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Editorial

Platinum Metals Review: Looking Back and Moving Forward

This will be the last issue of *Platinum Metals Review* to be published under that name. From the next issue, in July 2014, the journal will become known as the *Johnson Matthey Technology Review*. Some of our readers will be aware of this change as information has been announced previously (1).

Looking back *Platinum Metals Review* has covered many groundbreaking technology areas over the decades in which it has been published. Highly downloaded recent articles from the Journal Archive include the health applications of platinum in medical devices such as pacemakers, neurostimulation devices etc. (2); the use of platinum group metals (pgms) to disinfect water (3); platinum’s use in electrochemical measurements (4); the history of the pgms in the Periodic Table (5); preparatory techniques for pgm nanoparticles (6); the qualities of pgms that make them suitable for anticancer and other medical treatments (7); the uses of coordination chemistry in organic reactions, optical applications, hydrometallurgy and medicine (8); the reasons for the use of platinum in fuel cell electrocatalysts (9); a discussion of the relative importance of platinum, palladium and rhodium in gasoline automotive catalysts (10); and phosphorescent platinum complexes for promising organic light-emitting diodes (OLEDs) (11).

All past articles in *Platinum Metals Review* will remain available to access free of charge in electronic formats from the Journal Archive.

Of course during its publication *Platinum Metals Review* has been exclusively focused on pgm-containing technologies. From the next issue, the journal will have a much broader scope as it transitions into the *Johnson Matthey Technology Review*. The emphasis on pgms will cease, however the new, broader ethos will be to publish on selected topics of especial relevance to Johnson Matthey’s industry, and to those working towards industrially relevant applications.

SARA COLES, Assistant Editor

References


Johnson Matthey Technology Review

In mid-2014 there will be a new-look website. We have taken the opportunity to add some new functionality: authors will be pleased to know that we will offer faster publication as we will be publishing articles on a rolling basis, ahead of publication of the issue to which they are assigned. There will be Chinese translations of article abstracts, to help the rapidly growing research community in China to access the information that they need. It will also be possible to download...
articles on mobile devices such as a smartphone or tablet and it will be possible to sort articles by subject category to more easily find articles of interest.

The new website and journal will be found at: http://www.technology.matthey.com/. Please look out for further announcements.

Topics which will be eligible for submission to the Johnson Matthey Technology Review will include:

- Analytical techniques
- Biocatalysis
- Catalysis
- Chemistry
- Electrochemistry
- Electronics
- Emissions control
- Energy conversion & storage
- Historical
- Industrial processes
- Medical
- Metallurgy and materials
- Nanotechnology
- Pharmaceuticals and fine chemicals
- Sustainable chemistry

The full list with further details will appear on our website under Editorial Policy.

We are now inviting submissions to the Johnson Matthey Technology Review and these are not limited to people who already have a relationship with Johnson Matthey Plc. Contact us to submit a manuscript or if you would like more information.

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Recent Research and Developments Related to Near-Equiatomic Titanium-Platinum Alloys for High-Temperature Applications

Effect of partial substitution of titanium and platinum in Ti$_{50}$Pt$_{50}$ on strength and shape memory properties above 800°C

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Titanium-platinum (Ti$_{50}$Pt$_{50}$) (all compositions in at%) alloy exhibits thermoelastic martensitic phase transformation above 1000°C and has potential for high-temperature shape memory material applications. However, as has been previously reported, Ti$_{50}$Pt$_{50}$ alloy exhibited a negligible recovery ratio (0–11%) and low strength in martensite and especially in the austenite phase due to low critical stress for slip deformation. In order to improve the high-temperature strength and shape memory properties, the effects of partial substitution of Ti with other Group 4 elements such as zirconium and hafnium and the effect of partial substitution of Pt with other platinum group metals (pgms) such as iridium and ruthenium on the high-temperature mechanical and shape memory properties of Ti$_{50}$Pt$_{50}$ alloy were recently investigated. This paper reviews the transformation temperatures and high-temperature mechanical and shape memory properties of recently developed Ti site substituted (Ti,Zr)$_{50}$Pt$_{50}$, (Ti,Hf)$_{50}$Pt$_{50}$ and Pt site substituted Ti$_{50}$(Pt,Ru)$_{50}$ and Ti$_{50}$(Pt,Ir)$_{50}$ alloys for high-temperature (~800°C–1100°C) material applications.

1. Introduction

Equiatomic nickel-titanium (NiTi), also known as nitinol, is one of the best-known shape memory alloys. However, nitinol is limited to biomedical and room temperature engineering applications (1) and cannot be used at high temperature (for example, above 100°C) due to its low transformation temperature (2–4). Recently, partial substitution of Ni with Pt and Pd in NiTi was found to be effective for increasing the transformation temperature and it was reported that recently developed NiTi-Pt (5) and NiTi-Pd (6) have potential for high-temperature
shape memory material applications (4). Ti_{50}Pd_{50} and Ti_{50}Pt_{50} exhibit a thermoelectric orthorhombic (B19) martensitic phase transformation from the austenite (B2) phase. Austenite finish ($A_f$) (1085°C) and martensite finish ($M_f$) (1020°C) temperatures of Ti_{50}Pt_{50} were found to be ~500°C higher than those of Ti_{50}Pd_{50} whose $A_f$ was 550°C and $M_f$ was 480°C (7). Thus, Ti_{50}Pt_{50} can be used for much higher temperature (for example, above 1000°C) shape memory material applications than Ti_{50}Pd_{50}, which can be used for 400°C–600°C applications (5). (Ti,Zr)_{50}Pd_{50} (8) has a $M_f$ of 445°C, lower than that of Ti_{50}Pd_{50} (5, 7), showing that Zr acts as a B2 phase stabiliser in Ti_{50}Pd_{50}. Transformation temperatures of Ti_{50}Pd_{50} (7), Ti_{50}Au_{50} (9, 10), Ti_{50}Pt_{50} (7) and Ti_{50}Ni_{50} (3) are given in Table I. As shown in Table I, Ti_{50}Pt_{50} (7) alloy has the highest transformation temperature among the four alloys. Only Ta_{50}Ru_{50} and Nb_{50}Ru_{50} (11, 12) have high transformation temperatures similar to Ti_{50}Pt_{50} alloy (4, 7). Ta_{50}Ru_{50} and Nb_{50}Ru_{50} exhibit two-stage transformation from B2 to tetragonal B' phase, and then from B' to monoclinic B'' phase at low temperature (12), whereas Ti_{50}Pt_{50} (7) exhibits one-stage transformation from B2 phase to thermoelectric orthorhombic (B19) martensitic phase (7).

Biggs et al. found diffusionless twin oriented martensitic transformation at about 1000°C in Ti_{50}Pt_{50} alloy. Broad laths with well-developed midribs were observed close to the equiatomic composition (13). They also showed that the B2 (austenite) to B19 (martensite) phase field ranges from 46 at% to 54 at% Pt (14). Ti_{50}Pt_{50} phase, which had not been reported before, was shown to be 30%–45% Pt in the revised phase diagram for TiPt and the phase boundary for TiPt agreed well with the literature (15). The site preference behaviour of solute addition to TiPd and TiPt on the basis of theoretical calculations of energy gap was provided by Bozzolo et al. (16). The phase stability of TiPt at equiatomic composition was investigated theoretically using the heat of formation, elastic properties, electronic structure (density of states) and phonon dispersion curves of B2, B19 and B19' structures (17). The partial isothermal section of the Al-Ti-Pt phase diagram at 1100°C was studied in the compositional region below 50 at% Pt (18).

Due to the high transformation temperature of the Ti_{50}Pt_{50} alloy (4, 7, 14), the room temperature to high-temperature (for example, 50°C below $M_f$ and 50°C above $A_f$) mechanical properties and shape memory properties of Ti site substituted and Pt site substituted Ti_{50}Pt_{50} alloy were investigated. This article discusses and compares recently reported results from the present group related to the phase transformation temperatures, mechanical and shape memory properties of Ti_{50}Pt_{50}, Ti site substituted (Ti,Zr)_{50}Pt_{50}, (Ti,Hf)_{50}Pt_{50} and Pt site substituted Ti_{50}(Pt,Ir)_{50} and Ti_{50}(Pt,Ru)_{50} alloys.

### 2. Experimental Procedures

Alloys were created by arc melting homogenised at 1250°C for 3 h, and then quenched with ice water. The phase transformation temperatures were investigated using differential thermal analysis (DTA) between 600°C to 1100°C at a heating and cooling rate of 10°C min⁻¹ using a Shimadzu DTA-50 device. X-ray diffraction analysis was conducted at room temperature (~25°C) to high temperature from 20°–90° in 2θ using a Rigaku TTR-III X-ray diffractometer with CuKα radiation. For microstructural observation, sputter etching (dry etching) was carried out using a glow discharge optical emission spectrometer (GD-OES) and argon-nitrogen gas mixture. For shape memory effect measurements, rectangular samples of 2.5 mm × 2.5 mm × 5 mm were compressed to apply 5% strain at a temperature of

<table>
<thead>
<tr>
<th>Alloy</th>
<th>$M_p$, °C</th>
<th>$M_f$, °C</th>
<th>$A_p$, °C</th>
<th>$A_f$, °C</th>
<th>$A_f-M_p$, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti_{50}Au_{50} (9)</td>
<td>597</td>
<td>586</td>
<td>615</td>
<td>624</td>
<td>38</td>
</tr>
<tr>
<td>Ti_{50}Pd_{50} (7)</td>
<td>510</td>
<td>480</td>
<td>520</td>
<td>550</td>
<td>70</td>
</tr>
<tr>
<td>Ti_{50}Pt_{50} (7)</td>
<td>1070</td>
<td>1020</td>
<td>1040</td>
<td>1085</td>
<td>65</td>
</tr>
<tr>
<td>Ti_{50}Ni_{50} (3)</td>
<td>−19</td>
<td>−33</td>
<td>−4</td>
<td>7</td>
<td>40</td>
</tr>
</tbody>
</table>
50°C below \( M_f \) using a Shimadzu AG-X compression test system. Samples were then heated to 1250°C and held for 1 h under vacuum for shape recovery. The shape memory effect was measured by comparing the sample's length before deformation, after applying 5% strain and after heat treatment. For mechanical testing, cyclic loading-unloading compression tests were conducted for 20% applied strain at test temperatures of 50°C below \( M_f \) and 50°C above \( A_f \) with an initial strain rate of \( 3 \times 10^{-4} \) s\(^{-1}\).

3. Results and Discussion

3.1 Ti\(_{50}\)Pt\(_{50}\) Alloys

The transformation temperatures of Ti\(_{50}\)Pt\(_{50}\) alloy reported by the present research group (19) were found to be ~50°C less than those reported elsewhere (7). A 50°C difference in transformation temperatures is expected to be due to small composition variations, accuracy or the type and distance of the thermocouple from the specimen and experimental method used. The B2 phase structure was identified for Ti\(_{50}\)Pt\(_{50}\) alloy above \( A_f \) and B19 martensitic phase below \( M_f \) and the lattice parameters of B19 and B2 increased with increasing temperature (20). The lattice parameters of B19 and B2 reported by the present research group (20) were found to be close to those reported by H. C. Donkersloot and J. H. N. Van Vucht (7), as shown in Table II. The stress for reorientation of martensite at room temperature was found to be 200 MPa, decreasing to 50 MPa when tested at 50°C below \( M_f \) of Ti\(_{50}\)Pt\(_{50}\) alloy (20). The small non-linear strain recovery upon unloading of mechanically loaded Ti\(_{50}\)Pt\(_{50}\) alloy samples below \( M_f \) was related to pseudoelasticity caused by the reversion of a small fraction of detwinned martensite to twinned martensite upon unloading (20). In the case of superelasticity there is reverse transformation of deformation-induced martensite to the parent austenite phase upon unloading.

It was also found (19) that Ti\(_{50}\)Pt\(_{50}\) alloy exhibited negligible shape memory effect (~11%), due to the low critical stress for slip deformation compared to the stress required for martensite reorientation. The Ti\(_{50}\)Pt\(_{50}\) alloy exhibited the single yielding phenomenon and very low strength (20 MPa) in the B2 phase region (19). Thus, Ti\(_{50}\)Pt\(_{50}\) alloy is very soft in the B2 phase region. The single yielding phenomenon showed that slip is the dominant deformation mechanism. The drastic decrease in strength during phase transformation from B19 to B2 and negligible shape memory effect demonstrate that Ti\(_{50}\)Pt\(_{50}\) cannot be used for high-temperature shape memory material applications. The effect of partial substitution of Ti with the Group 4 metals Zr and Hf and of Pt with Ir and Ru to improve the high-temperature strength and shape memory properties are reviewed here.

