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Electrochemical Supercapacitors as Versatile Energy Stores

POTENTIAL USE FOR PLATINUM METALS

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“Supercapacitors” are a new category of electrical condenser which are based on the properties of charge distribution at the interface of an electrode/electrolyte solution. After an introduction to the features of such devices, a brief history of their development is followed by a description of some technical details. The latter part of the paper is devoted to some specific properties of ruthenium and iridium oxides, RuO, and IrO, which exhibit very interesting interfacial behaviour for their potential use in supercapacitors. In particular, these materials are very versatile in their method of preparation and in their surface properties. Prospects for changing the properties of the active layer of the superconductor by mixing two or more oxides are discussed.

Electrical energy is able to be stored either electrostatically in conventional capacitors, or electrochemically in cells or batteries (electrochemical power sources). For capacitors the electrical energy stored is given by:

\[ W_E = QAV = CAV^2 \]  

where AV is the electrical potential drop across the capacitor when electrical charge Q resides on its plates; C is the capacitance of the condenser defined as:

\[ C = Q/AV \]  

The amount of charge Q, as well as the capacitance C, is directly proportional to the surface area of the plates. For ideal capacitors, C is a constant and Q and AV are linearly related, see Figure 1a. During charge and discharge electrical charges do not cross the capacitor but move in and out through the external circuit.

Batteries store and supply electrical energy through a quite different mechanism. Electrical energy is stored as the chemical energy of reactants which are then transformed at the interface of the two electrodes of an electrochemical cell. For instance the global reaction at electrodes PbO, and Pb of a lead-acid battery during discharge is:

\[ \text{PbO}_4 + \text{Pb} + 2\text{H}_2\text{SO}_4 \rightarrow 2\text{PbSO}_4 + 2\text{H}_2\text{O} \]  

Discharge takes place (ideally) at the V value fixed by the AG, the change in Gibbs energy, of Reaction (iii):

\[ AG = -nFAV \]  

where n is the amount of charge transferred for the transformation of a mole of reactants and F is the Faraday constant.

In principle, current is supplied by a battery at constant AV as long as active material is still available in the device, see Figure 1b. In terms of electrical concepts, its capacitance would thus be infinite. However, during charging and discharging electrical charges cross the electrode/solution interface so that this device behaves electrically more like a resistor than as a capacitor. Nevertheless, the amount of electrical energy stored can be calculated by also
using Equation (i). Since $Q$ is very large, $W_n$ will be orders of magnitude higher than for conventional capacitors. However, the power density, that is, the power per unit volume or mass, will be orders of magnitude higher for conventional capacitors because of their smaller size. Moreover, the lifetime of batteries is limited by the number of charge/discharge cycles.

So-called double-layer or electrochemical capacitors fill the gap between the above two categories, see the Table overleaf (1, 2). Electrical energy can be permanently stored at the electrode/electrolyte interface due to the spontaneous charge separation occurring as the system attains electrostatic or electrochemical equilibrium. This is schematically shown in Figure 2. If the metal is negatively charged, for example, cations accumulate at the interface on the solution side at a distance of the order of magnitude of a few molecular diameters. In view of the high dielectric constant of the medium and of its thinness, the double-layer capacitor may have a capacitance of 20 to 100 $\mu$F/cm² depending on the natures of the metal and the solution. If the electrochemical interface is polarisable, that is, impermeable to electric charges, then the interface behaves as a “molecular” non-ideal capacitor (3), that is, because of the usually non-linear response of molecules to an electric field, the charge/potential relationship differs from that of a conventional capacitor (Figure 1). Thus, a mercury/aqueous solution interface, the “classic” polarisable electrode, may have a differential capacitance $dQ/d\Delta V$ of several tens of $\mu$F/cm² at some potentials, with corresponding lower integral capacitance $Q/\Delta V$. 

![Fig. 1](image1.png)  
**Fig. 1 (a)** Charging curves for ideal and non-ideal capacitors. **(b)** Discharging curves for an ideal capacitor and a battery

![Fig. 2](image2.png)  
**Fig. 2** The electrical double layer at the interface between an electrode and an electrolyte solution. OHP (Outer Helmholtz Plane) is the plane of closest approach of solvated ions to the electrode surface. The OHP acts as one of the plates, on the solution side, of the double layer capacitor.
The latter is of interest for practical situations.

An electrochemical interface cannot be charged by working with a single electrode. Thus, an electrochemical capacitor has the same features as a battery: two electrodes in contact with an electrolyte, see Figure 3a, but with dramatically reduced size, and with a fundamentally different mechanism of charging and discharging, Figure 3b. In addition, electrochemical capacitors carry no polarity under open-circuit conditions. It is to be noted that for such a system to work properly, interfaces are needed which behave reversibly to either direction of current flow; additionally, the total capacitance is half the value of a single interface, since the two electrodes are two capacitors in series, see Figure 3c.

Mention should be made of another class of condensers – the electrolytic capacitor – which could be confused with electrochemical capacitors since they are also based on an electrochemical mechanism. However, these in fact are conventional capacitors because they consist of two metal plates separated by a thin oxidic dielectric which is electrolytically grown on the metals. Aluminium or tantalum oxide is usually used as the dielectric. No spontaneous charge separation takes place at the interfaces – double-layer charge is not involved. Moreover, precautions must be taken with the electrical connections since wrongly connected electrolytic capacitors may explode (due to a breakdown of the dielectric). Furthermore, the relative permittivities of the dielectrics: aluminium oxide (7–10), tantalum oxide (25–27), titanium oxide (48) and other oxides are small, and the thickness of the dielectric is high, compared with their coun-

<table>
<thead>
<tr>
<th>Device</th>
<th>Energy density, Wh/dm³</th>
<th>Power density, W/dm³</th>
<th>Cycle life</th>
</tr>
</thead>
<tbody>
<tr>
<td>Batteries</td>
<td>50–250</td>
<td>150</td>
<td>10⁴</td>
</tr>
<tr>
<td>Electrochemical capacitors</td>
<td>5</td>
<td>&gt; 10⁵</td>
<td>&gt; 10⁵</td>
</tr>
<tr>
<td>Conventional capacitors</td>
<td>0.05</td>
<td>&gt; 10⁸</td>
<td>&gt; 10⁸</td>
</tr>
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Properties of Different Electrical Energy Stores

Taken from Ref. 1

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terparts in the electrical double layer capacitor.

From the above it is clear that batteries are needed when a supply of electrical energy is required for a long period of time at low current, whereas double-layer capacitors are useful for the rapid supply of large quantities of electricity over a short time. In order to improve the power delivered by these capacitors, the amount of charge stored per square centimetre of geometric surface area should be maximised while the potential window of operation should be enlarged as much as possible.

