°C under H$_2$ at atmospheric pressure. The supports used were a pure anatase TiO$_2$ and P25, consisting of ~4:1 anatase:rutile phases, and the catalysts were prepared by impregnation of RuCl$_3$·xH$_2$O onto the support before drying at 120°C for 12 h followed by oxidation at 400°C or 500°C under air for 4 h.

The BET surface areas of the TiO$_2$ supports and Ru catalysts were found to lie in the range 50–170 m$^2$g$^{-1}$ and it was apparent that the P25 support had a surface area almost three times lower than the pure anatase but that very little surface area was lost upon doping with Ru metal compared to the anatase. This is due to the anatase phase being less thermodynamically stable than the rutile phase so increasing calcination temperature results in greater pore collapse and concomitant loss of surface area, whereas P25 contains both rutile and anatase phases and is more stable to temperature increases. The metal loadings of the catalyst samples were determined by quantitative temperature programmed reduction (TPR) and this showed that the Ru loading was not affected by an increase in calcination temperature. The metal dispersion was probed by a combination of X-ray diffraction (XRD) analysis of the support crystal planes exposed for Ru binding, TEM analysis, infrared spectroscopy and CO hydrogenation reactions. These data led the authors to conclude that Ru supported on P25 was dispersed much better than on pure anatase TiO$_2$. It is proposed that the rutile component of P25 serves as an anchor point for the RuO$_2$ species since they possess similar crystal structures and that the poorer dispersion and particle agglomeration on pure anatase was due to the mismatch between anatase
Dihydroquinone (Q/QH2) couple stores two protons and acts as soluble electron/proton transport agents. For example, the hydroquinone/quinone processes and act as soluble electron/proton transport agents. Quinones are also present in plant metabolism to accomplish the necessary multi-electron oxidation processes and act as soluble electron/proton transport agents. Renewable Energy Storage

Finally, Ting Yang Nilsson (Linköping University, Sweden) gave an interesting talk on lignin modification for biopolymer/conjugated polymer interpenetrating networks as renewable energy storage materials (5). The premise behind this work is to develop low cost, renewable derived charge storage materials for use with intermittent energy sources which can match current battery technologies in terms of performance, without the use of expensive inorganic materials such as rare earth metals. In nature, redox functions contained within biopolymers are widely used in energy conversion processes in plants and make use of temporary proton storage on amino acid residues to accomplish the necessary multi-electron oxidation step. Quinones are also present in plant metabolism processes and act as soluble electron/proton transport agents. For example, the hydroquinone/dihydroquinone (Q/QH2) couple stores two protons and electrons in a six carbon/two oxygen structure, giving an electronic charge density of 496 mAh g–1. Considered alone, this charge storage capacity is superior compared to more conventional systems such as lithiated carbons (344 mAh g–1) and olivine iron(III) phosphate (FePO4) systems at 170 mAh g–1. It is known that incorporating quinone groups onto the main chain of conjugated polymers leads to increased charge storage, as does the inclusion of quinones into redox active anionic counterions in doped conjugated polymers. This work has successfully produced a class of materials based on the combination of polypyrrole and lignin derivatives containing redox active functional groups. The incorporation of lignin into a material with suitable electronic and ionic conductivity can enable charge transport to and from the quinone sites, opening up the possibility to use this redox function for charge storage. A three electrode system was used to electrochemically polymerise pyrrole at Au electrodes in an aqueous solution of lignosulfonate, generating a black [Ppy(lig)] conducting product coating on the Au surface. This layer can be grown to ~3 μm thick over the course of 2 h and with a conductivity of ~1 S cm–1 and elemental analysis yielded a N:S ratio consistent with a composition comprising ~1:1 ratio of polypyrrole and lignosulfonate. Cyclic voltammetry studies of the [Ppy(lig)] electrodes in 0.1 M aqueous perchloric acid (HClO4) revealed a well-defined and narrow redox wave at ~0.5 V vs. Ag/AgCl and a poorly defined wave in the typical potential range for polypyrrole. The presence of two redox waves, compared to just one present in polypyrrole, shows that the quinone groups of the lignosulfonate are readily accessible and are responsible for the second observed wave. Inclusion of pH buffers showed a systematic dependence of redox potential on pH with a value of 58 mV/pH unit, close to the 59 mV/pH unit anticipated for 1 electron/1 proton processes. The availability of charge stored in these materials and the rate at which it can be extracted was also studied by discharge under galvanostatic conditions in 0.1 M HClO4 for two film thicknesses, 0.5 μm and 1.9 μm. For the thinner film little dependence on the discharge rate is seen, whereas the thicker film shows limited capacity and rate in the range 1–17 A g–1. The thicker film in particular gives discharge curves with two different slopes, transitioning between 0.35–0.55 V which is likely due to contributions from the different redox potentials of the two component materials present in the film. Specifically, the transition should represent the reduction of the quinone groups from the Q to QH2 state and any remaining capacity due to the polypyrrole present. Following further measurements and data analysis the 1:1 polypyrrole/lignosulfonate composite material was estimated to have a charge storage capacity of ~80 mAh g–1 which is a very promising beginning. One area of future work with these materials is to address the issue of self-discharge, but the authors believe that this and other improvements can be achieved by examining different lignin sources and processing parameters which can have a large effect on the number of phenolic groups in the material.
Conclusions