3.2 Ti\(_{50}\)(Pt,Ir)\(_{50}\) Intermetallic Alloys

Ir has a high melting point (2447°C) compared to Pt (1769°C) (21). Both Pt and Ir have the face-centred cubic (fcc) crystal structure (22). The solubility of Ir in TiPt is expected to be high as Ir is a pgm. Ir was therefore selected to improve the high-temperature strength and shape memory properties of Ti\(_{50}\)Pt\(_{50}\) alloy. The nominal compositions of developed alloys were: Ti\(_{50}\)(Pt\(_{37.5}\)Ir\(_{12.5}\)), Ti\(_{50}\)(Pt\(_{25}\)Ir\(_{25}\)) and Ti\(_{50}\)(Pt\(_{12.5}\)Ir\(_{37.5}\)) (19, 23–25). It was found that the intensity of DTA peaks became weaker and the peak width became wider with increasing Ir content (23). As shown in Figure 1, the phase transformation temperatures were also increased by partial substitution of Pt with Ir and \( A_f \) which was 1057°C for Ti\(_{50}\)Pt\(_{50}\) alloy, was

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Temperature</th>
<th>Phase</th>
<th>( a, \text{Å} )</th>
<th>( b, \text{Å} )</th>
<th>( c, \text{Å} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti(<em>{50})Pt(</em>{50}) (20)</td>
<td>RT</td>
<td>B19</td>
<td>4.586</td>
<td>2.761</td>
<td>4.829</td>
</tr>
<tr>
<td></td>
<td>1200°C</td>
<td>B2</td>
<td>3.191</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>1300°C</td>
<td></td>
<td>3.196</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Ti(<em>{50})Pt(</em>{50}) (7)</td>
<td>RT</td>
<td>B19</td>
<td>4.55</td>
<td>2.73</td>
<td>4.79</td>
</tr>
<tr>
<td></td>
<td>1100°C</td>
<td>B2</td>
<td>3.192</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>
increased to 1218ºC for Ti50(Pt12.5Ir37.5) alloy (19). The transformation temperatures were increased by approximately 4ºC for 1 at% partial substitution of Pt with Ir (19, 25). The lattice parameter of B2 phase in Ti50Pt50 was decreased with increasing Ir content up to Ti50(Pt25Ir25). However, as the Ir content was increased further, the lattice parameter of B2 phase increased (25). Because the B19 phase is an orthorhombic structure, the lattice parameter ratios a/b, c/b and c/a were found to be larger than 1.0 and the largest values of a/b, c/b and c/a appeared in Ti50Pt50 and decreased with increasing Ir content. When the crystal structure is tetragonal, according to the adopted formula \( a = c \neq b \) lattice parameters \( a \) and \( c \) will have the same value, whereas \( b \) will have different values and \( c/a \) should be 1.0 (25). It was shown that the value of \( c/a \) approached 1 for Ti50(Pt37.5Ir12.5) alloy, indicating that the orthorhombic martensitic structure of Ti50Pt50 changed to a tetragonal phase with increasing Ir content to ~30 at% Ir in Ti50(Pt, Ir)50 alloys (25). Based on these results, the Ti50(Pt, Ir)50 alloys were divided into three groups. The first group for the alloys with Ir of up to approximately 10% was considered to be the Ti50Pt50 type orthorhombic structure because the lattice parameters and the lattice parameter ratios were close to those of Ti50Pt50. In the second group with Ir content of 10 at% to 30 at%, the orthorhombic structure changed to nearly tetragonal with increasing Ir content. In the third group, the Ir content of alloys was above 30 at% Ir, where the lattice parameter ratio c/a once again increased with increasing Ir content (25).

Microstructural analysis was used to observe the surface relief around the phase transformation temperature for Ti50Pt50 as well as Ti50(Pt, Ir)50 alloys. However, the surface relief, which was very clear in Ti50Pt50, became less clear in Ti50(Pt, Ir)50 alloys (24). The compressive strength at 1000ºC test temperature of Ti50Pt50 (300 MPa) increased to ~1000 MPa for Ti50(Pt12.5Ir37.5) alloy as shown in Figure 2 (24). Another study indicates that Ti50Pt50 exhibits the single yielding phenomenon (19). However, shape memory alloys exhibit double yielding, where the first yielding is related to deformation-induced martensitic transformation and the second yielding is related to permanent deformation due to slip (26). The single yielding phenomenon for Ti50Pt50 showed that slip is the dominant deformation mechanism (19).

The double yielding phenomenon, which is a characteristic of shape memory alloys (26), was analysed for Ti50(Pt, Ir)50 alloys (19, 24). A maximum recovery ratio of 57% due to the shape memory effect was observed for Ti50(Pt37.5Ir12.5) alloy after deformation at 850ºC and then heating above \( A_f \) (24, 25) as shown in Figure 2. However, the recovery ratio due to the shape memory effect decreased with further increase in Ir content (24, 25). Ti50Pt50 in the austenitic phase region exhibited very low strength (~20 MPa) when compression tested at 50ºC above \( A_f \) (19). It was also shown that the strength of Ti50Pt50 alloy in the austenitic phase region was increased from 20 MPa to 240 MPa by partial substitution of Pt with Ir in Ti50(Pt12.5Ir37.5)
alloys (19). However, the strength of Ti50(Pt,Ir)50 alloy in the B2 phase region was still much lower than that in the martensite phase region (~1000 MPa) (24); further research is required to improve the strength of Ti50Pt50 shape memory alloys.

3.3 TiPt-Zr, TiPt-Hf and TiPt-Ru Intermetallic Alloys

The transformation temperatures, high-temperature mechanical and shape memory properties of Ti site substituted (Ti45Zr5)Pt50 (27, 28), (Ti45Hf5)Pt50 (29) and Pt site substituted Ti50(Pt45Ru5) (27) shape memory alloys have recently been reported. Similar to Ti, Zr and Hf also belong to Group 4 of the periodic table, so Zr and Hf have the same number of valence electrons (i.e. four) as Ti. The group number, melting point, density and atomic radius of Ti, Zr, Hf, Ru and Ni are listed in Table III. As shown, the atomic radii of Zr and Hf are larger than that of Ti (30), so partial substitution of Ti with Zr and/or Hf is expected to improve the high-temperature strength and shape memory properties of (Ti45Zr5)Pt50 and (Ti45Hf5)Pt50 alloys due to the solid solution strengthening effect. Similar to Pt, Ru is also a pgm, its atomic radius is smaller than that of Pt (30). The density of Ru is also lower than that of Pt. The melting points of Hf and Zr are higher than that of Ti and the melting point of Ru is higher than that of Pt (Table III). Therefore, partial substitution of Ti with Zr and/or Hf in (Ti45Zr5)Pt50 and (Ti45Hf5)Pt50 alloys, as well as partial substitution of Pt with Ru in Ti50(Pt45Ru5) alloys is expected to increase the melting temperature of Ti50Pt50 alloys. The densities of Zr and Hf are higher than that of Ti, so partial substitution of Ti with Zr and/or Hf will increase the density of Ti50Pt50 alloy. However, the effect will be small for partial substitution of Ti with Zr compared to partial substitution of Ti with Hf due to the small density difference between Ti and Zr compared to that between Ti and Hf. Since Ru is less dense than Pt, partial substitution of Pt with Ru will decrease the density of Ti50Pt50 alloy. It was reported (27–29) that partial substitution of Ti with Zr and Hf, as well as partial substitution of Pt with Ru in Ti50Pt50 alloy effectively improved the strength in the martensitic phase as well as in the austenitic (B2) phase region when tested at 50ºC below Ms and 50ºC above Ms. The strength at 50ºC below Ms and 50ºC above Ms of Ti50Pt50 (19), (Ti45Zr5)Pt50 (27, 28), (Ti45Hf5)Pt50 (28, 29) and Ti50(Pt45Ru5) (27) alloys is given in Figure 3. Partial substitution of Ti with Zr in Ti50Pt50 was found to be more effective in improving the strength and shape memory properties (27, 28) than partial substitution of Ti with Hf (28, 29) and partial substitution of Pt with Ru (27). As revealed by the energy dispersive spectroscopy (EDS) composition analysis of matrix and precipitates (27), partial substitution of Ti with Zr in (Ti45Zr5)Pt50 results in precipitation of (Ti,Zr)Pt3. Such precipitates were not found for (Ti45Hf5)Pt50 (28, 29) and Ti50(Pt45Ru5) (27) alloys, so the higher strength and shape memory properties for (Ti45Zr5)Pt50 were due to the combined effects of solid solution strengthening and (Ti,Zr)Pt3.

Table III

Physical Properties of Ti, Zr, Hf, Pt, Ru and Ni Metals

<table>
<thead>
<tr>
<th>Metal</th>
<th>Group number</th>
<th>Atomic radius, nm (30)</th>
<th>Melting pointa, ºC</th>
<th>Density at room temperature, g cm–3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti</td>
<td>4</td>
<td>0.140</td>
<td>1670</td>
<td>4.5</td>
</tr>
<tr>
<td>Zr</td>
<td>4</td>
<td>0.155</td>
<td>1855</td>
<td>6.5</td>
</tr>
<tr>
<td>Hf</td>
<td>4</td>
<td>0.155</td>
<td>2231</td>
<td>13.2</td>
</tr>
<tr>
<td>Pt</td>
<td>10</td>
<td>0.135</td>
<td>1769</td>
<td>21.3</td>
</tr>
<tr>
<td>Ru</td>
<td>8</td>
<td>0.130</td>
<td>2334</td>
<td>12.4</td>
</tr>
<tr>
<td>Ni</td>
<td>10</td>
<td>0.135</td>
<td>1453</td>
<td>8.91</td>
</tr>
</tbody>
</table>

a Melting points are given from ASM Alloy Phase Diagram DatabaseTM

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precipitation resulting in an effective increase in critical stress for slip deformation. It was also reported that the transformation temperatures were decreased by partial substitution of Ti with Zr in (Ti45Zr5)Pt50 (27, 28) and by partial substitution of Ti with Hf in (Ti45Hf5)Pt50 (28, 29) alloys, as well as by partial substitution of Pt with Ru in Ti50(Pt45Ru5) (27) alloys. This showed that Zr, Hf and Ru act as B2 phase stabilisers in Ti50Pt50 intermetallic alloys.

4. Conclusions
The potential of equiatomic Ti50Pt50 as a high-temperature shape memory alloy was reviewed. Recent efforts to improve the high-temperature mechanical and shape memory properties of Ti50Pt50 alloy were also discussed. Partial substitution of Ti with other Group 4 elements such as Zr and Hf, as well as partial substitution of Pt with other pgms such as Ir and Ru, was found to be effective for improving the high-temperature mechanical and shape memory properties of Ti50Pt50 alloy. The higher strength and shape memory properties for (Ti45Zr5)Pt50 were related to the combined effects of solid solution strengthening and (Ti,Zr)Pt3 precipitation. It was also reported that the crystal structure of orthorhombic martensite (B19) changed to tetragonal structure with increasing Ir content in Ti50(Pt,Ir)50 alloys. 100% shape memory effect has still not been achieved and the strength of the developed TiPt-X alloys in the B2 phase is still much lower than that in the martensite phase. Work is ongoing to solve these challenges in order to use near-equiatomic TiPt based shape memory alloys for high-temperature (>800ºC) applications.

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Yoko Yamabe-Mitarai gained her PhD at the Tokyo Institute of Technology in 1994. After working on a JSPS fellowship in 1994 and 1995, she joined NIMS and engaged in research on the mechanical and functional properties of pgms, which are used in automotive engine spark plugs, aiming to grow single crystals for electronic devices in furnaces at ultra-high temperatures between 1400ºC and 2000ºC. Recent interests include high-temperature shape memory alloys using pgms which can operate at around 1000ºC.
Hydrogen and Fuel Cell Technologies at the Hydrogen South Africa (HySA) Systems Competence Centre

Technological achievements and breakthroughs with emphasis on platinum group metals beneficiation work to date under the HySA Systems Initiative

The Hydrogen South Africa (HySA) programme is based upon the beneficiation of South Africa’s large platinum group metal (pgm) resources. The present article summarises some of the progress by HySA Systems, one of the three Competence Centres under the HySA Programme, since 2008. Work has been carried out on membrane electrode assembly and stack development for high-temperature proton exchange membrane fuel cells (HT-PEMFCs) for use in combined heat and power (CHP) supplied by natural gas and hydrogen fuelled vehicle (HFV) applications. The emphasis is on improved carbon monoxide tolerance and simplified heat and humidity management, allowing simpler fuel cell systems to be designed. Metal hydrides modified with palladium are being explored as poisoning-tolerant hydrogen storage materials for stationary and special mobile applications, and metal organic frameworks (MOFs) modified with platinum as light-weight hydrogen storage with a high hydrogen storage capacity. Lastly research into hydrogen purification using Pd membrane reactors is focused on membrane support synthesis, hollow fibre seeding and development of the plating procedure.

1. Introduction

HySA Systems is one of three National Competence Centres which makes up HySA. Initiated by the Department of Science and Technology (DST) and approved by the Cabinet in May 2007, HySA is a long-term (15-year) programme within their Research, Development and Innovation (RDI) strategy, officially launched in September 2008 (1). This National Flagship Programme is aimed at developing South African intellectual property, innovation, knowledge, human resources, products, components and processes to support the South African participation in the nascent but rapidly developing international platforms in hydrogen and fuel cell technologies. HySA also focuses on: (i) the ‘use and displacement of strategic

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minerals’; (ii) ways of harnessing South Africa’s mineral endowments to promote both the hydrogen economy and renewable energy use; and (iii) seeking the most cost-effective and sustainable ways of incorporating pgm-based components in hydrogen fuel cell and other technologies, in turn resulting in commercialisation ventures and a viable industry around mineral beneficiation.

The principal strategy of HySA is to execute research and development (R&D) work, with the main aim of achieving an ambitious 25% share of the global hydrogen and fuel cell market using novel pgm catalysts, components and systems, since South Africa has more than 75% of the world’s known pgm reserves. In order to achieve this, the structure is aimed at the parallel development of knowledge and technology across all areas of the hydrogen and fuel cell value chain, allowing for the establishment of a strong R&D hydrogen and fuel cell technology and exporting added value pgm materials, components and complete products. The first five years of funding focused on developing infrastructures at each centre with a major emphasis upon human capacity development. Relevant international expertise was recruited by each centre to access technical support and well-established implementation networks and to ensure the programme and its deliverables remain market related and world-class. Collaborations with institutions and partners from R&D, academia and industry are underway (1, 2).

