# PLATINUM METALS REVIEW

_A quarterly survey of research on the platinum metals and of developments in their application in industry_


## VOL. 43  JULY 1999  NO. 3

## Contents

<table>
<thead>
<tr>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>The Oxidation of Alcohols to Aldehydes or Ketones</td>
<td>94</td>
</tr>
<tr>
<td><em>By Holger B. Friedrich</em></td>
<td></td>
</tr>
<tr>
<td>Ruthenium in Living Radical Polymerisation</td>
<td>102</td>
</tr>
<tr>
<td>Developments in Cisplatin Research</td>
<td>103</td>
</tr>
<tr>
<td><em>By Simon P. Fricker</em></td>
<td></td>
</tr>
<tr>
<td>Thin-Film Light-Emitting Ruthenium(II) Devices</td>
<td>104</td>
</tr>
<tr>
<td>Organometallic Chemistry and Applied Catalysis</td>
<td>105</td>
</tr>
<tr>
<td><em>By Berth-Jan Deelman</em></td>
<td></td>
</tr>
<tr>
<td>Sonochemical Platinum Reduction</td>
<td>108</td>
</tr>
<tr>
<td>Catalyst Enhanced Oxidation of VOCs and Methane in Cold-Plasma Reactors</td>
<td>109</td>
</tr>
<tr>
<td><em>By Muhammad Arif Malik and Salman Akbar Malik</em></td>
<td></td>
</tr>
<tr>
<td>Encapsulation of Platinum in Dendrimers</td>
<td>113</td>
</tr>
<tr>
<td>Combined Homogeneous and Heterogeneous Catalysts</td>
<td>114</td>
</tr>
<tr>
<td><em>By David T. Thompson</em></td>
<td></td>
</tr>
<tr>
<td>The Effects of Hydrogen on the Physical Properties of Palladium</td>
<td>116</td>
</tr>
<tr>
<td><em>By V. A. Goltsov</em></td>
<td></td>
</tr>
<tr>
<td>“Platinum 1999”</td>
<td>118</td>
</tr>
<tr>
<td>Aftertreatment for Low Emission Vehicles</td>
<td>119</td>
</tr>
<tr>
<td><em>By M. V. Twigg</em></td>
<td></td>
</tr>
<tr>
<td>Johann Wolfgang Döbereiner’s <em>Feuerzeug</em></td>
<td>122</td>
</tr>
<tr>
<td><em>By Professor George B. Kaufman</em></td>
<td></td>
</tr>
<tr>
<td>Noble and Rare Metals: NRM-2000</td>
<td>128</td>
</tr>
<tr>
<td>Abstracts</td>
<td>129</td>
</tr>
<tr>
<td>New Patents</td>
<td>134</td>
</tr>
</tbody>
</table>

**Communications should be addressed to**

*The Editor, Susan V. Ashton, Platinum Metals Review, jmpmr@matthey.com*

*Johnson Matthey Public Limited Company, Hatton Garden, London ECIN 8EE*
The Oxidation of Alcohols to Aldehydes or Ketones

HIGH OXIDATION STATE RUTHENIUM COMPOUNDS AS CATALYSTS

By Holger B. Friedrich
School of Pure & Applied Chemistry, University of Natal, South Africa

The oxidations of alcohols to aldehydes and ketones are vital reactions in synthetic organic chemistry, and high selectivity and mild conditions are important prerequisites for ease of product work-up and lower cost. Currently, many of the best oxidants for these conversions contain high valent ruthenium, with ruthenium acting as a catalyst for these reactions. It is important to have detailed knowledge and understanding of the mechanisms of the oxidation reactions and the factors that influence them, as only by completely understanding how these processes work will it be possible to design better or optimal catalysts. In this paper, the more viable oxidants currently available are reported and some investigations into the mechanisms of the reactions and factors affecting them are discussed.

As the catalytic conversions of primary alcohols into aldehydes and of secondary alcohols into ketones are essential for the preparation of many key synthetic intermediates in organic chemistry, there is currently much activity being undertaken in the search for catalytic systems which can perform these operations.

\[
\text{RCH}_2\text{OH} \xrightarrow{\text{oxidant}} \text{RCHO} \quad (i) \\
\text{RCH(OH)R'} \xrightarrow{\text{oxidant}} \text{RC(O)R'} \quad (ii)
\]

In particular, the reaction shown in Equation (i) does not usually stop at the formation of the aldehyde and over-oxidation to the carboxylic acid often occurs.

\[
\text{RCHO} \xrightarrow{\text{H}_2\text{O}} \text{RCOOH} \quad (iii)
\]

Historically, various oxidative systems have been available for these reactions, including chromium(VI) oxo compounds, copper chromites (often used industrially for bulk preparations), vanadium pentoxide, PtO₂, RuCl₃/Cu(II) (1, 2) and the Swern oxidation (3). However, there are various drawbacks to using these reagents; for instance, they are either rather aggressive, need relatively high or low temperatures, give unwanted and difficult to remove by-products, are difficult to separate from the product after the reaction is over, require acidic conditions which limit the choice of substrate, or, they do not give complete conversions in all applications. Thus, there is clearly a need to prepare milder and more selective oxidants with higher rates of conversion. Several oxidative systems which at least partially fit the above criteria have recently been reported, and many of these contain or are based on ruthenium.

The chemistry of high-oxidation-state ruthenium is less well developed than that of, for example, osmium (4) or rhenium (5). Specifically, reaction mechanisms and the factors which influence the performance of various oxidants are poorly understood. It is clear, however, that several of the high valent oxo ruthenium compounds made so far are active in transforming both primary alcohols into aldehydes and secondary alcohols into ketones. While many compounds will cause these transformations, few do so catalytically and this may be ruthenium's strength. Many of the known ruthenium-containing oxidants are also tolerant of other sensitive functional groups in organic molecules. It would be desirable to have a very

selective catalytic oxidant, which would not attack other potentially reactive groups, such as double bonds, halides, epoxides, esters, amides, or protecting groups, such as silyl or benzoate, amongst many others. Ideally, this catalytic oxidant would also operate at room temperature in an environmentally friendly solvent system (such as water) and use "green" co-oxidants such as oxygen (O_2) or hydrogen peroxide (H_2O_2). This ideal catalytic oxidant should also be easy to recycle. Designing such systems remains a challenge, although significant progress is being made. Other factors which influence the acceptance of new catalysts include the ease of operation and the ease of (synthetically or commercially) producing the catalytic oxidant.

**Ruthenium Oxide Catalyst Systems**

The only known well-defined stable ruthenium(VII) compound is ruthenium tetroxide, RuO_4, which is frequently far too vigorous an oxidant, as it attacks many functional groups, such as double bonds, and often forms carboxylic acids. Consequently, research has focused on ruthenium compounds in slightly lower oxidation states.

"Catalytic" systems reported in the literature with reasonably high selectivities, conversions (depending on substrates) and turnovers (measured as moles of product per mole of catalyst), are [RuO_2(py)_2].3.5H_2O (py = pyridine), trans-[4-'Bu-Hpy][RuO_2Cl_2(4-'Bu-py)] (Hpy is a protonated pyridine), [LPh][RuO_2Cl_2] (L = P, As) and trans-[RuO_2(py)_2][BF_4]_2, all having 4-methylmorpholine N-oxide, MNO, as co-oxidant (6-8). These compounds are obtained in moderate yield, and the first two are made by utilising RuO_2 as a gas, and require appropriate manipulative and experimental skills. The dinuclear compound also appears to have a limited "shelf-life".

A series of compounds, which appear to have considerable potential as viable catalytic oxidants are the compounds cis-[PPh_3]_2[RuO_2Cl_2(OCOR)] (R = Me, Et, Pr, CHF_3), (9). The cis-oxo arrangement is unusual because of the considerable electronic stabilisation associated with the trans-dioxo, d^2, configuration (10). The acetic acid derivative was shown to be a good catalytic oxidant with MNO as co-oxidant. No effects were observed on varying the length of the alkyl chain (R). It was felt that this system was worth further investigation and high yield routes to the compounds, where R = Me, CF_3, C,H_11, C,H_11F, and C,H_11, were developed, which avoided the need to use RuO_2 gas. The compounds were found to be stable and catalytically active with a wide range of co-oxidants (H_2O_2, NaOCl, 'BuOOH (tertiary-butyl hydroperoxide)) with MNO and tetrabutylammonium periodate being the best, amongst others. Fluorinated compounds often display very different properties to their protonated analogues, probably because fluorine and hydrogen, although being of similar size, have very different electronegativities. However, we found that apart from significantly affecting the synthetic yields of the oxidants, no effect on the oxidations was observed.

The most well-known ruthenium oxide catalyst, tetrabutylammonium perruthenate (TPAP) and its sister tetrabutylammonium per ruthenate (TBAP) are effective in many selective organic transformations of the type summarised in Equations (i) and (ii) using MNO as the co-oxidant. A comprehensive review has recently been published (11). TPAP is also almost the only ruthenium oxidation catalyst to have been studied kinetically. The reaction of TPAP with propan-2-01 was found to be autocatalytic, possibly due to the formation of colloidal RuO_2 which may form RuO_2-nRuO_2 (12). TPAP is a three-electron oxidant overall, but it is believed that the alcohol oxidation step is of the two-electron type. The fact that TPAP will oxidise cyclobutanol to cyclobutanone suggests that a one-electron oxidation process is not involved, since a one-electron oxidant would cleave cyclobutanol to acyclic products (13).

Other reported ruthenium(VI) oxidants will usually convert primary alcohols into acids, although internal alcohols will still be converted into ketones. Compounds reported to effect these transformations are K[RuO_4] and [RuO_4]^2- (really trans-[RuO_4(OH)_2]^+) (7, 14, 15). The yields range from moderate to good, depending...
on the substrate. Conversions are carried out in basic aqueous media, as ruthenate and per-

ruthenate are unstable at lower pH. This limits the reagents to substrates which are stable at

high pH. The reactions are rendered catalytic by using K\textsubscript{2}S\textsubscript{2}O\textsubscript{8} (persulfate) or BrO\textsubscript{3} (bromate) as the co-oxidant. Similar results are attained in the same media using trans-[RuO\textsubscript{2}(HIO\textsubscript{4})\textsubscript{4}]\textsuperscript{3-} as catalyst, with NaIO\textsubscript{4} as the co-oxidant (16). Even ruthenium tetroxide, RuO\textsubscript{4}, has been reported as oxidising secondary alcohols to ketones (1, 17). However, both RuO\textsubscript{4} and sodium ruthenate are known to attack double bonds, although sodium ruthenate will do so only if high temperatures or longer reaction times are employed (18, 19). Since RuO\textsubscript{4} is unstable at pH > 8, the active species in those reactions reported to involve RuO\textsubscript{4} and NaOCl is probably RuO\textsubscript{4}, see Equation (iv) (20).

4RuO\textsubscript{4} + 4OH\textsuperscript{-} → 4RuO\textsubscript{3} + 2H\textsubscript{2}O + O\textsubscript{2} \hspace{1cm} (iv)

At high pH (>12) though, ruthenate is the dominant species:

4RuO\textsubscript{3} + 4OH\textsuperscript{-} → 4“RuO\textsubscript{4}:+” + 2H\textsubscript{2}O + O\textsubscript{2} \hspace{1cm} (v)

The compound [RuO\textsubscript{2}(tetramesitylporphyrinato)] has been reported to oxidise alkyl alcohols to ketones, although its primary application is as an alkane oxidant (21).

Strictly speaking, few of the above mentioned ruthenium catalysts are true catalysts, since if the “catalytic” reactions are carried out with too little co-oxidant, the ruthenium compound remains in a reduced state. A catalyst should be unchanged after a reaction. Instead, the ruthenium oxo compounds are really primary oxidants, that is, they directly oxidise the substrate. The co-oxidant is the secondary oxidant – which regenerates the primary oxidant. A few of the commonly used secondary oxidants do react directly with alcohols (for example, MNO with primary alcohols), but the conversions are generally low.

Alcohol oxidations with transition metal oxo reagents probably mainly involve the same basic transformation as shown in Figure 1, involving an ester intermediate. For all of the catalytic oxidants mentioned above, primary alcohols react more rapidly than secondary alcohols, probably due to steric hindrance of secondary alcohols. It is generally thought that the reagents, reported above, which effectively catalyse the reaction in Equation (i), do so because of the presence of molecular sieves in the reaction medium. The molecular sieves efficiently remove water (formed in the reaction and present as water of crystallisation of MNO). It is known that an aldehyde hydrate is necessary for the reaction in Equation (iii) to occur. The mechanism for the oxidation by chromic acid of an aldehyde is shown in Figure 2 (22) and ruthenium oxide oxidations are presumed to be similar. Some preliminary results from our...
The stoichiometric oxidations of propan-2-ol with the sodium salts of ruthenate and per-
ruthenate have been investigated kinetically and me-
chanistically (23). Both reactions are believed to pro-
ceed via free radical-like transition states, 
although the subsequent steps differ. For both ruthenate and per-
ruthenate, an ester interme-
diate, as shown in Figure 1, is thought to be unlikely and instead it is assumed that the 
ruthenium salts add to an \( \alpha \)-C-H bond of the alcohol. The proposed mechanism is shown in 
Figure 3. Since HRuO\(_3\)\(^{+}\) is very reactive, it is believed that a single electron transfer would occur very rapidly, before the radical could diffuse out of the solvent cage. For the stoichiome-
tric oxidation of propan-2-ol with per-
ruthenate, as shown in Figure 3, it is thought likely that because the HRuO\(_2\) ion is less reactive, the product would move out of the solvent cage before further reaction. These proposed mechanisms fit theoretical predictions (24).

The reactions of [RuO\(_2\)]\(^{-}\) and [RuO\(_4\)]\(^{2-}\) with
cyclobutanol suggest that the latter is a two-electron and the former, unlike TPAP, is a one-electron oxidant, see Figure 4 (25).

The mechanisms of the catalytic oxidations of propan-2-ol using [RuO₄]²⁻ with a variety of co-oxidants have also been investigated. For the co-oxidants hexacyanoferrate(III), diperiodatocuprate(II) and periodate, the data imply that a complex is formed, as for the stoichiometric oxidation, Figure 3. The role of the co-oxidant is only to regenerate Ru(VI). The exception is when the co-oxidant is chloramine-T. In this case, the co-oxidant appears to react directly with the Ru(VI) ion, see Figure 5. This active complex then reacts rapidly with propan-2-ol to form acetone (26). It seems very likely, however, that these mechanisms are only valid in aqueous base and the mechanisms are probably different in non-aqueous media, as shown, for example, by the different reaction products obtained in the oxidation of cyclobutanol with TPAP and basic perruthenate.

The disadvantages of many of the catalysts that catalyse the reaction in Equation (i) and also of several which efficiently catalyse the reaction in Equation (ii) are that they require CH₂Cl₂ or CH₂CN as solvents (which are not "green") and that they require MNO as co-oxidant. However, the MNO co-oxidant is expensive, an irritant to the eyes, the respiratory system and the skin, and its final product, 4-methylmorpholine, is corrosive and causes burns to the skin, the eyes and mucous layers in the nasal tract. Apart from this, even the best known catalysts do not give quantitative or almost-quantitative transformations in all apparently suitable systems and, as such, there is a great need to develop more effective and more selective catalysts with higher turnovers.

In general, the activity of catalysts is affected by the steric bulk (for instance, cone angles) of the attached groups and the electron density on the metal. The significant effect of the groups attached to the Ru(VI) centre is demonstrated by the examples of Ru(VI)O₂ moieties bonded to porphyrins or to other bulky tetradentate ligands: many of these compounds are effective catalysts for the epoxidation of olefins (27). None of the other ruthenium(VI) oxo catalysts, referred to above, can perform this reaction. However, even Ru(VI)O₂ compounds, with bulky bidentate ligands, can catalyse epoxidation reactions (28).

**Towards Commercial Catalysts**

As part of a project to develop commercially viable catalysts for the oxidation of alcohols, we are interested in determining how various substituents affect the chemistry of ruthenium(VI) oxo compounds. One potential route would involve the synthesis of organometallic ruthenium(VI) oxo compounds. The possibility of being able to vary and fine-tune a wide range of alkyl or aryl substituents should offer much information on these systems and facilitate the design of highly specific catalysts. However, only a few
mono-oxo ruthenium(VI) organometallic compounds are known (29) and ruthenium(VI)
organometallic di-oxo compounds have so far proved to be totally elusive.

Alternatively, one can study the effects of substituents in inorganic ruthenium oxo compounds. This latter approach has the advantage that routes to discreet, fully characterisable compounds of this type are already available.