This review has taken only a small snapshot of the work presented on biomass related topics at the conference. It was apparent from the myriad talks presented and nationality of the presenters that biomass is a burgeoning area of research across the whole world with a focus in many different application areas. By and large the pgms were featured most prominently although base metals are becoming more widespread. As shown in this review, there is also research into applications which do not utilise a metal of any sort although these are distinctly more specialised. As with most ACS meetings, whilst massive in scale and number of attendees it was very well organised and, of the talks this reviewer attended, there were only a few issues with equipment or the speakers themselves.

References

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The Reviewer

Ian Casely graduated in Chemistry from Imperial College, London, UK, in 2005 with subsequent PhD studies at the University of Edinburgh, UK, focused on rare-earth metal N-heterocyclic carbene organometallic complex synthesis and reactivity. In 2009 he moved to the University of California, USA, as a postdoc to work on small molecule activation chemistry and established a project developing the organometallic chemistry of bismuth complexes. Returning to the UK in 2011 to work at University of Oxford, UK, on Group 4 metal based heterogeneous slurry polymerisation, in July 2011 he joined the PGM Applications group at Johnson Matthey Technology Centre, Sonning Common, UK. He is working on the conversion of biomass to chemicals as well as in the area of metal organic framework chemistry.
Introduction

“Advances in Biofuel Production: Algae and Aquatic Plants” is a compilation of papers that have previously been published elsewhere, presented as 12 chapters. These have been edited by Barnabas Gikonyo, whose research interests range from the application of biocompatible polymeric materials for the repair of spinal cord injuries to the development of non-food biofuels. The book is intended to provide an overview and evaluation of the current status and prospects for fuel production via algae, microalgae and aquatic plants. As such, the book should appeal to general researchers with an interest in this area, rather than just specialists working in the field.

The book is divided into three main sections. Part One provides an overview of the current status and challenges in producing sustainable fuels from algae. Part Two, which consists of seven chapters and makes up the bulk of the book, examines both the supply potential and some of the current technologies relevant to biofuel production. The final section comprises three chapters dealing with next generation research, with a focus on progress in genetic developments.

Current Status and Challenges

The two chapters in Part One, which provides perspectives on the challenges facing scale-up and economics, will be of interest to general readers. Chapter 2 provides quantification of a number of the challenges, in particular those related to process economics, energy consumption and environmental acceptability. Using a variety of published data and life cycle analysis (LCA) studies, the authors, Douglas Aitken and Blanca Antizar-Ladislao (University of Edinburgh, UK), review the current state of knowledge and technology readiness of algal biomass to fuels. Their analysis covers a range of key aspects: choice of algal species and species control; reactor technology for growing algae; harvesting and separation technologies; water usage; product (fuel) types; and the use and impact of fertilisers. The authors highlight a number of barriers that will need to be overcome if commercial algal biofuel production is to be realised. Significant amongst these are energy consumption in the production process, for example to effect separation of the algal products from the aqueous medium; the use of fertilisers to deliver algae growth; and water
requirements. Interestingly, most algal biofuels are stated as likely to be net contributors to greenhouse gas emissions, mainly due to the current energy inputs required for algal biofuel production. The development of enhanced, low-energy separation processes and the use of waste water or recovery of nutrients are highlighted as areas for further research. The authors also propose that improved energy recovery from the available (non-oil) biomass will require the use of anaerobic digestion or combustion, even to the extent that it may be beneficial to ignore biodiesel and to simply recover energy directly using these two methods.

