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Ruthenium Polyaminocarboxylate Complexes

PROSPECTS FOR THEIR USE AS METALLOPHARMACEUTICALS

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Ruthenium (Ru) complexes containing polyaminocarboxylate (pac) ligands (Ru-pac) have features which indicate they may be suitable for biological applications. For instance, Ru-pac complexes can bind to biomolecules through a rapid and facile aquo-substitution reaction, and Ru-pac has a range of accessible oxidation states. Ru-pac also has some notable catalytic properties that mimic enzymatic hydrocarbon oxidation by cytochrome P-450 in homogeneous conditions. This is of immense significance towards developing Ru-pac based agents for oxidative cleavage of DNA and artificial nuclease in DNA foot-printing experiments. This review aims to highlight the scope of Ru-pac complexes as metallopharmaceuticals, and outlines their potential for certain biological applications.

The chemistry of ruthenium complexes containing polyaminocarboxylate (pac) ligands (Ru-pac) is of continuing interest. The donor character of the pac ligand is comparable with that of many biological enzymes which make use of the carboxylate and amine donors from amino acids to bind to a metal centre. The pac ligand can form very stable 1:1 (metal:ligand) complexes with ruthenium.

Early studies (1-3), later confirmed by crystallographic evidence (4-8), showed that the pac ligands in Ru-pac complexes function as pentadentate ligands, see Figure 1. The sixth coordination site of the ruthenium centre in Ru-pac complexes is occupied by a water molecule at low pH or by an hydroxide ion at high pH. Figure 1 shows structures and formulae of some [Ru(pac)(H₂O)] complexes, and Table I contains data on spectral, electrochemical and acid-dissociation constants for these [Ru(III)(pac)(H₂O)] complexes.

The chemistry of [Ru(III)(pac)(H₂O)] complexes is dominated by their lability towards the aquo-substitution reaction, which affords a facile and straightforward synthesis to mixed-ligand complexes (8). The reasons that ruthenium complexes containing ‘pac’ ligands demonstrate potential applications in metallodrugs are because of:

- the number of stable and accessible oxidation states they possess,
- their rapid rate of ligand exchange, and
- their ability to bind to certain biological molecules.

Furthermore, these Ru-pac complexes exhibit catalytic properties, in homogeneous conditions in the presence of oxygen atom donors, that mimic the biological enzymatic oxidation of hydrocarbons by cytochrome P-450 (8). Although the significance of Ru-pac complexes as chemotherapeutic agents has been reviewed (9), this article aims to examine the prospects of Ru-pac complexes for promoting studies towards the development of Ru-pac based pharmaceuticals, for a range of diseases. A glossary of terms used in the review is appended at the end of the paper.

The Ru-pac Complex as a Model for Enzymatic Oxidation

Dioxygen complexes of transition metals play an important role in a number of biological reactions. The formation of a Ru(IV)-peroxo complex species in the reaction of Ru(III)-edta and dioxygen was first reported by Ezerskaya and Solovykh (10,
11) in the 1960s, while spectral, electrochemical, and kinetic evidence in favour of the formation of the \([\text{Ru}^{IV}(\text{edta})_2(O_2)]^{2-}\) peroxo species during catalytic hydrocarbon oxidation was reported by Taqui Khan and coworkers (12, 13). Ru-pac complexes (pac = edta, hedtra) in the presence of the single

**Table I**

<table>
<thead>
<tr>
<th>Complex</th>
<th>Spectral data, (\lambda_{\text{max}}), nm ((\varepsilon_{\text{max}}), M(^{-1}) cm(^{-1}))</th>
<th>Electrochemical data, (E_{1/2}) (V vs. NHE)</th>
<th>Acid dissociation constant, (pK_1), at 25°C</th>
<th>Acid dissociation constant, (pK_2), at 25°C</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{Ru}^{III}(\text{Hedta})(\text{H}_2\text{O})])</td>
<td>280 (2800 ± 50) 350 (680 ± 30)</td>
<td>−0.04</td>
<td>2.4</td>
<td>7.6</td>
<td>8</td>
</tr>
<tr>
<td>([\text{Ru}^{III}(\text{Hpdtta})(\text{H}_2\text{O})])</td>
<td>282 (2890 ± 50) 370 (940 ± 50)</td>
<td>−0.05</td>
<td>2.3</td>
<td>8.1</td>
<td>8</td>
</tr>
<tr>
<td>([\text{Ru}^{III}(\text{hedtra})(\text{H}_2\text{O})])</td>
<td>285 (1950 ± 20) 350 (850 ± 20)</td>
<td>−0.07</td>
<td>−</td>
<td>4.9</td>
<td>8</td>
</tr>
<tr>
<td>([\text{Ru}^{III}(\text{medtra})(\text{H}_2\text{O})])</td>
<td>290 (2400 ± 30)</td>
<td>−0.10</td>
<td>−</td>
<td>6.3</td>
<td>8</td>
</tr>
</tbody>
</table>

\(\text{Hedta and Hpdtta represent the protonated pendant COOH group in } [\text{Ru}^{III}(\text{Hedta})(\text{H}_2\text{O})] \text{ and } [\text{Ru}^{III}(\text{Hpdtta})(\text{H}_2\text{O})], \text{ respectively.}\)  

\(M\) is mol dm\(^{-3}\)
oxygen atom donors: NaOCl, PhIO, t-BuOOH, and KHSO₅, were found to be active in catalysing the epoxidation of olefins and the hydroxylation of the C-H bond (14, 15); both of these reactions resemble enzymatic oxidation by cytochrome P-450 monooxygenase (an enzyme catalysing oxo-transfer reactions). Further, a system comprising [Ru³⁺(edta)(H₂O)]⁺/ascorbic acid/H₂O₂ (or O₂) that was able to perform the hydroxylation of cyclohexane to cyclohexanol, as an analogue of the Udenfriend system (16), was also reported (17). Ferryl intermediates (FeV=O) are the active DNA cleavage agents in O₂-activated DNA cleavage by bleomycin. Bleomycin epoxidises stilbenes via its ferryl form. Similarly, [Ru⁷⁺(pac)O] was reported to be the active species in the olefin epoxidation and hydroxylation of saturated hydrocarbons (14, 15a). Reports that the oxo-functionalisation of the C=C/C-H bond in hydrocarbon oxidation is catalysed by Ru-pac complexes seem to be highly significant for developing Ru-pac based agents for oxidative cleavage of DNA and artificial nuclease in DNA foot-printing experiments (15b).

Prospects for Ru-pac Complexes as Antitumour Agents

Although in cell culture studies a correlation has been observed between the cytotoxicity of some ruthenium complexes and their DNA binding ability (18), the mechanism of the drug action of these ruthenium complexes is still largely unknown. Octahedral Ru(III) and Ru(II) complexes containing ligands, such as amines, N-heterocycles and dimethylsulfoxides, exhibited various degrees of biological activity, including antitumour action in vitro (19). Considering that the above Ru(III) complexes are more inert than the corresponding Ru(II) analogues, an ‘activation by reduction’ mechanism was proposed to explain the antitumour activity of such complexes (19).

Ru-pc complexes, due to their liability towards aquo-substitution, bind DNA constituents in a facile and straightforward manner (20-22) and thus have oncological significance. Antitumour activity has been reported for labile Ru(IV)-cdta (cdta = 1,2-trans-diaminoocyclohexan-N,N,N',N'-tetraacetate) (23, 24), while cis-[Ru³⁺(pdta)Cl₂] (pdta = propylenediaminetetraacetate) is known to damage nuclear DNA and inhibit DNA recognition by enzyme restriction (25). A crosslinking with a guanine base unit of DNA has been proposed as an explanation for the observed activity. However, the generation of a superoxide radical in NADPH oxidase, triggered by the presence of the Ru-pdta complex, may be another reason for the observed cytotoxicity (9).

Mixed-ligand complexes of Ru(II)-pac with a series of DNA bases have been reported by Shepherd’s group (15c) and the binding sites of the DNA constituents have been discussed with regard to their significance in chemotherapy. They reported a novel η²-coordination mode for Ru-pac (pac = hedtra, thta; thta = triethylenetetramine-hexaacetate) at the C5=C6 olefinic double bonds of uridine- and cytidine-related bases, along with coordination at the normal binding sites (N3 and N1). Although the ‘pac’ environment favours π-donation by the ruthenium centre, no experimental evidence for η²-attachment was observed in the case of thymidine. This assumes the pyrimidine structure is important for η²-coordination. The affinity of Ru(II)-pac complexes to the η²-pyrimidine site was shown to be linked to a balance between electronic and steric factors, and thus Ru-pac could be significant as a DNA crosslinking agent (15c).

Our Ru-pac Work

In our laboratory, kinetic and mechanistic aspects of the interaction of [Ru(pac)(H₂O)Cl] complexes with DNA have been explored in attempts to find mechanisms of possible drug activity. Our previous studies on the kinetics and mechanism of binding of [Ru³⁺(edta)(H₂O)]⁻ with DNA bases, nucleosides and nucleotides, led us to conclude that [Ru³⁺(edta)(H₂O)]⁻ binds an adenine base unit of single strand calf-thymus DNA in a kinetically preferred pathway (20-22).

Other kinetic studies (26) have suggested that there is rapid coordination through the N7 of the adenine moiety of adenosine monophosphate (AMP) followed by a ring closure step in which the exocyclic NH₂ group (at C6 in the adenine base) of AMP binds to the ruthenium centre by dislodging
the adjacent carboxylate group of the coordinated pac ligand, see Figure 2.

The order of reactivity of \([\text{Ru}^{III}(\text{pac})(\text{H}_2\text{O})]\) complexes towards binding nucleotides is:

\[
[\text{Ru}^{III}(\text{pdta})(\text{H}_2\text{O})]\geq [\text{Ru}^{III}(\text{edta})(\text{H}_2\text{O})]\gg [\text{Ru}^{III}(\text{hedtra})(\text{H}_2\text{O})]\gg [\text{Ru}^{III}(\text{medtra})(\text{H}_2\text{O})].
\]

All the Ru-pac complexes exhibit a similar order of reactivity towards nucleotides: AMP >> inosine monophosphate (IMP) > guanosine monophosphate (GMP).

The results of cell proliferation studies with Ru-pac complexes (26) using cell lines for MCF-7 (breast cancer), NCI-H460 (lung cancer) and SF-268 (central nervous system) revealed that \([\text{Ru}(\text{edta})(\text{H}_2\text{O})]^+\) and \([\text{Ru}(\text{pdta})(\text{H}_2\text{O})]^+\), are much more efficient inhibitors of these cell lines than complexes where pac = hedtra^+ and medtra^+. \([\text{Ru}(\text{hedtra})(\text{H}_2\text{O})]\) and \([\text{Ru}(\text{medtra})(\text{H}_2\text{O})]\) have insignificant activity which, presumably, is associated with a much lower rate of binding to purine-based nucleotides than in the case of the ‘edta^+’ and ‘pdta^+’ complexes.

The order of growth inhibition for these three cancer cell lines, due to \([\text{Ru}(\text{edta})(\text{H}_2\text{O})]^+\) is: SF-268 > NCI-H460 > MCF-7, and the estimated GI_{50} values (in mM) of \([\text{Ru}(\text{edta})(\text{H}_2\text{O})]\) are: 0.57 for SF-268, 0.65 for NCI-H460 and 0.78 for MCF-7, respectively.

Furthermore, in cancer cells, binding of an active agent with sulfur-containing biomolecules available in the cells is considered to be one reason for ‘drug resistance’ and ‘toxicity’ of cisplatin-like drugs in the postulated mechanism for activity (27). Binding with thio-macromolecules in the cell decreases the intracellular accumulation of metallo-drugs, so they cannot reach sufficient numbers to bind with the DNA in the cell to cause cell death. Thus it appears that understanding the kinetic interactions of these metal complexes with DNA fragments, with regard to sulfur-containing biomolecules, is important for understanding their antitumour activity as well as their toxicity.

We have recently reported that the binding rate of \([\text{Ru}^{III}(\text{pac})(\text{H}_2\text{O})]\) with such thio-ligands is much lower than the binding rate with AMP (28). This indicates that Ru-pac complexes could have a lower toxic effect, due to their lower reactivity with sulfur-containing biomolecules, and thus be of pharmacological significance. Such possible metallo-drugs could perhaps be tolerated at higher dosage with fewer side effects.
Ru-pac Complexes as NO Scavengers

The enzyme, nitric oxide synthase (NOS) catalyses the conversion of L-arginine to L-citrulline, during which reaction NO is produced (29). There are several isoforms of NOS and these are divided into the Ca²⁺-dependent constitutive NOS (cNOS) and the Ca²⁺-independent inducible NOS (iNOS) groups.

Effects of a Decrease in NO

NO seems to play a role in many disease states (30a); for instance, a decrease in NO production (from cNOS) can lead to severe hypertension. This is a disease state that is treated by vasodilators (NO donors), such as nitroprusside (30b). The route of NO production from nitroprusside is:

\[
[\text{Fe}^{II}(\text{CN})_{5}(\text{NO})]^{2-} \rightarrow (\text{RSH; ascorbate}) \rightarrow [\text{Fe}^{II}(\text{CN})_{5}(\text{NO})]^{3-} \quad (i)
\]

\[
[\text{Fe}^{II}(\text{CN})_{5}(\text{NO})]^{3-} \rightarrow \text{CN}^{-} + [\text{Fe}(\text{CN})_{4}(\text{NO})]^{2-} \rightarrow \text{NO} + [\text{Fe}(\text{CN})_{4}(\text{H}_{2}\text{O})]^{2-} \quad (ii)
\]

The NO produced acts as:

\[
\text{NO} \rightarrow \text{guanylate cyclase sites} \rightarrow \text{GMP production} \rightarrow \text{blood pressure control} \quad (iii)
\]

Effects of Excess NO

On the other hand, sepsis and toxic shock are caused in patients by the overproduction of NO – in response to a pathogenic invasion of the bloodstream (31-42). The result is a precipitous drop in blood pressure that could lead to multi-organ failure, including renal failure. The excess NO in the bloodstream is present due to action by macrophages (mononuclear phagocytic cells that reside in tissues). This situation with the pathogens may be treated by other antibiotics, while the excess NO can be absorbed by a metal complex acting as a scavenger. Ru-pac complexes meet the basic requirements for effective NO scavenging as they undergo a rapid substitution reaction and form stable nitrosyl complexes (43). In addition, the Ru-NO bond is reasonably stable, and persists through a variety of substitution and redox reactions. This allows the properties of the Ru-pac complex to be finely tuned so it can become an effective NO scavenger:

\[
[\text{Ru}^{III}(\text{edta})(\text{H}_{2}\text{O})]^+/\text{NO} \rightarrow [\text{Ru}^{II}(\text{NO})^{+}(\text{edta})] \rightarrow \text{H}_{2}\text{O} \quad (v)
\]

In vitro studies have shown that Ru-edta complexes are successful in scavenging NO in biological systems and suggest that they could play a role in novel therapeutic strategies aimed at alleviating NO-mediated disease states (44). For instance, the addition of Ru-edta complexes (100 µM) to gamma-activated RAW 264 cells (a murine macrophage cell line) was found to reduce NO levels. The effect of Ru-edta complexes on NO-mediated tumour cell killing by gamma-activated macrophages (RAW 264) was studied in a co-culture system. A non-adherent murine mastocytoma (P815) line was the ‘target’ cell. Ru-edta complexes (100 µM of JM1226 and JM6245) when added to the culture medium, gave some protection from macrophage-mediated cell killing. The ‘target’ cell viability increased from 54.5 ± 3.3% to 93.2 ± 7.1% and 80.0 ± 4.6%, respectively, (n = 6).

The vasodilator response of isolated, perfused, precontracted rat tail arteries caused by a one-off injection (10 µl) of S-nitroso-N-acetyl-penicillamine (SNAP) was attenuated by adding Ru-edta complexes (100 µM) to the perfusate. The ED₅₀ increased from 6.0 µM (Krebs only) to 1.8 mM (Krebs + JM6245) and from 7 µM (Krebs only) to 132 µM (Krebs + JM1226). Male Wistar rats were injected with bacterial LPS (4 mg kg⁻¹ intraperitoneal of lipopolysaccharide) to induce endotoxaemia. When the JM1226 Ru-edta complex (100 µM) was administered 20 hours afterwards, the LPS fully reversed the hypotension associated with the endotoxaemia.

A brief study of the kinetics of interaction of Ru-edta complexes with NO, aimed at understanding the mechanisms of drug action (45), showed that the rate of the aquo-substitution of [Ru^{III}(edta)(H₂O/OH)]²⁻/²⁻ with NO is very fast (1.95–3.29 x 10⁷ M⁻¹ s⁻¹ at 7.3°C) in pH range 6.5-8.0. However, at pH 8.0, the higher value for the rate of aquo-substitution (3.29 x 10⁷ M⁻¹ s⁻¹ at 7.3°C), than at pH 6.5 (2.18 x 10⁷ M⁻¹ s⁻¹ at 7.5°C), does not agree with the pH dependence of the rate constants for the aquo-substitution reaction of the
Ru-edta complex with other entering nucleophiles (8). This apparently anomalous observation (45) could probably be explained by assuming the pK₂ value for the acid-dissociation:

\[
[Ru^{III}(edta)(H_2O)]^- \leftrightarrow [Ru^{III}(edta)(OH)]^{2-} + H^+ 
\]

pK₂ would, at 7.3ºC, be higher than the value (7.6) reported at 25ºC. As a result, the concentration of the generally labile \([Ru^{III}(edta)(H_2O)]^-\) species would be higher at low temperature (7.3ºC) even at pH > 7.6. Therefore, the decrease in the rate constant at pH > 7.6 reportedly observed for the substitution of Ru-edta complex at 25ºC was not seen at 7.3ºC by Slade et al. (45).