The first system to be considered consisted of compounds of the type [RuO$_2$Cl$_2$(Y-py)$_2$] (Y = H, 4-'Bu, 3-CN, 4-CN, 2-Br, 3-Br, 4-Br, 4-Cl, 4-Me, 4-C(O)C$_2$H$_5$, 3-COOH, 4-COOH). This series was chosen because we thought that substituents on a flat aromatic ring, for which Hammett substituent constants were available, should show easily quantifiable electronic effects on the ruthenium centre. The first examples of compounds in this series (Y = H, 4-'Bu, 4-Cl) were prepared by Griffith and co-workers (6) and the rest by us (30). As can be seen from Figure 6, substitution at either the 3- or 4-position of the pyridine ring should have a significant effect on the charge on the pyridine nitrogen and consequently on the net charge on the ruthenium centre.

Similarly, the nature of the substituent Y (either electron pushing or electron withdrawing) should affect the charge on the pyridine nitrogen and hence on the ruthenium centre. These effects should be revealed by changes in the Ru=O stretching vibrations. This is confirmed by examining the IR spectra of these compounds.

Fig. 6 Localised relative charges on (a) 3-Br-pyridine and (b) 4-Br-pyridine and the resulting relative charge distribution in the complexes they constitute (c) and (d), respectively

Fig. 7 A plot of ν(Ru=O) values against σ* for the compounds [RuO$_2$Cl$_2$(Y-py)$_2$]; σ* is a description of the substituents. The magnitude of σ* gives the relative strength of the electron-withdrawing or electron-donating properties of the substituents. The value of σ* is positive if the substituent is electron-withdrawing and negative if it is electron-donating.

Platinum Metals Rev., 1999, 43 (3)
Excluding the compound where \( Y = H \), the \( \nu(\text{Ru}=O) \) stretches correlate linearly with the Hammett, \( \sigma \), and Taft, \( \sigma^t \), values, see Figure 7, and Pauling type electronegativity (X) values of the \( Y \) substituents. Since these values are due to an inductive effect, one would expect the inductive effect to increase with decreasing distance between the substituent, \( Y \), and the ruthenium centre. This is observed, with the slope of the graph for the 3-substituted compounds being much steeper than for the 4-substituted compounds.

Thus, these complexes are stoichiometric and “catalytic” oxidants for the conversion of alcohols to aldehydes, with the substituents, \( Y \), clearly affecting the performance of the compounds. The Table shows values for stoichiometric oxidations of 1-hexanol to hexanal by (Y)OCl₂Ru with a range of co-catalysts.

A sequence was observed of the oxidising ability for the stoichiometric oxidations: phen < 4-Me-py < benzoyl-py < 3-CN-py < 4-CN-py < 4′-Bu-py < 4′-Cl-py ≈ py < 3-Br-py = 4-Br-py < bipy. An almost identical sequence was observed for the “catalytic” oxidations, using H₂O₂, hypochlorite (OCl⁻) or t-butyldihydroperoxide ((CH₃)₃COOH) as the co-oxidants. Although the \( Y \) substituents clearly affect the \( \nu(\text{Ru}=O) \) values and hence the strength of the Ru=O bond and the electron density on the metal, no correlation between oxidising ability and substituent constants for \( Y \) is observed. This implies that electron density on the metal has no significant effect on these compounds as oxidants.

In addition, electronic effects do not appear to play a role in the performance of the Ru(VI) salts, \([\text{PPh}_3][\text{RuO}_2\text{Cl}_2(\text{OCOR})]\), as reported above. While most of the above compounds are mediocre oxidants, the performance of \([\text{RuO}_2\text{Cl}_2(4-\text{Br-py})]\) is exceptional and so is that of \([\text{RuO}_2\text{Cl}_2(3-\text{Br-py})]\), to a lesser extent. Both of these are far superior oxidants to any of the other compounds in this series. The 4-Br-pyridine derivative gives especially high rates of conversion with reasonable turnovers. We are at present investigating this clear ligand effect.

A study of the compounds \([\text{RuO}_2\text{Cl}_2L]\) (\( L = \)...
bipyridyl, 1,10-phenanthroline) indicates that the rigidity of the ligands may also play a role, as the bipyridyl compound is a reasonable oxidant, whereas the phenanthroline compound is a very poor oxidant, as shown in the Table.

One of the great disadvantages of many homogeneous catalytic systems is the problem of separating the product from the catalyst. For this reason heterogeneous catalysts remain very popular, as the catalyst can simply be filtered off and reused.

One way of attempting to combine the advantages of homogeneous and heterogeneous catalysts is by bonding soluble catalysts to insoluble supports, although these have yet to attain a large scale industrial breakthrough (31). We have supported ruthenate on poly-(4-vinylpyridine) and on zeolite-Y. Both these supported catalysts appear to be very selective in the oxidations referred to in Equations (i) and (ii), with a wide range of co-oxidants at room temperature (32). The catalysts can be filtered off and reused. We are currently investigating both the structures and the versatility of these catalysts. We believe that the ruthenate may be bonded to the polymer, as is the OsO\textsubscript{4}/poly-(4-vinylpyridine) system for oxidising alkenes to diols, rather than just being supported (33).

A ruthenium hydrotalcite heterogeneous competitor has recently been reported (34). This catalyst is reported to oxidise primary and secondary alcohols into aldehydes and ketones, respectively, in high yields with high selectivity. This catalyst appears to be easily prepared and the oxidations take place at 60°C in toluene, using molecular oxygen as co-oxidant. It would appear that a heteronuclear interaction between ruthenium and cobalt is responsible for the high activity, with ruthenium probably being oxidised to a +6 oxidation state within the Brucite, Mg(OH)\textsubscript{2}, layer.

The use of oxygen as co-oxidant, as in the system mentioned above, is very advantageous from an environmental point of view. We have carried out extensive studies on various co-oxidants for the catalysts [Ru\textsubscript{2}O\textsubscript{3}Cl\textsubscript{6}(Y-py)\textsubscript{3}], [PPh\textsubscript{4}]-[RuO\textsubscript{2}Cl\textsubscript{3}(OCOR)] and polymer or zeolite “supported” ruthenate. While these systems are active for a wide range of co-oxidants, consistently, highest conversions for these systems and many of those reported above, are usually obtained using MNO, although tetrabutyl-ammonium periodate appears to be an excellent co-oxidant for the immobilised systems and also for the oxidation of primary alcohols with the salts [PPh\textsubscript{4}][RuO\textsubscript{2}Cl\textsubscript{3}(OCOR)] (R = CF\textsubscript{3}, C\textsubscript{6}H\textsubscript{4}, and C\textsubscript{3}F\textsubscript{3}).

Concluding Remarks
Thus, it would seem that high oxidation state ruthenium catalysts are amongst the best mild oxidants for the oxidation of alcohols, with little or no over-oxidation products being obtained. Our information remains limited on the mechanism of the reactions and on which factors, besides having ruthenium in a high oxidation state, influence the efficiency of these compounds. Our best hope of discovering what influences the oxidation chemistry of ruthenium will come from using homogeneous catalytic systems, although environmental and economic concerns may ultimately favour supported, heterogeneous or genuinely two-phase catalytic systems.

Acknowledgement
Thanks to the Alexander von Humboldt Foundation, NMT Electrodes, Western Platinum Refineries, the University of Natal and the Foundation for Research Development for their support; also to Vikash Gokul.

References

Ruthenium in Living Radical Polymisation

Living radical polymerisation has become an important technique in precision polymer synthesis for the construction of new polymers with tailor-made structural complexities. In order to assemble structurally well-defined polymers, in terms of molecular weights and molecular weight distributions, their polymerisation must be controlled. However, the control of the reactivity of the propagating chain ends was difficult, until the recent discovery of living (controlled) radical polymerisation. Due to its unique tolerance to water, radical polymerisation can be performed as suspension, dispersion and emulsion processes.

Most of these living radical polymerisations are based on transition metal catalysis (via reversible activation of a carbon-halogen terminal) or nitroxide-mediated processes.

Recently, workers at Kyoto University, Japan, have examined the living radical suspension polymerisation of methyl methacrylate (MMA) in water and alcohols using RuCl2(PPh3)2 catalyst/activator and an organic halide initiator, such as PhCOCHCl or CCl3Br, in the presence and absence of aluminium(III) isopropoxide, Al(Ot-Pr)3, at 80°C (T. Nishikawa, M. Kamigaito and M. Sawamoto, Macromolecules, 1999, 32, (7), 2204–2209).

With ruthenium(II)-initiation, living radical suspension polymerisation of MMA proceeded to give poly(MMA) with controlled high molecular weights (Mn) and narrow molecular weight distributions (Mn/Mw = 1.1 to 1.3). In water, the PhCOCHCl/RuCl2(PPh3)2 initiating system gave poly(MMA) of Mn ~ 104 and Mw/Mn ~ 1.1, even in the absence of Al(Ot-Pr)3.

Polymersations were faster in water than in organic solvents, such as toluene. The radical mechanism of the polymerisation was confirmed and the high stabilities of the dormant carbon-halogen terminal and of the ruthenium catalyst in water and alcohols were demonstrated. Ruthenium complexes are known to be weakly oxophilic and sometimes water tolerant.

This living radical suspension polymerisation may also be used with other metal complexes or monomers and be applicable to the precision synthesis of block and random copolymers.
Developments in Cisplatin Research

Cisplatin: Chemistry and Biochemistry of a Leading Anticancer Drug
EDITED BY BERNHARD LIPPERT, Wiley-VCH, Weinheim, 1999, 563 pages,
ISBN 3-906390-20-9, £105

It is 30 years since Barnett Rosenberg and his colleagues published their seminal paper in Nature entitled "Platinum compounds: a new class of potent antitumour agents" (1). This initial paper marked the beginning of what was to become one of the most exciting uses of platinum, and initiated international research efforts in scientific fields as diverse as inorganic chemistry, cell and molecular biology, and oncology. The platinum drugs, cisplatin and carboplatin, are still at the forefront of anticancer therapy, and there are four major new compounds presently in clinical trials: JM216 being jointly developed by Johnson Matthey and Bristol Meyers Squibb, AnorMED's AMD473 being developed in collaboration with Zeneca, BBR3464 which is being developed by Roche-Boehringer Mannheim in collaboration with its inventor, N. P. Farrell of Virginia Commonwealth University, and Sanofi's oxaliplatin. Bernhard Lippert's excellent book reviews the achievement, progress, and new developments in cisplatin research over the last thirty years.

The book is divided into 6 Parts and contains 22 chapters, each written by current leaders in the field. The international aspect of the research is demonstrated by the choice of authors who come from Europe, the U.S.A. and Japan. The length of the book precludes a discussion of each individual chapter so selected highlights will be discussed. The choices are purely subjective and reflects the reviewer's own interests.

Discovery of Cisplatin

It is fitting that Part 1, "The Start", is a very personal account of the discovery of cisplatin by Barnett Rosenberg. The account is one of basic research and a physicist's fascination with the similarities between the physical appearance of chromosomes during cell division and the magnetic dipole field such as that seen with iron filings around a bar magnet. It was this unlikely coupling of ideas which gave rise to the experiments that ultimately led to the discovery of the anticancer activity of platinum compounds.

Part 2, "Cisplatin - How Good is it?" by P. J. O'Dwyer, J. P. Stevenson and S. W. Johnson, reviews the clinical use of platinum drugs. What is apparent from reading this chapter is not only the efficacy of the platinum drugs, but the wide range of cancers in which they are a component of the therapeutic regimen. One disappointing aspect of this chapter is that it ends without a concluding section and therefore does not answer the question posed in the title.

Biochemical Mechanisms and Chemical Interactions

Part 3 consists of 4 chapters describing the efforts that have gone into understanding the biochemical mechanism of cisplatin. D. B. Zamble and S. J. Lippard describe the response of cellular proteins to cisplatin-damaged DNA. A group of proteins that recognise the cisplatin-DNA lesion, HMG proteins, appear to be associated with enhanced sensitivity to cisplatin. Another protein of great interest is the product of the p53 tumour suppressor gene. This is discussed both in this chapter and the subsequent chapter by A. Eastman. Eastman discusses the mechanism by which cisplatin-DNA binding leads to cell death by apoptosis (programmed cell death).

Part 4 and Part 5 examine the chemistry of platinum compounds relevant to their anti-tumour activity. R. B. Martin describes the relevance of the hydrolysis of platinum complexes to their mechanism of action; Y. Chen, Z. Guo and P. J. Sadler exploit NMR to examine the interactions of platinum complexes with biomolecules. J. Reedijk and J. M. Teuben review platinum-sulfur interactions relevant to the biochemical mechanism of cisplatin. The reactions...
of platinum drugs with S-donor ligands are important for two reasons: [a] a mechanism of resistance to the platinum drugs is inactivation resulting from the reaction with S-containing biomolecules such as glutathione and methionine, and [b] thiol reagents can potentially act as "rescue agents" to prevent some of the toxicity of cisplatin.

The chapters in Part 5 illustrate how the discovery of the pharmacological properties of cisplatin have influenced the direction of coordination chemistry. Lippert takes a personal look at the "platinum blues", particularly those formed by the interaction of cisplatin and pyrimidine nucleobases. This theme is developed in the following chapters, written by L. Randaccio and E. Zan grando; G. Natile, F. P. Intini and C. Pacifico; and K. Matsumoto.

New Developments

The book ends with a description of new developments. The first two chapters of Part 6 focus on compounds in clinical trials. N. Farrell, Y. Qu, U. Bierbach, M. Valsecchi and E. Menta review the structure-activity relationships of di-and trinuclear platinum compounds undergoing Phase I clinical trials. L. R. Kelland reviews the development of orally active platinum drugs including JM216 and AMD473. The development of AMD473 takes up the theme of thiol reactivity as this compound was designed to have reduced reactivity with thiols, thereby overcoming this mechanism of resistance. K. E. Sandman and S. J. Lippard address the problem of new drug discovery in the light of the recent advances and application of combinatorial chemistry in drug discovery. They evaluate novel screening methodologies for testing libraries of platinum compounds.

One of the striking aspects of this book is the way in which personalities come through the description of the science. This is at its best in the dedication at the end of the chapter by Eastman in which he acknowledges the work of the late J. J. Roberts who was responsible for much of the early fundamental research on the biochemical mechanism of cisplatin. The discovery of cisplatin has inspired many scientists from diverse backgrounds and this is demonstrated throughout the many excellent reviews. Bernhard Lippert is to be congratulated on producing a book consisting not only of numerous scientific articles of high quality describing current research, but also a book that conveys the essence of scientific research. This book is recommended to all those with an interest in platinum chemistry, bioinorganic chemistry, biochemistry, and the clinical development of platinum anticancer drugs, and is a good illustration of their significance.

SIMON P. FRICKE

Reference

Thin-Film Light Emitting

Solid-state light-emitting devices, based on ruthenium(II) complexes and operating at low voltages, do not have the high brightness and efficiency of electrog engenerated chemiluminescence cells, also based on Ru(II) complexes. This is due to a slow electrochemical "charging" mechanism, which redistributes the counterions to create redox states for charge transport and light emission, and delays the device response after an applied potential bias. If solid-state devices are to be used in flat-panel displays, clearly shorter "charging" times (to brightness) are required.

Now, a team from Massachusetts Institute of Technology has produced single-layer, spin-cast films of small-molecule Ru(bpy)3(PF6)2 (1) complexes (bpy = 2,2'-bipyridine) with high-brightness at low voltage, and no need of "charging" or reactive cathode materials (E. S. Handy, A. J. Pal and M. F. Rubner, J. Am. Chem. Soc., 1999, 121, (14), 3525–3528).

Thin films (~ 1000 Å) of the Ru(II) complex were spin-cast onto an indium tin oxide (anode) patterned glass from pyridine solutions. An aluminium cathode completed the devices. All devices had luminance levels of 1000 cd m−2 at 5 V and 200 cd m−2 at 3 V and external quantum efficiencies of 1 per cent at low voltage. The emitted red light could be shifted to a more useful red with increased device stability on replacing ligands in (1) by esterified bpy ligands. Device response times can be shortened by using short, high-voltage pulses, and low voltage operation.
Organometallic Chemistry and Applied Catalysis

A REVIEW OF THE THIRD ANGLO-DUTCH SYMPOSIUM

By Berth-Jan Deelman
Elf Atochem Vlissingen B.V., Vlissingen, The Netherlands

The latest Anglo-Dutch Symposium on organometallic chemistry and applied catalysis was held at the University of Sheffield from 29th to 30th March 1999. It was the third symposium of these highly successful meetings between the Dutch and British communities involved in organometallic chemistry and catalysis. Previous meetings have been held in Amsterdam (1997) and in Sheffield (1996) following an initiative by P. M. Maitlis, K. Vrieze and G. van Koten (Universities of Sheffield, Amsterdam and Utrecht, respectively).

A total of 120 participants attended this symposium which covered a wide range of subjects in catalysis. In addition to lectures by a large number of well-known researchers, a poster session displaying more preliminary results also formed part of the programme. Below, highlights relevant to catalysis using platinum group metals are described, as well as some generally interesting developments in catalysis which were discussed during this meeting.