In practice an ideal double-layer capacitor can hardly be realised, since spurious surface redox reactions usually accompany double-layer charging and this is in fact the case with carbon capacitors, which is the prototype of this category (4). In these carbon capacitors surface redox structures (for example quinone groups) are always present (5). “Supercapacitors” are a particular category of electrochemical double-layer capacitors in which capacitive, \( Q_c \), and surface Faradaic, \( Q_f \), charges coexist. For instance, if a monolayer of atomic hydrogen is formed on a platinum electrode by cathodic discharge:

\[
\text{H}^+(\text{aq}) + e \rightarrow \text{H}_2(\text{Pt})
\]

Equation \( v \) resembles the reaction occurring in a battery, but is confined to the surface of the electrode. The charge associated with hydrogen adsorption is approximately 200 \( \mu \text{C/cm}^2 \) of real surface area. This charge, divided by the potential range from which it is transferred, constitutes a pseudo-capacitance since it is not associated with a purely capacitive phenomenon (2, 6).

However, \( Q_f + Q_c \), the latter being the “true” double-layer charge, dramatically increases the power of an electrochemical capacitor, while affecting the response time very little; hence the term “supercapacitor” which these devices are often called (2). The example described by Equation (5) would not constitute an excellent supercapacitor, since the potential range of effective operation is too narrow, being only about 0.3 to 0.4 V.

In this paper we will focus our attention on the transition metal oxides of the platinum group, particularly ruthenium and iridium, RuO\(_2\) and IrO\(_2\). The interesting and promising properties of these oxides will be illustrated for potential applications in supercapacitors.

**Background of Supercapacitors**

Although the capacitive properties of electrochemical interfaces have been known since 1879 from work by Helmholtz (7), practical applications of the electrical double-layer for energy storage have only recently become of worldwide interest (8).

Grahame’s pioneering studies on the electrocapillarity of mercury in 1947 (9) were completed in the early 1960s by investigations carried out on the adsorption of hydrogen on platinum, palladium, rhodium, iridium and gold (10). At that time the Standard Oil Company (SOHIO) was aware of the high value of the double-layer capacitance of carbon electrodes in fuel cells (11), and in the summer of 1962 a 3 cell/6 V carbon capacitor, the size of a large car battery, was able to power a canoe on a lake for about ten minutes. In April 1969 a brochure was prepared for their prospective customers entitled: “Non-polar Electrokinetic Capacitor, 0.6 Farad, 6 Volts”. However, the research was terminated in 1971 and the technology was later licensed to Nippon Electric Company, who have been manufacturing “Super Capacitors”, since 1979 (12). Almost at the same time, Matsushita designed their “Gold Capacitor” using activated carbons in organic electrolytes (13).

Electrodes based on platinum metals oxides were developed in the 1970s (14); they were designed originally for use as dimensionally stable anodes in chlor-alkali cells (15). Later ruthenium oxide was used in the Pinnacle “Ultracapacitor” (16), while in 1990 Giner Inc. presented their RuO\(_2\)/carbon/Nafion capacitor (1, 17).

**Future Applications of Electrochemical Capacitors**

Electrochemical capacitors seem to open novel dimensions in power engineering and power electronics, offering enormous specific capacitance as their particular advantage. Compact
electronic components with very large capacitances could be manufactured. Electrochemical capacitors have potential power densities of over 3 kW/kg and 10 kW/dm³ (1), exceeding the power densities of high-power batteries by a hundredfold. Energy densities of about 5 Wh/dm³ are higher than those of present-day ceramic and electrolytic capacitors. Conventional capacitors can store up to 1 C of charge, while batteries can store 10⁴ to 10⁶ C, therefore electrochemical capacitors could fill this gap. In contrast to accumulators, electrochemical capacitors can be charged and discharged in shorter times and their rechargeability is almost unlimited. Various applications for electrochemical capacitors have been proposed (8, 18):

- High power devices for energy storage systems, voltage stabilisers, power failure protection, pulsed lasers, satellite antennas, space communication systems, electric vehicle propulsion, starters in motor vehicles, regenerative braking, medical equipment such as defibrillators, electronic fuses in the mining industry and smart weapons.
- Battery substitutes for consumer electronics: memory back-up in computers, displays, video recorders, solar watches and toys.
- Replacing conventional capacitors in electronics for filters for power supplies, controlling equipment and alarm safety devices. Capacitors can protect sensitive electronics against power fluctuations, line transients and shutdowns.

The power system could be a hybrid arrangement with an energy storage capacitor for handling the peak power and a battery for handling the sustained load.

**Technical Details**

A simple electrochemical plate capacitor is formed from two plane electrodes dipping into an electrolyte. Two double-layer capacitances are thus combined in series and can be charged by applying a voltage. The initial high charging current decays to zero after a few seconds or minutes of charging. The charging voltage should not exceed the decomposition voltage of the electrolyte. Higher nominal voltages from the capacitor can be realised by combining in series several electrodes to form a bipolar stack.

Electrochemical capacitors display some features which are unknown to conventional capacitors, and some which can be compared to those of electrolytic capacitors (5, 19). An ideal double-layer capacitor would have a perfect dielectric with an infinitely large capacitive reactance which would cause a phase shift of 90° between the AC voltage and AC current flowing through. Owing to the internal resistance of electrodes and electrolytes actual electrochemical capacitors show a phase shift of less than 90°. In practice a pseudocapacitance is measured which is strongly dependent on frequency, temperature and voltage. The impedance of capacitors can generally be modelled by an equivalent electric circuit consisting of the isolated resistances and pseudo-capacitances of the electrodes, see Figure 3c, the electrolyte resistance and, if necessary, a series inductance (16, 17).

The ability to store energy increases as more bipolar electrodes are used and larger active electrode areas are chosen. The search for highly capacitive electroactive materials has led, among other materials (5), to ruthenium oxide (20) and iridium oxide (21, 22).

**Noble Metal Oxides as Active Materials**

The surface of an oxide in the presence of water molecules becomes covered by a carpet of OH groups, that is, it is hydroxylated, see Figure 4 (23). Platinum group metals are known to form oxides in a range of oxidation states from +2 up to +8. Thus, when RuO₂ is placed in solution and its potential is altered, for instance made more cathodic (reduction), the valency state of the surface metal atoms changes while being compensated by an exchange of protons with the solution (24):

\[
\text{RuO}_2(\text{OH})_6 + 6e^- + 6\text{H}^+ \rightarrow \text{RuO}_{2.5}(\text{OH})_{3.5} (\text{vi})
\]

Reaction (vi) is reversible for both RuO₂ and IrO₂, taking place over a potential range of about 1.4 V in aqueous solution, and limited only by the electrochemical decomposition of water – oxygen is evolved at more positive potentials, and hydrogen is formed at more negative potentials.
The pseudo-capacitive charge exchanged in Reaction (vi) involves all the active metal sites of the oxide surface. On the basis of a structural model, charge $Q$ can be calculated to be about 160 to 200 $\mu$C/cm$^2$ over a potential range of about 1 V when ruthenium ions are formally oxidised from +2 to +4. The associated capacitance is thus about 0.2 mF/cm$^2$ of real surface area. However, interest in utilising RuO$_x$ is due to the fact that this oxide, and also IrO$_x$, can be obtained in a morphological state, which increases its surface area enormously. A layer of a few micrometres thickness can carry a charge of up to 1 to 2 C/cm$^2$ of geometric surface, which is equivalent to a surface roughness of 500 to 1000. Thus, a RuO$_x$ supercapacitor could provide a capacitance of 0.5 to 1 F/cm$^2$, which is equivalent to about 25 to 50 F/g of active material.