The thermodynamics and kinetics of Ru-edta complexes as efficient scavengers of NO was recently reported by Eldik's group (46). The results of FTIR and \(^{15}\)N-NMR spectroscopy studies clearly afforded evidence of the NO\(^+\) character of NO coordinated to the Ru-edta complex. The value of the overall equilibrium constant (\(K_{NO}\)) determined from UV-Vis spectroscopic and electrochemical methods, is \(9.1 \times 10^7 \text{ M}^{-1}\) at 25ºC and pH = 5.0. The effect of buffer components (acetate buffer) became clear, while the value of the rate constant \((1 \times 10^5 \text{ M}^{-1} \text{ s}^{-1} \text{ at } 8\text{o}º\text{C and pH } 5.0)\) was two-orders of magnitude less than that reported by Slade et al. (45). An attempt to make direct measurements of the rate of NO binding, using laser flash photolysis was unsuccessful, though the formation of a disubstituted \([Ru^{III}(edta)(NO^+)(NO_2^-)]^+\) was detected by \(^{15}\)N-NMR spectroscopy. Laser flash photolysis of this complex was complicated by the number of chemical reaction steps.

In other recent reports, the preparation, characterisation, kinetics and biochemical activity of various species of Ru-pac complexes (pac = edta; dtpa) were reported (47, 48). The report reaffirmed the NO scavenging ability of Ru-pac complexes and reported similar rate constant data as Slade et al. for the Ru-edta complex (45). However, the binding of NO with Ru-dtpa was slower \((3 \times 10^5 \text{ M}^{-1} \text{ s}^{-1} \text{ at } 20\text{o}º\text{C and pH } = 7.4)\) (50 mM phosphate buffer) than that observed for the Ru-edta complex (45).

The reaction of \([Ru^{III}(edta)(H_2O)]^-\) with \(H_2O_2\) in the presence of arginine produces NO, in the form of \([Ru^{IV}(edta)(NO^+)]^+\), and citrulline (49). This affords a simple model of NOS. A working mechanism has been proposed for this reaction involving the hydroxylation of arginine by \([Ru^{V}(edta)(O)]^-\) species (formed by reaction of \([Ru^{III}(edta)(H_2O)]^-\) with \(H_2O_2\)) to resemble the first monooxygenase step of the NOS reaction (49). In a subsequent step, the oxidation of N-hydroxyarginine to citrulline and NO is proposed to take place via a 'peroxide shunt' mechanism (49).

**Organ Rejection Studies**

In 2002 it was reported that NO derived from the regulation of inducible NO synthase (iNOS) might play an important role in organ rejection (50). In experimental models of acute cardiac transplant rejection (without immunosuppression), treatment using NOS inhibitors to prevent acute rejection yielded conflicting results. This is suggested to be most likely due to potential inhibition of constitutive NOS (cNOS). Accordingly, agents that trap NO directly may have some advantage. The efficacy of the Ru-edta complex alone and in combination with low-dose cyclosporine (CsA, which is an immunosuppressive drug that delays graft rejection - a model of delayed graft rejection) for inhibiting the nitrrosylation of myocardial protein, and for prolonging cardiac allograft survival in a model of acute cardiac transplant rejection (without immunosuppression) has been evaluated (50). Treatment with the Ru-edta complex either prolonged the graft survival and/or caused a marked decrease in myocardial nitrosylprotein formation, as determined by EPR spectroscopy. In vivo scavenging of NO by the ruthenium complex was verified by high-performance liquid chromatography analysis of the nitrrosylated drug in plasma samples. Low-dose CsA given alone or in combination with the Ru-edta complex completely blocked the formation of myocardial nitrosylprotein complexes. While low-dose CsA alone prolonged graft survival, the combined therapy of CsA and the Ru-edta complex produced a synergistic effect on graft survival. The studies explored the possibility of using the
Ru-edta complex alone and in combination with CsA to protect myocardial proteins from post-transcriptional modification and to prolong cardiac graft survival.

**NO in Angiogenesis and Tumour Progression**

NO also plays a role in angiogenesis and tumour progression (51-62). These studies suggest that increased levels of NO correlate with tumour growth and spread in human cancers. Drugs that interfere in the nitric oxide synthase (NOS) pathway could thus be useful against angiogenesis-dependent tumours, and the Ru\textsuperscript{III}-edta complex was found to be effective in this regard (62). The key steps of angiogenesis, endothelial cell proliferation and migration stimulated by vascular endothelial growth factor (VEGF) or NO donor drugs, were reportedly blocked by the Ru\textsuperscript{III}-edta complex (62).

**Ru-pac Complexes as Protease Inhibitors**

Cysteine proteases (thiol protease in older literature) have recently been discovered in viruses of poliomyelitis and hepatitis A (63, 64), and their pathological role (65-69) in brain trauma, muscular dystrophy, arthritis, cardiac ischaemia and Alzheimer’s disease is reasoned to occur via degradation of concerned proteins by the enzyme. Cysteine proteases have a control aspect on HIV-1, myocardial repair, periodontal disease and cytomegalovirus (herpes).

Recently, evidence from molecular, immunological and pharmacological studies has indicated that cysteine cathepsins (peptidases belonging to the papain family) play a role in the malignant progression of human tumours (70). It has been suggested that cysteine cathepsins, most likely with serine proteases, degrade the extracellular matrix, thereby facilitating tumour growth into surrounding tissues and vasculature (70). Clinically, the levels, activities and localisation of cysteine cathepsins and their endogenous inhibitors have been shown to have diagnostic and prognostic value (70).

In order to achieve selective inhibition of cysteine proteases, cysteine protease inhibitor (CPI) should have an active site which could, selectively, be highly reactive with the cysteine residue of the enzyme to produce an inert covalent enzyme-inhibitor complex. In this context, the use of metal complexes is conspicuously absent from the literature. However, we have recently discovered that Ru-pac complexes possess cysteine protease inhibition activity (26, 71).

The protease inhibition activity of Ru-pac complexes was studied using three cysteine protease enzymes: bromalain, papain and ficin with azoalbumin as the substrate. In order to understand cysteine protease inhibition by Ru-pac complexes, the interaction of Ru-pac complexes with cysteine (a thio-amino acid and cysteine protease contain this unit) and other thio-amino acids was studied, leading to the formation of S-coordinated species. The ability of Ru-pac complexes to inhibit cysteine protease activity was attributed to the high affinity of the ruthenium complexes towards binding the –SH group in the cysteine residue of the enzymes via a rapid aquo-substitution reaction. The protease activity of the enzyme was thus inhibited by the formation of a stable Ru(edta)-enzyme complex, see Figure 3.

These studies demonstrate that the [Ru\textsuperscript{III}(edta)(H\textsubscript{2}O)]\textsuperscript{2-} complex effectively inhibits the protease activity of the three enzymes, whereas, the [Ru\textsuperscript{III}(hedtra)(H\textsubscript{2}O)] complex, although able to reduce the hydrolysis of azoalbumin by bromalain at a certain level, failed to do so with papain. The lower efficacy of the Ru-hedtra complex, than the Ru-edta complex, towards inhibiting protease activity of bromalain may be linked with the lower affinity of Ru-hedtra towards binding the –SH group in cysteine.

However, the absence of inhibition activity by the Ru-hedtra complex for papain, and the significantly lower efficacy for ficin suggest that the protease inhibition activity of the Ru\textsuperscript{III}-pac complexes is enzyme specific.

Very recently it has been reported (72) that the S-atom of cysteine reacts to bind the N-atom of the nitrosyl complex of Ru-edta to form a 1:1 intermediate species, which subsequently converts into another intermediate by reacting with another molecule of cysteine and ultimately produces
[Ru$^{III}$ (edta)($H_2O$]$^{-}$. Cysteine is returned to the reacting system together with the release of $N_2O$. This observation is of significance, implying the catalytic reduction of NO to $N_2O$ in a biological system.

Concluding Remarks

In this article, we have primarily reviewed the kinetics and mechanism of the interaction of Ru-pac complexes with biomolecules. The ability of Ru-pac complexes to perform hydrocarbon oxidation in a manner that resembles the enzymatic system, cytochrome P-450, appears to be useful for developing Ru-pac based agents for oxidative cleavage of DNA and artificial nuclease in DNA footprinting experiments. The ability of Ru-pac complexes to bind to DNA constituents at a faster rate than to sulfur-containing ligands, points towards exploring the possibility of a new family of ruthenium-based anticancer drugs of low toxicity. The [Ru(pac)(NO)] complexes offer a number of features as NO carriers or scavengers.

The discovery of the protease inhibition activity of Ru-pac complexes may be of significance in developing antiviral agents in which Ru-pac complexes could act as metallo-inhibitor agents for disease progression.

Although the above features make Ru-pac complexes promising for clinical application, a better mechanistic understanding of the different modes of drug action of Ru-pac complexes would probably yield more effective chemotherapeutic agents.

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Glossary
arginine is a nonessential amino acid in adults and supplies the amidine group for the synthesis of creatine. Arginine is also formed by the transfer of an N atom from aspartate to citrulline in the urea cycle. Arginine is important for NO production by the enzyme nitric oxide synthase. NO is important for maintaining cardiovascular health. However, most arginine is utilised in the liver and kidneys, and only a fraction is available for this purpose.

citrulline, L-citrulline is a nonessential amino acid that supports the body in optimising blood flow through its conversion to L-arginine and then, via nitric oxide synthase, to nitric oxide. Citrulline is synthesised in the intestinal tract from glutamine, and converts to arginine in the endothelial cells. Citrulline allows for increased and sustained NO production in the endothelium to support circulatory function.

cytidine is a purine nucleoside: cytosine linked by its N9 nitrogen to the C1 carbon of ribose. It is a component of ribonucleic acid (RNA) and its nucleotides are important in the synthesis of a variety of lipid derivatives.
**effective dose 50, ED<sub>50</sub>,** is the amount of drug required to produce 50 percent of the maximum response in a pharmacological test. It is usually calculated from a plot of log(Dose) vs. response.

**growth inhibitory concentration 50, GI<sub>50</sub>,** is the concentration required to inhibit growth of tumour cells in an *in vitro* test by 50 percent relative to a control.

**JM1226,** is now known as **AMD1226, K[Ru(Hedta)Cl],** potassium chloro[hydrogen(ethylenedinitrilo)tetraacetato]ruthenate.
A nitric oxide scavenger first developed at Johnson Matthey and now being further developed by AnorMED.

**JM6245,** is now known as **AMD6245, [Ru(Hedta)(H<sub>2</sub>O)],** aqua[hydrogen(ethylenedinitrilo)tetraacetato]ruthenium.
A nitric oxide scavenger first developed at Johnson Matthey and now being further developed by AnorMED.

**lipopolysaccharide, LPS** also known as endotoxin, is composed of lipid and polysaccharide moieties. LPS is a component of the cell wall of gram-negative bacteria that is released from dying bacteria and stimulates many of the innate immune responses, including synthesis of nitric oxide. Lipopolysaccharide from *Escherichia coli* is a commonly used immune cell activator in laboratory immunology.

**macrophage** is a mononuclear phagocyte found in tissues, and plays an important role in the innate and adaptive immune response. Macrophages are produced from stem cells in bone marrow which develop into monocytes, enter the blood, and later into tissue where they develop into macrophages. Macrophages kill ingested microorganisms. They can be activated by endotoxin and cytokines such as γ-interferon.

**NADPH** is nicotinamide adenine dinucleotide phosphate (reduced form).

**nucleoside** is a heterocyclic nitrogenous base, a purine or pyrimidine, in an N-glycosidic linkage with a pentose sugar. It is often used to denote a compound obtained by hydrolysis of nucleic acids, a purine or pyrimidine linked to ribose (in RNA) or deoxyribose (in DNA).

**nucleotide** is a phosphate ester of a nucleoside, particularly the 5' phosphate of a pyrimidine or purine in N-glycosidic linkage with ribose or deoxyribose, as occurs in the nucleic acids, RNA and DNA, respectively.

**pyrimidine** is a metadiazine, C<sub>4</sub>H<sub>4</sub>N<sub>2</sub>, which is the fundamental form of the pyrimidine bases. There are mostly oxy or amino derivatives, for example, 2,4-dioxypyrimidine is uracil, 2-oxy-4-aminopyrimidine is cytosine, and 2,4-dioxy-5-methylpyrimidine is thymine. Uracil, cytosine and thymine are constituents of nucleic acid.

**RAW 264 cells** are a murine macrophage cell line. RAW 264 can be activated with LPS to produce cytokines and nitric oxide.

**SNAP** is S-nitroso-N-acetyl-D,L-penicillamine, an organic nitric oxide donor molecule.

**thymidine** is a pyrimidine nucleoside, thymine linked by its N1 nitrogen to the C1 carbon of deoxyribose. It is one of the four nucleotides that make up DNA.

**uridine** is a pyrimidine nucleoside, uracil linked by its N1 nitrogen to the C1 carbon of ribose. It is a component of ribonucleic acid (RNA), and its nucleotides participate in the biosynthesis of polysaccharides and some polysaccharide-containing compounds.
Every four years, geologists from academia, national geological surveys, exploration and mining companies, interested in the platinum group elements (PGE) hold an international symposium to discuss the latest geological ideas, exploration targets and technical information. However, only three years separated the 9th meeting held near the Stillwater Complex in Montana, U.S.A. (1), and the 10th meeting held in August 2005 in Oulu, Finland (2), perhaps reflecting the interest in these commodities. The main organisers of the meeting were Tuomo Alapieti (University of Oulu) and Markku Iljana (Geological Survey of Finland). As Finland and western Russia have been centres of intense exploration for platinum during the last few years, Oulu was an interesting locale for the meeting.

As always, there was a variety of presentations (totalling over 200) covering discoveries and evaluations of mineralised areas, descriptions of the host rocks (usually layered igneous intrusions), characterisations of different platinum-group mineral assemblages, and ideas on the processes that induce platinum mineralisation.

What is new are the changes in reporting on exploration programmes to stock exchanges. This has meant that much more quantitative information is available about PGE developments than ever before. Unlike previous Platinum Symposia, exploration companies are now keener to report their results, and give ore body models. Many interesting areas were described, but none that is going to change the future of PGE mining (3).

The Baltic Shield

Starting in Finland and Russia (geologically called the Baltic Shield), many ancient intrusions carry some PGEs and copper-nickel (Cu + Ni) sulfides. Important resources occur in the Portimo Complex (over 200 Mt at 2 g t⁻¹ Pd + Pt + Au), Koillismaa, Penikat and Keivitsa Complexes. Despite drawbacks of variable grade and lack of local smelter, North American Palladium is interested in continuing exploration in these areas. Many other intrusions have been incompletely evaluated.

The Burakovka intrusion lies in western Russia, and at 720 km² is the largest in Europe. Good mineralisation occurs in a chromitite layer (like the UG2 in the Bushveld Complex) and at other levels in the igneous intrusion. Another large, but deformed intrusion, the Monchegorsk intrusion (550 km²), contained a high-grade, vein-like Ni-Cu sulfide-rich system, largely mined out, but now has been found to host two PGE-enriched layers with significant tonnage, although continuity of grade remains to be demonstrated. The Fedorova-Pana intrusion has a strike length of 40 km and thickness of 3.5 km. A thick mineralised zone up to 50 m wide, allegedly like the J-M Reef of the Stillwater Complex, has been traced for 1.4 km. Grades are quoted at 2–10 g and up to 0.5% Cu + Ni, but resource tonnages were not given.

Unlike these layered examples, the Keivitsa body is a massive ultramafic plug, 3 by 4 km, with a central ore body of 1 km², extending to at least 500 m depth. It has a resource of 315 Mt at 0.5% Cu + Ni and 0.2 g t⁻¹ PGE.

Canadian Occurrences

A jump to describing occurrences in Canada may seem a long way, but geological evidence was presented that Fennoscandia (Baltic Shield) and Ontario/Quebec (geologically called the Superior Province) were once joined before very ancient continental drift separated them over 2 billion years ago. Many small layered intrusions in that part of Canada may be part of the same igneous event as those just described. Examples, such as the River Valley intrusion (25 Mt at 1.4 g t⁻¹ Pd + Pt + Au) and the Shakespeare intrusion with a 14 km strike length and 7 Mt at 0.8% Cu + Ni and 1g t⁻¹ PGE.
PGE were documented. While such tonnages may not seem large, the occurrences are near Sudbury, and may be able to take advantage of the proximity to Sudbury’s mining and smelting infrastructure.

Exploration in Sudbury was (to our minds) the most important in terms of significant and probable further ore exploitation. Despite its geographic location, it is 600 m years younger than the previously described occurrences in the Baltic/Superior supercontinent. The deeper, distal, Cu-rich sulfides, with relatively higher PGE, have been known for a long time, but exploration programmes seem to be getting better at finding their targets, and a number were described (for example, McCreedy West and Podolksy). Tonnages were not given, but grades of up to 10 g t\(^{-1}\) were common. A smaller high-grade occurrence on the east rim has 13 Mt at 5% Cu + Ni and 4 g t\(^{-1}\) PGE. Particularly interesting are aureoles of low-sulfide but high-PGE mineralisation that have not been fully appreciated until recently. They have been recognised around some of the distal, sulfide-rich zones, and may exist around many more.

The Duluth Complex, on the shore of Lake Superior, has been extensively explored. It has a marginal zone that is sparsely mineralised. It has enormous but low-grade Cu, Ni and PGE deposits. Extraction by leaching of the metals is being developed, and is considered viable.

**New Discoveries**

A Ni-Cu-PGE discovery was reported from Western Australia. The Nebo and Babel intrusions are mafic rather than ultramafic and have a thick mineralised layer near their centre. Tonnages and grades are: 400 Mt, 0.6% Cu + Ni and 0.2 g t\(^{-1}\) PGE. Somewhat similar is the remote Ferguson Lake deposit in Canada. A deformed gabbroic sheet, 14 km long by 500 m thick has a sulfide-rich zone, 60 Mt at 1% Cu+Ni and 1.5 g t\(^{-1}\) PGE. A lower unit, poorer in sulfides, but richer in PGE, has recently been identified.

**Brazil**

A Brazilian intrusion, Serra da Onca, was described. It is extensive (25 km), with an ultramafic lower half and gabbroic upper half, like the Bushveld Complex. Near and above the boundary is a thick zone (200 m) with elevated PGE values, but generally not exceeding 1 g t\(^{-1}\).