General Developments in Catalysis

A promising new development using micro-reactors in catalysis was presented by R.W. K. Allen (University of Sheffield). The favourable heat and mass transfer properties in these reactors can lead, in some cases, to better selectivity (reactor control). These reactors appear to be especially promising for fuel cells but may be even more so for rapid parallel screening of catalyst libraries.

An overview on recent developments in combinatorial synthesis, especially in the area of catalysis, was given by M. L. Turner (University of Sheffield). Although the so-called “split and mix technique” is very effective for creating large libraries, containing over 10,000 members, there is a practical problem with identifying and keeping track of the many individual ligands or catalysts that are synthesised.

This problem does not occur in parallel syntheses, but the technique appears to be best suited for smaller libraries, typically with less than 1000 members, although equipment for the generation of larger libraries is being developed.

Current applications and developments in “combinatorial catalysis” are therefore mainly carried out using the parallel approach. It is clear that another very relevant issue, although not addressed by Turner, concerns how a ligand-metal complex library with sufficient diversity of ligands should be constructed, and how the feedback from the screening results should be incorporated into the library, so as to help focus the screening process.

Platinum group metal based homogeneous catalysts and the use of rapid screening techniques for finding catalysts for specific catalytic reactions is also of interest to Johnson Matthey, as reported by A. K. Keep. Often, each specific combination of substrate and desired catalytic reaction requires a particular catalyst and consequently a dedicated screening process. This observation explains the intense current interest in rapid parallel screening techniques for catalysis.

Workers at the University of Liverpool have developed a new high pressure gas flow cell for NMR spectroscopy. This has been developed for in situ spectroscopy and B. T. Heaton described the cell and its uses. It can, for example, be used to study intermediates in rhodium catalysed hydroformylation. The technique
allows NMR measurements to be made under catalytic conditions while gas is bubbling through the sample.

**New and Improved Catalysis**

R. A. van Santen (Technical University of Eindhoven, The Netherlands) described the oxidation of ammonia to dinitrogen and water, achieved using alumina-supported platinum, iridium or copper catalysts. The catalysts developed have a high tolerance to water and use oxygen as the promoter.

Interestingly, the detailed thermodynamics of every step of the catalytic cycle as well as those of deactivation pathways and side reactions (NOx formation) are well understood, based on high level molecular orbital (MO) calculations on low molecular weight model compounds. Pt(NH3)6 supported on HZSM-5 zeolite also proved to be an active ammonia reduction catalyst at low temperatures (473 K), with increased activity and selectivity when water is present in the feed. The group at Eindhoven is now developing catalysts for the electrochemical oxidation of ammonia.

Detailed accounts of recent improvements and better understanding of the BP/Amoco Ir/T catalysts for methanol carbonylation process were given by R. Watt (BP/Amoco) and A. Haynes (University of Sheffield). From a technical and process economics viewpoint, the iridium system has some major advantages over the older rhodium-based process. For instance, it has been found that deactivation of the catalyst takes place by the build-up of HI which enters the water-gas shift reaction to form inactive [Ir(CO)3H]. This can now be successfully suppressed using ruthenium carbyns (such as [Ru(CO)3H]) and other Lewis acidic I- acceptors (such as InI3 or GaI3) as promoters. It was demonstrated by model reactions that the role of the promoters is to abstract I- from the electronically unsaturated [Ir(CO)(Me)3] intermediate, which accelerates the migratory insertion of CO to form the iridium acyl complex, by ~800 times.

The selective hydroformylation of internal olefins to linear aldehydes was described by P. C. J. Kamer (University of Amsterdam). This was achieved using rhodium-xantphos and closely related complexes as catalysts under low carbon monoxide pressures. The catalyst first isomerises the alkene to the terminal olefin and then starts to hydroformylate it.

An elegant 3-component coupling of two equivalents of an electron-poor alkene, an alkyl halide and an alkyltin compound, using a Pd0 complex of the BIAN ligand (BIAN = bis(imino)acenaphthene), was described by C. J. Elsevier (University of Amsterdam), see Scheme I.

The selective partial hydrogenation of internal alkynes was also accomplished using (BIAN)Pd0(cis-CH2=CH-E) (E = CF3, C(O)OMe) (87 per cent selectivity for stilbene).
Compared to the well-known Lindlar catalyst, less E-alkene was synthesised, but sometimes more alkane is formed.

**Asymmetric Homogeneous Catalysis**

In an enthusiastic presentation, V. K. Aggarwal (University of Sheffield) explained that his group has developed a catalytic process for the direct synthesis of chiral epoxides from aldehyde and diazoalkane derivatives, see Scheme II. The catalytic process is believed to consist of two cycles, one involving a rhodium alkylidene and one involving a chiral sulfur ylide. In some cases, [Cu(acac)], was found to be more beneficial than [Rh,(OAc)],, although it is not clear which copper species are formed. Enantiomeric excesses (ee) were generally better than 90 per cent. Using a similar approach, chiral aziridines were also accessible, starting from a functionalised imine as reactant instead of the usual aldehyde.

Chiral cyclopentadienyl ligands with pendant -C₆H₄-2-C'(H)MeNMe₂ arms were reported by C. White (University of Sheffield) to be reasonably effective (ee > 71 per cent, using [C₆Me₆-C₆H₄-2-C'(H)MeNMe₂RhCl₃] as catalyst and a 10-fold excess of free ligand) for the asymmetric hydrogenation of non-functionalised 1-alkenes, a reaction which is known to be notoriously difficult.

**Supported Catalysts and Catalyst Recycling**

A number of presentations dealt with catalyst deactivation and methods for recycling. As explained by the symposium host, Professor P. M. Maitlis, catalyst deactivation in homogeneous catalysis is largely an undiscovered territory. Deactivation is understood for only a few well-known catalysts. The question remains why this is so. It may be that deactivation is not usually investigated because of the higher ratio of product:catalyst value, compared with heterogeneous catalysts which are often used in bulk applications. If this is the case, then homogeneous catalyst recycling may be less economically interesting. Nevertheless, there may be other reasons (environmental issues or optimising the use of noble metals) to explain the efforts going into developing methods for recycling homogeneous catalysts.

One such approach is the development of fluororous catalysts (fluorous refers to being soluble in a fluorinated solvent) which can be recovered by selective extraction with fluorous solvents. Some methods for rendering conventional noble metal catalysts fluorous, by the use of 4-C₆H₄C₆F₁₅ units to prepare triaryl phosphines and bis(diarylphosphino)ethane ligands, were presented by E. G. Hope, University of Leicester. In most cases the fluorous domain of the catalyst has a negative effect on catalytic activity, but at the same time preferential fluorous phase affinity requires the catalyst to have substantial fluorous character (> 60 weight per cent F). The “trick” in this branch of catalysis appears to be to design an ideal electronically insulating spacer to separate the large fluorous domain from the active metal centre. While better results were obtained using P(O-C₆H₄-4-C₆F₁₅), (for rhodium catalysed hydroformylation) and P(C₆H₄-4-OC₆F₁₅), (for rhodium catalysed hydrogenation), the retention of the fluor phase by the catalysts and ligands, and
consequently their efficient recycling, remain to be investigated.

Another approach to catalyst recovery is to anchor the catalyst to a well defined macromolecular support, which will keep the catalyst on one side of the microporous membrane in a membrane reactor. If the large support is soluble and indeed well defined, then fast single site homogeneous catalysis can take place. Professor G. van Koten, Utrecht University, described this technique and noted that carbosilane dendrimers may be the ideal support for this. In his group nickel- and palladium-functionalised dendrimers have already been prepared. The palladated derivative of a phosphine functionalised dendrimer has been successfully used as the catalyst in the codimerisation of styrene and ethylene, see Figure 1. Catalyst retention in a membrane reactor is already rather good for relatively low molecular weight dendrimers but catalyst deactivation is still a problem. Investigations into the origin of this deactivation, whether membrane or dendrimer-related, are now being performed.

Other interesting contributions, not concerned with the platinum group metals, were presented at the Symposium, but are not reviewed here.

In conclusion, the quality of the work undertaken in the U.K. and in The Netherlands and described at the Symposium should ensure that these Symposia will play an increasing role in the exchange of ideas on catalysis.

The fourth Anglo-Dutch Symposium is expected to take place in The Netherlands in the autumn of 2000, probably at the University of Utrecht.

**Sonochemical Platinum Reduction**

Platinum nanoparticle, of interest because of their high catalytic activity, were prepared in an aqueous system using high density ultrasound (200 kHz and 6 W cm$^{-1}$). The nanoparticles were found by researchers from Osaka Prefecture University (Y. Mizukoshi, R. Oshima, Y. Maeda and Y. Nagata, *Langmuir*, 1999, 15, (8), 2733–2737) to be smaller and more regular than those made radiochemically. Stable, homogeneously spherical, monodispersed Pt nanoparticles, of average diameter 2.6 nm, were formed at the rate of 26.7 μM min$^{-1}$ in a Pt(II)-sodium dodecyl sulfate system. Three kinds of reducing species are proposed to be formed in the sonicated system, near and/or in the hot bubbles, and these then react with the PtCl$_2$ complexes to form the platinum nanoparticles.
Catalyst Enhanced Oxidation of VOCs and Methane in Cold-Plasma Reactors

By Muhammad Arif Malik
Applied Chemistry Division, PINSTECH, PO Nilore, Islamabad, Pakistan

and Salman Akbar Malik
Department of Biological Sciences, Quaid-i-Azam University, Islamabad, Pakistan

Volatile organic compounds, VOCs, are used in a number of industrial processes in a variety of roles, for instance as solvents, cleaners and liquid fuels. During these processes, some of the VOCs, which are known to be air toxins, inevitably escape into the surrounding air. It is the release of this VOC-laden air into the atmosphere that is partly responsible for stratospheric ozone depletion, tropospheric ozone increase, global warming (the Greenhouse Effect) and some health problems. Here, we briefly review some applications of platinum metals catalysts in the abatement of VOCs and in the conversion of methane using cold-plasma techniques. Some information on the abatement of acid gases, the generation and application of non-thermal plasmas is also presented.

Volatile organic compounds, VOCs, which are toxic by nature and which are used in industrial processes as solvents, cleaners, thinners, degreasers, monomers and liquid fuels, can be converted into water and less harmful carbon dioxide by thermal incineration at high temperatures (> 700°C) (1). However, thermal incineration requires a lot of energy to heat up the ambient gas molecules. Some of this energy can be saved by incorporating a suitable catalyst into the incineration system, enabling the oxidation reaction to be performed at lower temperatures (~ 300 to 500°C) (2). Clearly, this still involves using elevated temperatures.

The use of cold plasmas can offer a promising alternative to the combustion of VOCs. By selectively channelling electrical energy into the desired plasma, chemical reactions occur at ambient temperature and pressure to break up the VOCs into smaller components (3, 4). Cold plasmas are produced by electrical discharge techniques (5–15), and have been utilised in a number of industrial applications (5–8, 16–23). In cold-plasma techniques, free electrons are accelerated under the influence of the strong electric field produced by electrical discharge. Heavier ions and the bulk of the neutral molecules remain close to room temperature (6, 7). The high-energy electrons undergo inelastic collisions with the ambient gas molecules to produce reactive species, such as 'O, 'OH, 'HO₂, 'H, 'N, O₂, N₂, O₂, O₂, O₂, OH, N₂, N, O₂, and O₂ (6–8, 14, 24, 25). These free radicals, ions and excited-state molecules in turn oxidise the targeted VOCs.

Cold-plasma techniques are rapidly being developed for the destruction of toxic VOCs in air (3, 4, 26–29), soil (30) and water (31, 32), as discussed in reviews (15, 33–43). They are also being developed for the abatement of other air pollutants, such as sulfur oxides, nitrogen oxides and carbon dioxide (7–9, 34, 35, 38, 44, 45).

Cold Plasmas with Catalysts
Combining cold plasmas with catalysis is an emerging technique which can oxidise VOCs at a much faster rate, at a lower temperature and with lower input energy, when compared with cold plasma or thermal catalysis techniques alone (15, 20, 46–49).

For example, when acetone-containing air was passed at a flow rate of 400 cm³ min⁻¹ through
a wire-cylinder type pulsed corona discharge reactor, the acetone concentration was reduced from 40 to 30 μmol min⁻¹. When the discharge gap of this reactor was packed with alumina pellets (3–5 mm diameter), the acetone concentration was found to be further reduced from 40 to 6 μmol min⁻¹, the other operating conditions being identical (48). The operating conditions were: room temperature, atmospheric pressure, 9 W power from a DC source (as high voltage pulses of 45 kV (positive polarity), 4 μs width, 0.4 μs rising time and constant frequency) and a reactor volume of 100 cm³ (48). There was, however, almost twice as much of the by-product ozone produced when alumina was present.

When the macroporous alumina was replaced by alumina having primarily meso- and micropores, the ozone was reduced to a negligible level, without affecting the efficiency of the VOC destruction (49). Alumina can therefore be used as the support for the active metal catalysts.

In a further example, palladium-coated spherical pellets of porous γ-alumina were shown to decompose methane in corona discharges (15, 50). The nitrogen oxides formed were significantly reduced when this palladium coated γ-alumina catalyst was employed.

By comparison with conventional catalytic reactors, excellent results have also been achieved using platinum, palladium and rhodium, for example, as catalysts in cold-plasma catalytic reactors (51), to convert Freon and methane into simpler molecules.

Electrode surfaces can also catalytically enhance the oxidation of VOCs, if a catalytically active material is incorporated into the electrode structure. When stainless steel electrodes were replaced by electrodes having catalytically active noble metal or noble metal alloy surfaces, the destruction of methane in cold plasma was improved (52).

The decomposition of air pollutants other than VOCs (sulfur oxides, nitrogen oxides and carbon dioxide) has also been improved by the addition of suitable catalysts in the cold-plasma environment (15, 53–55). As an example, sulfur dioxide could be removed with high efficiency after a very short treatment time when palladium- and platinum-coated γ-alumina were used in a corona discharge reactor (15).

Partial Oxidation of Methane

The partial oxidation of methane (a major component of natural gas) in cold plasma yields far more valuable products than its complete oxidation (to carbon dioxide and water). C₂ products (ethane, ethene and acetylene) (56, 57), hydrogen (58), synthesis gas (59–61), methanol (62–66) and formic acid (66, 67) are just some of these products.

There are two major obstacles to overcome in methane activation:

1. the tetrahedrally arranged strong C-H bonds of methane do not allow space for oxidising agents to attack and
2. the 'CH₂ produced from methane is likely to undergo further oxidation, which may convert it to carbon dioxide and water.

Consequently, conventional thermal activation of methane requires high temperatures (>1000°C), gives low yields and is costly. The addition of suitable catalysts, particularly supported noble metal catalysts, such as platinum, palladium, rhodium and ruthenium, can activate methane at relatively lower temperatures, at faster rates and with better selectivity to the desired products (68, 69).

Effects of Microwave Irradiation

Microwave irradiation of suitable catalysts, such as proton conductive catalysts, oxygen ion conductive catalysts, activated carbon or charcoal, can convert methane at lower temperatures and give higher yields of the desired products than conventional heating (70–75). Under certain conditions, microwave irradiation can generate cold plasma which selectively converts methane to acetylene (72). Methane conversion in plasma takes place faster, at lower temperatures (~500°C) and needs lower input energy (about one half) than the thermally driven process (76, 77).

Indeed, combining the cold plasma with catalysis can further improve the energy efficiency as well as the selectivity of the desired products.
In general, methane conversion in different reactors follows the order (80):

Plasma-catalytic > plasma > catalytic > thermal

High-energy electrons and oxidising species, such as \( \text{O}, \text{O}^\cdot \) and \( \text{O}_2 \), present in the cold plasma environment, can produce \( \text{CH}_2 \) radicals from methane by hydrogen abstraction (56, 82, 83). The catalyst adsorbs the free radicals and their target molecules, allows the desired chemical reaction to take place on a solid surface and finally releases the products (79, 80).

When catalytic materials, such as platinum, nickel, iron, manganese dioxide and molybdenum trioxide, were placed next to the microwave plasma cavity (79, 81), platinum was found to give the highest methane conversion of 55 per cent. Product selectivities of 54 per cent for ethane, 27 per cent for ethylene, 7 per cent for \( \text{C}_2 \) hydrocarbons, and 6 per cent for formaldehyde/methanol were achieved with platinum as the catalyst.

The application of an electric field inductance (EFI), used to evolve a high density of microwave plasma to the cold-plasma-catalytic reactor, results in further increases in the methane conversion (80). The highest methane conversion to \( \text{C}_2 \) hydrocarbons, of 63.7 per cent, was achieved by employing a palladium-nickel bimetal catalyst in the cold-plasma-catalytic reactor in the presence of EFI.