Biofuel for Today

Chapter 3, by Stijn Cornelissen (ZinInZin, Utrecht, The Netherlands), Michèle Koper (Ecofys bv, The Netherlands) and Yvonne Y. Deng (Ecofys UK), delivers a more positive perspective on the potential of algae routes to fuels. The authors take a similar broad overview of the role of bioenergy in a fully sustainable global energy system and present a model in which 95% of our energy needs are met by renewable energy, without a major reduction in activity levels, by 2050. Their analysis covers issues such as land use, food security, water requirements and greenhouse gas emissions and considers a wide range of renewable energy types. Recognising that significant development is still required for commercial production of biofuel from algal oil, the authors only include this as a technology option from 2030 onwards, from which point they allow algal oil to supply any remaining demands in oil routes after the use of residues, waste and bioenergy crops. Inherent in their model is the recycle of the non-oil components of algal biomass to provide nutrients and energy input into the growth and processing of the algae. They conclude that the amount of algal oil needed (equivalent to $21 \times 10^{18}$ J of energy) and associated land requirements ($3 \times 10^5$ km$^2$ of non-arable land) lie comfortably within the potential available and will result in a net reduction in greenhouse gas emissions.

Firoz Alam (Royal Melbourne Institute of Technology (RMIT) University, Australia) et al. in Chapter 4 provide further thoughts about the viability of algae routes to biofuel. While lacking the quantification of some of the earlier chapters, this short article concludes that microalgae offer immense potential for biofuel production. However, the authors re-emphasise a number of technical issues discussed in earlier chapters. In particular, they highlight the need for developments to reduce the huge energy losses (most of which is associated with extracting lipids) and to recover value from the majority (approximately 70%) of the biomass that is currently wasted, for example by the re-use of nutrients.

The theme of assessing the potential of algal biofuel production is further explored by Colin M. Beal (The University of Texas at Austin, USA) et al. in the next chapter, which focuses on two key criteria for success: the energy return on investment (EROI) and the financial return on investment (FROI). The analysis presented includes both direct (for example electricity usage in the process) and indirect (for example energy embedded in consumed materials) energy and operating costs. Results are presented for two scenarios: the experimental case (based on small scale lab data) and the highly productive case, a system with a greater biomass productivity ($40 \times$ increase) and higher lipid fraction in the biomass ($15 \times$ increase), as well as improved energy efficiency and re-use of 95% of cultivation water. These assumptions are described as optimistic but not unreasonable. As might be expected, the EROI for the highly productive case was significantly better than that of the experimental case, but still fell well short of that required to give a process that is competitive with conventional fuels. A similar result was reached for the return on investment criterion. Based on this analysis, the authors conclude that, even for the optimistic highly productive case, current technology falls well short of providing a route to fuels that can offer a profitable alternative to conventional energy sources. In addition, algal biofuel routes are stated to be more water intensive and resource intensive than conventional fuels. A number of technology limitations are identified by the model that will not be addressed by improving algal biomass productivity. For example, stoichiometry demands an increased nutrient requirement (with an increase in the associated energy embedded in fertilisers) with increased growth rates. On a more positive note, the model is used by the authors to generate a number of targets for research stakeholders to direct the development of commercially viable technology. These include the use of waste and recycled nutrients; the use of waste heat and flue gas as inputs to the process; development of energy efficient harvesting and separation methods; and development of ultra-productive algal strains. While the overall conclusion of this piece of work could be seen as highly negative.
for algal fuels, the authors finish by stating that algae represent one of the few alternative feedstocks capable of producing fuel substitutes directly. ‘Game-changing’ biotechnology advances (for example the development of ultra-productive algal strains) are needed to achieve sustainable, large-scale algal biofuel production.

The next four chapters in the book deal with specific aspects of technology of direct relevance to biofuel production from algae. Chapter 6, by Ryan W. Hunt (The University of Georgia, Athens, USA) et al., reviews the use of electromagnetic bio-stimulation as applied to bioenergy applications and provides a wealth of examples to show how growth may be stimulated by electromagnetic effects. The mechanisms responsible for these effects and the potential to apply to biofuel production are not fully understood; as the authors state, the aim of the paper is to stimulate interest in this field.