**Summaries**

New PGE information from the traditional areas: Bushveld, Noril’sk, Great Dyke and Stillwater, was sparse, except for the Platreef, about which one compilation suggested resources of 600 Mt with grades from 1 to 2.5 g t\(^{-1}\). In terms of this tonnage, all the other occurrences mentioned above are dwarfed into insignificance. In all recent reports of explorations, base metals have become an important component of any possible resource estimate, and it is anticipated that in the future exploitation will depend upon both precious- and base-metal extraction. Perhaps one general important observation about all these occurrences is that palladium exceeds platinum.

**References**


**The Authors**

Grant Cawthorn was born in England. He has geology degrees from Durham and Edinburgh Universities. After a post-doctoral fellowship in Newfoundland, he now teaches igneous petrology in the School of Geosciences at the University of the Witwatersrand, South Africa. His main interests lie in the formation and vast reserves (Pt, Cr, V) of the Bushveld Complex. His University post is supported by the mining industry, and he holds the title of the Platinum Industry’s Professor of Igneous Petrology.

Tony Naldrett emigrated to Canada from the U.K. in 1957. In 1987 he joined the Department of Geology, University of Toronto, retiring in 1998. He is a Professor Emeritus, continuing to research magmatic sulfide deposits. His most recent book is “Magmatic Sulfide Deposits: Geology, Geochemistry and Exploration”, Springer-Verlag, 2004. In 2002 the Society of Economic Geologists awarded him the Penrose Gold Medal. He is currently an Honorary Professor in the School of Geosciences, University of the Witwatersrand.
Mechanical Properties Data for Pt-5 wt.% Cu and Pt-5 wt.% Ru Alloys

WORK PRESENTED AS A BASIS FOR FUTURE COMPARISONS

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Scant data exist for the mechanical properties of commercial platinum jewellery alloys Pt-5 wt.% Cu and Pt-5 wt.% Ru. Here data from new evaluations are presented on 90% cold worked and fully recrystallised heat treated alloys at 800°C. Recommendations are made for procedures in reporting future evaluations including disclosure of full processing details.

Platinum-5 wt.% copper (Pt-5% Cu) and platinum-5 wt.% ruthenium (Pt-5% Ru) are widely used alloys for platinum jewellery manufacture. It is therefore surprising that their mechanical properties are not well documented, as the mechanical properties of jewellery alloys are of fundamental importance in determining: (a) the ease with which the alloy may be formed into a jewellery item; and (b) the strength and durability of the finished item in service. Knowledge of mechanical properties is therefore beneficial to both jewellers and materials’ developers. Equally important is knowledge of the processing and microstructural condition of the alloy for which data are quoted, but even when mechanical property data are available, this information is often missing.

Some mechanical properties of pure platinum, Pt-5% Cu and Pt-5% Ru obtained from a review of available literature are shown in Table I. It can be seen that hardness values are well documented for most conditions, probably because determination of hardness involves a simple, non-destructive test which is quickly and easily carried out. However, while hardness testing is useful, it does not yield

<table>
<thead>
<tr>
<th>Table I</th>
<th>Currently Available Mechanical Properties of Pt-5 wt.% Cu and Pt-5 wt.% Ru</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Vickers hardness strength, MPa</td>
</tr>
<tr>
<td><strong>Pure Pt</strong></td>
<td></td>
</tr>
<tr>
<td>Annealed</td>
<td>40–50</td>
</tr>
<tr>
<td>Cold worked</td>
<td>100</td>
</tr>
<tr>
<td><strong>Pt-5 wt.% Cu</strong></td>
<td></td>
</tr>
<tr>
<td>As cast</td>
<td>127</td>
</tr>
<tr>
<td>Annealed</td>
<td>110–120</td>
</tr>
<tr>
<td>50% cold worked</td>
<td>215</td>
</tr>
<tr>
<td>90% cold worked</td>
<td>?</td>
</tr>
<tr>
<td><strong>Pt-5 wt.% Ru</strong></td>
<td></td>
</tr>
<tr>
<td>As cast</td>
<td>127</td>
</tr>
<tr>
<td>Annealed</td>
<td>125–130</td>
</tr>
<tr>
<td>50% cold worked</td>
<td>200–211</td>
</tr>
<tr>
<td>Worked “hard”*</td>
<td>210</td>
</tr>
<tr>
<td>90% cold worked</td>
<td>?</td>
</tr>
</tbody>
</table>

* The amount of cold work is not specified in the reference; ? indicates no information is available.
easily interpreted results. Hardness is related to strength, ductility and elastic modulus, but these properties are not simply extracted from the hardness value. Conversely a properly conducted tensile test is easily interpreted, and the yield strength, tensile strength, elastic modulus and ductility can be more simply distinguished. For precious metals such as platinum, considerations of cost (tensile test specimens being relatively large) probably account for the paucity of tensile test data.

Table I also shows that most of the available information is for the annealed and as cast conditions, which are expected to exhibit similar values. With the exception of Lanam and Pozarnik (4), very few sources give processing information such as annealing temperature, or microstructural information, such as grain size. Also lacking are experimental details that allow other researchers to evaluate the data.

In order to test platinum jewellery alloys, a microsample tensile testing machine has been built at the University of Cape Town that can test samples of total length 8 mm. This paper reports on measurements of both the hardness and tensile properties of Pt-5% Cu and Pt-5% Ru, in the annealed and 90% cold worked conditions. The aim is to provide mechanical property values, averaged from multiple tests, from specimens for which detailed processing and microstructural information is provided.

**Experimental Procedure**

Although there is a pressing need to measure the mechanical properties of platinum alloys, it is not a very practical undertaking when the expense of the material is considered. Even the smallest specimens in the ASTM tensile testing standards (7) are beyond the means of many researchers. The approach used here: microsample tensile testing, has been used previously for other materials with success (8). It uses a very small sample that is as close to the ratios of the ASTM standard as possible while minimising the amount of material used. It is useful in this situation because it reduces the cost of carrying out multiple tests to provide adequate data. A schematic of the specimen design can be seen in Figure 1.

The specimen has a total length of 8 mm, with a nominal gauge width of 0.5 mm and a nominal gauge length of 2.26 mm. The thickness can be varied by the amount that the starting plate is rolled and is kept of the same order as the width. Typically the gauge width contains 5 to 10 grains but this is obviously determined by grain size.

The custom built apparatus is shown in Figure 2. A tensile specimen is positioned in the grips. The operation of the tensile testing apparatus is based on a screw driven actuator that applies a load to the specimen in the grips. Friction is reduced to a negligible amount with an air bearing. Load is measured with a 500 N load cell and displacement is measured with a miniature linear variable displacement transducer (LVDT) sensor. A computer records both displacement and load. Because displacement is not measured directly on the specimen, we do not regard the elastic strain data as reliable; furthermore analysis of the elastic response is complicated by elongation of the specimen ends in the grips. However, the recorded plastic elongation is reliable and compares well with direct measurements made on the specimens after testing. Examination of specimens after testing confirms that the plastic behaviour is concentrated in the gauge section.

To make the tensile specimens a plate is first rolled to the required thickness. If required, the plate is then annealed. This can take place before or after cutting. The cold worked specimens were cut with the tensile axis parallel to the rolling direction. The samples were cut using both a computer...
numerical control (CNC) mill and wire electro discharge machining. The choice of cutting method was found to have little effect on the materials. The Pt-5% Cu and Pt-5% Ru samples were measured at two extremes of mechanical behaviour: the recrystallised and 90% cold rolled states.

Specific information about their processing is as follows: the as received material was homogenised first at 1000ºC for 12 hours. It was then cold rolled to 90% reduction in thickness. Half of the material from each alloy was retained to perform testing of 90% cold rolled material. The remainder was heat treated at 800ºC for six hours under vacuum. Light micrographs of the grain structure were taken. Hardness and tensile specimens were polished to a mirror finish for consistency. Small sample tensile tests and Vickers hardness tests with a 100 g load were performed with each set of specimens.

**Results**

Light micrographs from each set of material are shown in the figures. Figures 3 and 4 show the microstructure of the materials in the 90% cold rolled and 800ºC heat treated conditions, respectively. As expected the 90% cold rolled material shows grains that are elongated in the direction of rolling. The heat treated Pt-5% Cu exhibits complete recrystallisation, with equiaxed grains of size ~ 100 µm. By comparison, the heat treated Pt-5% Ru alloy, Figure 4(b), shows finer grains, of size ~ 50 µm.

Figure 5 shows some typical tensile test results. As expected, the 90% cold rolled alloys exhibit a higher yield stress and significantly lower ductility than the recrystallised alloys.

The calculated average results of tensile tests are seen in Table II along with the hardness results.
It can be seen that the two alloys are not significantly different in strength, however, the Pt 5% Cu alloy is more ductile than the Pt 5% Ru alloy.

Discussion

If the new data in Table II is compared with the literature values quoted in Table I, it can be seen that the hardness and strength values obtained in the present work are consistently higher. This is expected for the cold rolled specimens, since the values obtained from the literature were for 50% cold worked alloys, and the results in the present work are for 90% cold work. The increased dislocation density in the 90% cold rolled specimens results in higher values for both hardness and strength, and very low ductility.

The difference in values for annealed specimens quoted in the literature and in the present work should also be evaluated on the basis of microstructure, but unfortunately heat treatment and microstructure data are not available for the values in the literature. The light micrographs in Figures 3 and 4 show that Pt-5% Ru has a finer grain structure than the Pt-5% Cu after heat treatment at 800°C. This suggests that the recrystallisation temperature of Pt-5% Cu is lower than that of Pt-5% Ru, consistent with the slightly lower melting temperature of Pt-5% Cu. The recrystallisation temperature for both materials is clearly 800°C or less after 90% cold work, and is certainly less than the 1000°C after an unspecified amount of prior cold work suggested in (3). The hardness and strength values in Table II show that the values for Pt-5% Ru are higher than for Pt-5% Cu.

![Fig. 4](image1.png)  (a) Pt-5 wt.% Ru in the 90% cold rolled state and (b) Pt-5 wt.% Ru in the 800°C heat treated condition

![Fig. 5](image2.png)  Tensile stress-strain curves from Pt-5 wt.% Cu and Pt-5 wt.% Ru alloys
Cu after the same heat treatment, which can be explained by the finer grain size of the Pt-5% Ru. Similarly, the difference in elongation may have more to do with the difference in grain size rather than real differences in the alloys. This illustrates the importance of both processing and microstructural information in evaluating mechanical property data.

The standard deviations of the strength data shown in Table II, illustrating the variation in values obtained in repeated tests of the same specimen type, are relatively large at around 10%. This underscores the necessity of carrying out multiple tests on each specimen type in order to obtain reliable average values for mechanical properties.

### Conclusion

The results presented provide data to serve as a basis for comparison in further research on platinum alloys. It has been shown that the two most widely used platinum alloys are not significantly different in mechanical properties, and in addition, microstructure information and hardness values for each tested sample have been included. This is the most comprehensive information available on mechanical properties of these alloys and can serve as a baseline for alloy development. It is recommended that published mechanical data should include full processing information, microstructural characterisation if possible, number of specimens measured, and standard deviation or range of values obtained. This will greatly assist in evaluation of data and comparison with other measurements.

### References

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### The Authors

Candy Lang is Associate Professor in the Department of Mechanical Engineering at the University of Cape Town (UCT). She is leader of the Hot Platinum research project, which is involved in developing novel platinum technology for the jewellery industry.

Dr Kamili Jackson was a Post Doctoral Fellow in the Department of Mechanical Engineering, UCT. Her work included the tensile testing of current and new platinum alloys for use in jewellery applications.
This book is Volume 5 in the open-ended “Catalytic Science Series”, dedicated to an in-depth description of catalysts and their extensive applications. Prior volumes are: “Environmental Catalysis”, “Catalysis by Ceria and Related Materials”, “Zeolites for Cleaner Technologies” and “Isotopes in Heterogeneous Catalysis” (Volumes 1 to 4, respectively). “Supported Metals in Catalysis” presents recent developments in characterisation and application of supported metals in heterogeneous catalysis – a truly mammoth task for one publication. While the book is not dedicated to the use of platinum group metal (pgm) catalysts, they do feature throughout, reaffirming their vital role in the world of heterogeneous catalysis.

As with many other publications on heterogeneous catalysis, this book can be divided into three main categories: preparation, characterisation and application. The first chapter describes the preparation methods used in the manufacture of supported metal catalysts, namely impregnation and precipitation. Even though this chapter is biased towards impregnation techniques, it provides a useful insight into the design and optimisation of catalysts prepared on various support media (powder and monolith).

Chapters 3 and 4 concentrate on various aspects of catalyst characterisation. The authors admit it would be impossible to describe in detail, in only a few chapters, all the methods used for the determination of the physical and chemical properties of metal catalysts. However, the reader is provided with a good foundation with which to explore the range of spectroscopic techniques available, with specific examples of their utilisation for in situ characterisation of metal catalysts. Chapter 4 is worthy of particular mention, where methods used to determine dispersion and support metal crystallite size are discussed. This subject matter has formed an integral part of many doctoral theses, and many would have undoubtedly benefited from reference to this book.

The remainder of the book is dedicated to specific areas of heterogeneous catalysis, with comprehensive reviews covering subject matter as diverse as the catalytic activation of C1 compounds and the reforming of naphtha, to the production of hydrogen and synthesis of fine chemicals. The catalytic abatement of pollutants emitted from the flame combustion of fossil fuels for transport applications is also introduced. It could be argued that a much more in-depth investigation than the book provides is required for a comprehensive understanding of the vast body of research carried out in this particular field over the past 30 years. However, for a relative newcomer to this area, the subject matter is well introduced and encourages the reader to delve further into automotive catalysis, as, indeed, do all the other sections for their particular fields. In essence, such encouragement forms the primary aim of this publication, and in this it excels brilliantly.

Catalysts for the manufacture of fine chemicals have been a major, and almost exclusive, focus throughout my career, and I have had the pleasure of working alongside the authors of Chapter 9, who deal with this topic. Dr Richard Wells, now at the University of Aberdeen, who advised me throughout my Ph.D., and my colleague, Dr Peter Johnston, whose pensmanship is recognisable, even under the name Peter Johnstone.

The greatest challenge posed by the fine chemical industry to catalysis is the need for ever-increasing selectivity to a desired product. Selective hydrogenation alone warrants many chapters in this series of books. In this volume, the authors...
cover the much publicised hydrogenation of butadiene and α,β-unsaturated carbonyl compounds, but I would encourage them (and those reading) to investigate further the role of heterogeneous catalysts in the selective hydrogenation of molecules containing functions such as aromatic rings, heterocycles, nitro groups and nitriles, halides and protecting groups. Catalysts capable of selectively hydrogenating the aforementioned groups, in the presence of others, are in high demand, and the pharmaceutical, agrochemical and fine chemical industries would value them greatly.

As Professor Geoffrey Bond states in the preface, no single mind can fully comprehend the entirety of a subject as diverse as supported metal catalysts. The book does not aim to do this, but presents each chapter in a readable manner, with overviews of the critical aspects of the subject and a thorough reference list for the reader to find greater detail if they wish. As a stand-alone publication, it provides good reference to aspects of heterogeneous catalysis. As part of the “Catalytic Science Series”, it is an invaluable tool to research students and industrial chemists in catalysis.

**The Reviewer**

Neil McGuire is a Senior Development Chemist (Catalyst and Chiral Technologies) at Johnson Matthey Catalysts in the U.K. His main interests are platinum group metal heterogeneous catalysts for use in the pharmaceutical, fine chemical and agrochemical industries.

**Effects of Completely Encapsulating Platinum in Ceria**

It is well known that for noble metal particles supported on certain oxides, catalytic activity and selectivity for certain reactions such as CO hydrogenation can be strongly enhanced by pre-reduction. This results in the migration of atoms from the support to the surface of the noble metal particle itself to build up a partial monolayer, and is known as the strong metal-support interaction (SMSI) effect. However, in general it has always been thought that some exposed metal surface atoms are necessary to allow chemisorption and subsequent reaction.

Now, for the first time, we have shown that the complete encapsulation of noble metal particles by a reactive support also leads to good activity and excellent selectivity for the water gas shift (WGS) reaction (1).

Using solution microemulsion techniques we have made CeO$_2$-encapsulated platinum (Pt) and Pt/Au (platinum/gold) particles and tested their WGS activity against Pt/CeO$_2$ catalysts made in more conventional ways. In contrast to the conventional catalysts, very few exposed Pt surface sites were found when CO was used as a probe to detect any surface Pt. On testing the catalyst using a typical WGS feed, better activity was found than with conventional catalysts, and more importantly there was no evidence of the competing reaction of methanation. This provides the strongest evidence of effective encapsulation of the Pt particles.

Characterisation of the encapsulated particles by UV spectroscopy showed a correlation of activity with CeO$_2$ electronic structure suggesting that the presence of Pt enhances the ability of CeO$_2$ to undertake redox chemistry and hence become active for the WGS reaction. Therefore, the encapsulation of noble metal particles by reactive oxide coatings such as CeO$_2$ represents a new class of catalytic material which has the ability to be tuned to achieve good activity and selectivity.

**Reference**


**The Authors**

S. C. Edman Tsang is Professor of Nanomaterials and Catalysis at the University of Reading, U.K. He is interested in fundamental and applied aspects of novel nanosize materials as heterogeneous catalysts, solid state absorbents and sensors, which includes synthesis, testing and characterisation of these materials. E-mail: s.c.e.tsang@reading.ac.uk

David Thompsett is a Scientific Consultant responsible for the Electrotechnology & Catalyst Preparation Department at the Johnson Matthey Technology Centre, U.K. His interests include fuel cells, catalyst preparation and characterisation, and the relationship between catalyst activity and structure. E-mail: thompd@matthey.com

DOI: 10.1595/147106706X95356
The 7th European Congress on Catalysis (EUROPACAT-VII – A Key to a Richer and Cleaner Society), organised by the Bulgarian Catalysis Club and the Greek Catalysis Society under the auspices of the European Federation of Catalysis Societies (EFCATS) took place in Sophia, Bulgaria, from the 28th August to 1st September, 2005. In all there were 773 registered delegates from 39 countries and 750 presentations – 170 oral and 580 posters. At the end of each oral session, selected posters were described in two-minute flash oral presentations, and 200 posters were covered in this way. The oral presentations were grouped into 11 different symposia covering most areas of heterogeneous catalysis from fundamental catalysis and surface science to industrial catalysis.