Effects of Corona Discharges

A disadvantage of microwave plasma is that it usually operates at pressures below atmospheric, which makes it less suitable for large-scale applications. Cold plasmas established at ambient conditions, such as by corona discharges, have proved successful for methane conversion (56–67). The addition of a suitable catalyst in the discharge gap of corona discharge reactors has achieved faster rates of methane conversion and better selectivity to the desired products, while requiring less input energy than when catalyst is absent (20, 84–86).

Replacing the stainless steel electrodes in the cold plasma reactor with ones containing some catalytically active metal can enhance methane conversion. Almost the same methane conversion (~ 6 per cent) and selectivity for \( \text{C}_2 \) products (~ 80 per cent) were achieved with about half the input power (35 kV, 4.6 W) by using copper instead of stainless steel electrodes (45 kV, 9 W) in a DC pulsed corona discharge reactor at a flow rate of 30 cm\(^3\) min\(^{-1}\) for a methane:oxygen feed of 95:5 (87).

Noble metal electrodes have the best results for the conversion of methane to \( \text{C}_2 \) hydrocarbons in a pulsed corona discharge. Results for the electrodes were in the following order (88):

\[
\text{Platinum} > \text{palladium} > \text{copper}
\]

Conclusion

From the above discussion, it may be inferred that using catalysts, particularly catalytically active platinum group metals, in cold-plasma reactors has become an active area of research in the last few years. The growing demand for controlling VOC emissions, for better utilisation of natural gas reserves, together with the rapid pace of development in this area, suggests that there may well be future applications for such catalysts on an industrial scale in cold-plasma reactors.

Acknowledgment

Financial support from the Ministry of Science and Technology, Government of Pakistan, is gratefully acknowledged (Ref. No. HRD-94/CH(1)298-ASA(Trg)).

References


*Platinum Metals Rev.*, 1999, 43, (3)
Encapsulation of Platinum in Dendrimers

The high surface:volume ratios of platinum nanoparticles enhances their catalytic properties, and makes their production and utilisation of great importance. A successful sonochemical preparation of platinum nanoparticles is reported on page 108 of this journal.

Conventional routes for nanoparticle preparation include evaporation and condensation, and metal salts reduction, both requiring stabilisers of polymers, ligands or surfactants to control particle size and prevent agglomeration, but which passivate the cluster surfaces. Clusters and colloids can also be prepared using templates of reverse micelles and porous membranes, but again passivation occurs unless the template is removed.

Now researchers from Texas A & M University have developed a method to produce a less passivated platinum catalyst by using a dendrimer as both stabiliser and template (M. Zhao and R. M. Crooks, Adv. Mater., 1999, 11, (3), 217–220). A fourth generation (G4) polyamidoamine (PAMAM) Starburst dendrimer was loaded with a predetermined amount of platinum(II) ions followed by reduction with BH$_4^-$. From 12 to 60 Pt nanoparticles may be inside each dendrimer without agglomeration for up to 150 days. The dendrimers are spherical, monodispersed, highly functionalised and branched, with an open centre and sterically crowded exterior. They can entrap the Pt ions and stabilise the clusters without totally passivating the surface. This hydroxyl-terminated dendrimer provides stability and size control to the Pt particles (diameter ~1.5 nm) and permits substrates to penetrate the interior and access the cluster.

When attached to gold electrodes, in the presence of O$_2$, Au/G4-OH(Pt$_{120}$) gives an enhanced catalytic current and a shift in peak potential to 75 mV, compared to a Au/G4-OH modified electrode. In the presence of O$_2$ only a small current is observed, confirming that O$_2$ reduction is taking place, and making this of potential interest for fuel cell catalysts.
A number of both large- and small-scale homogeneous catalytic processes have been in commercial operation for many years (1–3), and a significant proportion of these depend on platinum group metals catalysts, sometimes involving more than one metal. The Cativa process operated by BP Chemicals for the production of acetic acid from methanol, has recently been using a soluble iridium/ruthenium catalyst system which includes both of these features (4).

In general, homogeneous processes are characterised by both high chemical and high energy utilisation efficiencies but a major deterrent in the further exploitation of this methodology has been the perceived inability to readily separate the products from the catalysts. Attempts to overcome this difficulty have included ligand modification, biphasic catalysis and efforts to support homogeneous catalysts on polymeric and inorganic supports. The use of supports for the catalysts has in the past been only partially successful as most of these systems have lost catalytic metal species into solution during the reactions.

The recent results reported by R. J. Angelici and H. Gao of the Iowa State University, U.S.A., are therefore of particular interest, because they result from combining the attributes of a firmly tethered homogeneous catalyst with synergistic assistance from a silica-supported metal-particle heterogeneous catalyst (5–7). These effects were demonstrated in arene hydrogenation, and such a combination catalyst has been called a “tethered complex on a supported metal”, TCSM.

In the earliest of these three papers (5), the first examples of TCSM catalysts were reported. Activity for the hydrogenation of toluene to methylcyclohexane was substantially higher than that of the tethered complex or of the supported metal separately (40°C and 1 atm hydrogen). Rates and turnover frequencies, TOF, were low but the results indicated that there was potential for more combination reactions of this type. Two TCSM catalysts were prepared by tethering one of the rhodium isocyanide complexes, RhCl(CO)[CN(CH3)2Si(OEt)2], (Rh-CNR2) or RhCl[CN(CH3)2Si(OEt)2], (Rh-CNR2), to a silica supported palladium metal catalyst (Pd/SiO2) by refluxing in toluene for 4 hours, see Figure 1.

Hydrogenation of Arenes

In a more recent paper (6) on this topic, rhodium and platinum isocyanide complexes RhCl(CO)[CN(CH3)2Si(OEt)2], (Rh-CNR2), RhCl[CN(CH3)2Si(OEt)2], (Rh-CNR2), and PtCl2[CN(CH3)2Si(OEt)2], (Pt-CNR2) were tethered to the SiO2-supported platinum group metal heterogeneous catalysts M-SiO2 (M = Pd, Pt, Ru) to give the TCSM catalysts: Rh-CNR2/Pd-SiO2, Rh-CNR2/M-SiO2 (M = Pd, Pt, Ru) and Pt-CNR2/Pd-SiO2, respectively. These TCSM systems were used to catalyse the hydrogenation of arenes (Rh-CNR2/Pd-SiO2, and Rh-CNR2/M-SiO2) and cyclohexanone (Pt-CNR2/Pd-SiO2) under the same mild conditions of 40°C and 1 atm hydrogen. They again showed activities that are higher than those of the homogeneous Rh (or Pt) isocyanide complex by themselves, the SiO2-supported metal heterogeneous catalyst itself, or the Rh (or Pt) complex catalyst tethered to SiO2 itself. The activities of the TCSM catalysts were strongly affected by the nature and loading of the supported metal in the catalyst. Of the three SiO2-supported metal catalysts, M-SiO2 (M = Pd, Pt, Ru), the Rh complex Rh-CNR2 tethered on Pd-SiO2 gave the

highest activity for the hydrogenation of toluene (TOF = 5.5 mol H₂ (mol Rh min)⁻¹ and turnover number, TON = 2420 mol H₂ (mol Rh)⁻¹ during 8.5 h). The Rh-CNR/Pd-SiO₂ catalyst with 10 wt.% Pd is more active than its counterparts with higher or lower Pd loadings. Spectral studies using diffuse reflectance infrared Fourier transform (DRIFT) measurements on the TCSM catalysts before and after use for toluene hydrogenation showed that the isocyanide ligands remained co-ordinated to the Rh (or Pt) centre, even after extended use. Furthermore, atomic emission spectroscopic analysis of the hydrogenation solutions indicated that there was no leaching of Rh (or Pt) into the solutions.

One possible mechanism of these reactions, which may help to explain the high activities of the TCSM catalysts, involves considering the supported palladium particles as the sites at which hydrogen is dissociated and spills over onto the silica. The tethered homogeneous complex may bind and activate the arene substrate, and this then reacts with the spilled-over hydrogen, thus producing the synergistic effect.

**Hydroformylation of 1-Octene**

In another paper from the same laboratory, the hydroformylation of 1-octene was studied under atmospheric pressure using rhodium carbonyl thiolate complexes tethered to silica (7). It was shown that these catalysts are highly active for 1-octene hydroformylation in the presence of phosphate donor ligands at 60°C and 1 atm. The high activity resulted from the stabilisation of Rh(SR)(CO)₂PR₃⁺ (I) species on the catalyst surfaces. High selectivity to aldehyde was produced and the n:iso product ratios could be widely varied by choosing an appropriate phosphate (R' in (I)). The catalysts were easily separated from the reaction mixtures and the catalyst activity could be maintained through at least three cycles over a total period of 69 hours, during which time there were 1273 (mol aldehyde (mol Rh)⁻¹) turnovers. The hydroformylation rate, conversion, and chemo- and regioselectivity were markedly affected by the phosphate donor and the PR₃⁺:Rh mole ratio. With the P(OPh), phosphate ligand, a particularly fast reaction time and high TOF of 1.19 min⁻¹ was achieved, together with a high n:iso ratio of 12.0.

It can be anticipated that further investigations on the effective tethering of organometallic catalysts to inorganic supports which carry catalytic metal particles will lead to more examples of synergistic effects in TCSM catalysts. This could result in the emergence of a broad range of possible applications in both the speciality and large scale chemical processing areas.

**References**


*Platinum Metals Rev.*, 1999, 43, (3)
The Effects of Hydrogen on the Physical Properties of Palladium

HYDROGEN-PHASE “NAKLEP” PHENOMENON DURING THE HYDROGEN TREATMENT OF PALLADIUM

By V. A. Goltsov
Donetsk State Technical University, Donetsk, Ukraine

Palladium is not polymorphic, which is why the physical metallurgy of palladium and its alloys is quite poor in comparison with those of polymorphic metals (such as iron, titanium, and others). In recent years advances in the physical metallurgy of palladium and its treatment have been taking place. The changes are based upon the physical effects that hydrogen has upon palladium when it is taken into the metal (1). In Ukraine and Russia this has been called “hydrogen-phase naklep” and was first noted in 1972. This observation has led to an improved concept in materials science and engineering (1–5).

When palladium is saturated with hydrogen, it becomes a polymorphic material and hydride transformations may be induced in it by processes of heating ↔ cooling and/or saturation ↔ desaturation. As there are differences between the specific volumes of the α-hydrogen solid solution and β-hydride phases in the palladium, these hydrogen-induced phase transformations cause internal plastic deformation (relaxation) and controllable strengthening of the palladium. Some basic changes of structure also occur: the density of dislocations grows, the size of the ‘mosaic’ blocks decreases while their number increases, the angle of their disorientation increases, and so on.

Unlike the internal cold work which occurs during the martensitic transformations in iron alloys, the structure changes mentioned above in palladium-hydrogen alloys are not only caused by internal plastic deformation but also by the development of some very specific processes of interactions of the solute hydrogen in the palladium, generating hydrogen-containing phases and producing defects in the crystalline structure.

Because of the complex nature of this type of physical phenomenon, it has been described as “hydrogen-phase naklep” or the “HPN-phenomenon” (2, 5).

Strengthening Effects

Annealed palladium has relatively poor mechanical properties, namely:

- Ultimate strength $\sigma_u = 180–200$ MPa;
- Yield limit $\sigma_y = 50–100$ MPa;
- Relative elongation $\delta = 20–25$ per cent.

An early noted HPN-phenomenon (1) was achieved by thermocycling specimens of palladium wire in hydrogen (20 ↔ 250°C), after which the wire specimens (diameter 0.5 mm) were fully degassed. During the hydrogen treatment the strength properties of palladium increased by a factor of 2–4, but the plastic properties of palladium decreased. It was consequently surmised that the HPN-treatment could be effectively used for strengthening palladium articles, without noticeable changes to their dimensions and shape.

Superstrength Palladium Alloys: TRIP Alloys

Treating palladium alloys with hydrogen without immediate degassing can result in the formation of superstrength palladium-hydrogen alloys having high plasticities – the hydride TRIP-effect. (TRIP is transformation induced plasticity.)

The example shown in Figure 1 was achieved by a double (combined deformation-hydrogen)
treatment (3). First, 90 per cent of the possible plastic deformation of a palladium wire was induced, until it reached a specimen diameter of 0.5 mm. After this initial mechanical treatment, the palladium specimen had very high strength properties (points a and b) and very low plastic properties (point c). Samples were then HPN-treated. Hydride transformations, \( \alpha \rightarrow \beta \rightarrow \alpha \), were effected by a number (n) of pressure cycles (0.2 MPa \( \rightarrow 1.33 \) Pa \( \rightarrow 0.2 \) MPa) in a hydrogen atmosphere at 100°C. After this the specimens were not degassed and a new palladium hydrided material was obtained. From Figure 1 it is clear that this new hydrogen-containing material \((n = 1-2)\) is much stronger and has been found to be more plastic than the pure, annealed palladium.

The nature of HPN-strengthened metals having hydride TRIP-plasticity has been reviewed and detailed analysis of the hydrogen treatment of metals and metallic materials, based on hydrogen phase naklep has been more fully discussed (3, 4).

**Recrystallisation Treatment**

HPN-strengthened palladium material has undergone recrystallisation annealing and its grain structure has been refined.

Samples of palladium wire were annealed in vacuum (about \( 10^{-1} \) Torr) for 6 hours at 900°C. A metallographic investigation of the samples was then undertaken. The samples were found to have extremely large grains (generally, only two or three grains in the 0.5 mm cross section of the wire). Their size was in the range 0.25 to 0.15 mm.

The samples were then HPN-treated and metallographic investigation showed them to have the same grain size as did the annealed samples. Annealings at 100 and/or 200°C did not significantly change the microstructure or the character of the high angle boundaries.

However, for samples annealed at 300°C, the development of first-stage recrystallisations may be seen. Small, newly crystallised grains could be seen near the boundaries of the initially large grains. The dimensionally smallest of these newly changed grains was of the order of 15 \( \mu \)m; but others may be 3–5 times larger. Annealing twins have also been observed. Annealing at 400°C led to further development of these recrystallisation effects, while above 500°C the grain sizes became significantly larger (by about 7–10 times).

**Conclusion**

HPN is the experimentally observed phenomena of the transitions of metals and alloys, in particular palladium, into controllable high strength states with special physical properties during courses of charging with hydrogen and transformation of \( \alpha \)-phase solid solution \( \leftrightarrow \) \( \beta \)-phase hydride. Therefore, HPN-phenomena may form the basis for the hydrogen treatment of palladium materials aimed at improving their structure and properties without noticeably affecting their dimensions and shape. Based on this treatment, novel advanced palladium alloys have now been made (5).
References


Platinum 1999

During 1998 the world supply of platinum increased by 9 per cent to reach 5.4 million oz, while demand increased by 4 per cent to 5.35 million oz. Demand was higher mainly due to the increased fabrication of jewellery in China and the U.S.A. However, industrial demand weakened slightly. Supplies of platinum from South Africa declined slightly, but supplies from Russia, despite a four month suspension of exports during the first four months of 1998, rose by 400,000 oz to reach a record 1.3 million oz. These are just some of the facts contained in the latest Johnson Matthey annual market survey of the platinum group metals, “Platinum 1999”. The review covers the supply, mining and exploration, and demand for the platinum group metals during 1998, with most emphasis being on platinum and palladium.

The major industrial use of platinum is in catalytic converters, and in 1998 this was unchanged at 1.83 million oz, supported by a rising use of platinum for diesel engines. Demand in Europe rose by 5 per cent, due to increased sales of diesel cars. In North America demand for platinum rose by only 1.25 per cent as consumers showed a preference for larger sized gasoline vehicles which carry palladium-based catalyst systems. The implementation of tighter emissions standards and the selection by U.S. manufacturers of palladium to meet hydrocarbon limits caused a 50 per cent surge in palladium sales.

An increase in the use of platinum for the hard disks of personal computers, which incorporate a platinum-cobalt layer to improve data storage, outweighed a lower demand for thermocouples. In total, demand from the electrical sector increased by 15,000 oz to 320,000 oz.

Sales for platinum investment products rose by 75,000 oz to 315,000 oz in 1998, with higher demand for the platinum American Eagle coins in the U.S.A. and large investment bars in Japan.

Consumption of platinum by the chemical industry rose by 30,000 oz to 265,000 oz, with demand for platinum process catalysts being strong. Typical of this was the platinum used for the rising production of silicones for sealants and adhesives for the construction industries of North America and Europe.

Fuel cells accounted for only a small part of platinum consumption in electrical applications but the prospects for significant demand in the future is improving. Several car manufactures have demonstrated fuel cell cars, but further work is required.

Demand for palladium rose to 8.19 million oz in 1998, while supplies rose to 8.4 million oz. Greatest demand was from the auto industry which reached 4.47 million oz, an increase of 1.27 million oz compared with 1997.