There are a number of Key Programmes (five in total) including CHP and HFVs, among others. This article focuses on a selection of projects involving pgms, including MEA development, stack design, and the storage and purification of hydrogen.

2. Combined Heat and Power

Fuel cell based CHP systems have entered early commercialisation recently and are being deployed in thousands in Japan (Ene-Farm) and Europe (Ene.Field, Callux). In Japan, 34,000 units were installed at the end of 2012 and the objective is to have over 5 million units installed by 2030. Most of the CHP systems deployed so far are based on low-temperature PEMFC (LT-PEMFC).

HySA Systems, however, is focusing on HT-PEMFC based CHP systems in the range 1–2 kWel, fuelled by natural gas. Although the electrical efficiency of HT-PEMFC is lower than that of LT-PEMFC, the overall efficiency (electricity + heat) is higher for HT-PEMFC based CHP systems. Moreover, HT-PEMFC can tolerate carbon monoxide poisoning better than LT-PEMFC and does not require a complex water management system, making HT-PEMFC ideal for CHP applications. The main scope is to develop internationally competitive components, specifically MEAs and stacks for the CHP market, however, there is also a concerted effort to develop systems in the above specified range. The block diagram of the CHP system being developed is provided in Figure 1.

![Fig. 1. Block diagram of the HT-PEMFC based CHP system](image-url)
The red blocks show the core R&D areas carried out by HySA and the yellow block shows the level of system integration that is currently being carried out at the centre. HySA Systems has successfully completed a breadboard CHP test bench in collaboration with Zentrum für Sonnenenergie- und Wasserstoff- Forschung (ZSW, the German Centre for Solar Energy and Hydrogen Research), and is validating various HT-PEMFC stacks in this configuration. Currently the efforts are targeted at the integration of a natural gas reformer with the breadboard system, to study and analyse the operation of the system at various operating strategies and conditions. The plan is to integrate a 1 kWe CHP system by 2014 and then to introduce locally produced components including the reformer and fuel cell catalysts from HySA Catalysis. HySA Systems is collaborating and also extending collaboration with various other institutions and companies, locally and overseas, to realise the objective of this programme.

3. Hydrogen Fuelled Vehicle

The scope of this HySA Key Programme is to develop and integrate systems and modules that can be used in niche fuel cell vehicles, based on HySA technologies. This includes on-board hydrogen storage (including metal hydrides), the fuel cell system (the fuel cell stack and its controller), power electronics and the Li-ion battery system. Through a modular design and standardised interfaces the ‘HySA Power Module’ will be designed so that it can be retro-fitted into existing small battery-powered vehicles with minimal changes to the vehicle itself.

4. Research and Development and Key Technologies

4.1 High Temperature Membrane Electrode Assembly

MEAs are the core of fuel cells and detailed understanding of the phenomena within the MEA is necessary to improve the durability and reduce the overall cost of the fuel cell. Although extensive research and development has already been carried out in LT-PEMFC MEAs, HT-MEA is relatively new. HT-PEMFCs are gaining momentum with the number of publications nearly doubled in 2012 (~1100) as compared to five years ago (~650). Most of the R&D is dedicated to the development of the PEM, although efforts are also made to develop suitable catalysts and gas diffusion electrodes. Some of the R&D areas focus on:

- Novel membranes that can operate between 40°C and 200°C without humidification requirements
- Development of suitable pgm-based catalysts that are active and durable
- Suitable support materials for the catalysts, to overcome carbon support corrosion/dissolution
- Suitable MEA architecture to reduce catalyst loading, minimise acid leaching and improve durability

At HySA Systems, the focus is on the MEA architecture aiming at reducing the catalyst loading and improving the durability, with the membranes sourced from commercial suppliers. Various coating techniques are being developed and used for both catalyst coated substrate (CCS) and catalyst coated membrane (CCM) MEA preparation methods. This includes air assisted spraying, ultrasonic spraying and electrophoretic deposition (EPD).

MEA performances comparable to the best results reported so far have been achieved under similar conditions (3). The GDEs in this case were prepared by a novel automatic catalyst spraying under irradiation technique, at usual operating conditions (160°C, H2/air, ambient pressure). The peak power density of the single cell reached 0.61 W cm−2 and the current density at +0.6 V was up to 0.38 A cm−2 (Figure 2).

The main reason for the performance was found to be the preparation conditions of the MEA and is reported elsewhere (3). Another crucial factor for the MEA, apart from the performance, is its durability under standard operating conditions. A short term durability test was performed on the MEA at 160°C with H2/air and a constant load of 0.2 A cm−2, Figure 3. The cell voltage reached a steady state within 4 h of operation and was found to be stable for a period of about 100 h. Following this, intermittent operation of the fuel cell was carried out to mimic ‘real’ operating conditions, with cooling to room temperature while shutting down. During this study for about 275 h operation, no appreciable degradation was noticed.

Focused efforts are also targeted at improving and optimising the GDEs. Various binders, proton conductors and acid controlling layers are currently being studied and the effect of the various binders on the performance of the MEA was investigated (4). Five different binders: Nafton®, polybenzimidazole (PBI), polytetrafluoroethylene (PTFE), polyvinylidene difluoride (PVDF) and a PBI-PVDF blend, were studied

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As expected, Nafion® was found to be unsuitable for HT MEAs, obviously due to its proton conductivity limitations at the operation conditions of 160°C. PVDF was found to be a better binder at low current densities, whereas PTFE was found to be suitable for high current densities.

Other MEA fabrication methods are also being studied including the CCM and EPD methods. Recently some promising results have been obtained with the EPD method (5) and further studies are currently being carried out in this area. HySA Systems have also set up a pilot-scale MEA manufacturing line and the components and operation are currently being optimised.

**4.2 High Temperature Proton Exchange Membrane Fuel Cell**

HT PEMFC technology has been under fast and intensive development for the past two decades and is currently becoming an attractive alternative to conventional perfluorosulfonic acid (PFSA)-membrane based LT PEMFC technology. The developed materials and components exhibit performances that would allow commercialisation (6). The high operation temperature of HT PEMFC at 150°C–180°C leads to some of the key advantages of the technology over LT PEMFC. The main advantage is tolerance to CO in the anode gas supply which enables supply with reformate gas without the need for a complex
purification process. Tolerance of up to 5% CO in the anode supply gas was reported for a single HT-PEM cell (7). Secondly, the high operating temperature and temperature difference simplifies the heat management system thus the electrically generated waste heat can be efficiently removed and captured. Finally, the membrane conduction mechanism which is not dependent on humidity or water content but on phosphoric acid doping level simplifies the water management system and eliminates the need for the supplied reactants to be humidified (8). These properties enable the design of simple fuel cell systems, especially for small-scale power generation supplied with reformate fuel.

In the field of HT-PEM fuel cell technology HySA Systems focuses on R&D, technology development and applications. The main objective is to integrate and validate complete CHP systems. To achieve this goal the conducted work is divided into three main streams: (i) HT-PEMFC stack development, (ii) HT-PEMFC stack validation and characterisation and (iii) HT-PEMFC stack applications, focused mainly but not only on stationary applications.

4.2.1 Stack Development

Proper thermal management of the HT-PEMFC stack is a crucial issue. A steady temperature has to be maintained because degradation processes are strongly temperature dependent (9). Water cannot be used as a cooling medium due to the high operating temperature. For this reason, alternative stack cooling strategies have to be developed and suitable thermally conductive fluids have to be used. Externally oil-cooled stack design is one of the possible options for HT-PEMFC stack cooling that ensures a long lifetime (10). The design has been developed by ZSW and HySA Systems produces the stacks for laboratory testing and validation. The production of graphite bipolar plates requires high precision tooling as the tolerances of machining are in the micrometre range. To meet all the requirements of stack component production, a high precision micro milling computer numerical control (CNC) machine, KERN Evo-765, is available at the HySA Systems laboratory together with a three-dimensional (3D) laser scanner, GOM ATOS II Triple Scan System. Together these are used for the manufacturing and quality validation of the stack components.

In 2012, a 96-cell 2 kWel HT-PEMFC stack was manufactured in South Africa in HySA Systems labs (Figures 5(a) and 5(b)). The South African HT-PEMFC stack has been integrated within a CHP prototype breadboard system (Figure 5(c)) and tested. The test was performed at 160°C, atmospheric pressure, pure hydrogen and air conditions; the polarisation curve of the stack measured during the test is shown in Figure 5(d). A peak power of 2.2 kWel was measured at 0.4 A cm⁻². Further testing includes operation on reformate and long term steady-state will be performed to validate the quality of the product.
Systems R&D work in the field of HT-PEMFC stack will also focus on the development of stack design up to 1 kW_{el} power.

4.2.2 Stack Validation and Characterisation

The fuel cell stack is the key component of every fuel cell system, its performance, efficiency and lifetime depends strongly on operating conditions. At HySA Systems commercial and in-house built stacks are being tested and their performances are measured at a wide range of operating conditions. Testing and validation of HT-PEMFC stacks is performed with the aid of commercially available testing stations. The characterisation of stack units up to 5 kW_{el} can be performed. Short stacks up to 200 W_{el} are being tested with the use of in-house testing setups. The electrochemical impedance spectroscopy (EIS) method is employed to investigate electrochemical processes that take place during the stack operation. Short 5-cell stacks have been assembled and validated. Preliminary results of conditioning and performance testing of a 150 W_{el} unit are very promising; for example, a current density of 0.78 A cm$^{-2}$ and almost 0.35 W cm$^{-2}$ were measured. A 1 kW_{el} externally oil-cooled stack has been also thoroughly characterised. The tests focused on thermal and electrical output at various operating conditions as well as stack resistance to operation vs. CO concentration. The highest stack performance was obtained at a power density of 225 mW cm$^{-2}$, at 160ºC and at 0.4 A cm$^{-2}$ measured using pure hydrogen. The stack showed a reasonable CO tolerance of up to 0.5% CO at 160ºC. A more detailed description of the results of stack testing has been reported and is available elsewhere (11). The stack will be further characterised and long term stability operation and voltage degradation rate will be studied.

4.2.3 Stack Applications

The advantages of HT-PEMFC make the technology attractive for stationary applications. A very promising
area is natural gas supplied CHP systems in which the reformer is integrated as a fuel processor. To investigate the possibilities of HT-PEMFC applications in a CHP system, a 2 kWel CHP prototype breadboard system designed in cooperation with ZSW has been installed and tested at HySA Systems (Figure 6).

The system has been validated at various operating conditions. Figure 7 shows an example of results obtained at different operating temperatures. The highest power density of 0.22 W cm⁻² was measured at 160°C, +0.5 V mean cell voltage and 0.45 A cm⁻². As can be observed, the operating temperature has a significant influence on the stack performance and the increase in temperature from 120°C to 160°C results in a power gain of almost 10%. Operation at high current densities at low temperature is not possible because the cell voltage drops below the safe operation level. The stack was also tested at different carbon dioxide concentrations and no significant decrease in performance was observed at CO₂ concentrations up to 20%. A thorough characterisation of the 2 kW CHP test-rig with CO and simulated reformate gas will be performed and a FLOX® reformer will be integrated.

4.3 Solid State Hydrogen Storage and Related Applications

HySA Systems activities within this key technology are aimed at the development, testing and validation of safe and efficient technologies for hydrogen storage, compression and separation utilising solid-state hydrogen storage materials. Mainly, these activities are focused on materials and systems development for stationary and special mobile applications on the basis of ‘low-temperature’ metal hydrides. In addition, HySA Systems carries out exploratory R&D in light-weight hydrogen storage materials based on nanostructured magnesium hydride and MOFs. Note that all MOFs activities have recently been transferred to HySA Infrastructure since the financial year of 2013/2014.

4.3.1 Metal Hydrides

Hydrogen storage materials based on reversible metallic hydrides have found a number of promising applications in processes of considerable economic potential, such as hydrogen storage, separation and recovery, thermally-driven compressors, heat
Pumps and NiMH batteries (12, 13). Much of this work is on non-pgm systems utilising South Africa’s rich mineral reserves and established mining infrastructure. However, the focus of the present article is on those applications involving the use of pgms. These include poisoning-tolerant surface modified metal hydride materials.

The selectivity of reversible hydrogen interaction with hydride-forming materials allows for the development of simple and efficient pressure or temperature swing absorption-desorption systems for hydrogen separation from complex gas mixtures and its fine purification (12, 13). However, so far, this approach has been successfully implemented only for hydrogen-rich feed gases (vent streams in the ammonia synthesis loop, H₂ > 50%) which contain relatively innocuous admixtures, mainly nitrogen and argon (14). At the same time, the gases associated with processing coal, petrol, natural gas and other carbonaceous fossil fuel feedstock, in addition to hydrogen, may contain significant amounts of other components, mainly CO₂ and CO, which in most cases cause the deterioration of hydrogen sorption performances of metal hydrides (15). The poisoning tolerance of hydride-forming materials can be improved by modifying their surface. The existing surface modification methods use two approaches, the first of which is aimed at the improvement of surface catalytic activity while the second protects the surface from an impurity attack by the creation of protective coatings permeable for hydrogen but not permeable for the impurity species (16).

Surface modification with a pgm such as Pd has been shown to significantly improve hydrogen sorption kinetics and poisoning tolerance. Pre-functionalisation of the metal hydride substrate with water-soluble aminosilanes facilitates the electroless deposition of pgm resulting in denser and more uniform coatings than conventional deposition techniques. The improvements have been found to be due to chemical bonding between the pgm nuclei and surface oxygen, via functional groups formed from aminosilane molecules (16, 17).