Several symposia featured work on the platinum group metals, and the papers reported here are grouped into very general categories.

EFCATS Sponsored Awards

Two awards are made at this Congress. One is the Johnson Matthey Award for Innovation in Catalysis, which was awarded to Professor Valentin N. Parmon of the Boreskov Institute of Catalysis, Novosibirsk, Russia. The other award is the François Gault Lectureship, and Professor Graham Hutchings of Cardiff University, U.K. became the award holder for 2006. The holder of this position acts as an ambassador for catalysis by lecturing around Europe.

Catalyst Preparation

A one-step flame synthesis route to Pt/Ba/Al2O3 was described by Reto Strobel (ETH Zurich, Switzerland). The material was prepared using two flame spray pyrolysis nozzles, one for the Al precursor and the other for the Pt/Ba precursors. The resulting material was found to have good NOx storage capacity. However, material made with only one nozzle for the Pt, Ba and Al had no NOx storage capacity.

Plasma spraying and cold gas dynamic spray methods used in preparing palladium (Pd), Pd-Mn, Cu-Cr and Mn catalysts for methane combustion were described by O. Yu. Podyacheva and coworkers (Boreskov Institute of Catalysis), and O. P. Solonenko and V. F. Kosarev (Institute of Theoretical and Applied Mechanics, Novosibirsk, Russia). The cold gas method was employed to deposit the metals onto thin metal foils, although other types of support, such as sheet, metal plate and foam were also discussed. In the procedure, a layer of alumina was deposited onto the metal surface for good adhesion, this was followed by a second alumina phase, and then the catalyst. Samples were characterised by XRD, SEM and XPS. SEM and thermal testing confirmed excellent adhesion and thermal stability. It was suggested that the samples could be suitable for use in the catalytic chambers of gas turbines.

The design of a Pd/carbon coated asymmetric α-Al2O3 membrane catalyst for the production of hydrogen peroxide (H2O2) by direct synthesis was described by S. Melada and colleagues (University of Venezia, Italy) and G. Centi (University of Messina, Italy). The procedure involved coating an alumina tube with a ceramic layer then a carbon layer, followed by Pd deposition. The effect of the Pd oxidation state, H2 partial pressure and synthesis variables were discussed. Results indicated that both a high partial pressure of hydrogen and surface oxidised Pd particles were needed for high activity. H2O2 is extensively used in the pulp paper/textile industries and is currently produced by the anthraquinone process. This process is not ideal, but other methods of production need to
consider that potentially explosive mixtures can be generated on scale-up. As the demand for H₂O₂ is likely to increase in the future (2M tonnes production in 2003), alternative production routes are certainly of commercial interest.

**Catalyst Characterisation**

Professor M. Neurock (University of Virginia, U.S.A.) gave a plenary lecture entitled ‘First-principles elucidation and design of catalytic sites and their environments’. He discussed the necessity for understanding, on an atomic scale, the active sites that control catalytic behaviour and their local reaction environment, as both are important in the search for more active and selective catalysts. Defect surface sites, bimetallic alloys, promoters, poisons, coadsorbed intermediates and the catalyst support can all change the nature of the adsorbate/surface interactions. Professor Neurock used \textit{ab initio} quantum mechanical methods and theory to study alloys for catalytic and electrocatalytic systems, including lean NOx catalysis.

Professor R. Schlogl (Fritz Haber Institute, Berlin, Germany) emphasised the need for both static and dynamic characterisation of catalysts to improve functional understanding of catalytic systems. One example used to illustrate this was the selective hydrogenation of pentyne over a range of Pd surfaces: single crystal Pd(111), Pd foil and Pd/alumina. High resolution XPS identified the presence of surface, sub-surface and bulk dissolved carbon.

Microscopy with ‘SuperSTEM’ (scanning transmission electron microscope) was described by J. L. Casci (Johnson Matthey Catalysts, Billingham, U.K.) for characterising promoters in cobalt Fisher-Tropsch catalysts. The technique is capable of sub-Ångstrom resolution, and was used to find the location of promoter atoms in the Co/alumina catalyst. Catalyst samples, prepared by the cobalt ammine carbonate deposition-precipitation method, were post-impregnated with Pt, Ir, Re or Ru precursors. A high-angle annular dark-field detector produced atomic number contrast imaging, while electron energy-loss spectroscopy (EELS) was used for elemental spectroscopy. The Pt, Ir and Re promoters were mainly present as isolated atoms, while the Ru promoter was present both as isolated atoms and in regions of high concentration with Co particles. All four elements

The Johnson Matthey Award for Innovation in Catalysis

The Johnson Matthey sponsored “Innovation in Catalysis” award has been presented now at three EUROPACAT meetings. At EUROPACAT-VII, Professor Valentin Parmon of the Boreskov Institute of Catalysis, Novosibirsk, Russia, was granted the award for “his fundamental contribution to the development of catalytic and photocatalytic solutions to sustainable processes and energy”. The award is managed and administered by the European Federation of Catalyst Societies.

At EUROPACAT-V the award was conferred on Pierre Jacobs (Katholieke Universiteit Leuven, Belgium) and at EUROPACAT-VI on Giuseppe Bellussi (EniTecnologie, Italy).
promoted the reduction to metallic cobalt, but only Ru, Pt and Ir were effective in lowering the temperature of the Co3O4 to CoO transition. Later analysis, including in situ XRD, showed the reduction of Co3O4 to CoO to Co metal.

R. N. Devi (Queen’s University of Belfast, U.K.) presented work on preparative aspects of a 5% Pt-0.5% Fe catalyst coated with Na-A zeolite for the selective oxidation of CO in the presence of n-butane. The zeolite coating allows the CO to reach the Pt catalyst but inhibits the n-butane. This leads to a big difference in the catalyst light-off temperature.

Theoretical Methods and Fundamental Studies

Professor R. Burch (Queen’s University Belfast, U.K.) stressed, as did many presenters, the need for in situ characterisation to identify reaction mechanisms. Steady state isotopic transient kinetic (SSITK) measurements were combined with diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) to look at the forward and reverse water gas shift reaction over Pt/CeO2. The DRIFTS equipment was designed to minimise residence time, in order to give a time resolution of a few seconds, and to prevent gas bypassing the catalyst to give improved kinetic data. The data showed that the carbonyl and carbonate species on the catalyst surface decayed at the same rate as the labelled CO, but that formate decayed much more slowly, indicating it was a minor intermediate in the reaction pathway under the conditions used.

C. R. Henry (CRMCN-CNRS, Marseille, France) described a surface science approach for producing a model supported catalyst. A Ni3Al (111) single crystal was oxidised at 1000 K to give an alumina film surface with a regular array of defects. Pd was deposited, and then gold (Au), and the bimetallic particles gave an ordered array of clusters. The spatial distribution of the Au and Pd is controlled by the surface defects.

Photocatalysis

Two talks examined light-sensitive precious metals-promoted titania systems for hydrogen production. The first talk, by M. Kitano (Kansai University, Japan), described a visible light-responsive Pt/TiO2 thin film photocatalyst produced by magnetron sputtering of Pt onto a planar TiO2 substrate. This configuration allowed the Pt and TiO2 sides of the catalyst to be physically separate, to prevent recombination of the O2 (produced on the TiO2) and the H2 (produced on the Pt), and thus easy separation of the two gases. The titania was a mixture of rutile and anatase, and the coating procedure produced TiO2 slightly reduced at the surface. The TiO2 was sensitive to visible light.

The second talk, by Professor M. J. Bowker (University of Cardiff, U.K.) described a Pd/TiO2 (P25) photocatalyst for reforming methanol to H2 and CO2 using UV light. The Pd loading had a strong influence on activity, which reached a maximum at 0.5 wt.% Pd.

The photocatalysed degradation of pesticides and organic pollutants was discussed by D. Bahnemann (University of Hanover, Germany), and M. Muneer and colleagues (Aligarh Muslim University, India). They examined the degradation of pesticide derivatives, such as N,N-dimethyl-α-phenyl benzene acetamide (diphenamid), bromacil, terbacil and 2,4,5-tribromoimidazole (TBI), and other pollutants, such as benzidine. Aqueous suspensions of TiO2 were investigated under varying conditions of pH, substrate, photocatalyst concentration, type of TiO2 and the presence of H2O2 as an alternative additive to O2. Several factors were found to be important for electron transfer and it was speculated that in order to improve the electronic effects in the reaction, mixed semiconductors (TiO2/SnO2) and Pt, Pd, Au or Ag might have to be included.

Catalyst Deactivation as Part of Catalyst Design

Professor S. D. Jackson (University of Glasgow, U.K.) highlighted the role of catalyst deactivation as a key part of catalyst design. Examples of catalyst deactivation in industrial processes were given, including propane dehydrogenation for which Pt and Cr catalysts were compared. Both catalysts deactivate quite rapidly,
Pt in 3 to 5 days, and Cr in 15 to 25 minutes. Processes have been designed to manage this deactivation, for instance, the Oleflex process (propane to propylene) from UOP using a Pt catalyst, and the Catofin® process from Houdry, using a Cr-based catalyst.

**Fine Chemical Synthesis**

Two presentations examined the use of precious metal catalysts for the synthesis of fine chemicals and their intermediates.

H. Markus and colleagues (Åbo Akademi University, Turku, Finland) discussed the use of Pd supported on zeolites for the hydrogenolysis of the lignan hydroxymatairesinol to matairesinol (matairesinol is an antiproliferative and antioxidant lignan). The work described the extraction of hydroxymatairesinol from Norway spruce (Picea abies) knots, which in 1998 were found to contain up to 10% lignans, with hydroxymatairesinol being the most abundant. The synthesis was carried out in a stirred glass reactor under hydrogen flow with 2-propanol as the solvent. Several Pd/zeolite catalysts were investigated and characterised by metal dispersion, surface area, support acidity, pore size and metal content. A bifunctional mechanism for the hydrogenolysis was proposed, requiring both metal and acid sites. Relatively large pores in the zeolite were considered important to allow the bulky reactant molecules access to the active sites. The results indicated that the reaction rate was inversely dependent on the acidity of the supporting zeolite.

E. Sulman and coworkers (Tver Technical University, Russia), P. Valetsky and colleagues (Nesmryanov Institute of Orangoelement Compounds, Moscow, Russia), and P. Valetsky and L. Bronstein (Indiana University, U.S.A.) discussed the synthesis of vitamin intermediates and fragrant substances by metal-polymeric nanocatalysts. They looked at the use of stabilised precious metal nanoparticles for achieving high selectivity, activity and technological performance. Different types of metal-polymeric catalysts, in Pd, PdZn and PdPt systems, were reviewed and the importance of the stabiliser towards activity was emphasised. They claimed improved activity and good selectivity, compared to a commercially available Pd catalyst.

**Environmental Catalysis**

Professor R. Prins (ETH Zurich, Switzerland) gave a plenary lecture on ‘Hydrotreating catalysis: a contribution to cleaner air!’. He discussed hydrodesulfurisation (HDS) and hydrodearomatisation (HDA) over pgm/alumina catalysts. Although systems based on MoS2 are the main candidates for HDS catalysts, pgm-based catalysts may be useful to further reduce the sulfur levels in a secondary sulfur removal step. At 300°C and 50 atm the order of catalyst activity for the hydrogenation of dibenzothiophene (to produce mostly biphenyl) was found to be: Pd-Pt alloy > Pt > Pd. When the more sterically hindered 4,6-dimethylbifenzothene underwent HDS, Pd gave a better performance than Pt, and Pd also produced much stronger hydrogenation, in this case giving predominantly 3,3-dimethylbicyclohexyl.

Work on a reformer for producing hydrogen from dimethyl ether was described by L. J. Pettersson (KTH-Royal Institute of Technology, Stockholm, Sweden). The hydrogen could then be used for catalyst regeneration (such as in a NOx trap) and to feed PEM fuel cells acting as auxiliary power units. The latter could, for example, provide power to run air conditioning at idle.

The leaching of nitrates from soil into water supplies is known to be due to excessive use of nitrate-based fertilisers in agriculture. In 1998 the European Environmental Agency estimated that 87% of the agricultural land in the EU has nitrate concentrations above the guide level of 25 ppm. The EU has set an upper level of 50 ppm as the maximum permitted concentration of nitrates in drinking water, and amounts above this are deemed unacceptable. One method of nitrate removal is to convert the nitrate ions into nitrogen. This can be achieved by liquid phase nitrate hydrogenation over, generally, heterogeneous bimetallic catalysts. However, more recent work has looked at monometallic catalysts with a
semiconducting support, such as TiO₂. Professor J. A. Anderson (Aberdeen University, U.K.) presented work aimed at developing procedures to improve understanding of the catalyst under working conditions. He gave results of in situ FTIR and XAS examination of Pd/TiO₂ catalyst used to hydrogenate nitrates in aqueous solution. The Pd/TiO₂ catalyst was prepared from TiO₂ P25 (Degussa) and a Pd precursor (Johnson Matthey). His results suggested that the catalyst converts nitrates to N₂ without forming the nitrite. However, the selectivity was considered inadequate.

Work on hydrogenation and oxidation reactions on core-shell nanoparticles of Pd-Ni/MgO was presented by S. Sao Joao and colleagues (CRMNC-CNRS, France), and L. Piccolo and C. R. Henry (IRC-2, France). Generally, the deposition of a thin layer of metal A onto a bulk metal B is known to alter the valence band of bulk B due to coordination, the lattice strain of metal A and the nature of the metals. In this work, a Ni core was prepared on MgO, and Pd was deposited onto the surface by bubbling hydrogen through the precursors (Pd acetylacetonate and Ni/MgO) in toluene. TEM analysis showed the core-shell structure of a Pd shell around the Ni core. The materials were tested for butadiene hydrogenation and CO oxidation.

Electrochemical Promotion

Several presentations focused on the phenomenon of electrochemical promotion (EP), also known as NEMCA (non-Faradaic electrochemical modification of catalytic activity). This relies on the application of a potential across an ionic conductor to alter its surface composition. The conductor carries a deposited catalytic metal, and the altered composition affects the activity of the catalyst. Professor Richard Lambert (Cambridge University, U.K.) illustrated the EP effect with a substrate of ion conducting β''-alumina, where Na or K is pumped to and from the surface on application of potential. Several applications were discussed, including a Fischer-Tropsch reaction over Rh coated K-β''-alumina. The K promotion led to an increase in ethanol production. Recent work was also described on using Pt coated Na-β''-alumina as a NOx storage device (analogous to those used in automotive applications for NOx removal in lean burn engines) where the nitrate can be decomposed by pumping Na away from Pt on application of voltage.

A breakthrough in the practical applications for EP was presented by Professor Costas Vayenas (University of Patras, Greece) who described a monolith-type reactor consisting of 22 parallel plates of YSZ coated on one side with Pt and on the other with Rh. This would allow for the processing of large volumes of gas without significant bypass issues, in a compact device.

Conclusion

The vitality, breadth, and success in research and development in heterogeneous catalysis with the platinum group metals was well demonstrated at this congress.

The next congress, EUROPACAT-VIII, entitled ‘From Theory to Industrial Practice’ will be held from 26th to 31st August 2007, in Finland at Turku/Åbo. It will be run by the Nordic Catalysis Society, and will be a joint effort by Denmark, Finland, Norway and Sweden. More information can be found from: http://www.europacat.org/
Osmium – The Patent Landscape

A VISUALISATION OF THE TECHNOLOGY DESCRIBED IN PATENTS RELATING TO OSMIUM

By Richard Seymour

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Patents are a key source of technical and commercial intelligence, as described in a previous article in this Journal (1). Osmium is often seen as the forgotten member of the platinum group metals, but nevertheless still attracts interest (2, 3).

Modern software allows us not only to search out patents relating to osmium, but also to visualise the search results. The landscapes, (Figures 1 and 2) were created using the Aureka ThemeScape™ software (4) which uses statistical algorithms to analyse the usage of words and phrases, and discern themes and relationships among documents. They show the results of a patent search on osmium covering the period 1981 to 2005 in the US (United States), EP (European Patent), PCT (Patent Cooperation Treaty), GB (British) and JP (Japanese) patent collections. Figure 1 shows a ThemeScape map of the set of 3400 patent documents in which the word osmium appears in either the title, the abstract or the claims, once duplicate family members have been removed. The map labels represent key themes within particular sections of the map. Figure 1 clearly depicts clusters of patents relating to catalysis (e.g. “acid, acetic acid, carbonylation”; “metathesis, alkyl, ligand”), fuel cells and sensors (e.g. “electrode, reference, sensor”, “anode, cathode, electrolyte”), and electronic applications (e.g. ...

Fig. 1 A patent landscape based on ~ 3400 patents in which osmium is mentioned in the title, abstract or claims.
“capacitor, layer, device”, “layer, electroluminescent, device”). The search could be narrowed to display patents in which osmium occurs only in the title or abstract (just over 800 patents), or be broadened to show patents in which osmium appears in the full patent specification (> 14,000 patents).

In Figure 1, the dots in the map are examples of specific patents. Clicking on a contour will pick up all the patents within that contour line, which is useful when further analysis of an area is required. The blue “ocean” represents areas of low patent activity.

It is possible to use to use this map to identify trends in patent activity over time, or to illustrate the patent activity of a particular company (by means of coloured dots). For example, Figure 2 shows patenting by three companies selected at random: red, a pharmaceuticals company; green, a chemicals company; yellow, an electronics company. With this patent visualisation approach, a broad picture of the actual and potential uses of osmium can be obtained, and be followed by more detailed examination of clusters of specific interest.