The above figures are only an example. In fact, the properties of RuO$_x$ depend dramatically on the details of its preparation and on the chemical composition of the active layer which may contain other components. The good response of RuO$_x$ and IrO$_x$ is not only due to their surface and morphological properties but also to their excellent electrical conductivity. This prevents the penetration of electric field into the bulk which would lower the capacitance associated with space charge effects, which can be detrimental with carbon materials.

RuO$_x$ and IrO$_x$ can be prepared in various ways and several methods have been described. For instance, active electrodes for electrolysis cells can be prepared by the thermal decomposition of suitable precursors. The nature of the precursor, the way the precursor is applied to the support, the temperature of calcination, and other parameters, all have a marked effect on the final surface response, which requires several complementary experimental approaches for its full evaluation. However, the most straightforward technique for in situ characterisation of the surface response is cyclic voltammetry.

In cyclic voltammetry a potential, which changes linearly and periodically with time, is applied to an electrode, while the current response is recorded. The cyclic voltammetric response of an ideal capacitor is illustrated in Figure 5, where the constant capacitance results in charging at constant current while $\Delta V$ is linearly increased; $\nu$ is the potential scan rate:

$$I = \frac{Q}{\Delta t} = C\Delta V/\Delta t = CV$$  \hspace{1cm} (vii)

From Equation (vii) it is clear that for a non-ideal capacitor the current response will be
more non-linear the more the capacitor departs from ideal behaviour.

In Figure 6(a) a typical cyclic voltammetric curve for RuO$_x$ is shown (26). It is interesting to see how much the response approaches that of a conventional capacitor despite the dramatically different nature of surface charging. The broad humps are associated with surface redox transitions, as outlined by Equation (vi). The broadness of the peaks can be explained in terms of a large heterogeneity in the surface sites. Figure 6(b) compares the cyclic voltammetric curves of different materials. It is more difficult to distinguish definite redox transitions for IrO$_x$ although the response is still typical of a non-ideal condenser (27). Conversely, the cyclic voltammetric response of a battery-like material or of a homogeneous surface site distribution would result in sharp, high peaks which are unsuitable for use in double-layer capacitors. The response of a NiO$_x$ electrode is shown for comparison.

Ruthenium and iridium oxides can also be prepared by anodic electrolytic growth on the parent metals. A very high charge is also obtained in this case, but the voltammetric response indicates that hydrous oxides with bulk oxidation/reduction transitions are obtained in similar circumstances. In this state the electrode resistance, which is deleterious, increases, while the time response becomes slower (27, 28).

Integration of the cyclic voltammetric curves gives the surface charge density ($q^*$, measured in C/m$^2$) associated with charging/discharging, which is a primary parameter in the evaluation of oxide electrode properties. Much fundamental work has been devoted to the characterisation of oxide electrodes (24), and a decrease in surface charge density has been found as the calcination temperature is increased. Figure 7 illustrates the case for IrO$_x$: the maximum indicates the borderline temperature below which decomposition is incomplete (29).

The surface charge density has been observed to depend on the solvent in which the precursor is dissolved: thus, organic solvents produce a higher charge for IrO$_x$ probably because they favour the formation of particles of smaller size (30). In addition, RuO$_x$ prepared from the nitrate exhibits a higher value of surface charge density than when it is prepared from the chloride (31).

The various morphological analyses carried out on these oxides have shown that the layer possesses a compressed powder structure, see Figure 8 (24). In addition to pores being present, crystallites are joined at boundaries which may be permeable to the electrolyte solution. Therefore, the whole layer becomes impreg-
nated with the electrolyte solution and this results in a very high oxide/solution interface area.

Proton exchange is easy and fast at the outer (macro) interface, but it may be limited by mass transfer and other problems at the inner (micro) interfaces. This can be inferred in a number of ways, from the dependence of the surface charge density on the pH of the solution (surface charge density decreases if measured at intermediate pH), from the exchange rate of tritium in solution, from the in-depth profile of proton concentration, and in particular from the dependence of surface charge density on the rate of application of the electrode potential in cyclic voltammetry (24). Figure 9 shows an example for RuO₂.

A model to separate the inner from the outer surface charge has been proposed on a phenomenological basis (32). If the slow process is proton diffusion toward the inner surface, then surface charge density, q*, is expected to increase with √v, as semi-infinite linear diffusion can be assumed. This is strictly the case as steps in potential are applied. In cyclic voltammetry experiments semi-infinite linear diffusion is not in a steady state since the electrode potential is varied continuously. It is however intuitive, since v (measured in V/s) is proportional to 1/√t, that q* should vary linearly with 1/√v. Extrapolation of the plot to 1/√v → 0 provides a value of q* corresponding to v = ∞, that is to completely frozen diffusion. Hence, q- is the charge exchanged by outer surface sites only.

The extrapolation of q* to v = 0 is less obvious, but it has been found that a plot of 1/q* versus √v results in a fairly linear dependence over a broad range of v. These plots give q₀*, that is the charge exchanged under reversible conditions. It is thought that q₀* refers to the protons exchanged by all the surface active sites. In conclusion, (q₀* - q-*) gives the charge exchanged by the inner surface, which provides an estimation of the porosity of the oxide layer.

The importance of porosity in double-layer materials can hardly be over-emphasised. It is obvious that for pulse applications the response...
of a capacitor may depend dramatically on the nature of the inner surface as well as on the direction of polarisation, since a proton saturated layer may respond faster than a proton unsaturated layer.

**Mixed Oxide Layers**

Oxide layers used for supercapacitors must have a great ability to store charge, but they must also be resistant to electrolytic media and to charge/discharge cycles. The latter can induce mechanical instability; higher stability can be achieved by combining two or more types of oxides.

As RuO$_x$ is mixed with IrO$_x$, the surface charge turns out to depend on composition, and is usually higher at intermediate compositions, see Figure 10 (33). Moreover, the surface composition differs from the bulk nominal composition, Figure 11 (27). Both $q^*$ and surface composition can be evaluated *in situ* by cyclic voltammetry.

From proton exchange experiments, *inter alia* it is observed that IrO$_x$ is more "hydrous" than RuO$_x$ (24), and therefore, IrO$_x$ can improve AC capacitance at low frequencies. On the other hand, RuO$_x$ displays a very low resistance and can be used to dope insulating metal oxides for application as "diluents" in industrial electrodes. Mechanical "erosion" can also be monitored electrochemically; since $q^*$ is proportional to the oxide loading, erosion is observed to decrease $q^*$ (34). Dissolution of active sites will also decrease $q^*$ since this is accompa-
nied by smoothing of the surface (35).