AB₅-type material surface modified by fluorination and Pd electroless deposition (18, 19) were found to have good poisoning tolerances (Figure 8), even for large (~1.5 kg) batches. The feasibility of their application for H₂ separation from gas mixtures (up to 30% CO₂ and 100 ppm CO) was demonstrated by testing a prototype H₂ separation system. The H₂ separation was characterised by stable performances during hundreds of absorption/desorption cycles (20, 21).

### 4.3.2 Metal Organic Frameworks

MOFs are crystalline coordination materials attractive for their microporous channels (<2 nm) and high specific surface areas (for example, 3500 m² g⁻¹ for MOF-5), which can be significantly greater than that...
exhibited by zeolitic materials, and their subsequent high hydrogen storage capacities (22). They are constituted of divalent or trivalent metal ion centres connected by large organic linkers. A multitude of MOF structures exist, and their framework topology, pore size and surface area can be tailored simply by the exchange of linker groups or molecular bridges in the synthesis stage (23). The materials typically contain microporous networks, with microcavity diameters known to range from 10 Å –13 Å. The materials are typically prepared through a solvothermal route, in which the metal ion precursor and molecular ligand are incubated under mild thermal conditions. However, attractive storage capacities are only achieved under energy-intensive cryogenic conditions. However, applications of these materials for ambient temperature absorption of hydrogen proved ineffective, with IRMOF-8 exhibiting <2.0 wt% at 298 K and 10 bar H₂, thus failing to meet US DOE targets (24). This drastic decrease in the hydrogen storage capacities of MOFs is a direct result of the decrease in the binding energy between hydrogen molecules and the MOF surface.

HySA Systems R&D has been focused on both the synthesis of MOF materials exhibiting high specific surface area and the post-synthetic pgm treatment of these materials in order to facilitate high hydrogen storage capacities under ambient conditions of temperature and pressure (25). Syntheses of materials have been centred on the preparation of MOF-5, MOF-177 and IRMOF-8. Our post-synthetic treatment of the MOF materials has been dedicated towards catalytic additions to the MOF materials to make them suitable for room temperature adsorption of hydrogen for on-board storage systems of fuel cell electric vehicles (FCEVs). This is achieved through consideration of the ‘hydrogen spillover’ phenomenon, which has the potential to increase room temperature hydrogen adsorption properties of adsorptive materials. Pt catalysts are known to promote the hydrogen spillover effect and when supported on high surface area materials, such as activated carbon (AC), has the potential to enhance the hydrogen storage capacity of the MOF materials (26). During the hydrogen spillover phenomenon, Pt catalytic particles cleave the bond in the dihydrogen (H₂) molecule leading to dissociation and generation of hydrogen ‘atoms’ (Figure 9). The H atoms then migrate to a substrate material where they can be used for various surface processes or spillover again to a secondary receptor (27). In these types of composite hydrogen storage materials, AC could be considered a primary hydrogen atom receptor, after the dissociation of H₂ by the Pt nanoparticles, with the MOF as a secondary receptor eventually storing the H atoms in its microstructure (28).

The Pt-AC material can be prepared via a chemical reduction method or can be purchased as a fuel cell catalytic material with various metal loadings available. Further bridging of MOF with the Pt/AC materials can be enhanced by the carbonisation of simple sugars (for example, sucrose, fructose, glucose) and this has been demonstrated to significantly enhance hydrogen storage capacities (29). The enhancement is a direct result of an increase in the binding energy from 9.65 kJ mol⁻¹ for unmodified IRMOF-8 to 21.7 kJ mol⁻¹ for H on the ‘bridge’ site of IRMOF modified with Pt/AC and sucrose.

The catalytic particles can be deposited onto high-surface-area MOF receptors, for hydrogen storage by spillover, either by physically mixing the MOF material with a supported metal catalyst (such as Pt/AC) or by introducing the metal onto the receptor through chemical doping. In both cases, additional bridging between catalytic particles is needed for further enhancement of hydrogen spillover processes for room temperature hydrogen adsorption (30). However, it was observed that reproducibility of H₂ spillover storage on the bridged MOF samples is very difficult to bring into
fruition, based on the nature of bridge building and non-uniform Pt/AC particle interconnectivities and inconsistent mixing of Pt/AC, sucrose and MOF particles. MOF activities are no longer within HySA Systems’ Projects Portfolio since 2013.

4.4 Palladium-based Membrane for Hydrogen Purification

Roughly 96% of the global annual demand for H₂ is currently derived from fossil based fuels using reforming processes. The reformation reaction product stream is typically a mixture of H₂, CO, CO₂ and methane of which the composition is controlled by reaction equilibria. Major capital investment is required to increase the H₂ yield and to separate the H₂ from the reaction mixture to produce fuel cell grade H₂. The commonly applied process to convert high concentrations of CO with steam (H₂O) into CO₂ and H₂ is known as the high temperature water gas shift (HTWGS) process which is typically followed by a low temperature water gas shift (LTWGS) to reduce the CO levels in the product gas stream below 1000 ppm. Downstream of the LTWGS a pressure swing adsorption (PSA) system is needed to separate the H₂ from the CO₂ and traces of other gases. Needless to say, the CO conversion and gas purification cost greatly impact the cost of fuel cell grade H₂.

Continuous films of Pd material are known for their exceptionally high selectivity towards H₂. So called ‘Pd membrane reactors’ have these films applied in close proximity to the reforming catalyst enabling H₂ to be removed from the reaction zone, allowing a continuous shift of the reforming and WGS reaction equilibrium resulting in significantly higher H₂ production yield. With the use of Pd-based membranes, fuel cell grade H₂ can be produced without the need for HTWGS, LTWGS or PSA technology, offering a great cost reduction potential. The production of Pd films is rather challenging as a successful membrane must not exhibit any defects (to ensure high H₂ selectivity), must preferably be less than 5 μm in thickness (to show sufficient permeance) and finally should exhibit both the mechanical and thermal stability needed to survive the harsh gas reforming environment during its operational lifetime.

HySA Systems R&D has been focused on the following:

- Membrane support synthesis. The support material forms the foundation for the membrane and needs to form a smooth surface that is mechanically and chemically stable in a reducing environment up to 600°C. In order to achieve a highly permeable support structure with high packing density, phase inversion technology is used to produce thin asymmetric zirconium dioxide hollow fibre supports. The production system and SEM images of hollow fibres with the desired ‘sponge like structure’ are depicted in Figure 10.

- Investigation of the most effective seeding procedure of hollow fibres. Commonly applied seeding procedures are typically repeated ten times to form a sufficient number of seeds well distributed over the surface of

![Fig. 10. (a) Photograph of the phase inversion setup developed to produce the hollow fibre support; (b) SEM image of a fibre showing the desired sponge like structure of the fibre outer area](image-url)
the support. Figure 11 shows that the seed formation has a great impact on the formation of the film.

- Development of the plating procedure. After a large number of nanoseeds not contaminated with highly mobile metals such as tin are deposited on a smooth surface of ZrO₂ in a well dispersed manner, a coalescence film can be produced.

Results related to the membrane selectivity and permeance are currently being collected.

5. Publications and Patents
HySA Systems has been active in disseminating their work in high impact journals (Figure 12) and innovating. For example, since 2008 two major patents have been generated by the Centre (32, 33).

6. Conclusions
This limited review has only been able to cover the major steps in pgm beneficiation work – there is much other work that is outside the scope of the present Journal. Nevertheless it can be stated that HySA Systems is delivering successfully in all of its remitted areas. From 2013 onwards, a large emphasis has been on implementing and advancing R&D vehicular system integration and broadening systems engineering activities to improve HySA technology maturity and commercialisation. In areas from CHP to HFV, developments in the HT-MEA technology and stack design are making progress towards allowing a simplified design of fuel cell systems especially suitable for small scale applications. Improved hydrogen storage and purification, based on pgm technologies, will also enable the cost of H₂ fuel to be reduced. Work is ongoing in all these areas.

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Fig. 11. SEM images of seeded and electroless plated hollow fibres showing the influence of seeds on the electroless plating process of Pd: (a) unmodified support; (b) seeding method 1; followed by (c) electroless plated support; (d) seeding method 2; followed by (e) electroless plated support
Industry Programme which is jointly managed by the South African National Research Foundation and the Department of Trade and Industry (NRF; THRIP projects TP2010071200039, TP2011070800020 and TP1207254249). Finally, we would like to thank all our HySA partners (HySA Catalysis and HySA Infrastructure), Spoke Institutions and industrial partners.

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Bruno G. Pollet FRSC joined the University of the Western Cape as full Professor of Hydrogen Energy and Fuel Cell Technologies and as Director of HySA Systems Competence Centre in March 2012. Professor Pollet has extensive expertise in the research fields of PEMFC, fuel cell electrocatalysis and electrochemical engineering.

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Mario Williams graduated from Cape Peninsula University of Technology in 2003 with a BEng in Chemistry. He obtained an MSc in Chemical Sciences in 2005 with work on catalytic materials characterisation related to DMFC/PEMWE, and a PhD in 2008 on solid-state hydrogen storage. He was then appointed as a postdoctoral research fellow and joined HySA in January 2012 as a Key Technology Specialist on hydrogen storage materials for FCVs.

(Continued)
Piotr Bujlo has 13 years of experience in fundamental and applied research on PEMFC technology, specifically in materials aspects, cell construction, cell and stack testing and validation for stationary and automotive PEMFC applications. Currently he is a Key Technology Specialist at the University of the Western Cape where he works on HT-PEMFC technology, namely stack validation and stationary application for CHP systems.

Shan Ji started his career as a postdoctoral research fellow at the University of the Western Cape in 2002 and initiated the first Li-ion cell manufacturing activity in South Africa in collaboration with a number of research institutes and Li-ion secondary battery manufacturers in China. He is responsible for management of the HySA Li-ion battery key programme where he contributed to the design and construction of an industrial pilot plant battery cell manufacturing line at SAIAMC. He is currently developing advanced battery cells, supervising PhD and MSc students and he publishes prolifically.

As institute director, Vladimir Linkov is responsible for achieving objectives as defined in its constitution; supervising and directing all activities and the day-to-day running of the institute. He was appointed full Professor at the University of the Western Cape in 1997. He initiated the first hydrogen and fuel cell research programme in South Africa, which became the foundation of the HySA National Flagship programme.

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Highlights of the research and characterisation of platinum group metals and their compounds

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Introduction
The “XX International Chernyaev Conference on Chemistry, Analysis and Technology of Platinum Group Metals” was held at the Siberian Federal University in Krasnoyarsk, Russia, between 7th and 12th October 2013. This conference was dedicated to the 120th anniversary of Professor Ilya Il’ich Chernyaev (1893–1966) and the 70th anniversary of the Gulidov Krasnoyarsk Non-Ferrous Metals Plant; it was also a celebration of 70 years since the first International Chernyaev Conference on Chemistry, Analysis and Technology of Platinum Group Metals, which was held in 1943 in Sverdlovsk (now Yekaterinburg) under the chairmanship of Professor Chernyaev. All aspects of chemistry, analysis and especially refining of platinum group metals (pgms) are traditionally discussed during the conference. Strong industrial participation is an important part of the Chernyaev Conference series (1).

More than 200 participants attended Chernyaev2013 from Russia, Portugal, Norway, Finland, Latvia and Kazakhstan with 10 plenary lectures, 100 oral and 65 poster presentations divided into four sections:
• Chemistry of pgms and gold compounds;
• Analysis of pgms and Au;
• Production technology of pgms and Au;
• Application of pgms and Au in industry, catalysis and medicine.

The first school for young scientists followed after the conference and included four plenary lectures and thirteen oral presentations.

Chemistry of the Platinum Group Metals
Synthesis and investigation of various pgm coordination and organometallic compounds in
solid state and solution were the focus of the first session. Danila Vasilchenko (Nikolaev Institute of Inorganic Chemistry, Novosibirsk, Russia) and co-authors reported the first detailed characterisation of H₂[Pt(OH)₆] in chloride-free nitric acid solutions in a broad range of concentrations (2). Several monomeric [Pt(L)ₓ(NO₃)₆-x] (L = H₂O or OH⁻; x = 0–6) and dimeric [Pt₂(μ-OH)₂(NO₃)₈]²⁻ anions were detected by ¹⁹⁵Pt nuclear magnetic resonance (NMR) in solution. Individual compounds such as (PyH)₂[Pt(NO₃)₆] and (CH₃)₄N₂[Pt₂(μ-OH)₂(NO₃)₈] were also investigated structurally in solid state using Raman spectroscopy and single crystal X-ray diffraction (XRD). Solid H₂[Pt(OH)₆] and its nitric acid solution were proposed as starting species for the preparation of various Pt(IV) and Pt(II) coordination compounds and heterogeneous supported catalysts.

Ruslan Mullagaleev (Institute of Chemistry and Chemical Technology, Krasnoyarsk, Russia) and Sergey Korenev (Nikolaev Institute of Inorganic Chemistry) and co-authors showed the great potential of palladium solution in nitric acid (3, 4) and especially trans-[Pd(NO₃)₂(H₂O)₂] (5) for synthesis of various monomeric and oligomeric Pd(II) species with promising industrial applications (6, 7). A halogen-free Pd(II) solution can easily be prepared by heating Pd powder in nitric acid, leading to formation of trans-[Pd(NO₃)₂(H₂O)₂] in solution. Crystalline trans-[Pd(NO₃)₂(H₂O)₂] can be prepared by slow evaporation of the solution and further utilised as a starting Pd(II) compound with high reactivity. Figure 1 summarises possible reactions which can be used to synthesise coordination and organometallic compounds of Pd(II) with high yields.