References

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Mechanisms of Volume Diffusion of Gold into Single Crystal Iridium

EVIDENCE THAT VOLUME DIFFUSION, INTRINSIC OR EXTRINSIC, DEPENDS ON THE ATMOSPHERIC COMPOSITION WHICH OCCURS DURING ANNEALING OF SINGLE CRYSTAL IRIDIUM

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Prior Work

Theoretical and experimental studies of the atomic mechanisms of diffusion and of typical features of volume diffusion indicate that atomic mechanisms are an efficient tool for analysing microscopic interactions between point defects (vacancies and impurities) participating in diffusion. The parameters of volume diffusion in solids are determined by mutual interactions between such point defects (6–13).

The effect of substitutional and interstitial impurities on the diffusion parameters of atoms used as atomic probes in metals has previously been studied (13–19). Work has also been done on the thermodynamics of formation of vacancy-impurity complexes (VICs) in interstitial solid...
solutions, and thermodynamics has been used to describe the diffusion of substitutional atomic probes in interstitial solid solutions of carbon in iron (C(Fe)) and carbon in palladium (C(Pd)) (15–18).

The formation of a VIC flow during carbon diffusion in platinum has been vividly demonstrated (18, 19). Pores formed in the diffusion zone, where carbon had diffused into the platinum, due to the condensation of ‘extrinsic’ vacancies released during thermal dissociation of the VICs. The binding energy of the VIC components in the platinum is: \(|E_{VIC}| > 50 \text{ kJ mol}^{-1}\).

This paper presents results of a study of the volume diffusion of Au into single crystals of Ir (single-Ir) of 4N (99.99%) purity during annealing in an ultrahigh vacuum (UHV) and a technical grade vacuum (TGV). The single-Ir crystals were grown at the Ekaterinburg Non-Ferrous Metals Processing Plant. Single crystals do not have grain boundaries. Coefficients of volume diffusion in TGV, \((D_{Au}^{(Ir)}_{TGV})\), were measured in single-Ir annealed in a TGV at the working temperatures of Ir. The values obtained were several thousand times larger than coefficients of volume diffusion, \((D_{Au}^{(Ir)}_{UHV})\), measured for the same samples in UHV. This is due to a new diffusion mechanism found during annealing in TGV. The mechanism involves ‘extrinsic’ vacancies which arise from dissociation of the VICs.

**Theoretical Background**

The profile of diffusing species (the diffusant) within a homogeneous sample is described by Expression (1) (6):

\[
C(y,t) = C_0(t) \exp\left(-\frac{y^2}{4Dt}\right) \quad (i)
\]

where \(C(y,t)\) is the concentration of the diffusant (in this case gold) at depth \(y\) in the sample, and \(C_0(t)\) is the concentration at the surface where \(y = 0\); \(t\) is the diffusion annealing time, and \(D\) is the coefficient of volume diffusion. \(D\) is determined
from the slope of the linear function in (ii):

$$\ln C = -y^2/4Dt$$  \hspace{1cm} (ii)

The activation enthalpy, Q, for volume diffusion is given by the relationship (iii):

$$\ln D = -Q/RT$$ \hspace{1cm} (iii)

where \( R \) is the gas constant and \( T \) is the annealing temperature.

The interaction energy (binding energy) \( E_{VIC} \), of the components in the VICs is determined from Expression (iv) (12–14):

$$E_{VIC} = \left[ Q_{VIC} - Q \right]/2$$ \hspace{1cm} (iv)

where \( Q_{VIC} \) is the activation enthalpy for diffusion by ‘extrinsic’ vacancies dissociating from VICs.

**Results**

**Gold Profiles in Single-Ir after Annealing in UHV or TGV**

The volume diffusion of Au in Ir was studied using single-Ir. The materials, their preparation and measurement by secondary ion mass spectrometry (SIMS) are described elsewhere (20, 21).

The dependence of \( \ln I_{Au}/(y^2) \), where \( I_{Au} \) is the intensity of secondary Au ions, recorded during SIMS analysis of single-Ir annealed in TGV or UHV, and \( y^2 \) is the square of the depth \((y)\) in the Ir, is shown in Figures 1 and 2 (see Expressions (i) and (ii)). The same samples were annealed alternately in UHV or TGV in a random sequence of annealing temperatures.

The profiles of all the measured diffusion zones were characteristic of volume diffusion (7), that is, the dependencies, in \( I_{Au}/(y^2) \), were linear over a broad range of concentrations and remained linear up to the initial surface of the samples. In all cubic crystals the crystal orientation is not important for diffusion (6).

**Temperature Effects of Diffusion Coefficients in Single-Ir Annealed in UHV or TGV**

Diffusion in solids follows the Arrhenius equation, and the Arrhenius dependence of the coefficients of volume diffusion for Au in Ir, \( (D_{Au}^{Ir})_{UHV} \) and \( (D_{Au}^{Ir})_{TGV} \), are shown in Figure 3. At low temperatures \((1/T > 0.75)\) it can be seen that coefficients \( (D_{Au}^{Ir})_{TGV} \) are 3 to 4 orders of magnitude larger than coefficients \( (D_{Au}^{Ir})_{UHV} \). The parameters \( D_0 \) and \( Q \) of the Arrhenius dependencies of the coefficients of self diffusion, \( D_{SD} \), (3), and the coefficients of volume diffusion \( (D_{Au}^{Ir})_{UHV} \) and \( (D_{Au}^{Ir})_{TGV} \) are given in Table I.

**Discussion**

**Mechanism of Gold Diffusion in Single-Ir during Annealing in UHV and TGV**

The activation enthalpy for self diffusion, \( Q_{SD} \), (22) and the activation enthalpy for volume diffusion \( (Q_{Au}^{Ir})_{UHV} \) of Au in single-Ir under UHV conditions (see Table I) are related as Expression (v):
Expression (v) is characteristic of the volume diffusion of substitutional impurities assisted by equilibrium, ‘intrinsic’ vacancies in pure metals (6). The ‘intrinsic’ vacancies arise from thermal effects. However, for annealing Ir in a TGV we obtained:

\[ \frac{Q_{Au}^{Ir \text{ UHV}}}{Q_{SD}} = 0.43 \quad (\text{vi}) \]

It follows from Expressions (v) and (vi) that volume diffusion occurs by ‘extrinsic’ vacancies rather than by equilibrium ‘intrinsic’ vacancies during TGV annealing at temperatures below 2000 K (~ 0.73 Tm). Using Expression (iv) and the measured activation enthalpies for Au diffusion, the binding energy, \( E_{\text{VIC}} \), of the interaction between the components in the VICs can be determined from Expression (iv):

\[ E_{\text{VIC}} = 0.5 [(Q_{Au}^{Ir \text{ TGV}})^{\Delta} - (Q_{Au}^{Ir \text{ UHV}})^{\Delta}] \]
\[ = 0.5[(193 \pm 27) - (424 \pm 5)] \]
\[ = - (116 \pm 16) \text{ kJ mol}^{-1} \quad (\text{vii}) \]

The negative value indicates that stable VICs are formed during TGV annealing. The large value of \( |E_{\text{VIC}}| \) is important for determining the stability of point defect complexes. Stable VICs form in Ir during TGV annealing when \( T < 0.73 \text{ Tm} \).

Concentration of Interstitial Impurities and Excess Vacancies

Excess vacancies are induced by interstitial impurities in single-Ir during TGV annealing. The concentration, \( C_{\text{interm}} \), of the interstitial impurities which form VICs in single-Ir during TGV annealing is determined from the relationship of pre-exponential factors, \( D_0 \), in the Arrhenius dependencies of the corresponding diffusion coefficients:

\[ C_{\text{interm}} = \frac{D_{\text{VIC}}}{D_0} = 1.7 \times 10^{-10} \approx 3 \times 10^{-8} \text{ at. parts} \quad (\text{viii}) \]

This concentration of interstitial impurities that form VICs in single-Ir, \( C_{\text{interm}} \), is natural. The coefficients \( (D_0) \) of diffusion \( D_{\text{UHV}} \) and \( D_{\text{TGV}} \) of gold in Ir are related to the concentrations \( C_{\text{Vac,i}} \) of intrinsic or extrinsic types of vacancies and their diffusion coefficients \( D_{\text{Vac}} \) (6):

\[ D_i = D_{\text{Vac}} \times C_{\text{Vac,i}} \quad (\text{ix}) \]

\( D_i \) represents the gold diffusion coefficient in either UHV or TGV, \( D_{\text{Vac}} \) is the diffusion coefficient of vacancies which is the same for both \( D_i \). It follows from (ix) that the concentration \( (C_{\text{Vac,i}})^{\text{VIC}} = (C_{\text{Vac,i}})^{\text{extr}} \) of ‘extrinsic’ vacancies formed in TGV annealing is related to the concentration of equilibrium vacancies \( C_{\text{Vac}} = (C_{\text{Vac}})^{\text{intr}} \) formed in UHV annealing at each annealing temperature by the relationship between the corresponding diffusion coefficients \( D_{\text{TGV}} \) and \( D_{\text{UHV}} \), respectively. For example, at the annealing temperature of 1300 K:

\[ \{ (C_{\text{Vac}})^{\text{extr}} / (C_{\text{Vac}})^{\text{intr}} \}_{1300 \text{ K}} = (D_{\text{TGV}} / D_{\text{UHV}})_{1300 \text{ K}} \]
\[ \cong 2 \times 10^{-18} / 4 \times 10^{-22} = 5 \times 10^3 \quad (\text{x}) \]

Effects of VIC Participation in Mass Transfer of Impurities in Iridium

The industrial use of Ir for crucibles and sheathings that are heated in air at temperatures from 1300 to 1800 K, leads to the Ir being loaded...
with interstitial impurities, such as carbon, oxygen, hydrogen and nitrogen, from the ambient atmosphere or from the processed contents of the crucibles. Under these conditions, alloying of the iridium which contains these interstitial impurities causes, besides Ir embrittlement, saturation of the Ir volume with VICs and these, as described, supply excess ‘extrinsic’ vacancies that dissociate from the VICs.

Consequently, all substitutional impurities become capable of diffusing from the body of the Ir crucible through the walls. Their diffusion coefficients are several orders of magnitude higher than the diffusion coefficients for the same impurities in VIC-free Ir, see Figure 3. This explains the high permeability of Ir walls to impurities such as gold. In addition, the accumulation of VICs and pores adjacent to internal interfaces, including grain boundaries, causes fast creep in the Ir sheath (3) and intercrystalline fracture, which appears as a specific intercrystalline embrittlement (23).

In order to prevent the appearance and growth of VICs in Ir used at high temperatures in air, it is necessary to alloy the Ir with components that have a larger affinity for interstitial impurities than Ir, and form VICs with the impurities. Such VICs must possess the highest binding energies, E_{VIC}.

Typical components that will bind all interstitial impurities (oxygen, carbon and nitrogen) are hafnium or thorium, etc. Their melting points and their binding energy with the interstitial impurities (oxygen, hydrogen, nitrogen), that alloyed with single-Ir during TGV diffusion.

When products manufactured from Ir are heated to high temperatures in air, Ir alloys are doped with the interstitial impurities, which form the basis of the VICs and thus determine the ‘extrinsic’ mechanism of the volume diffusion of substitutional components in Ir.

Conclusions

The activation enthalpy of volume diffusion of Au in single crystals of Ir annealed in TGV is almost half the value of the activation enthalpy of the volume diffusion of Au into single crystals of Ir annealed in UHV. This difference is explained by the decisive contribution from ‘extrinsic’ vacancies that dissociate from the VICs, and is the cause of the large diffusivity of substitutional Au during TGV annealing.

The large negative binding energy of the VIC components, \(-116 \pm 16\) kJ mol\(^{-1}\), indicates that VICs are formed by vacancies with interstitial impurities (oxygen, hydrogen, nitrogen), that alloyed with single-Ir during TGV diffusion. When products manufactured from Ir are heated to high temperatures in air, Ir alloys are doped with the interstitial impurities, which form the basis of the VICs and thus determine the ‘extrinsic’ mechanism of the volume diffusion of substitutional components in Ir.

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2005 Nobel Prize in Chemistry
AWARDED FOR THE DEVELOPMENT OF THE METATHESIS REACTION IN ORGANIC SYNTHESIS

For creative, ingenious and skillful work in the field of olefin metathesis and organometallic chemistry, the Nobel Prize for Chemistry in 2005 was awarded to Yves Chauvin (Institut Français du Petrole), Robert H. Grubbs (California Institute of Technology) and Richard R. Schrock (Massachusetts Institute of Technology) (1).

The metathesis of alkenes is a remarkable catalytic process in which, under the action of a transition metal compound, denoted by M, two C=C double bonds in two alkene molecules are broken and two new C=C bonds are sequentially formed (2), according to a metallocarbene/metal-lacyclobutane mechanism first formulated by Chauvin (3). The two molecules may be identical (for example, two propene molecules afford ethylene and E/Z-2-butene), or different (for example, \( R_2C=CH_2 \) and \( R_2C=CH_2 \) yield ethylene and \( R_2C=CR' \)). In addition, an intramolecular ring-closing of a diene with two terminal double bonds, accompanied by the release of ethylene, has been developed. The preferred catalysts are based on \( M = \) tungsten, rhenium, molybdenum, or ruthenium compounds: with the last two types enjoying widespread applications in both organic and polymer synthesis, mainly due to extensive research by Schrock (4) and Grubbs (5). By varying substituents on the olefin substrate, a wide range of further olefinic products become readily accessible, while monocyclic or polycyclic olefins provide polymers with unprecedented structures and properties (6).

First observed in the 1950s by H. S. Eleuterio (7), and subsequently by R. L. Banks, G. C. Bailey, W. E. Truett and others, the alkene metathesis reaction (a term coined by Calderon) and the related ring-opening metathesis polymerisation (ROMP) were developed in the following decades by many scientists, each bringing remarkable contributions to this productive area of organic synthesis and catalysis (8).

However, it was only in 1971 that a metal-carbene intermediate was proposed by Y. Chauvin and his student J.-L. Hérisson, to explain – satisfactorily for the first time – the mechanism (3). This extraordinary mechanistic proposal, rationalising Chauvin’s astonishing new observations, was immediately embraced by the metathesis community and prompted studies on metal-carbene initiators culminating in the creation of the molybdenum-alkylidene catalysts by R. R. Schrock, see Figure 1 (9), and the 1st and 2nd generation of ruthenium-alkylidene catalysts, by R. H. Grubbs, see Figure 2 (10).

The 2005 Nobel Laureates in Chemistry

Yves Chauvin
Nobelprize.org; ©Nobel Web AB

Robert H. Grubbs
Courtesy of Caltech

Richard R. Schrock
photo: L. Barry Hetherington
These transition metal alkylidene complexes, in themselves a fine artwork in organometallic synthesis, allow extensive practical applications. Some are commercially available and used worldwide, applicable to large-scale or combinatorial syntheses. Full utilisation of these versatile catalysts is just beginning, and by efficient and environmentally-friendly protocols they have opened many ways for obtaining a large variety of organic compounds and natural products with intricate structures, routinely used pharmaceutical intermediates, pesticides, polymers, and composite materials.

Remarkably, the above two types of metathesis catalysts have their own merits and distinctive features thus broadening even more their areas of application. For instance, Schrock’s molybdenum-based catalysts, Figure 1, display high activity and selectivity, while Grubbs’ ruthenium-based catalysts, Figure 2, are more tolerant to water and functionalities. With these catalysts, the promise of “green chemistry” in organic synthesis is Dawning.

In addition to alkene metathesis and ROMP reactions, involving eight electrons (8e⁻), related processes are now known (11). These formally involve: 4e⁻ (σ-bond metathesis); 6e⁻ (alkane/alkene insertion); 10e⁻ (alkyne polymerisation, and enyne metathesis) (12), or 12e⁻ (alkyne metathesis).

Acronyms of other reactions based on metathesis are: ADMET (acyclic diene metathesis), RCM (ring-closing metathesis), ARCM (asymmetric ring-closing metathesis) and ROM (ring-opening metathesis).

Ruthenium has featured before in Nobel Prize work (13), and it plays a key role in building modern metathesis catalysts. Reviews reflecting the outpouring of rapid developments in ruthenium-based catalysis for metathesis have been and are being published in this Journal (14).

Lastly, over the past few years, metal-catalysed olefin metathesis has had an enormous impact on organic synthesis, and is emerging as one of the most often used chemical transformations (15). By awarding the 2005 Nobel Prize for Chemistry to Chauvin, Grubbs and Schrock, the outstanding contribution resulting from metathesis for the progress of human society has now been rightfully recognised.

V. DRAGUTAN, I. DRAGUTAN AND A. T. BALABAN

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Some prominent scientists who have worked on metathesis reactions


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**Fig 1. The Schrock catalyst**

**Fig 2 (a) First, (b) second generation Grubbs’ catalysts**

_R is phenyl or cyclohexyl; Mes is mesityl_
References


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The Ninth Grove Fuel Cell Symposium
BUILDING AND COMMERCIALISATION OF A FUEL CELL INDUSTRY – A PROGRESS REPORT

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The Ninth Grove Fuel Cell Symposium and exhibition was held at the prestigious Queen Elizabeth II Conference Centre in Westminster, London, from 4th to 6th October 2005. This bimannual event is now the largest fuel cell gathering in Europe, this one attracting 480 delegates from 38 countries (1, 2). Some 54 papers were presented, and 186 posters were displayed. A further 760 people attended the associated trade exhibition, and a half-day demonstration of fuel cell vehicles and technology was held in Trafalgar Square. The latter attracted considerable public and media attention. Because of the wide range of fuel cell types and applications is now available, this article is restricted mainly to those associated with the utilisation of the platinum group metals.

Facts on Global Warming
Professor Lars Sjunnesson, the Symposium Chairman, welcomed the delegates and introduced Professor Sir David King (Chief Scientific Adviser to the U.K. Government) who spoke on ‘The Science of Climate Change: the Challenge of Global Warming’ (3). As long ago as the 19th century, noted scientists, such as Fourier and Tyndall, began to speculate about the effects of increased carbon dioxide (CO₂) in the atmosphere, while in 1896 Arrhenius forecast that a doubling of CO₂ levels would result in a 5°C global temperature rise. This agrees well with the latest forecast of a rise of 3 to 7°C. Carbon dioxide levels, having remained stable at 180-270 parts per million (ppm) for millions of years, currently stand at 379 ppm and are forecast to exceed 500 ppm at our current rate of consumption of fossil fuels.