Chemical and mechanical stability in supercapacitors can be improved by mixing noble metal oxides with valve metal oxides, such as titanium oxide and tantalum oxide (36). On the other hand, mixing two or more oxides always results in some deterioration of the high-frequency capacitance since valve metal oxides do not contribute to the electrochemical proton exchange. However, titanium oxide increases the DC resistance, while tantalum oxide may improve the series inductance, see Figure 12.

Conclusions

The oxides of the platinum group metals, particularly RuO$_x$ and IrO$_x$, possess properties at their interface with aqueous electrolyte solutions which are of great value for their potential use in electrochemical double-layer supercapacitors. The optimisation of their in situ response depends on a large number of variables which can be critically controlled only if their surface structure is investigated by a number of complementary electrochemical and non-electrochemical techniques.

The most promising aspects are (a) the very high interfacial capacitance per unit oxide mass due to the specific morphology, which results in a very high surface area, as well as to the specific mechanism of surface charging involving proton exchange with the solution, (b) the fast response to charging/discharging cycles, and (c) the mechanical and chemical stability under repetitive cycles. Finally in order to optimise the response mixing two or more oxides allows the various properties of the oxide layer to be controlled.

Acknowledgement

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**Conducting Polymer Interconnects for Platinum Nodes**

Since the development of ultra-small electrical circuitry, molecular electronics and artificial neural networks, the search to find ways of providing electrical connections between such nanosize three-dimensional structures has become a priority. The use of conventional mechanical or photolithographic fabrication techniques is inadequate for direct linking of such structures. Connecting these “molecular wires”, by using various chemical techniques to direct the linkage such as conducting organic polymer strands, has been the most successful so far, but a general technique for connecting large numbers of “molecular wires”, independently of each other, has not yet been found.

Now, however, researchers at the University of California, San Diego, have demonstrated the ability to interconnect many individual platinum nodes in three dimensions by an electrochemical polymerisation technique (C. L. Curtis, J. E. Ritchie and M. J. Sailor, “Fabrication of Conducting Polymer Interconnects”, Science, 1993, 262, 2014-2016).

Their technique is based upon the ability of conductive polymers, such as poly(3-methylthiophene), to be electrochemically switched between electronically conducting and non-conducting states. Pairs of platinum wires in an array immersed in a solvent of monomer/electrolyte, were independently electrically linked by polymer dendrites on passing an alternating current between them. When an actively polymerising strand electrically contacts a non-conductive strand, the non-conductive strand switches into its conductive state in the region close to the connection. Further polymerisation then occurs in the contacted region to reinforce the connection. The process requires no external mechanical manipulation or lithographic patterning. By using a separate insulating step, sets of electrically independent nodes can be prepared. The insulation of the electrically active links was performed by subsequent electropolymerisation of 4-vinylpyridine or 2-methylthiophene or, more consistently, by dip-coating the connections into a tetrahydrofuran solution of polystyrene.

The polymer connections display several properties relevant to neural networks, fuzzy logic or other nanofabricated model systems. In theory, a large number of nodes could be connected by this method, with the strength of each connection being determined by the conductivity between the node and the network. Therefore, it is expected that with further research, this non-mechanical technique could lead to the construction of complex three-dimensional nanosize interconnected arrays.

**High Temperature Palladium Superconductor**

Since the first high temperature YBaCuO superconductors were found in 1986, there has been much research to establish their basic mechanism and to find modifying elements which would increase the critical temperature. Copper oxides have usually been employed in these superconductors since they have a very high transition temperature, but no new families of intermetallic compounds with high transition temperatures have been discovered since the niobium binaries in 1953.


The transition temperature of this palladium quaternary intermetallic is higher than that of any previously reported for a bulk intermetallic compound. The superconductivity was observed for a narrow range of compositions at relatively low carbon contents. The superconducting volume fraction was large, even though the material was not single-phase. In addition, superconductivity was observed in small quantities in yttrium-palladium-boron alloys with no added carbon. It is suggested that yttrium palladium-boride carbide may be a new family of high-transition temperature superconductors.
Substantial Emission Control Progress to Meet Future Legislation

SELECTIVE REPORT OF THE 1994 INTERNATIONAL SAE CONGRESS

The February Congress of the Society of Automotive Engineers (SAE) is traditionally the focal point for those involved in the field of emission control. It is the main annual opportunity for presentation of technical papers associated with mobile source emissions and their treatment. The 1994 conference, which was held in Detroit from 28th February to 3rd March, proved to be one of the strongest Congresses ever held, with literally dozens of papers devoted to emission control, and therefore to the development and application of autocatalysts containing the platinum group metals.

Forthcoming legislation in California, the so-called LEV (Low Emission Vehicle) scheduled to come into effect in 1997, the prospect of further tightening of the European exhaust emission limits in 2000, and also perhaps the driving force of fiscal incentives, have caused the technology to race to meet these demanding automotive emission standards.

Although this review focuses upon three specific papers concerned with platinum group metals, it is important to note that the relative stringency of current and forthcoming emissions legislation now means that much greater emphasis is placed upon a system approach to emission control, as compared with the contribution from individual components. This was a recurrent theme throughout the technical presentations and papers. Several papers were given, for example, which discussed the potential for platinum and rhodium catalysts in combination with electrically heated supports or burner systems; the objective being to enable catalytic activity, especially hydrocarbon reduction to begin within seconds after vehicle start-up.

The past three or four years have seen an increasing interest in the prospects for using palladium in automotive emission catalysis. The use of palladium is not new, having been used in oxidation catalysts (to oxidise carbon monoxide and hydrocarbons) in the United States in the mid 1970s and early 1980s. However, palladium has not been widely used in three-way catalysts (for the simultaneous control of carbon monoxide, hydrocarbons and oxides of nitrogen) for two main reasons: first palladium is generally more susceptible to poisoning by lead and sulphur than either platinum or rhodium, and second, palladium can form alloys with rhodium thereby suppressing the catalytic activity of the rhodium. Nevertheless, the lower cost of palladium, compared with that of the other noble metals, and the fact that palladium does have specific desirable catalytic properties have contributed to its continuing development.

Palladium-Only Three-Way Catalysts

Three papers in particular considered palladium, the first being “Development of Palladium Only Three-Way Catalyst Technology” a joint publication of work done by the Ford Motor Company, the Engelhard Corporation and Johnson Matthey, and presented by J. S. Hepburn from Ford (SAE 941058), which described recent developments. The original objective of the research was to utilise the high temperature durability properties of palladium to provide a more thermally stable washcoat for use in close coupled automotive catalyst applications. Initial work used alkaline metals and rare earth oxides in conjunction with palladium to obtain a catalytic performance similar to that of rhodium. This was achieved by the construction of stable catalytic sites comprised of specific ions in close proximity to palladium atoms, which has the effect of promoting the dissociative chemisorption of nitric oxide and enhancing the water gas shift reaction, that is, it provides hydrogen to reduce nitric oxide.