Nitroso-ruthenium compounds have promising future applications in ruthenium coordination chemistry and refining from ores and secondary sources as well as from nuclear wastes (8). Vyacheslav Emel’yanov (Nikolaev Institute of Inorganic Chemistry) showed a detailed overview of [RuNO]-chemistry in aqueous chloride, nitride and ammonia solutions including a characterisation of species in solution and solid state as well as their transformations (9). NMR spectroscopy on ⁹⁹Ru, ¹⁴N, ¹⁷N and ¹⁷O has been applied as the most informative tool for characterisation of various species in complex Ru–NO–CT–NO₂–NH₂–NO₃–H₂O systems (Table I). The detailed analysis of NMR spectra may not only lead to an understanding of the chemical nature of target complexes but also propose reliable mechanisms for their formation and transformation. Powder X-ray diffraction (PXRD) and single crystal analysis have been applied for the characterisation of more than 50 Ru-based complexes in solid state over 30 years of intensive research at the Institute.

### Analysis of Platinum Group Metals

Analysis of the pgms in various objects was discussed in the second session. Liudmila Zhitenko (the Russian State Precious Metals and Gems Repository Gokhran) discussed fundamental and practical aspects of the analysis of pgms, Au and silver in cultural heritage samples. The most significant challenge for such samples is the practical impossibility of performing analysis in the laboratory; the analysis can be carried out only in their permanent places of storage, and must also be non-destructive. However, the analysis is not usually restricted by the need for high precision. Nowadays, portable, easy to use and precise equipment has been developed for use outside the laboratory such as in field-based analysis and museums. X-ray fluorescence spectroscopy (XFS), neutron activation analysis, laser spark emission spectrometry, inductively coupled plasma-mass spectrometry (ICP-MS) with

<table>
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<tr>
<th>Species</th>
<th>⁹⁹Ru</th>
<th>¹⁴N</th>
<th>¹⁷O(NO)</th>
<th>¹⁷O(H₂O)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[RuNOCl₄]²⁻</td>
<td>4190</td>
<td>−36</td>
<td>379</td>
<td>−</td>
</tr>
<tr>
<td>trans-[RuNO(H₂O)Cl₄]⁻</td>
<td>3920</td>
<td>−18</td>
<td>411</td>
<td>0±10</td>
</tr>
<tr>
<td>cis-[Ru(NO(H₂O)Cl₄]⁺</td>
<td>4450</td>
<td>−</td>
<td>−380</td>
<td>−71; −4*</td>
</tr>
<tr>
<td>merc-[Ru(NO)(H₂O)₂Cl₃]</td>
<td>4130</td>
<td>−18</td>
<td>413</td>
<td>−</td>
</tr>
<tr>
<td>fac-[Ru(NO(H₂O)₂Cl₃]</td>
<td>4770</td>
<td>−</td>
<td>−</td>
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*a acetone solution
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<thead>
<tr>
<th>Main reaction</th>
<th>Side reaction</th>
<th>Side reaction</th>
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<tr>
<td>CH₃CO₂C₂H₅ (20ºC–50ºC) or NO (20ºC–40ºC)</td>
<td>CH₃COOH + CH₃CO₂C₂H₅ + HNO₃ (&gt;100ºC)</td>
<td>CH₃COOH (50ºC–80ºC)</td>
</tr>
<tr>
<td>catena-[Pd(NO)NO₂] (yield 45%–60%)</td>
<td>[Pd₂(CN)₂(CH₃COO)₂]₄ (yield 10%)</td>
<td>CH₃COOH (&gt;100ºC) or (CH₃CO)₂O (80ºC–90ºC)</td>
</tr>
<tr>
<td>NO + NO₂ (20ºC–60ºC) (yield 75%)</td>
<td>CH₃COOH (80ºC–100ºC) (yield ~100%)</td>
<td>catena-[Pd(CH₃COO)₂]ₙ (yield 70%–85%)</td>
</tr>
<tr>
<td>NO + NO₂ (30ºC–80ºC) (yield ~100%)</td>
<td>CH₃COOH (110ºC–120ºC) (yield ~100%)</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 1. Reactions of Pd(II) nitric acid solutions with acetic acid and of trans-[Pd(NO₃)₂(H₂O)₂] with acetylacetone (Hacac = CH₃COCH₂COCH₃). Inserts show fragments of the corresponding crystal structures (H atoms are shown in grey, C in black, O in blue, Pd in green and N in red) and a proposed structure for [Pd(acac)NO₃]ₙ polymer derived from NMR and infrared spectroscopies. Yields for solid individual compounds are shown in the initial Pd(II) nitrate solution or trans-[Pd(NO₃)₂(H₂O)₂] (2–5) (Courtesy of Ruslan Mullagaleev (Institute of Chemistry and Chemical Technology))
laser sampling and PXRD were said to be the most appropriate methods for analysis of cultural heritage species (10).

Chemisorption of pgm on silica modified with sulfur-containing functional groups was discussed by Victoria Parfonova (Scientific Research Engineering Centre «Kristall» of the Siberian Federal University, Krasnoyarsk, Russia) and Svetlana Kozlova (Institute of Chemistry and Chemical Technology). The species –SH, >S, –S– and –S_n – at a concentration of 1.3 × 10^-3 mol g^-1 were used for the chemical modification of the silica surface (Figure 2). As a result, –SH modified sorbents quantitatively extracted Pd(II) and Au(III) chloride complexes from 6 M aqueous hydrochloric acid solution. Di- and polysulphides extracted all pgms plus Au. Selective extraction of pgms from chloride solution was possible from 0.1 M–4.0 M HCl aqueous solutions and non-ferrous metals were extracted only at pH>4 (11).

Technology and Applications of the Platinum Group Metals

Processing technology for raw materials as well as pgm production and applications were discussed between academic and industrial scientists in two corresponding sections. Oleg Belousov (Institute of Chemistry and Chemical Technology) and co-authors reported the possibilities of autoclave-based processing of pgm concentrates. Either sodium hydroxide (NaOH) or sulfuric acid (H_2SO_4) can be used for pgm leaching in the presence of sodium sulfite (Na_2SO_3) or sodium formate (HCOONa) respectively as reducing agents in the temperature range 120°C–180°C for 0.5 h–4 h. Autoclave reactions and reactions with ultrasonic or microwave activation are now common practice and can be applied from microgram to ton scale. These techniques are promising as the next generation for activation of ores and concentrates.

The last session focused on applications of pgm in medicine, catalysis and materials production. Yuri Shubin (Nikolaev Institute of Inorganic Chemistry) presented recent results in the area of pgm nanoalloy preparation using soft methods such as thermal decomposition of single source precursors in the solid state. The method was actively developed during the past decade and allows various nanoalloys and supported particles to be formed under thermal treatment of solid single source precursors at 100°C–400°C in inert (helium, argon and nitrogen) and reductive (H_2) atmosphere (12). It has been shown for Au-Ir and Au-Pd metallic systems with a wide miscibility gap that thermal decomposition of [Ir(NH_3)_5Cl][AuCl_4]_2 and [Pd(NH_3)_4][AuCl_4]_2 as single source precursors may lead to the formation of metastable Au_{0.5}Ir_{0.5} nanoalloys, which can be further applied as active heterogeneous catalysts for CO oxidation or formic acid decomposition.

A novel method for the preparation of supported Pd-based catalysts was presented by Nikolay Chesnokov (Institute of Chemistry and Chemical Technology). Pd nanoparticles of diameter 2 nm–4 nm can be deposited on various carbon supports such as thermally and
chemically activated graphite using $\text{H}_2[\text{PdCl}_4]$ solution in water-ethanol mixture.

Concluding Remarks
The Chernyaev2013 conference has shown that pgm chemistry is a still hot topic with strong practical and industrial importance. The conference has a long history with its own style and traditions, and this is expected to strengthen in the future as the conference becomes more international. The next XXI Chernyaev Conference is planned for 2016 in Yekaterinburg, Russia, and will be dedicated to the centenary of Yekaterinburg Non-Ferrous Metals Processing Plant.

Acknowledgements
The reviewers are grateful to Ruslan Mullagaleev (Institute of Chemistry and Chemical Technology) for his help with Figure 1 as well as to Victoria Parfionova (the Scientific Research Engineering Centre «Kristall» of the Siberian Federal University, Krasnoyarsk, Russia) for providing Figure 2.

References

The Reviewers
Kirill Yusenko studied chemistry at the Novosibirsk State University, Russia, and received his PhD in 2005 from the Nikolaev Institute of Inorganic Chemistry in the area of coordination and material chemistry of pgms. After a year as a postdoctoral researcher at the University of Hohenheim, Stuttgart, Germany, he spent several years as a researcher at the Ruhr-University Bochum, Germany. Since 2012 he holds a position at the Department of Chemistry, University of Oslo, Norway. His scientific interests are focused on the chemistry of pgms and nanomaterials based on metallic particles, thin films and porous coordination polymers as well as solid-state chemistry of pharmaceutical materials. He attended Chernyaev2013 as a plenary speaker.

Sergey Metelitsa studied chemistry at the Krasnoyarsk State University, Russia, and received his PhD in 2009 from the Siberian Federal University (SFU) in Krasnoyarsk, Russia, in the area of luminescence analysis of pgms. After this he worked at the Scientific Research Engineering Centre «Kristall» of the Siberian Federal University in Krasnoyarsk, Russia, for 3 years. During this period, he studied the complexation of pgms and other non-ferrous metals with inorganic oxides as active supports. Now he is a permanent researcher at the SFU. His scientific interests are focused on the analysis and coordination chemistry of pgms as well as environmental chemistry. He was the academic secretary for Chernyaev2013.

Vladimir Losev studied chemistry at the Krasnoyarsk State University, Russia, and received his PhD and further Doctoral degrees in Chemical Sciences in 2007 from the Scientific Research Engineering Centre «Kristall» of the Siberian Federal University in Krasnoyarsk, Russia. Currently he is a professor of analytical chemistry at the SFU. His scientific interests are focused in the area of analytical chemistry, especially spectroscopic analysis of pgms in environmental and industrial objects. He was the chairman of Chernyaev2013 and head of the local organizing committee.
Dennis Dowden Commemoration: Catalysis – from Fundamentals to Application

Catalyst characterisation, design and applications highlighted in a commemorative symposium to appreciate an outstanding scientist

Introduction
A commemorative symposium was held at the University of Durham, UK, on 3rd–4th April 2013 to celebrate the career of Professor Dennis Albert Dowden (1914–2012). The meeting was organised by the Royal Society of Chemistry (RSC) Applied Catalysis Group (ACG) and the RSC Surface Reactivity and Catalysis Group (SURCAT) and sponsored by Johnson Matthey. The meeting was attended by approximately 100 attendees from industry and academia and consisted of a series of oral and poster presentations.

An Appreciation
'Dennis A. Dowden – An Appreciation of a Life in Catalysis' was presented by Martyn V. Twigg (formerly Johnson Matthey). Dennis Dowden was born in 1914, shortly after the direct catalytic synthesis of ammonia had begun on an industrial scale. Dowden won a scholarship to Merrywood School and afterwards to Bristol University, UK, where he obtained a first class degree in chemistry. He carried out some research with Professor William E. Garner at Bristol on heats of adsorption of gases on solids before moving to Amherst College, Massachusetts, USA, to continue his work with Professor Ralph Beebe. In a year, his careful study extended knowledge on the nature of adsorption processes and was published in the Journal of the American Chemical Society in 1938 (1). With the likelihood of war with Germany he returned to the UK and joined ICI. He worked for ICI for his entire career, mostly at Billingham, until he retired aged 62 in 1977.

During this period he brought together empirical information and used concepts such as the band structure of semiconductors to develop theories of catalysis, at a time when catalysis was considered more 'black art' than science. He regularly lectured at catalysis conferences and was awarded the Chemical Society Industrial Medal in 1973 and a
Frank G. Ciappetta National Lecturer of the American Catalysis Society in 1974. In 1996 Dowden was awarded the International Congress on Catalysis Diploma in recognition of a lifetime service to the community of catalytic scientists (2). After retiring from ICI, he continued lecturing at Imperial College London, UK, and became a research fellow at Edinburgh University, UK. Dowden continued to work into his late seventies as a consultant and expert witness in industrial patent litigation. A fuller treatment of his life and work will appear in a forthcoming issue of this Journal.

Electronic Structure of Catalysts
Long before modern methods of catalyst characterisation were commonplace, Dowden emphasised the importance of metal particle size, shape and electronic structure in determining catalyst performance. Professor Peter Wells (Cardiff University, UK) presented seven snapshots of work carried out at the University of Hull, UK, that were inspired by Dowden’s ideas in a talk entitled ‘Morphology and Selectivity in Catalysis by Metals’.

The influence of electronic structure on activity was illustrated by the correlation of the rate coefficients for C6H6/C6D6 exchange with densities of states at the Fermi level (E_F) for the majority of the transition elements, whilst the correlation of 1-butene yields in butadiene hydrogenation with Pauling electronegativity for the transition elements demonstrated the importance of electronic structure on selectivity (Figure 1). The role of bulk structure was considered using the examples of butadiene hydrogenation over rhombic and hexagonal forms of molybdenum disulfide (MoS2) and the selectivity patterns observed in the hydrogenation of di-unsaturated aliphatic hydrocarbons over the platinum group metals (pgms). Examples were also given that showed the importance of site congestion on selectivity (isopentene isomerisation), the impact of metal support interactions on crystal structure (unfolding of Os6(CO)18 adsorbed on alumina using Fourier transform infrared spectroscopy (FTIR) and extended X-ray absorption fine structure spectroscopy (EXAFS)) and the role of edge and terrace sites (the enantioselectivity of a Pt catalyst in the hydrogenation of MeCOCOEt).