In Chapter 7, Juan Carlos Serrano-Ruiz (Universidad de Córdoba, Spain) et al. present an excellent overview of the potential catalytic transformations of two biomass derived acids for the production of advanced biofuels. The initial part of the chapter gives a brief outline of the chemistry involved in the catalytic processing of these resources, including both deoxygenation and carbon–carbon coupling reactions. The chapter then focuses on two platform chemicals, lactic acid and levulinic acid with a range of different transformations described to produce liquid hydrocarbon fuels for diesel and gasoline applications (Figure 1). The article also provides a very useful reference source with a good selection of recent articles on a variety of catalytic routes. However, discussion of the limitations of current catalytic technology and the advances required to deliver economically attractive processes to advanced biofuels is limited and would have been a useful addition to this chapter.

In Chapter 8, the use of anion exchange resins for one-step processing of algae is presented by Jessica Jones (The University of Texas at Austin) et al. The study shows that anion exchange resins such as Amberlite can concentrate and dewater algae and then be eluted with 5% sulfuric acid/methanol reagent. Although probably interesting to researchers in the field, this chapter is possibly too in-depth for the general reader.

Fig. 1. Scheme of the catalytic routes required to convert biomass-derived acids such as lactic acid and levulinic acid into advanced biofuels
A comprehensive review of methods for microalgae isolation and selection for prospective biodiesel production is presented in Chapter 9. This is a useful, very readable general introduction to the subject for scientists working in this area who are not familiar with the fundamentals of isolation and selection of microalgae for commercial cultivation. The chapter highlights topics from isolation through to large-scale production. Subjects such as sampling and isolation of cultures as well as cultivation and lipid determination are thoroughly discussed using a number of examples. The chapter concludes with discussing lipid content and lipid extraction in microalgae. It highlights the range of lipid contents for various species and also explains that lipid productivity is not the only factor that should be considered during strain selection.

Next Generation Research

The final section of the book consists of three chapters under the theme of next generation research and the technical aspects of these chapters lie outside of the experience of the reviewers. Chapters 10 and 11, which provide a comparison of next generation sequencing systems and a review of an annotation tool, are likely to be of limited interest to the general reader. In contrast, the final chapter, which provides an example of the use of gene transcription to provide insight into metabolic pathways within microalgae, is more accessible. Even to the non-specialist, this paper illustrates the potential for future research into metabolic engineering to deliver microalgae with enhanced characteristics for sustainable fuel production.

Conclusions

Overall the book is an interesting combination of diverse papers dealing with the general topic of biofuel production from algae. This is a wide ranging subject and for the reader interested in detail of the latest technology in, for example, bioreactor design, upgrading catalysis and separations, the book will fall short of expectations. For those interested in a higher level overview of the opportunities for biofuel production from algae, the current limitations and the major themes where development effort is required, this book will provide a useful introduction to the subject.

"Advances in Biofuel Production: Algae and Aquatic Plants"

The Reviewers

Michael Watson is Technology Manager in the Johnson Matthey Technology Centre (JMTC) at Billingham, UK. His current research activities are focused on the development of catalysts for a wide range of industrial processes, including the use of biorenewable feedstocks.

Fiona Wigzell joined Johnson Matthey in 2011. She is currently a Research Scientist at JMTC, Billingham. She has worked on a range of biomass related projects including catalytic upgrading of fatty acids to transportation fuels.
Here we profile an upcoming researcher who has benefitted from Johnson Matthey’s support in the past. David Nelson is a newly appointed Chancellor’s Fellow and Lecturer at the University of Strathclyde, in Glasgow, UK. His research interests concern the development of useful transition metal catalysed processes for synthesis via a detailed understanding of mechanism, rate and selectivity in key steps.

About the Research

Transition metal complexes can perform an incredible range of chemical transformations, with new reactions, applications and processes being discovered and documented daily. However, many of these reactions are not well-developed enough for routine industrial application on a larger scale; while smaller-scale syntheses might employ these techniques, process chemists must often redesign synthetic routes to replace these reactions with more scalable or economical alternatives.