“Platinum 1999” contains two special feature on platinum in hard disks and on developments in automotive emissions legislation which describes the increasingly strict controls over vehicle emissions in Europe, Japan and the U.S.A.

Readers of *Platinum Metals Review* who wish to receive a free copy of “Platinum 1999” are invited to contact Ms Emma Johnson at Johnson Matthey PLC, 40–42 Hatton Garden, London EC1N 8EE; e-mail: johnse@matthey.com; fax: +44-(0)20-7269-8389.
Aftertreatment for Low Emission Vehicles

A SELECTIVE REPORT FROM THE 1999 SAE ANNUAL CONGRESS

The 1999 annual congress of the Society of Automotive Engineers (SAE) took place in Detroit from 1st to 4th March with 46,309 delegates and 1104 companies exhibiting new products. Some 1120 papers were scheduled for presentation covering all the automotive technologies, although fire curtailed some sessions. Papers on exhaust gas aftertreatment focused on tighter emissions requirements from conventional gasoline, lean-burn gasoline and diesel engines. Some new legislation and a selection of papers are reviewed here, with SAE numbers being given.

New Legislation

In 1998 a number of new emissions levels were introduced or proposed. In the U.S.A. National, NLEV, standards were adopted in 49 states, and the Environmental Protection Agency (EPA) concluded that the more stringent Tier II standards were needed. California adopted a LEV II programme, stringent standards for hand-held engines, a three-way catalyst (TWC) based standard for off-road spark ignition (SI) engines less than 25 hp, tight standards for recreational marine engines, and higher requirements for some motorcycles. The EPA announced plans to establish a voluntary heavy-duty diesel engine retrofit programme. The revised LEV and ULEV standards involve major hydrocarbon (HC) and nitrogen oxides (NOx) reductions, and the SULEV standard has exceptionally demanding emission levels.

In Europe gasoline car emissions have been agreed for 2000 (Stage 3) and 2005 (Stage 4). A range of measures will be developed for on-board diagnostics (OBD), cold start and in-service compliance along with tax incentives allowed for early introduction of Stage 4 standards. Gasoline and diesel fuel sulfur levels will also be markedly reduced.

Conventional Gasoline Engines

Low emissions demand that aftertreatment systems operate immediately after starting the engine. High activity catalyst formulations have low temperature light-off, and when combined with effective heat- and mass transfer and low heat capacity, respond quickly. Mounting the catalyst close to the manifold (close-coupled) minimises the time the catalyst takes to reach working temperature.

In the U.S.A., SWN and MECA (1999-01-0774) demonstrated that LEV II ULEV levels can be obtained by combining advanced catalysts on high cell-density substrates with insulated exhaust components. In examining systems for Europe – Elasis, Napoli University, Magneti Marelli and Fiat in Italy (1999-01-0775) concluded that a close-coupled starter catalyst and a main underfloor catalyst, or a closed-coupled main catalyst, are cost-effective solutions.

Thin Wall High Cell-Density Catalysts

These catalysts have high geometric surface area with lower heat capacity and backpressure than standard materials. BMW, NGK and Friedrich Boysen (1999-01-0767) developed a system with a relatively thin wall substrate (400 cps/4.3 mil, cells per square inch/thousandths of an inch) for a LEV/Stage 3 V8 engine. This had a close-coupled high palladium tri-metal catalyst on each air-gap insulated manifold, and an underfloor palladium/rhodium (Pd/Rh) catalyst. Corning, Johnson Matthey and DaimlerChrysler (1999-01-0273) compared physical durability of standard (400 cps/6.5 mil) and thin wall substrates (600 cps/4.3 mil and 400 cps/4.5 mil) coated with high temperature stable washcoats. Predicted and measured thermal shock parameters agreed, showing that the new catalysts have superior thermal shock resistance and are suitable for close-coupled positions.

Corning (1999-01-0269) confirmed improved thermal shock characteristics are due to a lower coefficient of expansion resulting from improved composition and manufacturing processes. Delphi, Corning, SWRI and ASE (1999-01-0271) had benefits using 600 cps/3.5 mil substrate over standard 400 cps/6.5 mil material;
but 600 cps/4.3 mil had more backpressure, restricting acceleration, which was not the case with the 600 cps/3.5 mil substrate.

DaimlerChrysler, Degussa and NGK (1999-01-0272) reported a similar study for V6 and V8 engines for Stages 3 and 4. Their system used close-coupled (600 cps/3.5 mil) and two underfloor catalysts (400 cps/4.3 mil). Contributions from the washcoat thickness to the backpressure of high cell-density catalysts were noted. Mazda (1999-01-0307) varied the amount and ratio of platinum group metals (pgm), catalyst promoters, catalyst layering and cell-density. Both 600 cps/4 mil and 900 cps/2 mil substrates were examined, the latter giving 35 per cent lower tail-pipe HC emissions. Honda and NGK (1999-01-0268) compared 600 cps/4.3 mil and 1200 cps/2 mil catalysts. High conversion was obtained with the high cell-density catalyst, but mechanical strength was a concern.

Honda's (1999-01-0772) ZLEV system (one-tenth of the ULEV limits) had reduced engine emissions due to high swirl with variable valve timing and lift, and improved spark plugs with durable small-diameter iridium centre electrodes. They maintained high temperature and prevented quenching. Fuel control was optimised during start-up, and precise air:fuel control was maintained by controlling the air:fuel ratio in each cylinder. Retardation of the ignition gave fast heating of a close-coupled high cell-density Pd-only starter catalyst (1200 cps/2 mil), followed by TWCs and a two layered catalyst comprising a HC-trap with a top layer TWC. At low temperature HC is trapped, but is released as the system warms to 100°C, when the TWC layer converts part of the released HC.

Electrically Heated Catalysts
Trapping HCs when cold then releasing them onto a working catalyst has several variations. Other methods of treating HCs include Exhaust Gas Ignition (EGI) when air-diluted rich exhaust gas is combusted ahead of a TWC, and the use of a special catalyst which oxidises carbon monoxide (CO) at low temperature. Electrical pre-heating has been widely researched and Emitec (1999-01-0770) reviewed the advantages of Electrically Heated Catalysts in SULEV systems. Increasing the gas temperature by electrical heating can offset thermal mass effects and shorten the catalyst light-off time.

Platinum Group Metals in Catalysts
Originally TWCs were predominately platinum/rhodium (Pt/Rh) formulations. Legislation, particularly in the U.S.A., emphasised attaining low HC emissions, and Pd-containing catalysts can achieve high HC conversions. Using these catalysts resulted in a wider use of Pd at increasingly higher loadings. Three types of Pd-containing TWCs are available: Pd-only, Pd/Rh, and tri-metal (Pd/Rh/Pt). The amount of Pd used in autocatalysts now exceeds that of Pt and Rh, and greater flexibility in the metals used might help future supply/demand considerations.

Johnson Matthey examined (1999-01-0309) conditions favouring Pd/Rh compared with Pd-only catalysts for NOx control. At low temperature both perform similarly, but high temperatures accentuated differences which give advantages to Pd/Rh catalysts in NOx conversions. This is because sulfide poisoning becomes more significant at high temperature when the exhaust is rich (reducing), so actual catalyst choice depends on the vehicle. Johnson Matthey (1999-01-0308) showed that increasing the Rh:Pd ratio in a standard lower loaded Pd/Rh catalyst maintained acceptable performance, but new improved formulations have lower Pd content. The activity of a new low-loaded Pd/Rh catalyst is better than the standard with twice the amount of pgm. This will allow Pd load reductions or improved performance at standard loadings. Pd/Rh catalysts with higher activities than standard Pd/Rh formulations have also been developed, thus giving options for managing pgm demand.

Lean-Burn Gasoline Engines
Direct injection (DI) gasoline engines capable of lean operation offer reduced fuel consumption, but their NOx control is a challenge. One method is to store NOx and release it for reduction over a TWC. A NOx-trap combines these. Ricardo (1999-01-1281) had a fast
light-off close-coupled catalyst and underfloor NOx-trap on a car with a stratified charge DI engine. With significant engine management modifications low tail-pipe emissions can be achieved, and effective NOx-traps allow engine calibration for fuel economy.

Control of operating parameters is critical for optimum performance and Ford (1999-01-1283) measured stored NOx from the quantity of fuel used in regeneration. Bosch (1999-01-1284) described a management system for DI gasoline engines, aftertreatment assumed a fast heated catalyst for early HC conversion, a NOx-trap with low oxygen storage (OSC) and a TWC with significant OSC. Temperature and oxygen sensors provided control inputs. Toyota (1999-01-1279) analysed NOx-trap sulfur poisoning, and suggested a hexagonal cell substrate of uniform washcoat thickness containing components which form hydrogen via steam reforming. While progress has been made, NOx-traps need low sulfur fuel, which should become increasingly available.

**Diesel Aftertreatment**

Diesel engines run lean with excellent fuel economy, but reduction of their NOx and particulate matter (PM) is difficult to achieve. Michael Walsh (1999-01-0107) reviewed diesel legislation and the tremendous progress in diesel combustion engineering, fuelling, and oxidation catalysts. A few modern diesel cars already meet Stage 3 emissions levels and a few small cars may meet Stage 4 requirements before 2005, but most vehicles will require effective NOx aftertreatment.

**NOx Reduction and Soot Removal**

Methods to remove NOx were discussed by the German FEV (1999-01-0108). Diesel exhaust contains only a small concentration of reducing species, limiting lean-NOx catalysts to about 15 per cent conversion. Injecting fuel, via the engine or directly into the exhaust, increases the available reductant and can increase NOx conversion to about 30 per cent. Degussa and ICT (1999-01-0109) showed how two Pt catalysts could be optimised. Unfortunately, such approaches will be insufficient in many situations, and methods able to provide high NOx conversions are needed, Selective Catalytic Reduction (SCR) being one. Ammonia, or a derivative such as urea, is injected into the exhaust before a SCR catalyst. This can give NOx conversions of 75 per cent, but there is no infrastructure for urea distribution and the weight and volume of an additional tank for refuelling must be considered. Another emerging technology is NOx-trap technology, similar to that for DI gasoline engines and operating at the lower temperatures of diesel exhaust. Sulfur tolerance, low temperature operation and obtaining regenerating conditions are concerns.

Soot (or PM) removal from diesel exhaust is necessary to meet future legislation. Major engine-based improvements have been successful, but more are needed. Hino (1999-01-0471) stated that with low sulfur fuel, high loaded Pt oxidation catalysts can remove some PM, but with high sulfur fuel sulfate forms over the catalyst and thus increases the PM. The Continuously Regenerating Trap (CRT™) uses a Pt catalyst to provide nitrogen dioxide which oxidises filtered PM at low temperature and prevents soot build-up in the filter and possible uncontrolled burning which can destroy filters. FEV described (1999-01-0108) a light truck fitted with a CRT™, cooled and filtered recycled exhaust gas, and fuelled by low sulfur fuel. The exhaust temperature of 200-500°C was suited to a CRT™ and is likely to be used more in future. FORTH/CPERI from Greece and Johnson Matthey (1999-01-0468) described design and selection criteria for sizing CRT™ filters. This employed a filter flow model that was validated by experimental measurement.

**Conclusions**

The Detroit SAE Congress has again been a focus for reviewing developments in emissions control technology; catalyst systems containing pgms clearly will still play a most crucial role in exhaust aftertreatment of low emission vehicles. SAE papers may be obtained from http://www.sae.org/products/sae99pap.htm or 400 Commonwealth Drive, Warrendale, PA 15096. M. V. TWIGG
On the Sesquicentennial Anniversary of his Death

By Professor George B. Kauffman
Department of Chemistry, California State University, Fresno

Johann Wolfgang Döbereiner, born in 1780, was the Professor of Chemistry and Technology at the University of Jena from 1810 to 1849. During this time he observed the action of platinum black on hydrogen, which led to his invention of the pneumatic gas lighter (Feuerzeug) and to Berzelius' concept of catalysis, besides making other contributions to pure and applied chemistry. On the one hundred and fiftieth anniversary of his death in 1849 a Festkolloquium was held to commemorate his work at the Friedrich-Schiller-University of Jena. Here we describe some aspects of his life and work.

On 7th May 1999, a Festkolloquium, in honour of Johann Wolfgang Döbereiner, was held at the Friedrich-Schiller-University Jena (Friedrich-Schiller-Universität Jena). The event was organised by the Chemisch-Geowissenschaftliche Fakultät, Institut für Anorganische und Analytische Chemie of the University, which was founded in 1558 and which has numbered among its faculty the illustrious philosophers Johann Gottlieb Fichte, Georg Wilhelm Friedrich Hegel and Friedrich Wilhelm Joseph von Schelling; the writer and critic Friedrich von Schlegel; and the dramatist and poet (Johann Christoph) Friedrich Schiller. The colloquium commemorated the 150th anniversary of the death, on 24th March 1849, of Johann Wolfgang Döbereiner, Professor of Chemistry and Technology at Universität Jena.

About 300 persons gathered in the Döbereiner-Hörsaal of the Chemistry Institute, where “Das Volk komite” presented a musical prelude beginning with a poem written specially for Döbereiner’s 36th birthday (13th December 1816) by his friend, the poet and dramatist, Johann Wolfgang von Goethe. The poem, “Dem Professor Döbereiner im Namen seiner Kinder, zum Geburtstag” (To Professor Döbereiner, in the Name of His Children for His Birthday), sung to the melody of Ludwig van Beethoven’s musical setting of Schiller’s “An die Freude” (Ode to Joy) from his Symphony No. 9, in D Minor, Op. 125, is as follows:

Wenn wir dich, o Vater sehen
In der Werkstatt der Natur
Stoffe sammeln, lösen, binden,
Als seist du der Schöpfer nur,
Denken wir: Der solche Sachen
Hat so weislich ausgedacht,
Sollte der nicht Mittel finden
Und die Kunst, die fröhlich macht?
Und dann, schauen auf nach oben,
Wünschen, bester Vater, wir,
Was die Menschen alle loben,
Glück und Lebensfreuden dir...

Whenever we see you, oh father,
In Nature's laboratory
Collecting, dissolving, combining substances,
As if you alone are the Creator,
We think: Should whoever has
So wisely invented such things,
Not find the means
And the art that makes us joyful?
And then, we behold on high,
Best father, wishes,
Which all people praise,
Good luck and joy in living to you...

Johann Wolfgang Döbereiner
1780–1849

After early struggles with solvency, Döbereiner was appointed in 1810 to be the Extraordinary (ausserordentlich) Professor of Chemistry and Technology at the University of Jena. In 1823, he observed the ignition, by finely divided platinum powder, of a stream of hydrogen directed at it, the platinum becoming white-hot. News of this work, later to be called catalysis, was quickly published and led to other scientists repeating his work.

The participants were greeted by Professor Christian Robl, Dean of the Chemisch-Geowissenschaftliche Fakultät, and Professor Klaus Manger, Speaker of the special research programme “Ereignis Weimar-Jena, Kultur um 1800”.

The scientific part of the programme consisted of two lectures by leading authorities in those fields of chemistry whose foundations were laid by Döbereiner – catalysis and the periodic system of the elements – “Heterocyclencarbenes: New Controlling Ligands in Catalysis” by Professor Wolfgang Anton Herrmann, President of the Technische Universität München, and “On the Nuclear Physical Limitation of the Number of Elements – The 100-Year Journey from Polonium to Element 112” by Professor Peter Armbruster of the Gesellschaft für Schwerionenforschung mbH Darmstadt. Armbruster headed the team that discovered the last seven elements of the Periodic Table up to element 112. The history of chemistry part of the programme consisted of the lectures, “Johann Wolfgang Döbereiner – a Pioneer for Modern Chemistry” by Professor Dietmar Linke of the Brandenburgische Technische Universität Cottbus and “Döbereiner’s Contemporaries – Chemists, Natural Scientists, Philosophers” by Professor Egon Uhlig of the Friedrich-Schiller-Universität Jena.

“The Most Brilliant Discovery”

As early as the 1820s, because of close relations between chemists across national boundaries and multiple publication of articles and abstracts in different languages, scientific information could be transferred with a speed and efficiency that is astonishing even to us in our Internet era. As an example par excellence of this phenomenon, Bill Brock cites Döbereiner’s discovery in 1823, which the great Swedish chemist, Jöns Jacob Berzelius, later called...
“catalysis” (1). On 27th July 1823, Döbereiner exposed hydrogen to powdered platinum prepared by igniting ammonium hexachloroplatinate (IV), \((\text{NH}_3)_2\text{PtCl}_6\), and observed that on admission of air, at room temperature or even at \(-10^\circ\text{C}\), “after ten minutes all the admitted air had condensed with the hydrogen to form water” (2–4).