There were an estimated 30,000 fatalities in Europe, in 2003, as a result of high temperatures, but because of global warming, by 2050 the average temperature is likely to equal the 2003 extremes. This is one of the main driving forces for finding more efficient ways to utilise fossil fuels and seek alternative renewable energy sources. Iceland is leading the way: having decided to move to a hydrogen economy. In future all vehicles there will be powered by hydrogen or fuel cells.

Grove Medal Presentation
Professor King then presented the Grove Medal for 2005 to Alan Lloyd (California Environmental Protection Agency) who described himself as “an environmental person with a job to do” rather than specifically a fuel cell advocate. The quality of air in California has improved in recent years, however, particulates have also increased. A number of organisations have been set up to introduce clean energy supplies and clean vehicles. Some 50 stationary fuel cells totalling 10 MW have been installed, and the California Fuel Cell Partnership is demonstrating a fleet of vehicles. The California Hydrogen Highway should result in 50 to 100 hydrogen fuelling stations able to supply 2000 vehicles by 2010. This fuel network is being extended up the west coast of the U.S.A. and into Canada. Other areas, in the U.S.A., Japan and Germany, are being equipped with hydrogen refuelling facilities.

The European Position
Professor Werner Tillmetz (ZSW, Germany) surveyed the technology being developed for fuel cells under the 7th Framework Programme organised by the European Commission. Within the European Union (EU), fuel cells are seen as important for job creation in the longer term, as well as facilitating a change to hydrogen and biomass fuels to safeguard energy supplies. Over 100 light passenger vehicles are in daily use, and 40 fuel cell buses have spent more than 2 years in passenger service. Worldwide, more than 350 vehicles are undergoing fleet tests and product development.
Early markets are envisaged for fuel cell motor cycles (see Figure 1) and scooters, go-carts, fork lift trucks, uninterruptible power supplies, marine and auxiliary power supplies, while military applications represent early niche markets for similar products. Over 3500 small portable units have already been sold for demonstration and niche markets. More than 100 units, each of 1-5 kW are currently installed in domestic combined heat and power applications within the EU, and many of these are providing over 80% thermal efficiency. These have electricity grid connection.

Michael Fübi (RWE Fuel Cells, Germany) provided an overview of the stationary fuel cell market. There is increasing interest in utilising renewable energy, with manure, sewerage and farm wastes, coal mine and landfill gases representing huge untapped energy resources, as well as presenting critical disposal problems. Molten carbonate fuel cells can utilise hydrogen derived from these sources. Several 250 kW plants built by MTU CFC Solutions have been extensively demonstrated, and one has been operating on natural gas in Magdeburg, Germany, since December 2002, accumulating over 23,500 hours of power generation. As operation on natural gas has been successfully demonstrated, a plant running on biomass anaerobic digester gas was begun in July 2005. Applications for these combined heat and power units include hospitals, telecommunications companies, the food industry and sewerage works. For smaller generators of up to 10 kW, there is an estimated demand for 50,000 units per year in the EU alone for commercial applications, while a much larger market exists for smaller fuel cells for residential use.

William Ernst (Plug Power, U.S.A.) described an early market for small fuel cells in his talk entitled ‘Small-Scale Dispersed Stationary Systems - a Status Report’. Generators of 1-20 kW, most of which are based on polymer electrolyte membrane (PEM) fuel cells catalysed by platinum, are rapidly finding an increasing range of uses for cell-phone network supplies, microwave repeater stations, pipeline monitoring stations, and cathodic protection. Plug Power have produced over 500 systems to date, and the eventual market for this type of device was quoted as $3.6 billion. Even at the current cost of $3000 kW$^{-1}$, economic niche markets are beginning to emerge as fuel cells can provide unique solutions for standby and auxiliary power supplies. In the United States, a Federal tax credit of 30% (up to $1000) of the capital cost is helping to develop a market that is expected to mature between 2010 and 2020.

**Road Vehicles and Auxiliary Power Supplies**

Yuji Kawaguchi (Honda Fuel Cell Power, Japan) gave details of their passenger vehicle development programme. This was begun in the 1980s, and has culminated in the latest Honda FCX which is now fully certified for road use, and offered for public rental. The high power density fuel cell

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**Fig. 1** This ENV motorbike, demonstrated by Intelligent Energy, features a 1 kW PEM-type power pack fuelled by compressed hydrogen. The hybrid design, when used in combination with lead acid batteries, gives a top speed of 80 kmph and a range of over 160 km. The power pack is easily removed for independent use.
developed by Honda for the purpose is suitable for volume production.

For peak power it is augmented by an ultra-capacitor giving a total of 80 kW. The fuel cell develops 50 kW, has a volume of 33 litres and a weight of 48 kg. It operates at 95°C and is capable of start-up from -20°C. This platinum-catalysed fuel cell has an aromatic electrolyte membrane containing sulfonate groups, providing conductivity twice that of conventional proton exchange membranes at -20°C. The stamped metal separator plates have a stainless steel base with an oxidised surface containing electrically conductive inclusions to provide contact resistance of less than one quarter of equivalent carbon plates, and weighing 20% less. Using the stamped separators halves the thickness of the cell compared to standard construction methods. Their inherent springiness means that fewer compression components are required. The Honda FCX vehicle has a weight of 1670 kg, and range of 430 km on hydrogen compressed to 350 bar, with a top speed of 150 km h⁻¹. The first models were delivered in 2002, in Japan and the U.S.A., and one vehicle is in use in California for personal daily commuting.

Massimo Venturi (NuCellSys, and formerly of Ballard Power Systems, Germany) described the progress made for buses during various demonstration programmes. The EU sponsored Clean Urban Transport Experiment (CUTE) trials involves 30 buses, see Figure 2. By July 2005 this fleet had operated for 60,000 hours and 850,000 km. The trials have shown that fuel cell engines have proven functionality and availability in commercial use. Reliability has been dramatically improved, with mean times between failures now about 3 times longer than at the start of the trials due to implemented improvements. For example, start-up times have been improved simply by making changes to computer software. Improvements still needed for a fully viable commercial product include longer fuel cell lifetimes (at least 5000 hours), increased power density and competitive cost.

Power for Consumer Electronics

According to George Apanel (SRI Consulting, U.S.A.) consumer electronics could provide one of the first large markets for fuel cells and provide a revolution in personal devices. Costs are already competitive – with rechargeable batteries for many applications – and, on a cost per watt basis, are up to 80% lower. At equal weights, fuel cells can provide 5-10 times the operating time of an advanced battery. However, the main advantage is the ability to recharge fuel cells instantly with a cartridge of liquid fuel, such as methanol. Commercially viable

Fig. 2 This DaimlerChrysler Citaro bus was used at the Symposium for taking delegates on tours of London sights. There are three such fuel cell buses in service in London. In total, 30 such buses are being evaluated in European cities under CUTE, the European Union sponsored Clean Urban Transport Experiment.
direct methanol fuel cells (DMFCs) are expected to be widely available within 2 years, and there is a huge opportunity provided by the 470 million consumer electronic devices sold worldwide. This market is growing at 10% per annum. A DMFC for portable use is in Figure 3.

Shimshon Gottesfeld (MTI Microfuel Cells, U.S.A.) explained that battery technology has traditionally lagged behind telecommunications technology. Ideally, power supplies with a five-fold power density are needed for devices such as wireless local area networks, digital television, hard disk drives and radio tuners. MTI have developed a method of operating DMFCs to overcome some of the limitations of this system. By running these cells at high current density, the methanol oxidation reaction reaches zero order. The Pt/Ru catalysed anodes can be fed with concentrated methanol, which is consumed before it has the opportunity to diffuse to the air cathodes (which have 6 mg cm$^{-2}$ platinum loadings), where it would otherwise cause mixed potentials. In addition, there is a spontaneous transfer of water from the cathode to the anode helping to suppress methanol diffusion. The cells provide power of 35 mW cm$^{-2}$ with 30% conversion efficiency of the fuel. These Mobion® cells are being used by an industrial customer to power a radio frequency identity (RFID) tag reader. The fuel cell has an output of 1 W for 35 hours (that is 35 W h), compared to the 8 Wh provided by the normal Li-ion battery.

The high energy density of methanol as an energy store explains the huge increase in interest in these devices in the past few years. The Mobion® cells yield around 1100 Wh l$^{-1}$ at 30% conversion efficiency, compared to 200 Wh l$^{-1}$ for advanced lithium prismatic batteries. This provides an enormous incentive and an opportunity for electrical device manufacturers to utilise this higher available power in an even wider range of devices. In the immediate future, the military domain is seen as the first large niche market for DMFCs from a cost point of view, in applications such as cord-free rechargeable power pack technologies. Hybrid battery/fuel cell applications are ideal since DMFCs are able to provide relatively low power outputs for long periods with high ampere-hour capacities.

Peter Gray (Johnson Matthey Fuel Cells, U.K.) reviewed some of the advances made in catalysts and membrane electrode assemblies (MEAs) for DMFCs, and explained how these are underpinning development of devices for portable power and consumer electronics. Applications being considered for DMFCs include recreational vehicles, boats and isolated dwellings, as well as remotely located telecommunications stations, traffic signs, weather stations, pipeline monitoring, etc. There are huge numbers of devices requiring less than 25 W, including laptop computers, personal digital assistants, camcorders and mobile telephones. These require MEAs giving high performance at temperatures close to ambient, and self regulation of water and fuel, as well as being of

**Fig. 3 A direct methanol fuel cell produced by Smart Fuel Cell. This was operated at the exhibition alongside the Symposium. Its output is 50 W at 4 A; methanol consumption is 1.3 l kWh$^{-1}$; and its overall weight is 8 kg.**
low cost. Activation polarisation at the methanol electrode is still the main performance limitation of DMFCs, despite the availability of catalysts, such as carbon supported Pt/Ru with upwards of 100 m$^2$ g$^{-1}$ surface area, and self-supported Pt/Ru alloy catalysts with 70 m$^2$ g$^{-1}$. MEAs have demonstrated lifetimes in excess of 4000 hours and power densities of 100 mW cm$^{-2}$. This equates to 500 mV at 200 mA cm$^{-2}$ at 60°C - a relatively high operating voltage that is desirable for good energy conversion efficiency.

Traditionally, the platinum metals industry has responded to increased demand for materials by increasing production. The emergence of the automotive catalyst industry posed no problems, and similarly, steadily growing demand for fuel cells should create no difficulty. Gray emphasised that there are substantial reserves of platinum available for fuel cell development, and also the fact that at the end of life, over 90% of the platinum group metals can be recovered and recycled. Products can be designed for ease of metal recovery as well as efficient manufacture. In fact, according to Philip Crowson, formerly Chief Economist of RTZ, at current rates of use, two-thirds of the metals in the Periodic Table will run out before platinum.

**Military Applications**

The power and energy demands for future U.S. Army programmes, such as Future Force Warrior and Future Combat System, require a revolution in power supplies, and fuel cells are viewed as a technology that may meet many of the military’s power needs. Chris Bolton (U.S. Army Research, Development and Engineering Command (RDECOM)) outlined three applications where fuel cells are being evaluated for possible military use. These are soldier and sensor power (under 100 W), man-portable power sources (100-500 W) and small mobile power units (0.5-10 kW). Fuel cells larger than 10 kW face competition from other power sources, such as diesel and Stirling engines. RDECOM is evaluating fuel cells supplied by a number of manufacturers and has drawn up preliminary specifications for a 20 W tactical power system for the Land Warrior Program, with a goal of 600-700 Wh kg$^{-1}$ (including fuel) for a 72-hour mission. However, the life of competing rechargeable batteries is reduced by high ambient temperatures, experiencing up to a 2-3 fold decrease in extreme environments, which further renders fuel cells even more economic as battery replacements.

George Cipriano (Protonex, U.S.A.) outlined some of their work on direct and reformed methanol fuel cells. Most of these are hybrid systems with batteries providing peak power, in a size range of 10-500 W. One 30 W continuous PEM fuel cell man-portable system designed for a 72-hour mission operates on sodium borohydride fuel which is decomposed to provide hydrogen when required. This provides an energy density of 380 Wh kg$^{-1}$, compared to 150 Wh kg$^{-1}$ for lithium batteries and 130 Wh kg$^{-1}$ for rechargeable cells. Further developments are projected to increase the fuel cell energy density to 800-1000 Wh kg$^{-1}$.

One major contrast with battery power is that for missions of longer duration, the fuel cell unit remains the same, and only additional fuel cartridges need to be carried. The use of portable fuel cell battery chargers for frontline soldiers is also being evaluated by the British Ministry of Defence, according to Angus Johnson (Thales Ltd., U.K.). Typically, a company of soldiers requires 183 batteries for a 48-hour frontline mission on the battlefield, under a wide variety of environments.

Great advances in reliability and safety enable fuel cells to be the sole power source for a new generation of submarines. S. Krummrich (HDW Fuel Cell Systems GmbH, Germany) stated that at least 16 Type U212A boats are being supplied to a number of navies, including those of Germany, Greece, Italy, Portugal and South Korea. These boats use platinum-catalysed PEM fuel cell modules, each of 72 cells, made by Siemens. Nine of these provide around 30 kW each, operating at 70-90°C with fuel conversion efficiencies of 72% at 20% of rated load and 62% at full load. Hydrogen fuel is stored on board the vessel in the form of hydrides, while the oxidant is liquid oxygen. The whole propulsion system must be self-contained, with navies using fuel cell submarines.
provision for disposing of waste heat, product water, purge gases, etc. Product water, for example, is used during the whole mission for the sanitary equipment on board. The fuel cell modules are connected in series by diodes using double bus bars to eliminate magnetic fields, and a hybrid arrangement with conventional lead-acid batteries is used for high speed operation. The propulsion load defines the main bus bar voltage, and the system normally operates using only the fuel cell assembly. For high current demands, as the bus bar voltage falls, an increasing load is taken from the batteries in combination with the fuel cells.

Darren Browning (DSTL, U.K.) outlined their programme on fuel cells for a variety of military applications, including propulsion systems for unmanned underwater vessels, unmanned aerial vehicles, sonobuoys and army equipment. Their target specification is 600-1000 Wh kg\(^{-1}\), which is 5 to 6 times the energy density of silver-zinc or lithium-ion batteries. For a variety of reasons, direct borohydride fuel cells have been selected for development. Sodium and potassium borohydrides are stable in highly alkaline solution, and these are used in alkaline electrolyte fuel cells with Pt/C catalysts for the cathode and an anion exchange membrane. For the anode catalyst, several materials have been evaluated, the optimum being high surface area gold dispersed on carbon, which exhibits good electrochemical activity, but low rates of spontaneous borohydride hydrolysis. In comparison, Pt/Ru or Au/Pt catalysts provide higher anode activity than gold, but hydrolyse the reagent. Work is underway to synthesise and evaluate suitable anionic membrane materials to minimise borohydride migration to the cathode.

A fleet of residential proton exchange membrane fuel cells, produced by manufacturers in the U.S.A., is being evaluated at military and civil facilities by the U.S. Army Engineer Research and Development Center/Construction Engineering Research Laboratory (ERDC/CERL). These premises include office buildings, hospitals, industrial facilities, barracks and gymnasiums, etc., all of which can benefit from improved power generation efficiency and security of supply. M. White (Jones Technologies, Inc., U.S.A.) introduced some of their preliminary findings. Domestically-produced proton exchange membrane fuel cells of 1-20 kW output are being evaluated at various U.S. military installations and embassies. Their manufacturers include Idatech, Plug Power, Nuvera, ReliOn, and Logan Energy. One fuel cell will be installed in the U.S. Embassy in Grosvenor Square, London. A great diversity of installations is being sought; units are required to provide a minimum of one year of fuel cell power with at least 90% availability. Although the program has been running for 4 fiscal years, delays in implementation mean that results are only available from the first two years. A total of 92 fuel cells will be sited at 56 DoD facilities. Results from 34 fuel cells at 24 sites are so far available.

The fuel cell units have achieved 82-90% reliability, although not all the units have completed the one-year demonstration. Overall, the project has accumulated 115,000 operating hours, with an average conversion efficiency for natural gas of 31.7%. The most commonly replaced components were steam filters, pumps, and supply lines, while the second most common were water filters, including reverse osmosis units, carbon filters, de-ionising units and other associated parts. Fuel cell stacks were replaced on average after 2485 hours, although 4 of the 11 natural gas fired units that ran for over a year did not require replacement stacks. One stack has operated for over 10,250 hours to date. All of the stack replacements took place before they failed completely. However, it has been concluded that the weakest parts of the installation are the steam and filtration systems. The study will continue for at least another two years, and improvements in designs resulting from information feedback should considerably improve the systems during this time.

Residential Combined Heat and Power

Small fuel cells are being demonstrated as a prelude to commercial exploitation. J. Heinen (RWE Fuel Cells GmbH, Germany) explained they are one of the companies active in this field, with partners BBT Thermotechnik (Germany) and IdaTech.
LLC (U.S.A.). Currently, twelve 4.6 kW units are being evaluated in multi-family houses and small commercial applications, with a further 25 units planned for the end of the year. Operating on natural gas, they provide 30% conversion of natural gas to electricity, with an overall 80–83% efficiency including heat recovery. The devices can be connected to the electric utility grid to enable optimum utilisation of the generating capacity. RWE is exploring the possibility of acting as an energy service supplier who owns and maintains the devices, selling electricity and heat to the consumer.

**Individual Homes**

The single family house is also a possible market for fuel cells. In his talk entitled 'Micro Combined Heat and Power Generation', G. Gummert (European fuel cell gmbh, Germany, now part of the Baxi Group) detailed their programme to develop residential fuel cells. The potential scale of this market is illustrated by the fact that Baxi produce 800,000 central heating boilers and 500,000 water heaters annually. A 1.5 kW reformer/proton exchange membrane fuel cell system has been developed, and provides an additional 3 kW of recovered heat. Natural gas, their preferred fuel, is now supplied to 75% of new houses in Europe. While 1.5 kW represents 70% of the total power requirements, 3 kW provides 65% of the need for heat.