The aim of the group’s research is to develop promising catalytic technologies to the stage that they can be deployed in an industrial setting on a large scale. The aim is to do this by conducting rational and quantitative studies of these catalytic reactions and key steps therein. The tools are those of synthetic organometallic and organic chemistry and of physical organic chemistry; including nuclear magnetic resonance (NMR), infrared (IR) and ultraviolet (UV)/visible spectrosopies, inductively coupled plasma mass spectrometry (ICP-MS), gas chromatography (GC), liquid chromatography (LC) and mass spectrometry (MS). Investigations into the rates and selectivities of key steps, how these depend

on catalyst structure and how these influence the overall performance of the reaction can provide useful information. Most importantly, this information can be used to inform the selection or design of catalysts and reaction conditions.

Dr David Nelson, group leader, has a background in the study of transition metal catalysed reactions, having held positions at the University of Strathclyde (PhD with Jonathan M. Percy) and the University of St Andrews, UK, (postdoctoral work with Steven P. Nolan FRSE). The work at Strathclyde looked at alkene metathesis reactions, predominantly using kinetic experiments. The effect of target ring size on the rate and selectivity
of alkene metathesis, mediated by ruthenium carbene complexes, was probed (Scheme I); the latter study also showed that the selectivity for cycloalkene over oligomer (the effective molarity) could be predicted from density functional theory (DFT) calculations. Mechanistic understanding regarding the initiation event in Grubbs-Hoveyda type catalysts and deleterious isomerisation side reactions was also provided.

The work at St Andrews consisted of various studies of organometallic chemistry and catalysis, using late transition metals such as iridium, ruthenium, palladium and gold. Highlights include: the preparation and study of N-heterocyclic carbene (NHC)-bearing iridium species, including \([\text{Ir(OH)(COD)}(\text{I}^\text{iPr})]\) and \([\text{IrCl(COE)}(\text{I}^\text{iPr})_2]\) (see Figure 1) and derivatives and analogues thereof; the study of the decomposition processes that ruthenium metathesis catalysts undergo; and the application of these decomposition products in catalysis.

Current work in the Nelson group is focused on ruthenium-catalysed C–H activation and nickel-catalysed cross-coupling, aiming to bring together both organometallic and physical organic approaches in the research.

![Scheme I. Partitioning between cycloalkene and oligomer in alkene metathesis (Mes = 2,4,6-trimethylphenyl)](image)

How does \(n\) affect the ratio of products?

![Fig. 1. Complexes \([\text{Ir(OH)(COD)}(\text{I}^\text{iPr})]\) and \([\text{IrCl(COE)}(\text{I}^\text{iPr})_2]\)](image)
Selected Publications


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EMISSION CONTROL TECHNOLOGIES

Kinetic Evaluation of Direct NO Decomposition and NO-CO Reaction over Dendrimer-derived Bimetallic Ir-Au/Al2O3 Catalysts


The performance of a dendrimer-derived bimetallic Au-Ir catalyst for the reduction of NO by CO and also for direct NO decomposition were studied and compared to a more conventional bimetallic catalyst, prepared using incipient wetness impregnation. Analysis of the dendrimer-derived catalyst showed highly dispersed Ir-Au particles and it exhibited better catalytic performance for both reactions when compared to the conventional catalyst. A structural effect due to Au was noted for the conventional catalyst which was not seen for the dendrimer-derived catalyst due to the fact the Au was so highly dispersed. On the conventional catalyst, Au particles appear to dilute the surface Ir sites, resulting in higher TOF when compared to monometallic Ir catalysts prepared using the same incipient wetness technique.

Prediction of Diffusivity and Conversion of \(n\)-Decane and CO in Coated Pt/\(\gamma\)-Al2O3 Catalyst Depending on Porous Layer Morphology


The effects of diffusion in the catalytic layer, especially if there are multiple coated layers, can limit the conversion in monolith reactors for automotive exhaust gas aftertreatment. Therefore a good understanding of the internal diffusion effects is required for designing an optimum catalytic coating. A detailed multiscale modelling technique including the use of 3D digital reconstruction is used to predict the effective diffusivity based on the actual structure of a porous coating. A 3D digitally reconstructed porous layer structure enabled the simulation of diffusion and oxidation of CO and \(n\)-decane on a microscale. The simulations were then compared with experiments which involved the coating of several layers with uniform thickness on flat metal foils and controlling its macroporous structure by changing the alumina particle size distribution, pore templates and compaction methods. The reactor outlet conversions were calculated using a macroscopic 1D plug-flow model. The comparison shows good agreement: the predicted effective diffusion coefficients through the tested Pt/\(\gamma\)-Al2O3 layers were 1.4, 3.6 and \(6.4 \times 10^{-6}\) m\(^2\) s\(^{-1}\) for CO at 298 K in compact, standard and macropore-templated sample, respectively.