When Döbereiner substituted pure oxygen for air, the reaction intensified to the extent that the filter paper holding the platinum charred. That same week he reported his discovery to his patron, close friend and most famous student, Germany’s greatest poet and playwright Johann Wolfgang von Goethe (1749-1832), who also served in Grand Duke Carl August’s court as Qualified Minister (zuständige Minister) for the Universität Jena. At the same time, he also reported it to the editors of several scientific journals.

On 3rd August, Döbereiner observed that if a jet of hydrogen was directed at the spongy platinum from a distance of 4 cm so that it was pre-mixed with air, the platinum became red-hot, then white-hot and the jet ignited spontaneously. This was the basis for what was to be called the Döbereinersche Feuerzeug (lighter) (5–10). This discovery, in which fire was produced without flint and tinder, quickly created an international sensation and was immediately tested and confirmed by many chemists and physicists.

**Rapid Publication of his Results**

By August, Döbereiner’s account had appeared in the *Journal für Chemie und Physik* (2), *Annalen der Physik* (3), *Annales de Chimie* (9), *Neues Journal der Pharmacie, Isis*, and *Bibliothèque Universelle* (11). That same month Karl Wilhelm Gottlieb Kastner (1783–1857), Professor of Chemistry and Physics at the Universität Erlangen, wrote about it to Justus von Liebig (1803–1873), who was then in Paris (12).

At the suggestion of the German naturalist and explorer Alexander von Humboldt (1769–1859), Liebig showed Kastner’s letter to Louis Jacques Thénard (1777–1857), who had also seen a brief report of Döbereiner’s work in the *Journal des Débats* of 24th August. Thénard reported it on 26th August to the Académie des Sciences in Paris. On 13th September, Döbereiner demonstrated his discovery at the meeting of the Gesellschaft Deutscher Naturforscher und Ärzte at Halle. Additional experiments by Thénard and Pierre Louis Dulong (1785–1838), who described them to the Académie on 15th September (13), prompted Jean Nicolas Pierre Hachette (1769–1834) of the École Polytechnique to write on 16th September 1823 to Michael Faraday (1791–1867) in London. Faraday began experiments of his own and related them in the Royal Institution’s *Journal of Science and Arts* in October, the month in which Döbereiner published his own monograph on the subject (14). That same month English translations of Döbereiner’s and Dulong and Thénard’s articles appeared in the *Philosophical Magazine*.

Thus, within three short months Döbereiner’s discovery had been reported in a monograph and in about a dozen European scientific journals. Berzelius, then the supreme authority on matters chemical, in his *Jahres-Bericht*, a series of annual reports that he had begun in 1821 in order to review advances in physical science during the previous year, wrote for 1823: “From any point of view the most important and, if I may use the expression, the most brilliant discovery of last year is, without doubt, that...made by Döbereiner” (15). This appraisal is even more remarkable in view of the fact that Berzelius had previously held Döbereiner in the lowest esteem: “I do not know whether...[Thomas Thomson] or Döbereiner...is the worst chemist in existence at the moment” (16).

**Döbereiner’s Life and Career**

Who was this man who was suddenly thrust into the limelight by his unexpected discovery? Born on 13th December 1780 in Hof an der Saale in Bavaria, Döbereiner — a self-made man in every sense of the word — was the son of a coachman who was not financially able to provide the bright boy with any but the barest essentials of schooling (17–24). However, his mother encouraged him, and, after three years of an apprenticeship with an apothecary, he began,
The great German poet, Johann Wolfgang von Goethe, who was a Minister for Grand Duke Carl August of Sachse-Weimar-Eisenach, and the Duke in the courtyard of the castle at Jena. Goethe was a friend of Döbereiner. The Grand Duke appointed Döbereiner to be Professor of Chemistry and Technology at the University of Jena at the age of seventeen, five precarious Wanderjahre, eventually reaching Karlsruhe and Strasbourg, where he attended lectures on the sciences. He returned home and at the age of twenty-three married Clara Knab, a childhood friend.

Although he was now an apothecary, Döbereiner had neither the money nor licence to buy a pharmacy. He opened an agricultural produce business and began to produce pharmaceutical-chemical preparations. By 1803 he was reporting his experiments with white lead, sugar of lead, magnesium sulfate and other commercially valuable products in the Neues allgemeines Journal der Chemie, edited by Adolph Ferdinand Gehlen (1775–1819), which brought him to the attention of other chemists.

When Döbereiner lost his licence and his business, his relatives gave him a position in charge of bleaching and dyeing in their textile mill, but the Napoleonic war forced the plant to close. He then began to supervise agricultural estates, but these were discontinued in 1810, and once again, the twenty-nine year old father of a family found himself unemployed and unable to pay his debts.

At this lowest point in his life, Döbereiner was surprised to learn from the Senate of the Universität Jena that he had been nominated to be Extraordinary (ausserordentlich) Professor of Chemistry and Technology. Grand Duke (Grossherzog) Carl August (1757–1828) of Sachse-Weimar-Eisenach, an enlightened and liberal ruler and patron of the arts and sciences, had asked Gehlen to recommend a successor to Professor Johann Friedrich August Göttling (1753–1809) who had died the previous year. Gehlen, who knew that Döbereiner was out of work, proposed his name with little hope of success for he did not have a high school (Gymnasium) certificate, nor any higher education. Only after Döbereiner arrived in Jena did he learn that he needed a doctorate to occupy the position. He was granted a doctorate on 10th November 1810 at half the usual fee and because of his poverty was allowed to pay this debt in installments. Döbereiner was so grateful for the position that, despite more remunerative offers from five other universities, he remained at Jena until his death on 24th March 1849.

Research on Platinum

Döbereiner’s most significant discovery was an extension of his interest in platinum, which was necessary for laboratory vessels resistant to chemical reagents. As early as 1812 he began to extract and isolate platinum metals from two pounds of American platinum ore (5, 6).
Döbereiner's Feuerzeug, the gas lighter in which hydrogen gas, produced by the action of sulfuric acid on zinc, ignites after passing over platinum sponge hanging from a platinum wire. The Feuerzeug was used to light candles.

In 1823 platinum ores were discovered in the Ural Mountains of Russia, and this new source greatly facilitated his work. Carl August’s court in Weimar had close family connections with the Czar’s court, and the Grand Duke’s daughter-in-law, wealthy Russian Grand Duchess Maria Pavlovna (1786–1859), was a patroness of Döbereiner and made generous donations of ore to his laboratory (7).

In 1816 Humphry Davy (1779–1829) observed that flammable gases, such as methane (“fire damp”), burned without producing a flame in the presence of platinum, when mixed with air. This was the basis for his invention of the miners’ safety lamp, which brought him in 1817 the Royal Society’s coveted Rumford Medal for work in the applications of modern science (25). In 1820 Sir Humphry’s younger cousin, Edmund Davy (1785–1857), found that finely divided platinum (later called Platinschwarz by Justus von Liebig and Platinmohr by Döbereiner – both meaning platinum black) prepared by reducing platinum sulfate with boiling ethanol, reacted with ethanol vapour and remained white-hot until all the ethanol was consumed (26).

In 1821, after reading Edmund Davy’s article in a German translation which appeared in that year, Döbereiner repeated this experiment and found that the ethanol was oxidised to acetic acid. Because the platinum was not consumed, he suggested that the reaction could be used “for the large-scale preparation of acetic acid” (Essigäure) (27), and he even designed a vinegar lamp (Essiglampe), in which ethanol was supplied by a cotton wick to a small funnel containing platinum black. He spent the Christmas vacation of 1822 in Weimar with Goethe, who was not only a patron of the natural sciences but also made a number of original scientific contributions (28), and demonstrated these experiments to him. Döbereiner continued to work with platinum black and the finely divided metal prepared by ignition of ammonium hexachloroplatinate(IV) and extended this work to include other vapours and gases, particularly hydrogen, which led him to “the most brilliant discovery” discussed above (2–4).

Döbereiner first suggested that the reaction was “an electrical one, whereby hydrogen forms an electrical chain with the platinum”, but he later considered it to be “probably of a quite special nature, i.e., neither mechanical nor electrical nor magnetic” (14). In 1835 Berzelius named the phenomenon “catalysis” (29).

Döbereiner’s Platinfeuerzeug

Following this discovery, Döbereiner quickly applied it to construct the pneumatic gas lighter (Döbereinersche Feuerzeug) that bears his name (30). In this ingenious device hydrogen gas, generated from zinc and sulfuric acid, streams through a narrow opening toward a holder in which platinum sponge is suspended on a thin platinum wire, whereupon it ignites. The flame can then be used to light a candle. If the platinum becomes inactive, it can be activated by heating. By 1828 about 20,000 of these lighters,
some elaborately ornamented by decorative artists, were in use in Germany and England, and they soon became typical objects in many Biedermeier-style households. However, Döbereiner refused to patent his invention, declaring “I love science more than money, and the knowledge that with it I have been useful to many mechanical artists makes me happy” (4, 6).

Various types of phosphorus matches were sold during the 1820s. Those with tips composed of a “percussion powder” of potassium chlorate and antimony sulfide and called “friction lights” by their inventor John Walker (1781–1857) had been marketed in England since 7th April 1827. By the middle of the nineteenth century these, and so-called “safety matches” (Sicherheits- or schwedische Zündhölzer), which were invented in 1848 by Rudolph Christian Bottger (1806–1881), one of Döbereiner’s students, began to replace Döbereiner’s lighter. Bottger was originally a candidate of theology, who became so enthusiastic about Döbereiner’s lighter that he turned to chemistry, dedicating himself to the improvement of the lighter. He eventually became Professor of Chemistry and Physics at the Physikalische Verein at Frankfurt am Main (1835–1875) (5, 6). In 1831 he found that the ignition power of platinum sponge is destroyed by ammonia or ammonium sulfide vapours but that it can be restored by heating. Döbereiner called this property of ammonia “depotentiating action” (depotenzierende Wirkung). Döbereiner’s lighter was still in use at the beginning of World War I (4).

Other Research

Almost equal in importance to his work on the catalytic action of platinum was Döbereiner’s recognition of the relationship between atomic weights and chemical properties, making him the first of the many predecessors of Dmitrii Ivanovich Mendeleev and his periodic classification of the elements. As early as 1817 he demonstrated that the equivalent of strontium (42.5) is the arithmetic mean of those of calcium (20) and barium (65) (31). In 1829 he extended this so-called “law of triads” to many other families of elements such as sulfur-selenium-tellurium, lithium-sodium-potassium and chlorine-bromine-iodine (32, 33). These relationships can also be observed with atomic numbers as well as atomic weights (34).

Döbereiner also discovered the catalytic action of manganese dioxide (pyrolusite, Braunstein) on the thermal decomposition of potassium chlorate, the basis for the preparation of oxygen known to every introductory chemistry student (35). His discovery that hydrogen escaped from a cracked flask (36) led Thomas Graham (1805–1869) to his law of diffusion (37). In Graham’s words, “The original observation of Döbereiner...will always hold its place in scientific history as the starting-point of the experimental study of gaseous diffusion” (38).

Among his numerous organic experiments, Döbereiner prepared carbon monoxide by heating formic acid with sulfuric acid (39) and a mixture of carbon monoxide and carbon dioxide by heating oxalic acid with sulfuric acid (40). He also used copper(II) oxide in organic combustion analysis (41). He was one of the first to observe the fermentative conversion of starch paste into fermentable sugar, and he gave a correct explanation of alcoholic fermentation (42). These are only a few of the numerous contributions that Döbereiner made to the pure and applied science that he loved so much.

Acknowledgements

I am indebted to Professor Ernst-Gottfried Jäger, Chairman of the Döbereiner Festkolloquium Preparation Committee, Friedrich-Schiller-Universität Jena, and Diane Majors and Randy Vaughn-Dotta of California State University, Fresno, for assistance in the preparation of this article.

References

2 J. W. Döbereiner, J. Chem. (Schweiz), 1823, 38, 321
3 J. W. Döbereiner, Ann. Phys. (Gilbert), 1823, 74, 269
4 P. M. D. Collins, Platinum Metals Rev., 1986, 30, (3), 141
The conference, which is entitled "Current Status and Strategy of Development in the XXI-st Century" is aiming to cover such topics as the geology and refining of the noble and rare earth metals; metal recovery, assaying and analysis; the science and technology of the platinum group metals and their alloys and a broad spectrum of their industrial uses and engineering applications.

The First Circular and further details on the conference may be obtained from the organising committee, Chairman: Professor Victor A. Goltsov, Donetsk State Technical University, 58 Artem Street, Donetsk 340000, Ukraine; e-mail: goltsov@physics.dguu.donetsk.ua; tel: +380-(0)622-910-314; fax: +380-(0)622-921-278.

Noble and Rare Metals: NRM-2000
THIRD INTERNATIONAL CONFERENCE

The third in these broad ranging conferences, which take place every three years, is being held from 19th-22nd September, 2000, at the Donetsk State Technical University, Ukraine. The conference, which is entitled "Current Status and Strategy of Development in the XXI-st Century" is aiming to cover such topics as the geology and refining of the noble and rare earth metals; metal recovery, assaying and analysis; the science and technology of the platinum group metals and their alloys and a broad spectrum of their industrial uses and engineering applications.

The First Circular and further details on the conference may be obtained from the organising committee, Chairman: Professor Victor A. Goltsov, Donetsk State Technical University, 58 Artem Street, Donetsk 340000, Ukraine; e-mail: goltsov@physics.dguu.donetsk.ua; tel: +380-(0)622-910-314; fax: +380-(0)622-921-278.
ABSTRACTS
of current literature on the platinum metals and their alloys

PROPERTIES
Enhancement of Surface Self-Diffusion of Platinum Atoms by Adsorbed Hydrogen
STM of H₂-promoted self-diffusion of Pt on the Pt(110)-(1×2) surface has been carried out. An activated intermediate Pt-H complex (1) with diffusivity enhanced by a factor of 500 at room temperature, relative to the other Pt adatoms was observed. Density-functional calculations indicated that (1) consists of a H atom trapped on top of a Pt atom, and that the bound H atom decreases the diffusion barrier.

Polymerization and Decomposition of C₆ on Pt(111) Surfaces
The interaction of C₆ with Pt(111) was studied by AES, XPS, UPS, HREELS and LEED. At submonolayer coverages, C₆ is polymerised on Pt(111) at ≥ 300 K. Annealing multilayer C₆ films on Pt(111) to ≥ 600 K leads to a C₆ adlayer that is quite different from 1 monolayer C₆/Pt(111). On annealing C₆ films on Pt(111) to 900 K, graphite domains appear on the surface, and total fragmentation occurs at 1050 K.

Temperature-Dependent Segregation on PtₓRhᵧ(111) and (100)
Surface segregation was studied on PtₓRhᵧ(111) (1) and PtₓRhᵧ(100) (2) by LEED and LEIS. The Pt concentration grew continuously on (1) until 1000°C, whereas it reached a maximum enrichment at ~500°C on (2) and decreased thereafter. This contrasting behaviour resulted solely from the kinetic limitations in the low temperature regime.

Superconductivity Mediated by Spin Fluctuations in the Heavy-Fermion Compound UPd₂Al₃
Tunnelling spectroscopy has been used to investigate the superconducting order parameter of a heavy-fermion superconductor: epitaxial thin films of UPd₂Al₃. A strong-coupling feature in the tunnelling conductivity was observed, and when combined with inelastic neutron scattering data suggested a pairing interaction mediated by antiferromagnetic spin fluctuations. These induce a presumably d-wave order parameter without any unconventional symmetry reduction.

CHEMICAL COMPOUNDS
The First Experimental Evidence for the cis-trans Isomerism of Metal Chelates with Oxyazo Ligands
The cis- and trans-isomers of bis(2-hydroxy-4'-methylazo benzene)Pt(II) have been isolated and identified for the first time. A special feature of the separation of the isomers is that the cis form needs to be rapidly removed from solutions because it spontaneously converts into the trans form. The existence of the cis structure was proved by XRD analysis.

Synthesis, Structure, Chemical Bonding, and Properties of CaTln (T = Pd, Pt, Au)
CaTln, (T = Pd, Pt, Au) (1) were prepared by reacting the elements in glassy C crucibles under Ar. (1) crystallise with the MgCuAl₂ structure type (space group Cmcm). Magnetic susceptibility measurements of compact polycrystalline samples of (1) indicate weak Pauli paramagnetism. (1) are metallic conductors.

Synthesis and Characterization of Allyl(β-ketoiminate)palladium(II) Complexes: New Precursors for Chemical Vapor Deposition of Palladium Thin Films
Treatment of β-ketoiminates with [(allyl)Pd(μ-Cl)]₃ afforded volatile, air-stable allyl(β-ketoiminate)Pd(II) complexes, which are excellent precursors for the CVD of Pd thin films. In solution ¹H NMR analyses indicate either a direct rotation of a planar allyl ligand about the allyl-Pd axis or a solvent-assisted exchange process involving the transient formation of a monodentate ketoiminate ligand.