M. Kawamara (Tokyo Gas, Japan) described the Japanese national effort to develop proton exchange membrane fuel cell systems for residential applications. One was installed in the Japanese Prime Minister’s official residence in April 2005. The units, built by Matsushita Electric Industrial Co. Ltd. and Ebara Ballard Corporation, consist of a 1 kW reformer/fuel cell unit and a hot water unit. The device is grid connected, with an inverter to provide AC mains power for the consumer. A 200 litre storage tank provides hot water for domestic use. Over 400 units have been built this year; 175 were installed in the first 6 months. It is planned to build up to 10,000 units by 2008, and tens of thousands of units after 2010. Ultimately, the Japanese market is seen as up to 1.5 million units per year at prices of less than $10,000 each.

**The Future of Fuel Cells and Hydrogen**

The final session of the Symposium looked forward to the challenges and future prospects for hydrogen and fuel cells. Pablo Fernandez-Ruiz, a member of the Advisory Council of the Hydrogen and Fuel Cell Technology Platform of the European Commission in Belgium, stressed that the EU currently imports 50% of its energy needs, which is forecast to rise to 70% by 2030. In an effort to stem this rise, under the 7th Framework Programme for 2007-2013, EU funding for energy research will be doubled to 10 billion Euros, with basic research attracting 1.5 billion per year.

Valri Lightner (U.S. Department of Energy) detailed the Hydrogen Fuel Initiative which commits $1.7 billion for the first five years (2004-2008) of which $1.2 billion is for the realisation of the hydrogen economy and fuel cells. The United States is focusing on energy supplies, particularly the energy needs for transportation, as two-thirds of oil is used for this purpose. Surprisingly, heavy vehicles and light trucks account for higher fuel usage than private cars. Natural gas is one of the best distributed and cheapest sources of energy for hydrogen production in the U.S.A., while coal (combined with CO₂ sequestration) is also regarded as a potential fuel. Fuel cell costs need to be reduced to a target of around $30 kW⁻¹, compared to a current estimated cost of $110 kW⁻¹, when a production rate of 500,000 units per year is assumed. The barriers to achieving wide scale deployment of fuel cells are thought to be codes and standards, the investment required for a hydrogen generation and distribution network, and educating the public, rather than any technical hurdle.

**Summary**

A host of manufacturers of fuel cells, components and associated equipment is emerging, and many of their products were exhibited at the Symposium. Small fuel cells of up to 5 kW are already finding niche markets as standby generators in residential combined heat and power applications and consumer electronics. In the latter example, there are considerable incentives for con-
sumers, and customers are likely to be willing to pay a premium price. However, it is evident that costs must be substantially reduced for widespread transport applications to emerge, even for buses. But for stationary applications, increasing manufacturing capacity is likely to reduce costs considerably.

**Associated Exhibitions and Demonstrations**

On the afternoon preceding the Symposium, a demonstration of fuel cell technology was held in Trafalgar Square. This attracted wide public and press interest, and included an Intelligent Energy motorcycle (Figure 1), a DaimlerChrysler Citaro fuel cell bus (Figure 2), a DaimlerChrysler F-Cell A-class car (Figure 4), a BOC Echo2O car, a Microcab fuel cell taxi, and a Ballard Airgen unit, and on a trailer the London Hydrogen Partnership fuel cell, and a Tees Valley fuel cell powered mobile information sign. The exhibition included a large marquee open to the public containing a host of displays and smaller exhibits including: MTU CFC Solutions, Baxi Group, siGEN, Johnson Matthey, three U.K. universities, Ceres Power, Voller Energy, the London Hydrogen Partnership, and Transport for London. Fuel Cells Canada featured a Scalextrix miniature racetrack which the adults present reluctantly allowed children to use.

The Trafalgar Square exhibits were later moved to the Queen Elizabeth Conference Centre where the exhibition attracted over 85 organisations, including fuel cell manufacturers (many with working demonstrations), component suppliers and users. The DaimlerChrysler bus proved very popular, taking delegates for regular sightseeing tours around London. A special edition of the *Journal of Power Sources*, will carry the full papers.

**Bibliography**


**The Reviewer**

Don Cameron is an Independent Consultant on the technology of fuel cells and electrolyses. He is a member of several Working Groups of the International Electrotechnical Commission, Technical Committee 105 on fuel cell standards. He is also Secretary of the Grove Symposium Steering Committee.

Other fuel cell conferences can be found by visiting the PMR Events Calendar and browsing the listings or selecting ‘Fuel Cells’ from the drop down menu at: http://www.platinummetalsreview.com/dynamic/event/list

A list of all PMR fuel cell articles is freely available at: http://www.fuelcelltoday.com/FuelCellToday/PMR Links
ABSTRACTS

of current literature on the platinum metals and their alloys

PROPERTIES

Nanoscale Precipitates and Phase Transformations in a Rapidly-Solidified Fe–Pt–B Amorphous Alloy


XRD and calorimetry were used to study the phase transformations on heating of rapidly solidified (Fe0.75Pt0.25)75B25. TEM established the existence of nano-scale cubic cF4 Fe(Pt) solid solution particles within the as-solidified amorphous matrix. The particles of the cF4 Fe(Pt) phase start growing at elevated temperature and undergo ordering to form a tP4 FePt compound followed by the precipitation of a t12 Fe2B phase from the residual amorphous matrix.

The High-Pressure Modification of CePtSn – Synthesis, Structure, and Magnetic Properties


High-pressure (HP) modification of CePtSn was carried out under multianvil high pressure (9.2 GPa) and high temperature (1325 K) conditions from the normal-pressure modification. Both modifications are built up from Pt centred trigonal prisms. Together, the Pt and Sn atoms form different 3D [PtSn] networks in which the Ce atoms fill channels. Susceptibility measurements of HP-CePtSn indicate Curie-Weiss behaviour above 40 K with an experimental magnetic moment of 2.55(1) μB/Ce atom, indicating trivalent Ce.

Chemical Synthesis and Magnetic Properties of Well-Coupled FePt/Fe Composite Nanotubes


Heating a porous Al2O3 template loaded with an alcohol solution of a Fe chloride and Pt chloride mixture in flowing H2 at 670ºC gave L10 FePt nanotubes. TEM showed the existence of nano-scale cubic cF4 Fe(Pt) solid solution particles within the as-solidified amorphous matrix. The particles of the cF4 Fe(Pt) phase start growing at elevated temperature and undergo ordering to form a tP4 FePt compound followed by the precipitation of a t12 Fe2B phase from the residual amorphous matrix.

Heats of Displacement of Hydrogen from Palladium by Noble Gases


Noble gases (He, Ne, Ar) produced heat evolution when contacted with Pd powder partially saturated with H. The noble gases displace the adsorbed H species from the Pd surface, causing their reabsorption in the Pd lattice with the exothermic heat of Pd–H bond formation, or the formation of H2.

Properties of the Quaternary Amorphous Alloy

Pd48Ni4B24P18


The title alloy (1) was prepared in bulk form, without the use of B2O3 flux, by 50% substitution of B for P in the Pd48Ni4B24 system. (1) was shown to be largely amorphous by neutron and X-ray diffraction and DSC. The XPS data suggest partial substitution of B for P. With the addition of B, glass-forming ability without any fluxing compound was demonstrated.

Stress Evolution in Sputter-Deposited Fe–Pd Shape-Memory Thin Films


Fe-26–30 at.% Pd films (1) were deposited by magnetron sputtering. (1) are highly saturated solid solutions of Pd in Fe with a b.c.c. crystal structure and very fine grain size. (1) undergo an irreversible densification at > 100°C. The high-temperature austenite phase can be retained at low temperature by annealing (1) at 900°C followed by rapid cooling. Depending on the composition of (1), the metastable austenitic phase transforms to either a b.c.t. or a f.c.t. martensite at room temperature. Formation of the f.c.t. martensite is reversible.

Reactive Diffusion between Pd and Sn at Solid-State Temperatures


Sn/Pd/Sn diffusion couples (1) were prepared by a diffusion bonding technique. (1) were isothermally annealed between T = 433 and 473 K for various times in a silicone oil bath. PdSn1, PdSn2 and PdSn3 compound layers were observed at T = 433 K, but only PdSn2 and PdSn3 layers were found at T = 453 and 473 K. Volume diffusion was the rate-controlling process of the reactive diffusion between Pd and Sn.

Saturated Solid-Solution Hardening Behavior of Ir–Hf–Nb Refractory Superalloys for Ultra-High Temperature Applications


In Ir–3Hf–5Nb the solubility limitation of solutes Hf and Nb in the Ir solid solution is close to Ir–3Hf5Sn1 (1). (1) has a monolithic saturated f.c.c. structure, and a 0.2% yield strength of 140 MPa, even at 1950°C, compared with 19.7 MPa for pure Ir. A large solid-solution hardening effect is obtained in the Ir alloys, in which the solutes have a large misfit parameter with Ir and a small solubility limitation.
CHEMICAL COMPOUNDS
Solvent-Induced Supramolecular Isomerism in [Pt(S=MeCp)Cl]Cl2 and [Pt(S=MeCp)Cl]Br2

Slow diffusion of acetone into a 1:1 mixture of tetrakis(thiourea)Pt(II) dichloride and croconic acid dissolved salt in DMSO–H2O gave crystals of [Pt(SC(NH2)2)2][C6H6]·2DMF. (1) forms a 3D H-bonded assembly containing two types of channels that accommodate the solvent molecules. The DMSO molecules within the smaller channels are held by two H bonds; the larger channels contain solvent held by only one H bond.

Electrochemical Detection of Organohalides

Pt-Zn porphyrin nanocomposites (1) were synthesised using zinc porphyrin and H2PtCl6 in MeOH. The magnetic properties of [Ru(CH2NO)3]·MeOH (1) relate to the antiferromagnetic coupling of the Ru centres in the crystal lattice. The EPR spectrum of (1) indicates a single isotropic line only, characteristic of Ru 2+, with spin equal to 1/2.

PHOTOCONVERSION
Red Electrophosphorescence of Conjugated Organoplatinum(II) Polymers Prepared via Direct Metalation of Poly[(fluorene-co-tetraphenylporphyrin)] Copolymers

PL decay studies indicated that polyfluorene-co-tetraphenylporphyrin Pt(II) (PFO-PtTPP) is a triplet emitter. EL emission from the fluorene segment was completely quenched for copolymers with PtTPP content as low as 0.5 mol%. The external quantum efficiency of ITO/PEDT/PVK/PFO-PtTPP (1 mol%) + PBD (40 wt.%)/Ba/Al was 0.43%.

Single-Layer Electroluminescent Devices and Photoinduced Hydrogen Production from an Ionic Iridium(III) Complex

[Ir(df(CF3)ppy)2(dtbbpy)](PF6) (df(CF3)ppy = 2-(2,4-difluorophenyl)-5-trifluoromethylpyridine; dtbbpy = 4,4’-di-tert-butyl-2,2’-dipyridyl) can be used as a chromophore in single-layer electroluminescent devices and as a photosensitiser for H2 production. The blue-green electroluminescent emission (500 nm) and relative quantum yield of H2 (2025 µmol H2) were at the time of publication the highest values to date.

SYNTHESIS, CHARACTERIZATION AND FABRICATION OF SOLAR CELLS USING [Ru(dcbpy)(tptz)X]X (WHERE X = Cl–, SCN–, CN–) COMPLEXES

Dye-sensitised TiO2 solar cells were fabricated using [Ru(dcbpy)(tptz)]X (dcbbpy = 4,4’-dicarboxy-2,2’-bipyridine; tptz = 2,4,6-tris(2-pyridyl)-s-triazine; X = Cl–, SCN–, CN–) attached to sol gel processed TiO2 electrodes. The tptz functions as a spectator ligand, whereas the dcbpy functions as the anchoring ligand with sufficient visible light absorption.

SURFACE COATINGS
Al–Pt MOCVD Coatings for the Protection of Ti6242 Alloy Against Oxidation at Elevated Temperature

Al–Pt coatings (1) were obtained by MOCVD using Me3(MeCp)Pt and AlH3·N(C3H7)(C3H4). The isothermal oxidation at 873 K of (1) on Ti6242 coupons was carried out for 90 h. Oxidation kinetics revealed a strong transient oxidation regime followed by a diffusion driven parabolic one. (1) are dense, develop scales composed of γ-Al2O3 and δ-Al2O3 and they prevent Ti diffusion from the alloy to the surface.

ELECTROCHEMISTRY
Light-Assisted Synthesis of Pt–Zn Porphyrin Nanocomposites and Their Use for Electrochemical Detection of Organohalides

Pt–Zn porphyrin nanocomposites (1) were synthesised using zinc porphyrin and H2PtCl6 in the presence of light and ascorbic acid. The Pt nanoparticles were embedded within the Zn porphyrin matrix. A glassy C electrode was modified with Nafion-stabilised (1) and used for dehalogenation of carbon tetrachloride, chloroform, pentachlorophenol, chlorobenzene and hexachlorobenzene. The modified electrode exhibited catalytic activity for the reduction of the organohalides at −1.0 V vs. Ag/AgCl.

Electrochemical Behaviour of Amorphous and Nanoquasicrystalline Zr–Pd and Zr–Pt Alloys in Different Environments

Melt spun amorphous and nanoquasicrystalline Zr–Pd85 (1) and Zr50Pt20 (2) alloy ribbons show better corrosion resistance than Zr in all solutions studied. Both are susceptible to chloride attack and pitting has been observed. Complete passivation was observed in H2SO4, while gradual breakdown of the passivating layer occurs in NaOH. In general, the nanoquasicrystalline state in (1) and (2) shows better corrosion resistance than the amorphous state.
**HETEROGENEOUS CATALYSIS**

**XAFS Characterization of Pt-Fe/Zeolite Catalysts for Preferential Oxidation of CO in Hydrogen Fuel Gases**


Pt-Fe/mordenite catalyst (1) showed high activity and selectivity for the oxidation of CO in H₂-rich gas compared with Pt/mordenite. The states of the metallic components in ion-exchanged, H₂ pre-treated and post-PROX samples were studied by XAFS. Pt forms metallic clusters after H₂ pretreatment or the PROX experiment, whereas a large part of the Fe exists as oxides even after H₂ treatment. Preferential CO adsorption onto Pt on (1) was demonstrated.

**Characterization and Catalytic Performance of a Bimetallic Pt–Sn/HZSM-5 Catalyst Used in Denitratation of Drinking Water**


Pt-Sn/HZSM-5 zeolite (1) was characterised by TPR, H₂ chemisorption, XPS and Sn Mössbauer spectroscopy to examine its role during the catalytic reduction of nitrate ions in H₂O (denitration). These techniques showed a significant decrease in the H:Pt ratio upon Sn addition, Sn surface enrichment, the formation of PtSn alloys and Pt catalysis of the Sn reduction. (1) exhibits high catalytic activity for the reduction of nitrate to form N₂. The role of Sn is to reduce nitrate or nitrite according to a redox process, while the Pt maintains Sn in the metallic state.

**Catalytic Activities of Pd-TiO₂ Film Towards the Oxidation of Formic Acid**


Pd-TiO₂/ITO films (1) were prepared by a dip-coating and subsequent photodeposition (UV light) procedure. (1) were characterised by XRD, SEM and open circuit voltage. (1) not only exhibited higher photocatalytic and photoelectrocatalytic activities, compared with a TiO₂/ITO film, but also showed non-photocatalytic activity towards HCOOH degradation at room temperature and atmosphere pressure.

**Catalytic Properties of Several Supported Pd(II) Complexes for Suzuki Coupling Reactions**


Pd(II) complexes with N-ligands were synthesised and tested for the Suzuki coupling reaction. These complexes were also heterogenised on silica. Immobilised dichloro(N-3(3′-trimethoxysilyl)propyl-1,2-ethanediamine-N,N′)-Pd showed high catalytic activity, which makes it a useful system for biaryl compound synthesis. Leaching of the Pd into DMA/H₂O was negligible.

**HOMOGENEOUS CATALYSIS**

**Synthesis, Reaction, and Recycle of Fluorous Palladium Catalysts for an Asymmetric Allylic Alkylation without Using Fluorous Solvents**


A chiral fluorous aminophosphate (1) bearing two fluorous ponytails was prepared from (3)-prolinol and applied to the Pd-catalysed asymmetric allylic alkylation of 1,3-diphenyl-2-propanol acetate with a dialkyl malonate/N,O-bis(trimethylsilyl)acetamide/LiOAc system with ≤ 97% ee. The Pd catalyst formed from (1) and [Pd(η⁵-C₅H₅)Cl]₂ was easily separated from the reaction mixture and could be reused five times.

**Heck and Suzuki Coupling Reactions in Water Using Poly(2-oxazoline)s Functionalized with Palladium Carbene Complexes as Soluble, Amphiphilic Polymer Supports**


Three amphiphilic, H₂O-soluble diblock copolymers based on 2-oxazoline derivatives with pendant N-heterocyclic carbene/Pd catalysts in the hydrophobic block (1) were investigated. (1) in the Heck coupling of iodobenzene with styrene in neat H₂O gave high activities with TOF ≤ 2700 h⁻¹ at 110ºC. The Suzuki coupling of phenylboronic acid with iodobenzene and bromoarenes in neat H₂O exhibited even higher catalytic activity with TOF ≤ 5200 h⁻¹ at 80ºC.

**A Preparative Route to Methyl 3-(Heteroaryl)-acylates Using Heck Methodology**


Methyl 3-(heteroaryl)acylates were prepared using Heck coupling of heteroarene halides with methyl acrylate catalysed by Pd(OAc)₂/P(OCH₃)₃. A 3-fold excess of methyl acrylate and a bromoheteroarene in DMF were heated under N₂ with either triethylamine or diisopropylethylamine. P(OCH₃)₃ and Pd(OAc)₂ were used in a 2:1 ratio with a catalyst loading of 1–5 mol%. The highly volatile P(OCH₃)₃ is readily separated during the removal of the DMF.