First generation palladium-only three-way catalyst formulations demonstrated improvements, when compared to current three-way catalyst
technologies, in the hydrocarbon light-off and in an equivalent reduction of the nitrogen oxides. Second generation development focused upon improvements in the oxygen storage capability of the catalyst system to achieve an improved conversion capability for carbon monoxide and nitrogen oxides. Additional optimisation in the positioning of catalytically active sites further improved the water gas shift reactions described earlier.

Vehicle and laboratory reactor testing demonstrated the relative performances of palladium-only and palladium-rhodium catalyst formulations after ageing at various high temperatures. Data were presented showing that a palladium-only catalyst at 1200°C can have a broadly equivalent performance to a palladium-rhodium catalyst aged at 1000°C. The paper concluded that, when used in Ford vehicle applications, the palladium-only catalyst formulations demonstrated the capacity to reduce substantially the tailpipe emissions of hydrocarbons, carbon monoxide and oxides of nitrogen and this technology will be released into limited production in 1995.

**Durability Aspects of Palladium Only Catalysts**

Aspects of palladium-only three-way catalysts were reviewed by M. Härkönen and colleagues from Kemira Metalkat Oy in their paper, "Performance and Durability of Palladium Only Metallic Three-Way Catalyst" (SAE 940935). A palladium-only formulation, designed specifically for low temperature light-off and high temperature application, with a relatively high metal loading per catalyst, was found to be superior for the conversion of hydrocarbons, when compared with a conventional platinum-rhodium three-way catalyst. It was noted however that the control capability for oxides of nitrogen was lower than that of a platinum-rhodium system. Differences between palladium-only and platinum-rhodium catalyst performance are caused by changes to the air:fuel ratio of the engine. Higher air:fuel perturbation amplitudes showed that there was a capability for improving the conversion of nitrogen oxides using palladium-only catalysts without compromising other catalytic properties. In addition the performance of the catalyst can be further optimised by calibrating the air:fuel ratio exactly for this system.

**Extensive Work on Tri-Metal Catalysts**

This result tends to suggest that the use of palladium-only or palladium containing three-way catalysts will be specific to each application, and this was one of the main conclusions from the third paper which considered palladium, "Recent Trends in the Application of Tri-Metal Emission Control Catalysts" a joint paper from Degussa AG, International Catalyst Technology Co. and Nippon Shokubai Co. Ltd., which was presented by E. S. Lox of Degussa (SAE 940928).

The authors noted that the catalyst-relevant properties of fuels available in the United States of America and in European markets have improved considerably, and especially that the lead content has decreased. Advanced engine management systems are now available which allow a much tighter control of the air:fuel ratio. In addition the use of air pumps to add air to the exhaust to give a net oxidising exhaust gas composition at engine start-up creates a condition which is advantageous to palladium.

The report described an evaluation of combinations of various noble metals: platinum/rhodium, palladium-only, palladium/rhodium and platinum/palladium/rhodium for a range of loadings and ratios. The catalysts were evaluated under a range of test conditions, including synthetic gas, engine bench and by vehicle evaluation.

The effect of hydrocarbon speciation upon the catalytic activity was highlighted. Under lean conditions, palladium exhibits lower light-off temperatures for an olefinic hydrocarbon (butene) than platinum or rhodium based catalysts. Increasing the partial pressure of the oxygen lowers the light-off further. However palladium has no advantage over platinum for the light-off of a paraffinic hydrocarbon (butane) and the light-off temperature of a paraffinic hydrocarbon is not affected by an increase in the partial pressure of oxygen.
Thus the authors note that the improvements in the performance of engine hydrocarbon light-off, observed for palladium-only catalysts when used in conjunction with a secondary air-pump, are due to the present generation of gasoline engines emitting a higher proportion of olefinic hydrocarbons from utilising the currently available fuel specifications.

The performance of three metal autocatalyst systems was also considered in this paper. The authors noted that to combine platinum, palladium and rhodium into one catalyst would involve complex impregnation techniques. Therefore for this study combinations of different metal catalysts within the vehicle exhaust system were evaluated. Results indicate that the best conversion performance for carbon monoxide and hydrocarbons is achieved with those systems that place a palladium catalyst first, but the best compromise for simultaneous conversion of carbon monoxide, hydrocarbons and oxides of nitrogen is achieved by using a platinum-rhodium catalyst followed by a palladium-only catalyst. Within the context of European legislative requirements it was demonstrated that a platinum-rhodium catalyst followed by a palladium-rhodium catalyst gave the best results. However, in the context of United States legislative requirements it is noted that a single catalyst combining all three noble metals gives the best vehicle test results.

The Congress held this year has shown the determination and capability of the automobile manufacturers to meet the forthcoming stringent emission standards. It has also demonstrated that the use of platinum group metals can meet this challenge for application in vehicle exhaust systems.

C.J.

Encapsulation of Palladium Crystallites in Carbon

The growth in carbon nanotechnology has produced carbon in the form of giant clusters, large nested fullerenes, bamboo-like structures and nanotubes. Metals and metal carbides have been successfully included into these structures, and carbon clusters in tubular form encapsulating a metal are expected to result in new technology. However, encapsulating a metal has generally been selective with respect to the metal. Palladium is an important catalyst and is used in many chemical reactions, often supported on carbon. Now a researcher at the DuPont Company in Delaware, has succeeded in encapsulating cubic palladium crystals inside giant carbon clusters and produced worm-like carbon nanotubes ("nanoworms") (Y. Wang, "Encapsulation of Palladium Crystallites in Carbon and the Formation of Wormlike Nanostructures", J. Am. Chem. Soc., 1994, 116, 397-398).

The carbon-encapsulated palladium was found in the cathode deposit produced from arcing between a hollow carbon anode filled with palladium oxide/graphite cement paste and a carbon cathode within a chamber filled with flowing helium at 500 Torr. The ratio of the palladium oxide:carbon, in weight per cent, was from 0.05 to 1.0. The worm-like structures were mainly observed in the core of the cathode deposit and rarely found in the shell.

Deposits formed at the tip of the cathode were analysed by transmission electron microscopy. The head region of the "worm" was examined by energy dispersive X-ray analysis and was found to consist of palladium encapsulated in carbon clusters; electron diffraction of the body of the "worm" showed that it consisted of many sections of carbon tubes 20–50 nm in diameter and several hundred nanometres long. The tubes had mostly cone-shaped internal voids, with the tip of each void always pointing to the back of the worm.

Palladium appears to act as the seed for the growth of the "nanoworm"; the cone-shaped internal void being the result of tube closure caused by pentagonal ring formation due to the presence of palladium. Each closure is followed by new growth from the outer layer which forms the next section. This periodic tube closure and regrowth eventually produces the worm-like structure. Some worm-like bodies were without palladium in the head, but the internal cone-shaped voids indicated that palladium had once been present.