![Selectivity for 1-butene formation from 1,3-butadiene over films of second and third row transition metals](image)

Fig. 1. Correlation of selectivity during hydrogenation reaction and Pauling electronegativity for transition elements (Adapted from (2) and reproduced with kind permission from Professor Peter Wells, Cardiff University, UK)
The theme of electronic structure in alloys was developed further by Professor Michael Bowker (Cardiff University, UK). In a talk entitled ‘Catalytic Reactivity of Single Crystal Cu-Pd Alloys and the d-band Theory’ he used the decomposition reaction of formic acid and ethanol on copper-palladium alloys to interrogate local electronic vs. non-local ensemble effects on reactivity. Ultraviolet photoelectron spectroscopy (UPS) shows that the d-band of Cu-Pd is shifted below the E_F and for formic acid decomposition the alloy appears more ‘Group 11 like’ with the decomposition energy intermediate between the two metals, i.e. there is evidence of non-local electronic effects. However, for ethanol decomposition, the reactivity patterns for both Cu metal and Pd metal are observed, suggesting that it is localised electronic structure that determines reactivity notwithstanding the apparent d-band shift. Thus for Cu-Pd alloys, any theory that related reactivity to d-band position is apparently disproved.

Professor Richard Catlow (University College London, UK) described the application of computer modelling methods based on both interatomic potentials and density functional theory (DFT) to the determination of crystal, surface and active site structures in a range of oxide and microporous catalysts.

**Catalyst Design**

Dowden’s methodology for catalyst design viewed different forms of lattice and chemisorbed oxygen as possible selective or unselective species in partial oxidation reactions. Professor Ken Waugh (University of Manchester, UK) reviewed the role of oxygen species in maleic anhydride production from butane using a vanadium pyrophosphate ((VO)_2P_2O_7) catalyst and ethylene oxide production from ethylene over a silver/alumina catalyst using temperature-programmed reduction (TPD) and temperature-programmed desorption (TPD) studies.

Professor Graham Hutchings (Cardiff University), in his talk ‘Alkane Activation by Selective Oxidation’, discussed alternative approaches to methane activation and highlighted a patent published in 1971 by Dowden and Walker which used a Fe_{2}O_{3}(MoO_{3})_{3} catalyst for the direct synthesis of methanol (4). The group at Cardiff Catalysis Institute have shown that AuPd supported nanoparticles can activate CH_{4} with hydrogen peroxide for the production of methanol. By ‘confining’ any radical intermediates and by introducing acidic functionality, zeolites and especially ZSM-5 promoted with Fe and Cu are shown to be very effective for methane activation. However, H_{2}O_{2} is a more expensive chemical than methanol and so oxygen is preferred as an oxidant. AuPd can convert toluene almost exclusively to benzoyl benzoate and is suggested as a model for selective C–H bond activation by O_{2} without the stoichiometric use of H_{2}O_{2} (or other terminal oxidants).

The performance of gold catalysts supported on carbon for reactions such as hydrochlorination of ethylene and H_{2}O_{2} synthesis is known to be strongly dependent on the pretreatment of the support – in particular the process of acid washing before the addition of the active component. The fundamental changes that occur at the nanoscale during these processes have been studied using atomic force microscopy (AFM), scanning tunneling microscopy (STM) and X-ray photoelectron spectroscopy (XPS) on a highly ordered graphite sheet by Phillip Davies (Cardiff University). Mild acid treatment of the graphite sheet results in local delamination that resembles a ‘surface bubble’ in the AFM (Figure 2). Au^{0} nucleation then occurs at defect sites at the edge of the bubble. Hydrochloric acid pretreatment enhances Au nucleation and deposition, whilst nitric acid pretreatment produced larger particles. When the Au was deposited in the acid, HNO_{3} treatment led to larger particles compared to HCl.

Professor Jim Anderson (University of Aberdeen, UK) described how photocatalytic treatment of water pollutants produces minimal undesired byproducts and also overcomes the need for substantial quantities of hydrogen in catalytic hydrogenation in his paper ‘Simultaneous Removal of Organics and Nitrates from Aqueous Environments using Photocatalysis’. Metal doped titania (Ag, Au) shows enhanced photocatalytic reactivity and selectivity compared to titania alone. In this study, the enhanced textural properties of sol-gel produced tin doped titania was studied by porosimetry and by high-resolution transmission electron microscopy (HR-TEM). FTIR was used to probe surface hydroxylation and CO adsorption and the band gap determined by ultraviolet-visible (UV-vis) spectroscopy. High Sn loadings enhance UV photocatalytic performance whilst low loadings enhance the visible photocatalytic performance for nitrate depletion. The addition of a hole scavenger (such as oxalic acid) enabled the simultaneous removal of organic and nitrate components from aqueous feeds.
Hydrogen Production and Storage

Dowden published a patent claiming the use of pgms and other modifiers for the production of hydrogen by the steam reforming of naphtha in 1966 (5). Today hydrogen is produced by the steam reforming of natural gas, and in the future biomass may become an important source. Some of the challenges associated with these alternative feedstocks were addressed in a paper by Professor David Jackson (University of Glasgow, UK), entitled ‘Steam Reforming of Ethane and Ethanol over Rh/Alumina: a Comparative Study’, that examined activity, selectivity and deactivation during the steam reforming of two apparently simple and similar molecules, ethane and ethanol, over Rh/alumina, under similar conditions. No significant deactivation of catalysts was observed at 873 K although carbon filaments were formed during ethanol reforming (Figure 3).

Fig. 2. Local delamination caused by acid treatment of a highly ordered graphite sheet observed using AFM: (a) attack by acid leads to local delamination; (b) surface contours detected by AFM; (c) schematics showing graphite lattice extending over feature (Reproduced with kind permission from Phillip Davies, Cardiff University, UK)
For ethane, steam reforming and hydrogenolysis are the primary reactions and a high methane selectivity was observed, whilst the reaction of ethanol is much more complex involving a number of pathways including steam reforming and ethanol dehydration and dehydrogenation reactions. High hydrogen selectivity was observed.

Professor Julian Ross (University of Limerick, Ireland) described his recent work, ‘Formic Acid Decomposition over Pd/C Catalysts: Promotion and Change of Mechanism caused by Doping with Alkali Metals Ions’. Formic acid has been proposed as a medium for storing hydrogen. K/Pd/C is a highly active and selective catalyst for the decomposition of formic acid to hydrogen and CO₂. Energy dispersive spectroscopy (EDS), X-ray diffraction (XRD) and carbon monoxide chemisorption results showed that mobile K species were uniformly distributed over both Pd and C while TEM did not show any noticeable change of the Pd particle size upon alkali doping. Catalyst activation experiments suggest that the formation of potassium formate species occurs, possibly in the liquid phase containing formic acid, within the pores of the C support. Pd appears essential for this process to occur. The reaction occurs on both alumina and silica supports.

**Industrial Applications**

A number of industrial contributions were given that demonstrated the need for both fundamental and applied science for the successful development and application of new technology. Martin Hanton (Sasol Technology UK Ltd) gave a perspective on how fundamental science and exploration is a requisite for the creation of robust new industrial processes. Using the example of selective ethylene tetramerisation the research and development (R&D) path was traced from initial discovery and patent filing in 2003 to operating plant in 2013. David Johnson (Lucite International, UK) gave a presentation entitled ‘Commercialisation of a Novel Methyl Methacrylate Process – Catalyst Design and Development’. The talk described the development of a novel palladium phosphine catalyst which gives methyl propionate in 99.9% selectivity and a caesium/zirconia/silica catalyst that reacts methyl propionate with formaldehyde. The key to the success of the condensation reaction was an understanding of the reaction mechanism and achieving the right balance of acidity and basicity in the catalyst to minimise byproduct formation. Chris Mitchell (Huntsman Polyurethanes, Belgium) described an approach for the evaluation of catalyst for phosgene manufacture. Gas phase reaction of chlorine with an excess of CO over an activated carbon catalyst produces peak temperatures of over 500°C which makes this reaction very difficult to study in the laboratory. Comparison of the performance of full size catalyst pellets vs. crushed catalyst allowed catalyst effectiveness factors and therefore effective gas diffusivities to be estimated. These data have been combined in a two-dimensional (2D) reaction engineering model incorporating a description of heat and mass transfer to predict catalyst performance in industrial scale phosgene reactors. The reactor model was used to help improve catalyst lifetimes. Finally Rob Parry (BASF Catalysts, UK) gave a marketing perspective on the challenges for catalysis associated with the shift from non-renewable to renewable feedstock in the fuels and energy industries.

**Summary**

This was a very successful meeting, that brought together both young researchers and contemporaries of Dennis Dowden. As an industrial chemist, Dowden knew the importance of both fundamental understanding and the challenges of taking science through to industrial implementation. The range of contributions at the meeting demonstrated the breadth of these requirements well. Whilst modern methods have subsequently contradicted Dowden’s hypothesis that bond formation during chemisorption at metal...
surfaces occurs by ionisation or electron transfer, the importance of his ideas and the depth of thinking and insight that he showed for all aspects of catalysis were emphasised in the meeting by all who knew his work or had the fortune to work with him.

References

The Reviewer
Martin Fowles obtained a DPhil at University of Oxford, UK, in the area of gas phase kinetics. He joined Johnson Matthey (formerly ICI) in the Research and Technology department at Billingham in 1984 and has worked in a number of areas of high temperature catalysis, developing catalysts and innovative reactor concepts in the field of steam reforming and catalytic combustion. His current role is Research Associate, with interests in new opportunities for syngas developments.
“Palladium-Catalyzed Coupling Reactions: Practical Aspects and Future Developments”

Edited by Árpád Molnár (University of Szeged, Hungary), Wiley-VCH Verlag GmbH & Co KGaA, Weinheim, Germany, 2013, 692 pages, ISBN: 978-3-527-33254-0, £125.00, €150.00, US$190.00

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“Palladium-Catalyzed Coupling Reactions”, published by Wiley in 2013, is a comprehensive handbook and guide to modern aspects of this reaction type. The book focuses on state of the art techniques. The use of different reaction media, catalyst recycling, supported catalysts, microwave assisted synthesis and continuous flow reaction systems are all examined, making this book an excellent resource. The book avoids delving into the specifics of each type of coupling reaction and instead presents a variety of topics, discussing recent progress and potential future work in each given area. It was edited by Árpád Molnár, a Professor of Chemistry in the University of Szeged, Hungary, who has no less than 200 publications to his name. Numerous research papers in the field of catalyst development, coupled with review papers on many of the subjects covered in this book, qualify Professor Molnár for his position of editor.

The content of this book covers five general topics: an introduction and background to Pd-catalysed coupling reactions, Pd catalysts on various support materials, coupling reactions in different reaction media, reaction conditions for coupling reactions and industrial applications of Pd catalysed coupling reactions.

Introduction
The area of Pd-catalysed coupling reactions has experienced a huge growth in popularity and has swiftly increased in maturity in its relatively short lifetime, having moved from using stoichiometric amounts of Pd-based reagents to achieving impressively high turnover numbers (TONs) in just a few decades. Since the initial Pd-catalysed coupling reactions described by Heck (1), Negishi (2) and Suzuki (3) during the 1970s a wide range of coupling reactions, using different organic halides and organometallic compounds have been discovered (Figure 1).
The first chapter of this book gives a comprehensive introduction to the area of Pd-catalysed coupling reactions, covering the history and characteristics of the reactions and classification of the various reaction types, which numbered 72 in a recent review (4). A mechanistic overview is given along with considerations to be taken with regards to the effect of the halides and nucleophiles employed, the nature of the Pd species, ligands employed and other related topics. The introduction is concluded with a section on future challenges for Pd-catalysed coupling reactions. Here aspects relating to practical, real world applications are discussed along with developments that will enable these reactions to be brought into common usage. Even though this introduction is relatively brief it gives an excellent and comprehensive overview of Pd-catalysed coupling reactions, explains why Pd is the catalytic metal of choice and provides a basis for the following chapters.

**Support Materials**

There are four chapters that discuss the effects of the support material on the performance of Pd-catalysed coupling reactions. These are dealuminated ultrastable Y (USY) zeolites, magnetically separable nanocatalysts, ordered porous solids and polymers. In the first chapter, written by Kazu Okumura (Tottori University, Japan) the high TONs achievable by the use of USY zeolites is discussed. These materials are widely available due to their use in alkane cracking and make a suitable support for Pd due to nanometre sized pores within the zeolite structure. The preparation of USY zeolites, the dealumination process of the zeolite framework and the preparation of Pd/USY zeolite catalysts are discussed briefly followed by a number of examples of coupling reactions performed using these catalysts. As an introduction to this support type the author describes a typical Suzuki-Miyaura coupling of bromobenzene and phenylboronic acid in o-xylene with potassium carbonate as a base, used by Durgun et al. (5) to screen activity of Pd salts loaded on USY zeolites. \([\text{Pd(NH}_3\text{)}_4\text{Cl}_2/\text{USY} \text{exhibited high activity and using } 0.7 \times 10^{-4} \text{ mol% of catalyst for the coupling reaction a TON of } 1.3 \times 10^6 \text{ and a } 99\% \text{ yield were obtained. Work by the same group proved this catalyst type suitable for Suzuki-Miyaura coupling of heterocyclic compounds. High TONs and good yields were achieved in the coupling of 2-bromothiophene and thiophene-2-boronic acid indicating the possible use of Pd/USY catalyst in the synthesis of organic semiconductors.}

The second chapter in this section, written by Kifah S. M. Salih and Werner R. Thiel (TU Kaiserslautern, Germany), concerned magnetically separable nanocatalysts. Using magnetically separable supports offers an easy solution to what can be a difficult problem – removing the catalyst from the reaction mixture. In the introduction the authors describe the solid state properties required of the paramagnetic particles, factors affecting the lifetime of the supported catalyst, some of the characterisation techniques employed and the types of catalyst attached to the magnetic particles. For example, Manorama et al. reported nickel ferrite particles with a dopamine functionalised surface on which they grafted Pd nanoparticles (6). This Pd catalyst was employed in high yielding Suzuki coupling reactions between aryl chlorides and phenylboronic acid and also Heck reactions between aryl chlorides and styrene. Once the reaction was complete the catalyst was magnetically removed from the reaction mixture and successive reactions were performed with similar yields (Figure 2).