Synthesis of Poly(oxyethylene)-Grafted Palladium Clusters
A polymer-grafted Pd cluster (3–5 nm) was prepared by stirring an acetic acid solution of Pd(II) acetate and bipyridyl-terminated poly(oxyethylene) (bpy-POE₃₀₀) under 1 atm H₂ at room temperature. The cluster was soluble in CH₂Cl₂, CHCl₃, MeOH, acetone and H₂O. ¹H NMR spectra indicated the terminal bpy ligand is fixed at the surface of the Pd cluster. The calculated formula is Pdₙ bpy (bpy-POE₃₀₀)ₓ Oₙ₋ₓ.
PHOTOCONVERSION

Self-Assembly of Predesigned Trinetallic Macrocycles Based on Benzimidazole as Nonlinear Bridging Motifs: Crystal Structure of a Luminescent Platinum(II) Cyclic Trimer


Nonlinear N-deprotonated benzimidazole on reaction with square-planar cyclometalated Pt(II) precursors gave cyclic trimers with metal vertices, related to calixarenes. [Pt(thpy)(bzim)], (1) was formed from [Pt(thpy)(Hthpy)Cl] (Hthpy = 2-( thienyl)pyridine) on treatment with Na benzimidazolate. (1) photo-luminesces in solution at room temperature.

Phosphate Anion Binding and Luminescent Sensing in Aqueous Solution by Ruthenium(II) Bipyridyl Polyaza Receptors


A new class of anion luminescent sensor consisting of a series of new Ru(II) bipyridyl polyaza receptors was prepared and can bind and detect phosphate and ATP anions in aqueous solution via MLCT luminescent emission quenching. The receptors were prepared by refluxing bipyridyl substituted amine compounds with (bipy)RuCl₂.2H₂O in aqueous EtOH then by HCl addition.

Electronic and Light-Emitting Properties of Some Polyimides Based on Bis(2,2′:6′,2′″-terpyridine) Ruthenium(II) Complex


Novel polyimides that contain the bis(2,2′:6′,2′″-terpyridine) Ru(II) complex were synthesised, and their optoelectronic properties were studied. The absorption of the polymers at 500 nm was strongly enhanced by the Ru complex. The polyimides exhibited electroluminescent behaviour when the polymer films were fabricated into single-layered LEDs. The external quantum efficiency and maximum lumiance of the devices were 0.1% and 120 cd m⁻², respectively.

ELECTRODEPOSITION AND SURFACE COATINGS

Structure and Electrochemical Properties of Pt/C Catalytic Electrodes Manufactured by Ion Beam Sputtering

B. YANG, S. XU, Y. ZHANG, Y. JIAO AND Y. YU, Precious Met. (Chin.), 1999, 20, (1), 14–19

Pt/C catalytic electrodes (1) have been prepared by ion beam sputtering. The consumption of Pt in (1) was reduced to 0.19 mg cm⁻². It was established that the Pt films in (1) have f.c.c. structure, and that the catalytic activities of Pt coatings on graphite cloths is better than that on C papers. Application of high beam voltages and high beam current during ion beam sputtering further improved the catalytic activity of (1) with no degradation after 1000 h working.

On-Site Characterization of Electrocrysrallized Platinum Nanoparticles on Carbon and Sol-Gel Thin Film Modified Carbon Surfaces


Pt nanoparticles were electrocrysrallised on amorphous C film and on sol-gel modified C film deposited on Au mesh grids. These Pt-modified surfaces were characterised by TEM and energy dispersive spectroscopy. The particles deposited on bare C surfaces exhibited polytetrahedral crystallographic morphology. Subsequently, laterally dendritic growth of Pt formed by aggregation of primary particles (3 to 5 nm) was found on the sol-gel modified C surfaces. This was reported to be a new type of morphology for electrodeposited Pt with a high surface area.

Fabrication of Poly(diphenylsilylenemethlyene) and Poly(diphenylsiloxane) Thin Films Using Fine Metal Particles


A new technique for the ring-opening polymerisation of 1,1,3,3-tetraphenyl-1,3-disilacyclobutane (1) has been developed. (1) was first evaporated on Si substrates and then exposed to metal particle deposition by sputtering prior to heat treatment. Catalytic activities of Pt, Pt/Pd, Au, Cu and Ag particles were examined; the metal had no effect on the chemical structure of the film; but the polymerisation efficiency and film crystallinity depended greatly on the kind of metal, for identical sputtering and heating conditions.

Chemical Fluid Deposition: Reactive Deposition of Platinum Metal from Carbon Dioxide Solution


Chemical fluid deposition was validated for the deposition of CVD-quality Pt metal films on Si wafers and polymer substrates via hydrogenolysis of the complex dimethylcyclooctadiene/Pt(II) in supercritical CO₂ at 80°C. This reduction yields continuous metal films on solid substrates and discrete metal clusters within the 200 nm pores of an A1O₃ membrane.

The Electrodeposition & Material Properties of Palladium-Coalt


Mechanically stable, mirror-like Pd-Co films with 10–30% Co were produced at current densities of < 50 to > 700 mA cm⁻². In addition, any desired composition can be maintained within ± 5% over a wide range of operating conditions and plating bath ageing. The material properties of the Pd-Co deposits compared well with Hard-Gold and Pd-Ni finishes, but the Pd-Co alloy was harder and had superior durability. Thus, it proved to be an excellent material for contact finish applications.
Reactive Pulsed Laser Deposition of Iridium Oxide Thin Films


Highly conductive IrO, thin films have been deposited on Si(100) substrates by reactive pulsed laser ablation from an Ir target in an O, atmosphere. At 200 mTorr of O, ambient pressure, IrO, films deposited at substrate temperatures in the 400–550°C range are polycrystalline and exhibit a granular morphology with average size feature increasing (from ~90 to 170 nm) with the substrate temperature. The room temperature resistivities, 39 ± 4 μΩ cm, of these IrO, films compare well with those of bulk single-crystal IrO.

Properties and Application Feasibility of an Osmium-Oxygen Thin Film Prepared by DC-Glow-Discharge Deposition from Osmium Tetraoxide


An Os-O thin film (OsO,) was deposited by d.c.-glow-discharge from OsO,. The prepared films had a homogeneous amorphous structure and 10 nm order of resistivity. Since the transparency of a 20 nm thick film was ~ 80% for visible light, a transparent conductive film could be obtained on glass or plastic substrates. Fundamental properties are reported.

APPARATUS AND TECHNIQUE

Gas Sensor Materials Based on Metalloendrimers


Pt complexes (1) containing a terdentate “pincer” ligand [C,H, (CH,NMe,)-2,6] were synthesised. When coupled to a dendrimer core consisting of a benzene centre substituted with acid chloride functionalities as rigid linkage units, trimetallic macromolecules with containing 6-adsorption-active metal sites. These metalloendrimers had selectivity towards SO2.

Probing Organometallic Structure and Reactivity by Transition Metal NMR Spectroscopy


Transition metal NMR chemical shifts are readily measured and serve as a probe into electronic and steric effects of ligands and substituents in complexes. Quantitative correlations of metal chemical activities, both experimental and as a result of quantum chemical calculations, are reported to give new mechanistic insights and permit reactivity predictions and a screening of homogeneous catalysts. Examples involving the spin-1/2 nuclei *’Rh and *’Os are discussed.

Electrochemical Detection of Single-Stranded DNA Using Polymer-Modified Electrodes


Glassy C electrodes modified by reductive electropolymerisation of a thin film of poly[Ru(vbpy),] or poly[Ru(vbpy),]/vba] (vbpy = 4-vinyl-4-methyl-2,2'-bipyridine; vba = p-vinylbenzoic acid) were prepared. The modified electrodes were active towards the oxidation of guanine in solution in both a mononucleotide and a polymer.

HETEROGENEOUS CATALYSIS

High-Throughput Synthesis and Screening of Combinatorial Heterogeneous Catalyst Libraries


The catalytic activity and selectivity of 120 catalysts were measured, in < 1 minute, in combinatorial triangular libraries of Rh-Pt-Cu and Rh-Pd-Cu alloys, via the catalytic oxidation of CO and the reduction of NO, by scanning mass spectrometry. The elements of the libraries (~ 2 to 4 μg of material) were sputter-deposited in an array, annealed, then heated for test.

Ethyl Acetate Production from Water-Containing Ethanol Catalyzed by Supported Pd Catalysts: Advantages and Disadvantages of Hydrophobic Supports


Hydrophilic and hydrophobic Pd catalysts were investigated for the selective oxidation of H2O-containing EtOH in the presence of excess EtOH, a one-step preparation of ethyl acetate, in a continuous fixed-bed reactor. The conversion of EtOH catalysed by Pd/styrene-divinylbenzene copolymer was found to be 20 times more than that by Pd/y-Al2O3. However, it may have been caused by weak metal-support interactions and the formation of Pd(II) acetate.

Characterization of Model Automotive Exhaust Catalysts: Pd on Ceria and Ceria-Zirconia Supports


PdCeO, SiO2–CeO2, CeO2–ZrO2 solid solutions, and CeO2–ZrO2 solid solutions with partial incorporation of Pd were prepared and used as supports in model Pd automotive three-way catalysts. After ageing, catalysts prepared on the solid solution materials provided much more oxygen storage capacity (OSC) than those based on pure CeO2 or SiO2–CeO2. Addition of 5 wt.% Pd as a substitute for CeO2 improved the thermal stability of the CeO2–ZrO2 but did not increase the OSC of the model catalysts.

*Platinum Metals Rev.*, 1999, 43, (3) 131
Combustion of a Trace Amount of CH₄ in the Presence of Water Vapor over ZrO₂-Supported Pd Catalysts

Combustion of a trace amount of CH₄ over Pd/ZrO₂ catalyst was studied under nearly exhaust gas conditions (at temperatures 523–773 K) where H₂O vapour coexists. High catalytic activity was obtained with a ZrO₂ support calcined at 1073 and 1273 K. Durability tests at 673 K for 100 h revealed that the activities of these catalysts hardly decreased, while those of Pd/calcined Al₂O₃ were much decreased.

In Situ FT-IR Study of Rh–Al–MCM-41 Catalyst for the Selective Catalytic Reduction of Nitric Oxide with Propylene in the Presence of Excess Oxygen

Rh/Al-MCM-41(1) was studied for the selective catalytic reduction of NO by C₂H₆ in the presence of excess O₂. (1) showed a high activity in converting NO to N₂ and N₂O at low temperatures. In situ FTIR indicated that a Rh-NO₂ species is formed on (1) in flowing NO/He, NO + O₂/He and NO + C₂H₆ + O₂/He at 100–350°C. This species is quite active in reacting with propylene and/or propylene adspecies at 250°C in the presence or absence of O₂, leading to the formation of isocyanate species, CO and CO₂.

Study on Sol-Gel Derived Rh-Based Catalysts for Synthesis of C₂-Oxygenated Compounds Through CO Hydrogenation

Rh/CO₃/SiO₂ catalysts prepared by a sol-gel process were characterized and studied in CO hydrogenation at 2.0 MPa for the synthesis of C₂ oxygenated compounds. In CO hydrogenation, 2% Rh/CO₃ mainly catalysed the formation of acetaldehyde. Addition of CeO₂ increased the selectivity for both EtOH and acetaldehyde. CeO₂ decreased the catalytic activity, but increased appreciably the selectivity for MeOH.

Hydrodenitrogenation of Pyridine over Alumina-Supported Iridium Catalysts

Ir/Al₂O₃ catalysts obtained from various Ir precursors (Ir(AcAc)₃, Ir(CO)₃, HIrCl₄, and (NH₃)IrCl₃) were studied in the hydrodenitrogenation (HDN) of pyridine at 320°C and 20 bar of pressure in the absence and presence of a parallel hydrodesulphurisation (HDS) of thiophene. Ir(CO)₃ gave the most active catalyst, due to fewer contaminants in the starting Ir compounds rather than to better Ir dispersion. Ir dispersion was decreased by sintering in air, substantially decreasing the rate of C-N bond hydrogenolysis but with negligible change in the rate of pyridine hydrogenation. Ir/Al₂O₃ catalysts had much higher HDN activity and HDN/HDS selectivity than NiMo catalysts.


K[Ru(CO)₅]₂, K₂[Os(C₂H₄CO)₅] and K[Fe(CO)₅] catalysts were deposited from THF on graphite-like active C "Sibunit" followed by drying at 20°C in vacuum. The highest efficiency in NH₃ synthesis was displayed by K[Ru(CO)₅]₂ at ≥ 250°C (1 atm). Replacing "Sibunit" by commercially active C SKT sharply decreases the activity and stability of the catalysts, whereas NH₃ synthesis is greatly accelerated on adding metallic K.

Novel Supported Catalyst for Hydrodesulphurization Reaction

Ru/MgF₂ (1) was highly active in the hydrodesulphurisation (HDS) reaction. (1) was prepared by conventional impregnation with Ru(CO)₅. The specific properties of MgF₂ of hardness, resistance to calcination in O₂ and well-developed porous structure, contribute to its use as an active support. (1) is more selective for HDS and much less hydrogenation occurs simultaneously with HDS than when using Ru/Al₂O₃.

HOMOGENEOUS CATALYSIS

Cross-Coupling Reactions of Hypervalent Siloxane Derivatives: An Alternative to Stille and Suzuki Couplings

Bis(dibenzylideneacetone)Pd-catalysed cross-coupling of phenyl, vinyl and allyl siloxane derivatives was found to proceed in good to excellent yield with aryl iodides, electron-deficient aryl bromides, and allylic benzoates. Methyl and 2,2,2-trifluoroethyl siloxanes could be employed in the coupling reaction. Electron-donating and -withdrawing groups were tolerated on the aryl halide without affecting the coupling.

Use of Fluorinated Palladium Sources for Efficient Pd-Catalysed Coupling Reactions in Supercritical Carbon Dioxide

Pd sources, Pd(OCCF₃)₃, and Pd(F,acac), with fluorinated ligands were shown to be superior to non-fluorinated sources, Pd(OCONH₂)₃, and Pd(dbq), for Pd catalysed coupling reactions in supercritical CO₂. Significantly reduced temperatures and catalyst loadings were possible. The range of phosphine ligands used was increased to include PCy₃ and PPh₃, often considered to be poor ligands for coupling reactions.
Biphasic Synthesis of Hydrogen Peroxide from Carbon Monoxide, Water, and Oxygen Catalyzed by Palladium Complexes with Bidentate Nitrogen Ligands


Effective and stable Pd catalysts for the biphasic synthesis of H₂O₂ from CO, O₂, and H₂O are obtained by using a suitable bidentate nitrogen ligand. The best turnover number (578) for this reaction was achieved with a Pd complex with a 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline ligand. The reaction was carried out in a biphasic system in which the catalyst is soluble in the organic phase and the produced H₂O₂ is soluble in the aqueous phase. The biphasic system minimises the ligand oxidation.

Unprecedented Efficient Hydrogenation of Arenes in Biphasic Liquid-Liquid Catalysis by Re-usable Aqueous Colloidal Suspensions of Rhodium


A reduced aqueous colloidal suspension of Rh showed efficient activity for the catalytic hydrogenation of benzene derivatives under biphasic conditions at room temperature and atmospheric H₂ pressure. The aqueous phase containing the Rh(0) particles can be reused. The Rh nanoparticles are protected by hydroxyalkylammonium salts containing at least 16C atoms leading to electrosteric stabilisation.

Homogeneous Hydrogenation of Maleic Anhydride to Succinic Anhydride Catalyzed by Rh Complex Catalyst


Hydrogenation of maleic anhydride using various homogeneous transition metal complex catalyst systems was investigated. Typical experimental conditions were: 353–383 K; H₂ pressure 0.5–2.5 MPa; PPh₃;RhCl(PPh₃)₃ = 0–16; 0.03 mmol RhCl(PPh₃)₃; 20 mmol maleic anhydride; 8 ml of liquid; and 30–360 min reaction time. RhCl(PPh₃)₃ was the most active catalyst precursor for the hydrogenation of maleic anhydride to succinic anhydride. The optimum ligand and solvent were PPh₃ and ethylene glycol dimethylether, respectively.

RuCl₂(PPh₃)₃, Catalyzed Isomerization of the Baylis-Hillman Adducts


The RuCl₂(PPh₃)₃ catalysed isomerisation of Baylis-Hillman adducts was investigated. The Baylis-Hillman reaction typically produces functionalised allyl alcohols. Methyl 3-aryl-3-hydroxy-2-methylpropanoates in the presence of RuCl₂(PPh₃)₃ catalysts were converted to methyl 3-aryl-2-methy-3-oxopropanoates (~50% yield) by further reaction. This methodology is a new direction for Baylis-Hillman chemistry.