**Palladium Catalysed Aryl Amination Reactions in Supercritical Carbon Dioxide**


Pd-catalysed C–N bond formation in sc-CO₂ has been achieved. Formation of carbamic acid was avoided by the use of an N-silylamine as the coupling partner. The system Pd₃dba₃ (1 mol%) with X-Phos (2 mol%) enabled the catalytic amination of aryl bromides and chlorides with N-silylanilines. The methodology was extended to N-arylation of N-silyldiarylamines, N-silylazoles and N-silylbromatones.
Microwave-Assisted Organic Synthesis: Scale-Up of Palladium-Catalyzed Aminations Using Single-Mode and Multi-Mode Microwave Equipment


Batchwise scale-up of Buchwald-Hartwig aminations under microwave irradiation was investigated. Pd(OAc)₂ was combined with 2-(dicyclohexylphosphanyl)biphenyl or 2-(di-tert-butyolphosphanyl)biphenyl. Multi-mode (several vessels irradiated in parallel per batch) as well as single-mode (one vessel irradiated per batch) platforms were successfully used. The single-mode platform is the most convenient since it allows automatic continuous batchwise production.

**FUEL CELLS**

Optimization of the Sputter-Deposited Platinum Cathode for a Direct Methanol Fuel Cell


Equilibrium concentrations of dissolved Pt species from Pt/C electrocatalyst in 0.5 M H₂SO₄ at 80°C increased with applied potential from 0.9 to 1.1 V vs. reversible H electrode. The Pt surface area loss for a short-stack of PEMFCs, operated at open-circuit voltage (~0.95 V), was higher than another operated under load (~0.75 V). The formation of soluble Pt species (such as Pt²⁺) is claimed to play an important role in Pt surface loss in PEMFC electrodes.

On the Preparation and Stability of Bimetallic PtMo/C Anodes for Proton-Exchange Membrane Fuel Cells


Bimetallic PtMo/C (1) electrocatalysts were synthesised via reductive coprecipitation with either formaldehyde or formic acid as reducing agent. The electrochemical behaviour of (1) was characterised by CV in H₂SO₄ solutions as well as in MEAs. (1) were electrocatalysts with small amounts of In and Pd as matrix; (b) InPd phase as particle-like structures; and (c) Pd-rich phase as lamellar precipitates. Ageing (1), the very fine Pd-rich intergranular precipitates grew toward the grain interior as a lamellar structure, and finally the coarsened Pd-rich precipitates covered a large part of the Au–Ag based matrix.

Synthesis of Platinum Nanoparticles and Then Self-Assembly on Nafion Membrane to Give a Catalyst Coated Membrane


A catalyst-coated membrane (1) for a PEMFC with Pt loading of 2.8 µg cm⁻² was prepared by self-assembling charged Pt particles at SO₃⁻ groups on the membrane surface. Proton conductivity of (1) was 0.0932 S cm⁻¹. The performance of the self-assembled MEA achieved 2.3 mW cm⁻². This corresponds to Pt utilisation of 821 W per 1 g Pt.

**MEDICAL USES**

Surface PEGylation and Ligand Exchange Chemistry of FePt Nanoparticles for Biological Applications


By covering magnetic FePt nanoparticles (1) with PEGylated thiol and dopamine ligands, H₂O-soluble (1) of great stability were synthesised. The surface thiol ligands are readily exchanged with other thiols bearing chain-end functionalities. The surface binding of both DNA and protein to (1) was achieved.

Tumour-Inhibiting Platinum(II) Complexes with Aminoalcohol Ligands: Biologically Important Transformations Studied by Micellar Electrokinetic Chromatography, Nuclear Magnetic Resonance Spectroscopy and Mass Spectrometry


The existence of equilibrium between the ring-opened and ring-closed species. An appreciable increase in binding in the presence of sodium dodecyl sulfate (SDS) micelles was explained in terms of the activation of (1). There is a shifting of the equilibrium towards the ring-opened species, induced by adluct formation between SDS and (1).

Precipitation Hardening of a Cu-Free Au–Ag–Pd–In Dental Alloy


Three phases were observed in the solution-treated title alloy (1): (a) Au–Ag based phase with small amounts of In and Pd as matrix; (b) InPd phase as particle-like structures; and (c) Pd-rich phase as lamellar precipitates. By ageing (1), the very fine Pd-rich intergranular precipitates grew toward the grain interior as a lamellar structure, and finally the coarsened Pd-rich precipitates covered a large part of the Au–Ag based matrix.
NEW PATENTS

PHOTOCONVERSION

Photocatalytic Substrate Active under Visible Light
SAINT-GOBAIN GLASS FRANCE. World Appl. 2005/102,952

A transparent glass substrate, used for glazing, contains a mechanically resistant, long-lasting coating, of a photocatalytic active compound containing a thin layer of Pt, Rh or Pd, closely associated with a doped GaP, CdS, TiO₂, etc. An energy jump of 1.55-3.26 eV occurs between the upper level of the valence band and the lower level of the conductive band, corresponding to a wavelength in the visible field.

APPARATUS AND TECHNIQUE

Titania Nanotube Arrays for Use as Sensors
THE PENN RES. FOUNDATION. U.S. Appl. 2005/224,360

An electrical resistive device (1) for sensing H₂ gas includes: an array of TiO₂ nanotubes (1) formed by anodising a Ti layer; and a plurality of Pd (or other noble metal) clusters on top, mechanically supported by an integral member. (1) may contain dopant of < 1 mass% of Pd, Pt, Ru, Sb, etc. In O₂, (1) photocatalytically removes contaminants (liquid crude petroleum, pathogens, etc.) by exposure to radiant energy emitted within frequency range from visible to ultraviolet.

Integrated Capacitive Microfluidic Sensors
CALIFORNIA INST. TECHNOL. U.S. Appl. 2005/243,500

A microfluidic device for capacitive pressure sensing, includes a fluid channel, a cavity region, and a polymer-based membrane in between. Additionally, the device includes two capacitor electrodes, consisting of Pt, Au, Al, Cr, Ti and doped polysilicon, coupled to the membrane and the cavity region, and an electrical power source placed between which causes an electric field within the cavity field.

VCSEL Structure with Platinum Sublayer
HONEYWELL INT. INC. U.S. Appl. 2005/243,886

A vertical cavity surface emitting laser (VCSEL) with high reflectivity and heat dissipation characteristics includes a bottom distributed Bragg reflector (1) on a substrate; a metal layer (2), including a reaction barrier sublayer of Pt, W and/or Ti interposed between (1) and the substrate, forming a composite mirror structure. A patterned dielectric layer may be interposed between to reduce a deleterious chemical reaction between (2) and (1).

Ammonia Gas Sensor Having Improved Detection
FIS INC. Japanese Appl. 2005/127,743

An NH₃ gas sensor, with improved accuracy, comprises a semiconductor embedding a coil-like heater made of Pt or a Pt alloy acting as a substrate and a conductor-like electrode in a gas sensitive body (1) formed into a spherical shape. (1) is mainly made of Sn oxide and contains Au, to suppress the disturbance of NH₃ detection output by Pt.

HETEROGENEOUS CATALYSIS

Elimination of Aldehydes by Catalytic Oxidation
HENKELE KG. European Appl. 1,591,156

Aldehydes are eliminated by catalytic oxidation in the presence of a three-component catalyst comprising a catalytic composition of Ru/ZrO₂-MO₃ where M is Ca, Mn, Cu and/or In; n = 0.2-3, especially 0.5-2 (the respective upper and lower limiting values are included). The process may be run at relatively moderate (for example, ambient) temperatures leading to a high conversion rate of aldehydes, thus resulting in harmless degradation products, especially CO₂ and H₂O.

Platinum Catalysts Formed by in Situ Reduction
DE NORA ELETTRODI SPA. World Appl. 2005/097,314

A C-supported Pt black catalyst (1) is obtained by chemical reduction of in situ-formed Pt dioxide (2) by conversion of dihydrogen hexahydroxyplatinate precursor on a C black support, with an active area of 50 m² g⁻¹. The reducing agent is H₂, formaldehyde, etc. (1) is obtained by variation of pH and/or temperature (120-500°C) and can be incorporated in a gas diffusion electrode or in a coated membrane.

Catalyst Used for the Oxidation of Hydrogen
BASF AG. World Appl. 2005/097,715

A supported catalyst (1) for the oxidation of H₂ in a hydrocarbon dehydrogenation process comprises α-Al₂O₃ carrying 0.01-0.1 wt.% Pt and 0.01-0.1 wt.% Sn, with the Pt:Sn ratio being 1:4 to 1:0.2, relative to the total weight of the catalyst. Also disclosed are methods for oxygenating H₂ and for dehydrogenating hydrocarbons using rows of integrated reactors with (1).

Removal of Carbon Monoxide and Hydrocarbons
HTE AG. World Appl. 2005/102,513

Simultaneous removal of CO and hydrocarbons from O-rich exhaust gases is carried out in the presence of a catalyst (1) containing SnO₂ and Pd supported on a carrier oxide, such as a zeolite, being in a roentgenographically amorphous or nanoparticle form. (1) contains 3-50 wt.% SnO₂ and 0.2-10 wt.% Pd and, optionally, Pt, Rh, Ir and Ru; based on the mass proportions relatively to the carrier oxide. (1) may also contain B oxide and/or other promoters.

Catalyst Prepared by Microwave Heating
DOW GLOBAL TECHNOL. World Appl. 2005/102,525

A hydro-oxidation catalyst (1) for the hydro-oxidation of a hydrocarbon, preferably a C₃-C₈ olefin, such as propylene, by O₂ in the presence of H₂ to the corresponding partially-oxidised hydrocarbon, such as propylene oxide is presented. (1) comprises Pt group metal(s), and/or Au, Ag, lanthanide rare earth metals, deposited on a titanosilicate, preferably TS-1, which is prepared by microwave heating.
Supported Ruthenium Nanoparticle Catalyst
UNIV. HONG KONG World Appl. 2005/102,971

Oxidation of alkenes is carried out on Ru nanoparticle catalysts (1-100 nm in size), with Mn and Fe nanoparticles, grafted on an inert solid support, such as hydroxyapatite. The reaction yields a cis-1,2-diol from an alke, an oxidant and acid at –78 to 40ºC. The catalyst effects cis-dihydroxylation and oxidative cleavage of alkenes to give the respective cis-diols and carbonyl products. The catalyst can be separated by filtration or centrifugation, and reused.

Modified Carbon Supported Palladium Catalyst
CSIR U.S. Patent 6,963,016

A highly active modified C supported Pd catalyst (1) containing 2-6 wt.% Pd, is produced by the simultaneous impregnation of activated C with Pd and organic Al precursors, such as Pd chloride and Al isopropoxide, respectively, in a tetraethyl ammonium hydroxide aqueous solution. (1) is used for the hydrodechlorination of dichlorodifluoromethane to hydroxide aqueous solution. (1) is used in the field of pharmaceuticals and more specifically in processes for making substituted indole compounds.

Homogeneous Catalysis
Palladium Catalysed Indolisation
BOEHRINGER INGELHEIM INT. World Appl. 2005/090,302

Substituted indole compounds (1) were synthesised by reacting a 2-bromoaniline or 2-chloroaniline with a substituted acetylene in the presence of a Pd(OAc)2 catalyst, 1,1′-bis(di-tert-butylphosphino)ferrocene ligand, and K2CO3 base, in 1-methyl-2-pyrrolidinone solvent at 110-140ºC. (1) are used in the field of pharmaceuticals and more specifically in processes for making substituted indole compounds.

Optically Active Polymers
NAT. INST. ADV. IND. SCI. TECHNOL. U.S. Patent 6,962,962

An optically active polymer (1) is obtained by polymerising a chiral alkoxy-substituted phenylacetylene, such as (S)-(2-methylbutoxy)phenylacetylene in the presence of a Pd(OAc)2 catalyst, 1,1′-bis(di-tert-butylphosphino)ferrocene ligand, and K2CO3 base, in 1-methyl-2-pyrrolidinone solvent at 110-140ºC. (1) are used in the field of pharmaceuticals and more specifically in processes for making substituted indole compounds.

Fuel Cells
Production of Platinum-Ruthenium Alloy Catalyst
HITACHI MAXELL LTD Japanese Appl. 2005-177,661

A Pt-Ru alloy catalyst is made by dissolving a Pt and a Ru salt or complex in an organic alcohol solvent. C powder is dispersed in the alcohol solution, which is then heated while refluxing alcohol. The Pt-Ru/C powder is filtered, then heat treated at 300-500ºC in an inert atmosphere. Pt-Ru/C exhibits high activity when MeOH is oxidised and used in a fuel cell.

Electrode Catalyst for PEFCs
NISSAN MOTOR CO LTD Japanese Appl. 2005-196,972

Electrode catalysts (1) for use in PEFCs are manufactured by mixing Rh chloride-containing and Pt ion-containing reversed micelle solutions. Reducing agents, such as hydrazine, Na borohydride, etc., are added and conductive C supports are dispersed in the solution for loading composite metal particles onto the support. (1) have high activity and durability.

Electrical and Electronic Engineering
Ferroelectric Capacitor with a Template
TEXAS INSTRUMENTS INC U.S. Appl. 2005/230,725

A ferroelectric capacitor (1) comprises: a first electrode layer, including Ir, located over a substrate. An oxide electrode template (2) (20-100 nm thick) is located on the first electrode layer and includes perovskites: SrIrO3, SrRuO3, PbIrO3, PbRuO3, etc. (1) may include a ferroelectric dielectric layer over the oxide electrode template and a second electrode layer over the ferroelectric dielectric layer (2). (1) is used in ferroelectric random access memory devices.

TiW Platinum Interconnect
ANALOG DEVICES INC U.S. Patent 6,956,274

A metallisation stack used as a contact structure in integrated MEMS devices, particularly optical MEMS and Bio-MEMS, comprises a Ti-W adhesion and a barrier layer (1) with a Pt layer on top. (1) is formed by sputter etching the Pt in Ar, followed by a wet etch in aqua regia using an oxide hardmask. Alternatively, the Ti-W and Pt layers are deposited sequentially and patterned by a single plasma etch process with a photoresist mask.

Medical Uses
Radiopaque and MRI Compatible Nitinol Alloys
ADV. CARDIOVASC. SYST. INC World Appl. 2005/102,407

A medical device, such as a stent, is made from radiopaque and magnetic resonance imaging compatible alloy, for use with, or implanted in, a body lumen. It has improved radiopacity, retains superelastic and shape memory behaviour, and has a thin strut/wall thickness for high flexibility. The stent is made from alloy (1) such as Ni-Ti (nitinol), and includes a ternary element of Ir, Pt, Pd, Rh, Ru, Au, Re, etc. A balloon-expandable stent made from (1) is claimed.

Supramolecular Photoactivated DNA Cleavage
VIRGINIA TECH INTELL. PROP. U.S. Patent 6,962,910

Replication of hyperproliferating cells is decreased by using a supramolecular metal complex as a DNA cleaving agent to transfer charge from MLCT light absorbing metal, Ru or Os, to electron acceptor metal, Rh, by a bridging π-acceptor ligand. A bioactive MLCT state that can cleave DNA is thus generated. The complexes are tunable and can cleave DNA by low energy light in the absence of O2.
Catalysts play a crucial part in the successful operation of many processes, and are a major contributor to the overall economics. Precious metal-based catalysts are extensively used in chemical applications and refining, such as catalytic reforming units utilising platinum or platinum-rhenium catalysts. The trend is towards employing catalysts of even higher activity and stability, so an installed catalyst inventory could be worth several million dollars. In a chemical process, even small changes in catalyst formulations, preparation techniques or operational conditions can strongly enhance or harm catalyst performance, and hence the overall process economics.

Today the market place is ever more competitive and it is imperative that chemical plants operate at maximum efficiency. Additionally, the conditions of operation and regulation in processing industries are becoming increasingly severe. This necessitates close cooperation between the catalyst supplier and the operator, and a solid basis of trust has to be established between them to achieve the maximum benefits. The provision of technical service is also a vital aspect of a catalyst suppliers' remit.

Catalyst abuse, misuse or mal-operation are major problems for a catalyst supplier to contend with. Operating companies have a tendency to downsize, and this can result in chemical processors having less personnel to monitor and supervise units. The consequence has been an increasing number of 'catalyst incidents'. Catalyst suppliers must therefore provide appropriate technical service and after-sales support, and include, for instance, training for operators, troubleshooting if needed, and impartial advice for technical enquiries. All this is aimed at preventing unplanned shutdowns and premature catalyst change-outs.

The level of technical service should always be agreed between the operator and the catalyst supplier at the outset, to share expectations and avoid later disappointment. As a minimum, the process operator should expect the catalyst supplier, on a quarterly basis, to evaluate process data and perform requisite laboratory analyses of any spent catalyst samples from the process. This evaluation will provide the best evidence of events during service and it remains the most conclusive and reliable means of assessing the condition of used catalyst, and how the catalyst has performed and responded to the operating conditions.

**Recommended Evaluations**

For precious metal catalysts the evaluations should include:

- **Physical analysis**, including the crush strength, pore volume and porosity; the BET and/or the metal surface area should be obtained for comparison with typical fresh catalyst batches. This can provide evidence of sintering through thermal/hydrothermal ageing mechanisms.

- **The level of any contaminant on the catalyst surface** should be accurately measured (ICP, AA, XRF, etc.) and compared to recommended maximum permissible levels for those particular poisons. These levels are often based on invaluable information the catalyst supplier has acquired through years of experience. Catalysts are very sensitive, even to low levels of contaminants in feedstocks being processed. Many common contaminants (sulfur, halides, alkalis, heavy metals, etc.) can have a significant deactivating effect on the achieved activity/selectivity, even if their inlet concentrations are below the level of detection (1).

- **Finally, a pilot plant or microreactor test of catalyst activity and selectivity** should be made on a used sample and compared to a retained sample of fresh catalyst from the batch provided to the customer. This will help determine the remaining useful service life of the catalyst.

**Reference**


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