Ease of separation of this catalyst type is key to its functionality. Pd leaching was looked at in several of the examples described. There was low or negligible leaching of metal from the nanoparticles after several uses of the catalyst. In one case, leaching of Pd was observed during the reaction with reabsorption of the metal back onto the support occurring after the reaction mixture had cooled to room temperature. A number of other magnetically separable catalysts are described, including catalysts based on Pd nanoparticles and also Pd complexes supported on magnetic particles.

The third chapter in this section discussed the use of ordered porous solids as a support for Pd
catalysts and was written by the editor of the book, Árpád Molnár. The physical properties of ordered porous solids make them ideal for use in catalysis: high surface area, uniform pore size and a defined, tunable structure. Materials that fall under the category of ordered porous solids include zeolites, ordered porous silica-based materials and metal organic frameworks amongst others. The chapter opens with an in-depth look at the synthesis and characterisation of these materials, focusing on two examples: the mesoporous silicas MCM and SBA. A background to the materials, techniques employed to control pore size and distribution, methods to tailor properties and functionalisation are all covered extensively. An Ullmann coupling of iodobenzene using a range of mesoporous silica-based materials performed by Li et al. highlighted the catalytic performance and ability to tailor a catalyst to a reaction (7). Under the selected reaction conditions a conversion of 27% and a yield of just 7% were obtained using Pd supported on SiO2. By altering the ordered porous silica materials to suit the reaction, with large pores of SBA-15 to accommodate the biaryl product and aluminium doped MCM-41 to increase the Lewis acidity, promoting adsorption of the iodobenzene, much improved conversion and reaction yields were obtained. The chapter concludes with a summary of the current state of these materials together with a discussion of future prospects and challenges.

**Reaction Media**

Chapters six and seven discuss reaction media employed for coupling reactions, namely ionic liquids (ILs) and aqueous media. The solvent employed as reaction medium has a considerable effect on the performance, outcome, cost and environmental impact of a chemical transformation, so it is appropriate that some consideration is given to the solvent selection. Traditional solvents used for Pd-catalysed couplings include dimethylformamide, N-methylpyrrolidinone and other polar solvents, many of which have undesirable health implications, and as with most volatile organic solvents, are flammable and environmentally unfriendly.

Chapter six, written by Michael T. Keßler, Frank Galbrecht and Martin H. G. Prechtl (Universität zu Köln, Germany) and Jackson D. Scholten (Universidade Federal do Rio Grande do Sul, Brazil), is dedicated to the use of ILs as a reaction medium for Pd-catalysed coupling reactions. ILs are organic salts with low melting points, generally below 100°C. The author cites a number of reasons for their use: tunable combination...
of anions and cations to suit a particular reaction, stabilising effect of ILs on ligands and Pd complexes, solubility of organometallic compounds and ease of separation of reaction products once the reaction is complete. Again here, the authors detail a number of coupling reactions performed in ILs, discussing the use of both Pd complex-catalysed and Pd nanoparticle-catalysed reactions. The emphasis is on the advantages of ILs over more traditional solvents and the authors use a number of examples to highlight this, often with very high conversion rates, mild reaction conditions and excellent catalyst reuse and recycling potential.

In chapter seven, written by Kevin H. Shaughnessy (The University of Alabama, USA), cross-coupling reactions in aqueous media is the topic. Water being a cheap, non-toxic, non-flammable, renewable solvent makes it a sensible solvent choice. However, with organic compounds, problems of solubility along with often water labile reaction systems mean that the use of aqueous media is frequently avoided. The author discusses the resurgence of aqueous based organic chemistry, aspects of Pd that lend it to aqueous reaction systems and developments in water soluble ligands. The actual need for solubility is also discussed with efficient organic reactions being performed ‘on water’, that is, where solubility in the solvent is not required to achieve chemical transformations. A range of examples are given: firstly in aqueous media, then in biphasic systems of water and organic solvent mixtures. An example of a water-only mediated Suzuki reaction was performed by Basu et al. (8). A ligand free coupling of tropolone with an aryl trihydroxyborate allowed Pd(OAc)\textsubscript{2} and tetrabutylammonium bromide to catalyse the reaction at low temperatures and short reaction times in water (Figure 3).

**Reaction Conditions**

The next section of the book, consisting of three chapters, covers reaction conditions of coupling reactions. The topics covered here are microwave assisted synthesis, catalyst recycling and continuous flow reactions. Despite microwave assisted reactions and catalyst recycling appearing in numerous described reactions in previous chapters the editor considered the exceptional results possible when employing these techniques worthy of separate chapters. In the chapters on microwave synthesis and catalyst recycling the ‘green’ aspects of the subject are highlighted. In the case of microwave synthesis, reduced reaction times, minimised side products and improved yields are cited as reasons for its consideration.

As in other chapters the authors, Ke-Hu Wang and Jun-Xian Wang (Northwest Normal University, China), discuss a range of microwave assisted coupling reactions, most of which were reported within the previous decade. In most cases the short reaction times (with some reactions completing in a matter of minutes) are emphasised as a unique feature of microwave assisted synthesis, often coupled with excellent yields.

In the chapter on catalyst recycling Árpád Molnár places the focus on some of the shortcomings in reported recyclable catalysts. In the lengthy introduction, some common misconceptions with regards to what is a stable, recyclable catalyst are addressed. Where at times, efficacy is maintained while catalytic metal is being lost, the true recyclable nature of the catalyst is brought into question. This topic is covered in detail along with some techniques that can be utilised to monitor low levels of Pd loss. Nanoparticle, complex-based and polymer immobilised catalysts are covered along with a number of other reusable catalyst types. Here, numerous impressive examples of robust catalysts are discussed, with some performing twenty runs of a Heck coupling reaction without loss of performance (9). The design of reactions is also brought into question here. Low numbers of repeat runs using

![Fig. 3. A ligand free coupling of tropolone with an aryl trihydroxyborate catalysed by Pd(OAc)\textsubscript{2} and tetrabutylammonium bromide using water as reaction solvent (8) (Image courtesy of Wiley and Sons, Copyright 2013)](image-url)
the more reactive halides give impressive results, whereas for transformations performed with less reactive compounds, high numbers of test reactions and adequate characterisation to ensure no loss of catalyst are required to truly call a catalyst recyclable.

Chapter eleven written by William R. Reynolds and Christopher G. Frost (University of Bath, UK) covers the use of continuous flow reactors as a reaction system for coupling reactions. In previous chapters reactions were performed in batch style flasks or vessels. Excellent reaction efficiencies, both in yield and cost reduction, have been seen in bulk chemical processes for years. In recent decades considerable time has been dedicated to continuous flow reactors for organic synthesis and good reaction efficiencies have been achieved as a result. Lower energy requirements, better temperature control, improved mass transfer, lowered reaction volume giving greater control over the chemical reactions and ease of scaling from lab to industrial scale are cited as some reasons for continuous flow being an attractive alternative to batch type reactions. An effective example of improved reaction efficiency was conducted by Li et al. (10). In this example efficiencies of flow reactors were compared to batch reactors in the Suzuki coupling of aryl chlorides with phenylboronic acids using Pd(OAc)₂ as catalyst and DABCO (1,4-diazabicyclo[2.2.2]octane) as a ligand. After a 4 h residence time continuous flow reactions of both electron-rich and electron-poor aryl chlorides had completed with almost quantitative yields. The batch reacted counterparts had considerably lower conversions after 4 h and reaction times of 24 h were required to bring the reactions to completion (Figure 4). Reactor technology and design is also discussed, along with catalyst immobilisation techniques, continuous separation and the use of microreactors.

All of the chapters so far have presented impressive results but only in research scale coupling reactions. The final chapter in the book, by Andreas Dumrath, Christa Lübke, and Matthias Beller (Leibniz-Institut für Katalyse e.V. an der Universität Rostock, Germany) concerns industrial applications, mainly focusing on examples from the recent past. The focus of the introduction differs from the other chapters in that it includes a discussion based on real life reaction scale-up along with economic considerations, metal prices, the cost of the base and reactants employed, intellectual property implications and toxicity of catalysts where pharmaceutical products are concerned. A slightly different approach to examples is taken in this chapter, often presenting a background to the desired product, along with different reaction options and routes taken to catalyst and reaction selection. A Heck-Mizoroki coupling of benzyl acrylate with a bromonaphthalene was used in the synthesis of an oral pharmaceutical by GlaxoSmithKline (11). By replacing a late stage reaction with this coupling, the downstream chemistry was simplified resulting in better scalability along with a large reduction in processing time.

Fig. 4. Comparison of a flow vs. batch process for a Suzuki reaction (Image courtesy of Wiley and Sons, Copyright 2013)
in raw material cost. Other techniques covered in other chapters in this book are also used in industry including microwave assisted synthesis, continuous flow coupling reactions and reusable catalysts. This chapter exhibits a number of excellent examples of improvements to reaction rates and conditions achieved by incorporating Pd catalysed coupling reactions. Despite the complexity of a number of these compounds, equivalent or improved yields and stereocontrol was achieved by using these coupling reactions, often with an economic benefit due to fewer side products, the use of lower quantities of reagents and a reduced need for purification steps.

Summary

This book is an excellent, modern summary of the state of Pd-catalysed coupling reactions. The focus on highly efficient reactions and recyclability of the catalysts is in tune with the ethos being adopted by many in the chemical industry. Atom efficiency and the application of cleaner, less wasteful chemistry is now very achievable. This book would be an excellent starting place for an organic chemist who is interested in reducing costs and increasing efficiencies of existing reaction processes or one who is designing new synthetic routes.

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The Reviewer

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“Palladium-Catalyzed Coupling Reactions: Practical Aspects and Future Developments”
New Diphosphines for Molecular and Nanoparticle Catalysis

Here another researcher whose work has benefited from the support of Johnson Matthey and Alfa Aesar, a Johnson Matthey company, is profiled. Piet van Leeuwen is a Professor and Group Leader at the Institute of Chemical Research of Catalonia (ICIQ), Spain. His interest ranges from fundamental aspects to applied catalysis utilising mainly late transition metals.

About the Research

The main research interest of the group is the development of new and more efficient catalytic systems via a thorough study of ligand effects in homogeneous and nanoparticle catalysis with metals such as ruthenium, rhodium, palladium and platinum. Their research strategy is based on ligand design and a combination of classic synthetic methodologies and modern combinatorial and supramolecular approaches for fast generation of diverse catalytic entities. For instance, diphosphine based chiral assemblies containing simple chiral diols as modifiers are easily formed (Scheme I). The corresponding chiral assemblies are used as ligands to form versatile asymmetric hydrogenation catalysts based on rhodium or iridium (Figure 1).

In metal nanoparticle catalysis the group’s aim is the introduction of control over the nanoparticle formation with the aid of ligands, similar to that of...
homogeneous systems, while the catalytic reactions being studied are typical of heterogeneous catalysts. Ruthenium nanoparticles (RuNPs) stabilised by phosphorus containing ligands (diphosphines and secondary phosphine oxides) and N-heterocyclic carbenes (NHC) were synthesised and used successfully for hydrogenation of aromatic derivatives. RuNPs stabilised by benzofurobenzofuran diphosphine 1 are highly active for hydrogenation of aromatics at room temperature. In Figure 2, a model of the complex Ru$_{55}(1)_4$ shows how benzene could easily and nicely fit at the RuNPs surface, explaining their high catalytic activity and productivity for aromatic derivative hydrogenation.

Currently, the group is extending their work on metal nanoparticle synthesis to gold, rhodium and platinum with applications in (enanto)-selective hydrogenation among other reactions, as well as designing new ligand systems for nanoparticle stabilisation.

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Enhancing the Low Temperature Oxidation Performance over a Pt and a Pt-Pd Diesel Oxidation Catalyst


Hydrogen has been reported to have a positive effect on the oxidation kinetics of CO, HC and NO over Pt and Pt-Pd DOCs. The aim of this work was to determine whether this effect is due to the temperature rise during hydrogen oxidation or a change in reaction kinetics due to the influence of intermediate species. The research suggests that small amounts of hydrogen improve catalyst light-off and also promote NO oxidation over both catalyst types. The authors claim these benefits are due to both exothermic reactions increasing local catalyst temperatures and also a result of hydrogen increasing reaction rates and accessibility to catalyst active sites therefore promoting CO, HC and NO oxidation at lower temperatures.

HCN Emissions in Fluid Catalytic Cracking


FCC reactors are common components in refineries around the world with these reactors being fed with either heavy streams from other refinery units or other low-value components. By their nature these feeds contain a large number of contaminants, such as heavy metals and heteroatoms like S and N, which must be removed in order to meet emissions regulations; recently HCN has fallen under scrutiny in the USA and therefore added to the existing restrictions of SOx, NOx and particulate emissions from these reactors. This research evaluates the trade-off between HCN and NOx emissions and highlights that flue gas emissions control is a combination of factors arising from both the choice of additive and the design of the regenerator unit.