Critical Role of Water in the Direct Oxidation of CO and Hydrocarbons in Diesel Exhaust After Treatment Catalysis


The oxidation of CO and C\(_3\)H\(_6\) over a Pd/Al\(_2\)O\(_3\) catalyst were studied using isotopically labelled \(^{18}\)O\(_2\). Water was found to promote CO and cause C\(_3\)H\(_6\) to be oxidised at lower temperatures compared to a dry feed. The reaction mechanism was elucidated by adding a labelled \(^{18}\)O\(_2\) as the reactant, revealing that the main pathway in the presence of water is via water activation, while O\(_2\) plays a secondary role. D\(_2\)O significantly decreased this effect compared to H\(_2\)O, further supporting the importance of water activation (see Figure).
The Role of Pore Size on the Thermal Stability of Zeolite Supported Cu SCR Catalysts


*In situ* XRD has been used to carry out a comparison study on the effects of pore size on the hydrothermal stability of zeolite supported Cu SCR catalysts. Small pore catalysts were found to be more stable than large or medium pore catalysts. The supports studied were an 8-ring small pore chabazite (CHA) and a 12-ring large pore beta zeolite (BEA). Even though the parent zeolite frameworks have comparable stability and can maintain their structure after hydrothermal exposure at 900°C, the presence of Cu increased the rate of collapse of the BEA framework above 800°C while having little effect on the CHA framework. This is thought to be due to a harmful Cu/Al2O3 interaction. The steric restriction of the small pore zeolite structure may hinder this interaction allowing the stability to be improved.

Local Structure and Speciation of Platinum in Fresh and Road-Aged North American Sourced Vehicle Emissions Catalysts: An X-Ray Absorption Spectroscopic Study


The Pt species present in a range of fresh and road-aged three-way and diesel oxidation catalysts from North America were studied using Pt and Cl XAS in order to identify the Pt compounds that may be released into the environment from such sources. The main species present in the fresh catalyst were found to be oxides. In the road-aged catalysts, the main species were metallic. There were also some bimetallic components such as Pt-Ni, Pt-Pd and Pt-Rh. Significantly, there was no evidence of chloroplatinate species in the solid phase for any of the catalysts studied.

FINE CHEMICALS: CATALYSIS AND CHIRAL TECHNOLOGIES

An Efficient Catalytic Asymmetric Synthesis of a β2-Amino Acid on Multikilogram Scale


Research was carried out to tackle the challenges surrounding a kilogram-scale production of chiral β2-amino acid derivatives by catalytic asymmetric hydrogenation. The authors developed a short and efficient synthesis of an unsaturated N-Boc protected β2-enamide precursor and chiral catalyst screening was then carried out on common and readily available chiral metal complexes of Rh, Ru and Ir which would generate β2-amino acid in high enantiomeric excess. Optimisation experiments were then conducted to identify optimum reaction conditions and investigate the effectiveness of additives in terms of improvements in reactivity and enantioselectivity. A simple Ru-BINAP catalyst system was found to generate the (S) product in high enantiomeric excess (>99% ee) and yield. Production on a multikilogram scale resulted in >99% ee.

NEW BUSINESSES: FUEL CELLS

The Origin of High Activity But Low CO2 Selectivity on Binary PtSn in the Direct Ethanol Fuel Cell


DEFCs are an attractive technology as they can use carbon-neutral bioethanol as a fuel. The challenge is to find a more efficient electrocatalyst for the anode, in terms of both activity at low overpotential and CO2 selectivity. In this study, variable temperature electrochemical *in situ* FTIR was applied to the study of an active binary PtSn DEFC catalyst at 20°C and at 60°C. The binary PtSn catalyst was found to be better than Pt at inhibiting ETOH dissociation to CO, but to promote the partial oxidation to acetaldehyde and acetic acid. At 60°C there was enhanced CO2 selectivity due to an increase in both ETOH dissociation to CO and further oxidation to CO2. The main products were still found to be acetaldehyde and acetic acid at 60°C. Density functional theory (DFT) calculations were used to derive the potential-dependent phase diagrams for surface oxidants of OH formation on Pt(111), Pt(211) and Sn modified Pt(111) and Pt(211) surfaces and the results provide insight into these experimental results at the atomic and molecular levels.
PRECIOUS METAL PRODUCTS: COLOUR TECHNOLOGIES