As it is already known that chemical methods and electron beam radiation can open the ends of nanotubes and nanowires it is suggested that such carbon-encapsulated palladium could become very useful. The carbon protects the palladium in a pristine form and only needs to be able to release it periodically under controllable conditions. This would allow the palladium to be introduced into a chemical reaction with regulated and timed release.
Polymer-Immobilised Clusters of the Platinum Group Metals

By Professor A. D. Pomogailo
Institute of Chemical Physics, Russian Academy of Sciences, Chernogolovka, Russia

In this review major developments associated with the synthesis, properties, structure and applications of polymer-immobilised clusters of platinum, palladium, iridium, rhodium, osmium and ruthenium, are presented. Special attention is paid to polymer analogous reactions with metal clusters and new directions involving the polymerisation and copolymerisation of cluster-containing monomers. Some specific features of fixing heterometallic clusters on polymers are examined and the more interesting application of PCNM in catalysis, and future developments in this direction, are discussed.

Polymer-immobilised clusters of the noble metals (PCNM) are of great interest for at least two reasons; first, they are a new type of catalyst which can be used in many organic syntheses and second they can be widely used as a basis for the production of different polymeric materials with unusual properties. In addition polymer-immobilised clusters can act as a convenient model of metal catalyst surfaces. Studying immobilised clusters can provide information about the structure of the catalyst surface, such as metal-substrate bond energies, the stereochemistry of the active centre and structural transformations occurring during catalytic reactions, and also about the mechanism of the catalytic reaction.

At least three fields of chemistry are linked by PCNM: cluster co-ordination chemistry, polymer chemistry and catalysis. There are three major methods for the preparation of PCNM; these are the physical insertion of small metal particles into a polymer, chemical insertion and (co)polymerisation of cluster-containing monomers, see Table I.

**Preparation of PCNM Clusters of Unidentified Structure**

The methods of preparing platinum metals clusters immobilised on polymers having unidentified structure are based on forming small metal particles from fine powders, salts and mononuclear complexes in the presence of polymers, which act as protective covers. The specific features of these methods are the direct route and the relative simplicity of preparation of the products. PCNM prepared in this way have a wide size distribution, typically 10 to 700 Å, which can change during use. By comparison with typical mechanical mixtures of polymer and large metal particles of micron size, the polymer immobilised clusters additionally have a relatively high dispersion, a uniform size distribution of metal particles within the bulk of the polymer, and a substantial irreversible sorption of macromolecules on the surface of the metallic particles. Such PCNM have a tendency to encompass metal particles within the natural hollows of the polymer matrix, and their formation is often accompanied by chemical reactions. However, the PCNM produced by these methods may be of single-phase metallopolymeric compositions due to the high dispersion of the metal particles. Various methods for preparing polymer immobilised noble metal clusters are shown in Table I.

Another method for preparing clusters with unidentified structures is by the reduction of mononuclear complexes. This method uses carbon chain polymers or polymers produced by polycondensation as the organic medium for...
Table I

Methods of Preparing Polymer-Immobilised Noble Metal Clusters (PCNM)

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<tr>
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<tbody>
<tr>
<td>1</td>
<td><strong>PCNMs with Unidentified Structure</strong></td>
<td></td>
</tr>
<tr>
<td></td>
<td>a Decomposition of volatile metal salts, metal carbynyls,</td>
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<td></td>
<td>organometallic derivatives in polymer matrices as well as in</td>
<td></td>
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<tr>
<td></td>
<td>melts followed by cluster formation</td>
<td></td>
</tr>
<tr>
<td></td>
<td>b Chemical, photochemical and electrochemical reduction of</td>
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<tr>
<td></td>
<td>mononuclear complex in active medium in the presence of</td>
<td></td>
</tr>
<tr>
<td></td>
<td>polymers</td>
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</tr>
<tr>
<td></td>
<td>c Spraying of metal atoms (at low temperatures and pressures)</td>
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<tr>
<td></td>
<td>on thin polymer films</td>
<td></td>
</tr>
<tr>
<td></td>
<td>d Mixing clusters with polymer (microencapsulation)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>e Mechanochemical insertion of highly dispersed metal</td>
<td></td>
</tr>
<tr>
<td></td>
<td>particles, metal salts or metal oxides into polymer matrix</td>
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<tr>
<td>2</td>
<td><strong>Polymer analogous reactions with cluster participation</strong></td>
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<tr>
<td></td>
<td>a &quot;Assembly&quot; of polynuclear complexes from mononuclear ones</td>
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</tr>
<tr>
<td></td>
<td>including reduction of polymer-immobilised complexes</td>
<td></td>
</tr>
<tr>
<td></td>
<td>b Cluster immobilisation by functionalised polymers</td>
<td></td>
</tr>
<tr>
<td></td>
<td>c Immobilisation of heterometallic clusters</td>
<td></td>
</tr>
<tr>
<td></td>
<td>d Cluster immobilisation by polymer compounds</td>
<td></td>
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<tr>
<td>3</td>
<td><strong>(Co)polymerisation reactions in PCNM synthesis</strong></td>
<td></td>
</tr>
<tr>
<td></td>
<td>a Vibrational milling or other dispersive methods (decomposition of metal salts or metal oxides, metal dissolution, etc.) in a vinyl monomer medium followed by polymerisation reactions</td>
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</tr>
<tr>
<td></td>
<td>b (Co)polymerisation of cluster-containing monomers</td>
<td></td>
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<tr>
<td></td>
<td>c Polycondensation of metal cluster complexes</td>
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</table>

The process. For example, the reduction of palladium chloride, absorbed on polyheteroarylenes, by NaNBH, or hydrogen leads to the formation of Pd$^0$ clusters of size 1 to 3.5 nm (4). Such small particles interact so strongly with the polymer matrix that positive charge, Pd$^+$, appears on the palladium atoms as a result of electron transfer. The $\pi$-electron system of the polymer chain promotes this process and subsequently transforms into an ion-radical state.

Similar interactions between formed clusters and the polymer matrix are characteristic of many other metallopolymeric systems (5, 6), including clusters produced by spraying solvated metal atoms in vacuo at 77 K (7). The polymer matrix in such cases acts to stabilise the highly dispersed metal particles and prevents the subsequent enlargement of the clusters.

Metal particle growth prevention by the polymer matrix can be shown by examples from the formation of cluster-, or colloidal particles of palladium, ruthenium, rhodium, osmium, iridium, silver or gold, in protective polymer coverings (8, 9).

The following transformation sequence occurs on boiling RhCl$_3$ with polyvinyl alcohol (PVA) or polyvinylpyrrolidone solutions: in the first stage RhCl$_3$ is co-ordinated by the polymer, then oxoniene RhCl$_3$ complex is formed followed by fixing the hydride complexes as the alkoxide form; alkoxide groups being precursors of hydride forms. This sequence is necessary to form homogeneous colloids and is accompanied by consecutive growth of the particles, see Scheme I.

The clusters formed with thirteen rhodium nuclei have a face centred cubic lattice, and the
co-ordination number of rhodium is 12. They are attached to the protective colloid by electrostatic attraction or physical absorption and possibly by co-ordination bonds. The dimensions of the cluster particles may be changed by using a different polymer as well as by the reaction conditions.