Homogeneous Dehydrodysulfurisation under Ambient Conditions. Harnessing the Facile Polyhedral Rearrangement in the Ruthenium Carbonyl Cluster Ru₂(CO)₁₃


Reactions of Ru₂(CO)₁₃ (1) with H₂S affords the bridged butterfly species (μ-H)Ru₂(CO)₆(μ-SH) in which H and SH co-ordinate with simultaneous cleavage of one Ru-Ru bond and displacement of CO. Subsequent reaction with CO regenerates (1) and eliminates S₈ and H₂. These reactions take place at ambient pressures under vigorous stirring. The Ru=Ru bond rupture is quite facile. The CO in the system is not consumed and can be recycled indefinitely.

Room Temperature Operating Allenylidene Precatalyst [L,Ru=C=C=CR₂]⁻X for Olefin Metathesis: Dramatic Influence of the Counter Anion X⁻


Ru(II) [p-cymene(PCy₃)ClRu=C=CPh₂]⁻X⁻ (X⁻ = CF₃SO₃⁻) (1) was produced from commercial [RuCl₂(p-cymene)]. (1) catalyses the ring-closing metathesis (RCM) of N,N-diallyltosylamide at room temperatures whereas (X⁻ = BF₄⁻) (2) favours the cyclisation of the 1,6-diene into a 5-membered heterocycle without loss of atoms. The addition of BF₄⁻, OEt₂ to (2) restores its selectivity in the RCM reaction. (1) also promotes the metathesis of an ene-yne to produce the 3-vinyl-2,5-dihydrofuran.

FUEL CELLS

In Situ and Model EXAFS Studies of Electrocatalysts for Methanol Oxidation


EXAFS of as prepared Pt/C electrocatalysts for the DMFC indicated that the preparation of the dispersed Pt by the oxidation of Pt(SO₄)₄ forms dispersed PtO₄ species. After reduction by flowing H₂ in the gas treatment cell or potentiostatically in the electrochemical cell, small Pt particles are formed, shown by the presence of Pt neighbours in the first coordination shell.

Improvement in the Diffusion Characteristics of Low Pt-Loaded Electrodes for PEFCs


Low Pt loading electrodes were obtained by the direct mixing of electrocatalyst and ionomer (for the catalyst layer) and by the introduction of an intermediate hydrophobic C layer to optimise gas distribution. An optimum content of 20 wt.% PTFE in the C layer at a Pt loading of 0.1 mg cm⁻² gave, for air operation at 5 bar absolute pressure and 95°C, a maximum in the power density of ~ 450 mW cm⁻².
NEW PATENTS

ELECTROCHEMISTRY

Cathode for Electrolysis
CSIR COUNCIL SCI. IND. RES. U.S. Patent 5,855,751
A cathode for the electrolysis of an aqueous alkali chloride solution comprises a conductive steel substrate with a three component coating wherein: the first component is Ni oxide, the second is one or more of Rh, Ir, Pd and Os or their oxides, and the third is Au and/or Pt oxides, to reduce the H₂ overpotential. The electrode is used for non-mercury chloride cells, which currently use mild steel cathodes. The coating has catalytic activity and long term stability.

APPARATUS AND TECHNIQUE

Gas Sensor for Automotive Applications
ARMINES ASSOC. RECH. DEV. METHODES European Appl. 899,563A
A gas sensor for use in automotive applications, especially for measurements of CO, NOx and hydrocarbons, comprises a solid electrolyte of β-Al₂O₃ upon which two electrodes, one made of Au and the other of Pt, are arranged to be exposed to the gas, a measurement device and a thermo-regulation system. The response of the sensor to the pollutants can be changed as a function of temperature, giving improved accuracy.

Platinum Electrode Manufacture
GENERAL MOTORS CORP. U.S. Patent 5,887,240
A Pt electrode for use in a vehicle exhaust gas sensor is made by mixing Pt-, ceramic- and C-powders to form an ink which is applied to a green body. The green body is then sintered to form the electrode. The electrode has high porosity and high current density, even when sintered at > 1500°C.

Air Purifier
A W. ASIN CO. LTD. Japanese Appl. 10/296,082
A catalyst used as a filter for air purifiers consists of an optically active catalyst carrying 0.01-2.0 wt. parts of Pd as a photocatalyst for difficult-to-decompose volatile organic compounds (VOC). The VOC are quickly decomposed in the gaseous phase under optical irradiation at normal temperature. Energy consumption is reduced and catalytic activity is maintained.

HETEROGENEOUS CATALYSIS

Automobile Diesel Engine Catalyst
MAZDA MOTOR CORP. European Appl. 899,002A
An exhaust gas purifying catalyst for diesel engines comprises metal oxide particles containing Ce supporting dispersed Pd oxide particles. A Ce-containing coating layer covers the Pd oxide particles. Noble metals are fixed to the oxide by heat treatment. The catalyst gives enhanced purification and captures hydrocarbons in exhaust gas to crack and modify them to higher active hydrocarbons suitable as a reductant for NOx.

Production of Shell Catalyst
DEGUSSA A.G. European Appl. 904,838A
A shell catalyst, used for selective hydrogenation of C=H in gas streams, has a non-porous inorganic support (BET surface area < 80 m² g⁻¹) and is prepared by drying a suspension of H₂O-soluble Ru, Rh, Pd, Os, Ir, Pt, Ag and/or Au compound(s) and a coating compound on the support and then activating the shell-coated support in a reducing gas stream. Simultaneous application of active and coating material is simple, giving a shell catalyst with an effective surface, suitable for use at high gas spatial velocities of > 3000 h⁻¹.
Production of 1,1,2,2,3-Pentafluoropropane
ALLIED-SIGNAL INC. U.S. Patent 5,856,594
Production of 1,1,2,2,3-pentafluoropropane (1) comprises contacting H₂ and 1,3-dichloro-1,1,2,2,3-pentafluoropropane over a catalyst supported on Al₂O₃. The catalyst is Pd, Pt, Ru, Rh and/or Ir, preferably Pd. The reaction is performed in the vapour phase at 185–260°C with a contact time of 10–25 s. (1) is used as a refrigerant, solvent, foam blowing agent or aerosol propellant. Very little reduction of the F atoms occurs.

Hydrogenation of Hydroxylaldehyde
ARCO CHEM. TECHNOLOGY LP U.S. Patent 5,874,652
An aqueous mixture of 4-hydroxybutanal and 3-hydroxy-2-methylpropanal over a catalyst supported on Al₂O₃. The reaction is performed in the vapour phase at 185–260°C with a contact time of 10–25 s. The bimetallic catalyst is supported on Al₂O₃. The catalyst is Pd, Pt, Ru, Rh and/or Ir, preferably Pd. The reaction is simple and has sufficient activity and productivity to be used industrially. Phenol is used to prepare antioxidants, synthetic resins and insecticides.

Bimetallic Catalyst
FORD GLOBAL TECHNOLOGIES INC. U.S. Patent 5,876,680
A bimetallic catalyst used for converting exhaust gases from a lean-burn engine, especially automotive engines, consists of a porous γ-Al₂O₃ support, and 0.1–0.5 wt.% W oxide and 0.5–4 wt.% Pt deposited on the support; the amount of metals being based on the weight of the support. The catalyst has excellent ability to reduce exhaust gases at lower temperatures than prior catalysts.

Catalyst for Exhaust Gas Purification
NE CHEMCAT K.K. Japanese Appl. 11/28,359
The base structure of a catalyst for exhaust gas purification comprises a ferritic stainless steel containing in wt. % ≤ 0.2 C, 0.4–3.0 Si, ≤ 2.0 Mn, 13.0–20.0 Cr, 0.3–3.0 Mo, remainder Fe and impurities. The catalyst contains active ingredients chosen from Pt, Pd and Rh and a γ-Al₂O₃ carrier. A CeO₂ stabilised ZrO₂ is supported on the base. The catalyst has excellent corrosion resistance with high adhesion between the base and the catalyst.

Decomposition of Nitrous Oxide
KYOCERA CORP. Japanese Appl. 11/33,401
A catalyst for decomposition of nitrous oxide in exhaust gases of I.C.E. comprises a spinel crystalline multiple oxide of 0.5–20.0 wt.% Pd, and Ga and Ni. About 5–75 wt.% CeO₂ is added to the multiple oxide. NO is decomposed into N₂ and O₂, without using a reducing agent, thus saving energy.

Cyclohexanone Compounds
BAYER A.G. German Appl. 1/97/27,712
Cyclohexanone compounds (1) are prepared in consistent high yield by the catalytic hydrogenation of phenol compounds using Pd/C catalyst pre-mixed with a base component and H₂O₂ at 100–250°C and 1–20 bar H₂ pressure. (1) include intermediates for pharmaceuticals and plant protectants and is obtained with high selectivity and in good reproducible yields.

HOMOGENEOUS CATALYSIS
Synthesis of Phenol
ENICHEM S.P.A. European Appl. 894,783A
Phenol is produced by the catalytic oxidation of benzene and H₂O using Ti-silicalite, with H₂O being prepared in situ by the reaction of O₂, CO and H₂O in the presence of a Pd salt, a nitrogenated ligand and a non-co-ordinating organic acid. The process is simple and has sufficient activity and productivity to be used industrially. Phenol is used to prepare antioxidants, synthetic resins and insecticides.

Production of Unsatuated Alcohols
MITSUBISHI CHEM. CORP. Japanese Appl. 10/298,124
Unsaturated alcohols are produced with high yields and selectivities by reacting conjugated alkenes and H₂O using a catalyst of a Pd compound and a phosphine. The skeleton of the unsaturated alcohol is obtained by the polymerisation. Of the unsaturated alcohols, octa-2,7-diene-1-ol and other octadienols are used as intermediates for n-octanol or its esters.

Preparation of Aromatic Aldehydes
TOSOH CORP. Japanese Appl. 10/330,307
Preparation of aromatic aldehydes (1) comprises reacting halogenated aromatic compounds with CO and H₂ in the presence of a catalyst comprising a Pd compound and a phosphine. (1) are prepared under milder conditions than previously.

Production of DMUDO
DEGUSSA A.G. German Appl. 1/97/30,546
Production of 6,10- and 6,9-dimethyl-5,10-undeca-diene-2-ones (DMUDO) comprises the telomerisation of isoprene with alkyl acetoacetates in the presence of a Pd compound, and a P component as the catalyst system (optionally in the presence of a protic additive). The resulting β-keto esters are then saponified and decarboxylated to produce DMUDO, with good, controlled selectivity, for Vitamin E synthesis.

Rhodium-Based Hydroformylation Catalyst
HOECHST A.G. German Appl. 1/97/40,672
A Rh-based hydroformylation catalyst contains Rh in elemental or bound form, polyethylene glycol, a P-containing ligand and H₂O. The catalyst enables a high yield production of aldehydes by reacting 9–18C olefins with H₂ and CO. The organic phase and the aqueous catalyst phase can be rapidly separated, with no significant loss of Rh or ligands in the organic phase.

FUEL CELLS
Platinum Alloy for Fuel Cell Electrodes
EXXON RES. & ENG. CO. European Appl. 899,348A
A C-supported, Pt-dispersed Zn alloy for fuel cell electrodes has 10–40 wt.% Pt particles, 20–30 Å in size, on a C support of surface area 100–500 m² g⁻¹. A soluble Zn source is deposited on the Pt/C, and is calcinated and reduced to Zn. The alloy has good CO tolerance and can oxidise CO at low potentials.
Phosphoric Acid Type Battery
TOSHIBA K.K. Japanese Appl. 10/334,928
The anode plate of a PAFC has a transition noble metal alloy catalyst layer and a Pt catalyst layer on corresponding sides of the oxidation-gas outflow and the inflow side of the reservoir. The PAFC reduces the current density distribution gap, the amount of phosphoric acid used and the phosphoric acid vapour on the oxidation-gas outflow side.

Solid Polyelectrolyte in DMFC
JAPAN STORAGE BATTERY CO. LTD. Japanese Appl. 11/16,588
A polyelectrolyte used in DMFC consists of a double layered negative electrode catalysed layer. A Pt layer is formed on the inner side of the polymer electrolyte film. Another layer containing Pt and Ru is formed on its outer side. The amount of waste catalyst not participating in the reaction is reduced.

Double-Layer Capacitor
SIEMENS A.G. German Appl. 1/97/24,712
An electrochemical double-layer capacitor (1) has a porous double-layer electrode made of C containing an electrolyte of poly(perfluoroalkyl)sulfone acid, and a porous H electrode made of Pt or a Pt alloy. The contact layers are C paper. (1) is used in combination with PEMFC for electrotraction. It has a high capacity in relation to volume and weight.

ELECTRICAL AND ELECTRONIC ENGINEERING

Piezoelectric Actuator
TOYOTA CHUO KENKYUSHO K.K. Japanese Appl. 10/273,361
A composition for a piezoelectric (PZT) actuator includes PZT ceramic with added precipitated Pt, Pd, Rh, Ru, Os, Ir or Au. Precipitation from solution occurs on the ceramic by heating and baking. Excellent displacement characteristics are obtained at lower cost, due to lower amounts of metal being used.

Optical Recording Medium
KAO CORP. Japanese Appl. 11/25,515
An optical recording medium, such as for optical disks, has an optical reflex layer of Ag-Ru alloy, containing 0.5–20 at.% Ru laminated with a protective layer on a substrate. About 0.1–10 at.% of Rh, Pd, Ir or Pt are included in the alloy layer. The medium has a high reflecting rate and improved service life. The chemical stability of the optical layer is improved.

Optical Recording Medium
KAO CORP. Japanese Appl. 11/25,515
An optical recording medium, such as for optical disks, has an optical reflex layer of Ag-Ru alloy, containing 0.5–20 at.% Ru laminated with a protective layer on a substrate. About 0.1–10 at.% of Rh, Pd, Ir or Pt are included in the alloy layer. The medium has a high reflecting rate and improved service life. The chemical stability of the optical layer is improved.

Structure of a Semiconductor Electrode
FURUKAWA ELECTRIC CO. LTD. Japanese Appl. 11/26,396
A p-type compound semiconductor electrode has an Al layer partially formed on an insulating layer covering a Pt layer, and a Ti or Cr layer which are on the exposed surface of the semiconductor. Peeling of the electrode boundary surfaces and the insulating layer is prevented during wire or die bonding.

Thick Film Conductor
SANKEN DENKI K.K. Japanese Appl. 11/31,872
A Ag-Pd thick film conducting paste for hybrid IC is printed and baked on a circuit board forming a thick conductor layer of 93.4–99.5 wt.% Ag and 0.5–6.6 wt.% Pd. A Ni layer is formed on the conductor layer by non-electrolytic plating and an Al wire is bonded to the Ni layer using ultrasonic oscillation. The connection strength is improved and embrittlement of the conductor layer is prevented.

Perovskite Structured La-Sr-Ru Oxide
FUJITSU LTD. Japanese Appl. 11/53,935
A thin film electrode of perovskite crystal structure, La$_x$Sr$_{1-x}$RuO$_3$, x = 0–1, is formed on a Si board by sputtering a target of SrRuO$_3$ and La. It is used as an electrode of a ferroelectric random access memory. The film may be deposited on a Pt coated substrate.

Sputtering Target Manufacture
TANAKA KIRINZOKU KOGYO K.K. Japanese Appl. 11/61,392
Ru for sputtering targets for the formation of Ru thin film is manufactured by melting Ru powder on a plate several times. A highly pure Ru ingot of > 99.9% purity is formed by cutting the plate. The Ru thin films are use in the manufacture of semiconductor devices. Bubbles of H$_2$ and O$_2$ gas formed on the film are removed together with impurities.

Thin Film Magnetic Head
YAMAHA CORP. Japanese Appl. 11/66,514
A thin film magnetic head for a magnetic recording disk has a Pt spacer layer interposed in the multilayered magnetic core along the width direction of the magnetic layer. Magnetic field response occurs to high frequency, thus stratification becomes simple and complicated manufacture is avoided.

Ruthenium-Doped Semiconductor
D. RIMBERG ET AL. German Appl. 1/97/47,996
Epitaxial production of Ru-doped semi-insulating III-V compound semiconductors is achieved using a Group V precursor having < 3 H bonded directly to the Group V element. The Ru layer is highly ohmic on both electron and hole injection and has low capacitance to avoid degradation of h.f. properties.

MEDICAL USES

Ceramic Material Composition
NIPPON HASHTOKUKYOKU K.K. Japanese Appl. 11/1,738
Ceramic material for artificial teeth contains in wt.\%: 19–20 Au, 19–30 Pd, 9–20 Cu, 0.02–0.03 Ir, 0.4–4.5 Sn, 0.5–4.5 Ga, 33–48 Ag, and impurities; the total amount of Sn and Ga is 2–5 wt.\%. The alloy has excellent heat conductivity and improved chemical stability, and wear- and corrosion-resistance.

The New Patents abstracts have been prepared from material published by Derwent Information Limited.