Process Technologies

Use of an Areal Distribution of Mixing Intensity to Describe Blending of Non-Newtonian Fluids in a Kenics KM Static Mixer Using PLIF


The blending of Newtonian and time-independent non-Newtonian fluids in KM static mixers was evaluated using PLIF. The effect of a number of mixing parameters, fluid rheology and apparent viscosity ratio was investigated for two-fluid blending conducted at constant superficial velocity (0.3 ms⁻¹) and measured from images taken at the mixer outlet after introducing a stream of dye at the inlet. The PLIF images were analysed to determine the log variance and maximum striation thickness and this revealed conflicting trends. It was found that for two-fluid blending the PLIF image showed unmixed spots of a high viscosity material when introduced into a lower viscosity component.

Characterization of Au³⁺ Species in Au/C Catalysts for the Hydrochlorination Reaction of Acetylene


The preparation of a set of Au/C catalysts for the gas phase hydrochlorination of acetylene to vinyl chloride monomer was carried out using a range of impregnation solvents and variation of the drying temperature. A range of strong acids were evaluated as impregnation solvents and the use of aqua regia in combination with an intermediate drying temperature of 140°C resulted in the most active catalyst. XPS and TPR were used to evaluate the effects of the catalyst preparation parameters on catalytic activity and thermal reduction methods in particular were found to assist with the determination of the kinetic parameters for the reduction of Au³⁺ to Au⁰ using hydrogen.

Catalytic Syngas Purification from Model Biomass Gasification Streams


The production of clean biomass-derived syngas remains an important goal in the commercial manufacture of biofuels. A range of Ni and Rh containing catalysts were evaluated for the conversion of model tar components (toluene and naphthalene or benzene) in a simulated biogas feed containing up to
100 ppm H2S and 5 vol% CH4 at temperatures between 700ºC and 900ºC. H2S was found to significantly reduce hydrocarbon conversion but near complete conversion of CH4 and tar could be achieved on a Rh-based catalyst at 900ºC with a very high GHSV of 150,000 h⁻¹. At a more realistic GHSV of 60,000 h⁻¹ and higher CH4 levels (5 vol%) the effect of H2S concentration on catalyst activity followed an apparent linear activity decay law. The catalyst deactivation by H2S was found to be fully reversible and attributable to a transient site-blocking mechanism. A selection of catalysts were evaluated for tar and methane conversion using oak modelled syngas and the best candidates were then tested using oak derived syngas generated using a pilot-scale gasification unit. Rh catalysts were found to exhibit the best performance in terms of hydrocarbon conversion when compared to the Ni catalysts under similar conditions. The best Rh catalyst had a methane conversion of 95% over a 200 hour test showing little or no loss of activity when using the oak modelled syngas.

**Ethane Steam Reforming over a Platinum/Alumina Catalyst: Effect of Sulfur Poisoning**


The effect of H2S and CH3SH as poisons for Pt catalysts during the steam reforming of ethane was evaluated. Both poisons were shown to deactivate the catalyst over a number of hours, but of the two CH3SH proved more detrimental, reducing conversion rates almost by an order of magnitude. Selectivity was also affected, showing that the effect of S was not uniform on all reactions occurring over the catalyst and the production of CH4 was reduced the most, while the watergas shift reaction was affected to a lesser extent. A slight regeneration of the catalyst was seen upon removal of the CH3SH, but no regeneration was observed after removal of H2S. Overall, the poisons reduced activity and improved selectivity for hydrogen.

**Selective Hydrogenation of Acetylene over Pd–Boron Catalysts: A Density Functional Theory Study**


Density functional theory was used to investigate the hydrogenation of acetylene over B-modified Pd(111) and Pd(211) surfaces. This reaction has exhibited excellent performance experimentally using these catalysts. The selectivity of the reaction for ethylene formation was studied in two ways, firstly a comparison between the desorption and hydrogenation of ethylene and secondly a comparison between the formation of ethylene and 1,3-butadiene. The formation of sub-surface carbon and hydrogen on these catalysts has also been reported to affect the activity and selectivity of ethylene production from acetylene and the authors also evaluated the formation of these species. The results showed that these B-modified catalysts show similar activity and selectivity to C-modified Pd surfaces, the formation of 1,3-butadiene on the B-modified catalysts was slightly suppressed and the formation of sub-surface carbon and hydrogen was eliminated.

**Fundamental Aspects of H2S Adsorption on CPO-27-Ni**


Gas storage in MOFs has been an area of interest for many years both due to their high surface areas and chemical modularity. This research studied the adsorption of H2S on Ni2(dhtp)(H2O)2•8H2O MOF (known as CPO-27-Ni or MOF-74-Ni) which was characterised using *in situ* PXRD, FTIR, Raman and UV-vis spectroscopy and also by first-principles periodic boundary conditions calculations. The results demonstrated high stability of the MOF in the presence of H2S, but a clear colour change was observed in the sample which shows that H2S strongly coordinates to the Ni sites in the structure. Good agreement was seen between experimental and computed energies of interaction.

**New Methods in Biomass Depolymerisation: Catalytic Hydrogenolysis of Barks**


The conversion of biomass into useful chemical...
feedstocks is of increasing interest in the development of a sustainable chemical industry. This paper looks at the conversion of suberin, a material of low commercial value thought to be responsible for the waterproofing properties of bark. The hydrogenolysis of three species of tree bark (sycamore, spruce and cork) was studied using heterogeneous PGM catalysts and produced two major product streams. The lignin and lignin-like regions of suberin produced aromatic substituted guaiacols and the polyester regions yielded a range of saturated fatty acids and alcohols, including \( \alpha, \omega \)-functionalised species. The authors claim advantages to catalytic hydrogenolysis over conventional base hydrolysis both in terms of selectivity and conversion.

Characterisation of Platinum-based Fuel Cell Catalyst Materials Using \(^{195}\text{Pt} \) Wideline Solid State NMR

A novel FSFT method was used to acquire wideline \(^{195}\text{Pt} \) NMR data of Pt nanoparticles and Pt-Sn intermetallics/bimetallics. These nanoparticles can be used to catalyse oxidative reactions in fuel cell applications and the literature in this area of wideline NMR data is dominated by the alternative technique of SEHS (or SEIS). The FSFT method allowed for the mean number of atoms in a Pt nanoparticle to be estimated and also for detailed information about the number of atoms effectively present in each layer from the surface to be determined. The authors compared the FSFT technique to SEHS and saw advantages to using FSFT. Also presented here is the first \(^{195}\text{Pt} \) NMR characterisation of diamagnetic Pt\(_{13}\) nanoclusters which have no metallic character. This technique allows for a direct measure of isotropic chemical shift and is a better means of measuring the actual Knight shift when compared to referencing against the primary IUPAC shift standard.

Flame Spray Pyrolysis Generated Transition Metal Oxide Nanoparticles as Catalysts for the Growth of Carbon Nanotubes

The growth of MWCNTs using three transition metal oxide nanoparticles (Fe\(_2\)O\(_3\), Co\(_3\)O\(_4\) and NiO) was investigated. Synthesis of the nanoparticles was conducted using FSP and since the syntheses for both the CNT and nanoparticles were identical, a direct comparison of the products was possible allowing for the identification of links between the catalyst
and the morphology of the resultant nanostructures. Conventional CNTs were grown on Fe₂O₃ nanoparticles, no discernible growth was detected on Co₃O₄ and a mixture of conventional and coiled CNTs was observed on NiO. The authors investigated the effect of temperature, time and acetylene/hydrogen gas mixtures on the morphology, yield and purity of the CNTs and found that the yield of coiled CNTs can be increased to approximately 70% of the CNT yield.
Characterisation of Catalysts Using Secondary and Backscattered Electron In-lens Detectors

Heterogeneous catalysis often involves the use of metal nanoparticles, often between 1–10 nm in size. These particles are usually finely dispersed onto high surface area supports and act as an active centre during a catalytic reaction. The performance of a supported catalyst can be directly related to the size and spatial distribution of the metal nanoparticles. Therefore, it is of increasing importance to understand the structures and dispersion of metal nanoparticles. Traditionally this requires the use of transmission electron microscopy (TEM) which is not limited by the electron beam interaction volume limitations that are experienced by scanning electron microscopes (SEMs). However, imaging nanoparticles using SEM is an easier and lower cost option. Recent developments in the detection systems, specifically secondary and backscattered in-lens detectors, favour the use of low energy beams in SEMs which in turn allows the imaging of nanoparticles on supports.

Here we give a quick review of new detection principles and instrument design, the effects of the use of secondary and backscattered electron (BSE) in-lens detectors on imaging catalysts.

In-Lens Secondary Electron Detection

Figure 1 shows the principle of in-lens secondary electron (SE) detection (1). The beam is decelerated by an electrostatic lens and the field applied to decelerate also causes the acceleration of the scattered electrons in the other direction back into the lens on a helical path. The in-lens SE detector is placed on top of the final pole piece in the SEM chamber. The traditional SE detector (Everhart-Thornley (ET)) is also shown in the image, positioned outside the lens system and positively biased to draw SEs. The positioning of this detector favours both SE1 and SE2 electrons but the in-lens detector system favours mostly SE1s. For image generation in an SEM, a large number of secondary scattering products are generated by the interaction of the primary electron beam with the specimen material. To image the actual surface of a sample, SE1 electrons that have experienced one scattering event should be detected. Only SE1 electrons are generated in the upper range of the interaction volume and therefore contain direct information on the sample surface. These electrons can be detected very efficiently by the in-lens SE detector, whose detection efficiency results from its geometric position in the beam path and from the combination with the electrostatic/electromagnetic lens. As a result, high contrast images are easily achieved, even from a lower escape depth and energy. SE2 generation increases with decreasing atomic number, and consequently is worse for most of the catalyst supports such as carbon and alumina.

Figures 2(a) and 2(b) show images which were collected from a palladium on carbon sample. The contrast differences between SE and in-lens images can clearly be distinguished. In Figure 2(a), the image was acquired at typical 20 kV high tension and shows a lesser degree of detail, mainly due to the blurring effect of SE2 electrons as they originate from inner parts of carbon. In Figure 2(b), the image is acquired at low voltage using an in-lens detector, so it is much sharper and more detailed as this is mainly contributed by SE1 electrons which originate from the sample surface and the beam centre.

From a detector point of view, the standard ET SE detector picks up a mixture of SE1, SE2 and BSEs, which carry depth information as well as surface morphology information. This reduces the contrast and the resolution from the carbon particles. One of the reasons why the differences in contrast shown in Figure 2 are so stark...
is that the sample is made up of low atomic number atoms which cause larger interaction volumes for SE2, which in turn causes blurring.

**Energy Selective Backscattered Detection**

The in-lens backscattered detector (also known as an energy selective backscattered (EsB) detector) is placed on the top of the in-lens SE detector (2) (as shown in Figure 3). When compared with a normal BSE detector, the EsB detector collects the low loss (LL)-BSEs which originate directly from the beam spot centre (3). The EsB image would avoid the contrast which is contributed by those BSEs originating in ranges relatively far away from the beam spot centre.

In order to clearly understand the meaning of the LL-BSE detection, it is necessary to explain a little bit about the energy distribution of all possible electron scattering processes. **Figure 4** shows the whole energy spectrum of the secondary and BSEs (conventionally energies >50 eV) plotted with increasing energy (4).
Figure 4 also shows a number of defined features in the spectrum such as Auger electrons, multiple inelastic scattered electrons, plasmon losses and low loss events which are shown by the sharp low loss peak at the right side of the spectrum. Under the low voltage primary beam energy conditions as shown
in Figure 4, the SE and LL-BSE intensities become relatively high when compared with the broad saddle of multiple inelastic scattered electrons in between. The regions in the low loss peak coloured blue, green and yellow represent the discrimination areas set by the filter grid voltage of the EsB detector shown in Figure 3. In practice, it is possible just to cut off the SEs and the whole blue spectrum area when the filter grid is set to an optimum threshold. It would then result in a LL-BSE image with a good signal to noise ratio and good contrast. These fine contrast differences are obtained from electrons with very little energy loss generated in a very shallow region beneath the surface away from the area where multiple inelastic scattered electrons are produced.

Figure 5 shows the images which were collected from platinum particles on a carbon support. It is possible to distinguish the contrast difference between Pt and C due to their large atomic number difference \((\text{Pt}=78, \text{C}=6)\) in both images. But the main difference is the level of detail and the difference in the number of particles that can be observed between the two images.

In Figure 5(b), it is clear that the EsB image better shows the placement and morphology of Pt particles on carbon. By using lower energy electrons it is possible to reduce the interaction volume and therefore the contrast from the surface layer is exposed in this image. This is the reason that we only see the particles near the surface whereas in the BSE image in Figure 5(a), the carbon is blurred and we can see all the particles as the signal comes from deeper parts of the sample. The natural deduction would be that it should be possible to change the voltage and observe particles at various depths (5).
also associated with the filtering of the LL-BSE which seems to make the biggest difference in the way the carbon is imaged as distinct particles rather than a blurred background.

**Conclusions**

The in-lens imaging technique using both SE and BSEs gives a distinct advantage to catalyst imaging. The two examples demonstrate that the SEs provide a more detailed and surface sensitive topography and the BSEs provide a more depth sensitive characterisation of the metal nanoparticles as well as helping to visualise these on individual units of support material.

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