The same method was used to prepare palladium particles of diameter 1.8 nm within the protective colloid, polyvinylpyrrolidone. Natural polymers, such as β-cyclodextrine (10), different functionalised cellulose derivatives, oligo- and polysacharides (11), Indian silk (12), chitin and chitosane (13), may also be used as stabilising agents for colloidal particles of rhodium, platinum and palladium of diameter 1 to 100 nm.

**Synthesis by Polymer Analogous Reactions**

The development of new methods is needed to create materials composed of individual clusters or metal atom assemblies of diameters 1.5 to 5 nm with a narrow size distribution. In one method the assembly of polynuclear complexes from mononuclear complexes often occurs during the immobilisation or mononuclear complexes, by functionalised polymers, from highly concentrated solutions, as well as by fixation by unfunctionalised polymers. However, published data show that the nuclearity of the initial complexes can be preserved by fixing binuclear or trinuclear ruthenium complexes on ion-exchange resins, such as Amberlite IR-20 or Dianion CR-10, which contain iminodiacetate groups (14).

More elaborate methods of producing PCNM are based on fixing individual clusters of known structure by polymer macroligands. Macroligands, such as "popcorn" polymers (phosphorilated copolymers of styrene and divinylbenzene, \( \text{P-PPh}_3 \), or sometimes variations (triple block-copolymer styrene-divinylbenzene-vinyltrimethylphosphine) in the form of thin membranes or grains with size dimensions of 200 to 400 mesh are usually employed. Fixing the clusters can be performed by ligand- or ion exchange, oxidative addition, decarbonylation, ligand addition, and so on. Some of the more interesting PCNM prepared by these methods, grouped according to similarities in their preparations, are listed in Scheme II (15–20).

Polymer-immobilised clusters with a one-centre bonded cluster, for example iridium, are formed at low concentrations of phosphine groups, where less than two per cent of the benzene rings are functionalised, or at a statistical distribution of \( \text{PPh}_3 \)-groups. A convenient method of showing the structure of immobilised clusters is by comparison of the infrared spectra of the initial substances and the products formed. However, for macroligands with rather high concentrations of \( \text{PPh}_3 \)-groups, where more then three per cent of the benzene rings are functionalised, a mixture of clusters connected to the polymer by one and two \( \text{PPh}_3 \) groups is formed. Clusters connected to the polymer by two \( \text{PPh}_3 \) groups are produced as the sole product when the block-copolymer styrene-divinylbenzene-divinylphenylphosphine, containing 8 to 15 per cent of \( \text{PPh}_3 \)-groups, is used. Clusters connected to three \( \text{PPh}_3 \)-groups, are prepared in this way (for instance \( \text{P-PPh}_3 \text{RuCl}_3 \), see Scheme II).

It is important that immobilised complexes of Ir, are synthesised by assembly from \( \text{Ir(CO)}_3 \text{Cl-p-toluidine} \) or from \( \text{IrCl}_3 \text{(C,H}_2)_2 \), in situ in the presence of zinc and carbon monoxide. Attempts to fix \( \text{Ir(CO)}_3 \), dissolved in toluene, permanently with \( \text{P-PPh}_3 \) were unsuccessful; a mix-
ture of mono-, bi- and trisubstituted forms was obtained.

More complicated cluster transformations have been observed; for example, when Rh\(_4\)(CO)\(_{12}\) was reacted with PPh\(_2\) in hexane at 50°C binuclear clusters were formed (19). However, when this procedure was carried out with Rh\(_4\)(CO)\(_{12}\) in benzene, a precipitation of black spots of metallic rhodium was observed on the walls of the reactor (20). The black spots were of size 25 to 40 Å, and each spot contained about 100 rhodium atoms. The same effect has also been observed for anionic ruthenium clusters. At higher temperatures of 100 to 150°C the immobilised clusters dissociate to form metal crystallites in the polymers.

Cluster fragments of Ir\(_4\)(CO)\(_{12}\) can be fixed by other phosphorus containing macroligands on polymers which have been modified with the optically active groups 2,3-(o-isopropylidene-2,3-dioxi)-1,4-bis(diphenylphosphino)-butane (21).

The processes for immobilising noble metal clusters by other polymers have been studied less. In particular, the immobilisation of cluster Os\(_3\)(CO)\(_{11}\) on poly(4-vinylpyridine) (P4VPy) in dimethylformamide at 110°C in an atmosphere of carbon monoxide occurs by means of two pyridine rings, one of which is chelated (22):

The mechanism for bonding Rh\(_4\)(CO)\(_{12}\) with poly(4-vinylpyridine), as well as the structures of the products formed by the interaction of Rh\(_4\)(CO)\(_{12}\), Rh\(_4\)(CO)\(_{11}\) and Rh\(_4\)(CO)\(_{11}\)Cl, with NH\(_2\)-groups of the polymer (aminated polystyrene), requires further study (23). This also applies to the immobilisation of Ru\(_4\)(CO)\(_{12}\) on cross-linking macroporous chelating polymers, functionalised with the following: bipyridine,
2-aminopyridine, 2-aminophenol, 2-iminopyridine and sodium anthranilate (24), for example; and to products formed by the interaction of Rh$_2$(CO)$_3$Cl$_2$ with copolymers of styrene and divinylbenzene, modified by N,O-chelating nodes (25).

The interaction of Rh$_2$(CO)$_3$ (the first cluster to be immobilised (16)) with resin Amberlyst A-21 proceeds in a more complicated manner and leads to the formation of immobilised rhodium clusters of different nuclearity, see Scheme III (26).

The formation of HO$_2$(CO)$_3$N’Et.CH$_2$.P from Os$_2$(CO)$_3$. has been identified (27). Sulphur- and oxygen-containing matrixes are rarely used to immobilise clusters; polymeric alcohols and acids are the more often used macroligands. Thus, the addition of trismium clusters to polymeric alcohols proceeds, as in the case of inorganic oxide, by oxidative addition, see Scheme IV (28).

Very stable compounds, for example the binuclear acetate complex Ru$_2$(OOCCH$_3$)$_2$ (29), can be fairly easily fixed on the ion-exchange resin Diaion CR-10 (14). It is important to note that the preservation or dissociation of their polynuclear structure depends on the nature of the ligands. Thus, during the heterogenisation of the binuclear acetate complex Rh$_2$(OOCCH$_3$)$_2$, on a polymer which contains ligands of 3(5)-methylpyrazole or imidazole groups (29), the binuclear structure and the degree of oxidation of the rhodium (+2) remain on the polymer. In contrast, for rhodium binuclear complexes of sulphate, acetonitrile and hexafluoroacetyleacetonate the rhodium-rhodium bond breaks and the degree of oxidation on the central atom increases. An analogous result has been obtained during fixing the cluster anion Ru$_4$Cl$_4$ (30) on P-PPh$_3$ : the cluster anion can not penetrate into the polymeric matrix and so, for steric reasons, dissociates forming fixed mononuclear and dimer complexes.