Aerosol-Assisted Deposition of Gold Nanoparticle-Tin Dioxide Composite Films


Aerosol assisted chemical vapour deposition (AACVD) was used to investigate the formation of tin oxide films with embedded gold nanoparticles. The purpose of the study was to find out if gold could be used as a colourant in a CVD derived film. In this study, AACVD involves the growth of composite gold nanoparticle/tin oxide films from a one-pot precursor solution containing monobutyltin trichloride and auric acid in methanol. Two films were formed: gold nanoparticle films on the top plate and gold/tin dioxide composite film on the heated substrate. Depending on the position from the inlet, different amounts of gold incorporation were shown on the composite film thus a graded film was formed, therefore enabling the authors to assess the functional properties of the films. 0.03–0.15 Au:Sn molar ratio was found to be the optimum location where a mix of desirable properties such as blue colouration, reasonable optical transparency as well as reflectivity in the IR were observed.

PROCESS TECHNOLOGIES

Understanding the Optimal Adsorption Energies for Catalyst Screening in Heterogeneous Catalysis


In this research a two-step model was used by the authors to understand the kinetics of heterogeneous catalysts and help to predict which catalysts will perform best. The model provides a simplified description of real-world systems, only modelling those systems with a single rate-determining step. Detailed analysis of volcano curves was carried out, and related to adsorption energies and other terms from the Brensted–Evans–Polanyi (BEP) relation. The authors derive conditions in terms of the energy window which should allow for optimal catalysts to be designed.

Improving Sensitivity and Accuracy of Pore Structural Characterisation Using Scanning Curves in Integrated Gas Sorption and Mercury Porosimetry Experiments


An integrated gas sorption and mercury porosimetry technique is demonstrated which can detect pores within disordered solids which are undetectable when using conventional scanning experiments. On its own gas sorption was not sensitive enough to detect these pores, but the combined technique proved more powerful than either of the two individual methods on their own. Pore-filling mechanisms were found to vary in disordered solids, and so this integrated technique allows for a more accurate calculation of pore size distribution by avoiding the introduction of systematic errors due to the assumption of a single filling mechanism taking place.

Mechanistic Study of 1,3-Butadiene Formation in Acetylene Hydrogenation Over the Pd-based Catalysts Using Density Functional Calculations


During the selective hydrogenation of acetylene in commercial processes, one deactivation route for the palladium catalyst is due to the formation of green oil. The mechanisms behind the formation of this catalyst poison are not well known, but the formation of 1,3-butadiene is thought to be a precursor for green oil. This research uses density functional theory to investigate the likely reaction pathways over Pd(111) and Pd (211) surfaces for the formation of 1,3-butadiene in an attempt to understand the mechanisms of green oil formation. A combination of hydrogenation and coupling reactions of C₂ groups is believed to take place and therefore three potential routes to the formation of green oil were modelled resulting in a general explanation for the deactivation process of industrial catalysts. The effect of subsurface carbon atom formation was also studied, as well as that of Ag alloying on the 1,3-butadiene formation using Pd-based catalysts with the results comparing well with experimental results.

Moving from Batch to Continuous Operation for the Liquid Phase Dehydrogenation of Tetrahydrocarbazole


The liquid phase processing of fine chemicals is usually carried out using batch operation. However, the benefits of continuous operation such as decreased times for start-up and cool-down cycles, improved process safety and more stable reaction conditions should be taken into consideration. In this paper, the authors study the liquid phase dehydrogenation reaction of 1,2,3,4-tetrahydrocarbazole under continuous operation using a trickle bed reactor. The experiments were performed using realistic liquid velocities with and without the presence of a hydrogen acceptor. Under continuous use a commercial 5 wt% Pd/Al₂O₃ catalyst was found to slowly deactivate, however this problem is overcome when the catalyst is washed with sodium hydroxide. It was observed that the use of propene as a hydrogen acceptor gas can increase the overall catalytic activity of the operation.
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