There is no data available at present about bonding noble metal clusters by polymer-polymer compositions, unlike mononuclear complexes for which data which is available.

**Polymer-Immobilised Bimetallic Clusters**

A heterometallic polynuclear centre is preferable to a mononuclear one for many catalytic processes. Such systems can be considered as models of bimetallic catalysts, for example as the contact crystallites on the surface of catalysts used for refining oil distillates industrially. However, PCNM, in contrast to fused catalyst are of uniform structure. As a rule the same methods that are used to immobilise mononuclear complexes are used both to immobilise heterometallic clusters and to identify the structure of the products. The most widely used method is the assembly synthesis of clusters from monometallic complexes. A co-operative dissociation of H$_2$PtCl$_2$.Fe(NO)$_3$, and/or Rh$_3$(CO)$_12$.CoCl$_2$.6H$_2$O in polymeric matrixes has been carried out.

Bimetallic clusters can be formed in a colloidal dispersion of platinum and palladium stabilised by polyvinylpyrrolidone, if the ratio of palladium:platinum is 41; the dispersion being pre-
pared by the combined reduction of PdCl₂ and H₃PtCl₆ in a water-ethanol solution in the presence of polyvinylpyrrolidone (10). Clusters of different metals, for example, a mixture of the clusters Co₆(CO)₁₈ and Rh₆(CO)₁₈, in molar ratios from 1:1 to 3:1, can be fixed on amino-containing ion-exchange resins to use as a model of a bimetallic catalyst (31).

Heterometallic clusters of known structure are of greater use in the same way that immobilised monometallic clusters of known structure are. Phosphorilated polystyrenes are polymer matrixes of optimal structure, and ligand exchange or sometimes ionic exchange is widely used to immobilise clusters on them. The structure of the products is always determined by analysis of the infrared spectra of the carbonyl group clusters and by a comparison of the spectra of individual molecular compounds. Typical examples of immobilised heterometallic clusters are summarised in Scheme V (3, 17, 32–34). Other examples show the immobilisation of H₃FeOs₆(CO)₁₉ on cross-linking macroporous chelating polymers (24). There is also data about the immobilisation of Co₆Rh₆(CO)₁₈ on the ion-exchange resin Dawex-1 (35), as well as for H₂FeRu₆(CO)₁₉, [FeRh₄(CO)₁₉][NMMe₄]₂ and H₃Co₆(CO)₁₈, where x = 2 or 3, on macroligands. The mechanism of these processes has not yet been studied, and it is very possible that there are no examples of immobilisation of trimetallic type clusters.

PCNM Formation in the Course of Polymerisation

The formation of polymer-immobilised noble metal complexes during the preparation of the polymeric matrix has advantages both in simplifying the synthesis of the complexes and in determining their structure. The methods for preparing PCNM which were considered earlier are generally accompanied by numerous processes, the most important of which is an increase or decrease in their nuclearity.

The polymerisation of vinyl monomers in the presence of formed small dispersive particles of the platinum metals is not a commonly used method at present. However, in recent years methods for the polymerisation of cluster-containing monomers (as for other types of metal-containing monomers (36)) have aroused great interest. As this area of study is presently

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undergoing development, we shall demonstrate its possibilities with some examples.

The cluster monomers listed below were synthesised by the interaction of trinuclear clusters \( M_3(CO)_{12} \) (where \( M \) is osmium or ruthenium), \( Os_3(CO)_{10} \)(CH\(_2CN\), \( Os_3(CO)_{10} \)(CH\(_2CN\)), and \( (m-H)Os_3(m-OR)(CO)_{10} \) (where \( R \) is hydrogen or phenyl) with conventional monomers, such as 4-vinylpyridine, acrylic acid and allyl-sulphide, see Scheme VI (37).

It is interesting to note that in such monomers the pyridine ring is chelated as in the case for the product of the interaction of \( Os_3(CO)_{12} \) with poly(4-vinylpyridine) (P4VPy) (see above). At the same time the interaction of \( Rh_6(CO)_{12} \), with P4VPy in the presence of (N-oxide of trimethy-lamine) proceeds under mild conditions and is accompanied by the formation of the basic product, the monosubstituted derivative \( Rh_6(CO)_{12}(4VPy) \), and small amounts of di-substituted compounds \( Rh_6(CO)_{12}(4VPy) \), (38). These are easy separated by chromatography and may be isolated individually. In contrast to the \( Os_3 \)-derivatives the monomer \( Rh_6(CO)_{12}(4VPy) \) is an octahedron cluster with 11-end and 4-µ-bridge carbonyl ligands, and 4-vinylpyridine is connected to the rhodium atom only through the nitrogen atom, and occupies the co-ordination position of the twelfth terminal carbonyl group. The average length of the rhodium-rhodium bond is 2.762 Å and is similar to that of other rhodium clusters.

Polymer-immobilised noble metal clusters may also be produced by polymerisation and more often by copolymerisation of cluster-containing monomers, for example according to Scheme VII (39).

The composition of the polymers and their molecular weights are controlled by the usual methods, such as the composition of the monomer mixture and the polymerisation conditions. It is important that in such PCNM mutual thermal stabilisation of the polymer and the cluster in its chain, is observed. For example, the temperature of dissociation of clusters in copolymers containing the \( Os_3 \), complex and 4-vinylpyridine increases from 295 to 450°C, but the temperature for the thermal destruction of the polystyrene framework increases by 50 to 100°C (the cluster units are 0.5 to 1.0 mol per cent of the contents). The effect of the polymer chain is such that it can dissipate the diffusion of energy from the free rotary-oscillatory movement of the cluster into translation in the polymer segments, which therefore increases the thermal stability of the polymer.
Table II

Some Catalytic Reactions Which Use PCNM

<table>
<thead>
<tr>
<th>Catalysed reactions</th>
<th>PCNM</th>
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<tbody>
<tr>
<td>Reduction of nitrobenzene to aniline</td>
<td>Rh₆(CO)₁₆ on Amberlyst A-21</td>
</tr>
<tr>
<td>Ethylene hydrogenation</td>
<td>P-PP₃Rh₄(CO)₁₁</td>
</tr>
<tr>
<td>Hexene-1 hydrogenation</td>
<td>Rh/PVA (particle size 4 nm)</td>
</tr>
<tr>
<td>Selective hydrogenation of cyclopentadiene</td>
<td>Colloid particles of Pd on P4VPy</td>
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<tr>
<td></td>
<td>(particles size 1.8–5.6 nm)</td>
</tr>
<tr>
<td>Isomerisation of alkenes</td>
<td>Os₃ clusters on polymers with OH groups</td>
</tr>
<tr>
<td>Electrochemical oxidation of CH₂OH</td>
<td>Pd on solid polymer electrodes</td>
</tr>
<tr>
<td>H₂-D₂ exchange</td>
<td>Rh, Pd, Pt on P4VPy</td>
</tr>
<tr>
<td>Photoelimination of H₂ from H₂O</td>
<td>Colloidal particles protected by polymers</td>
</tr>
<tr>
<td></td>
<td>(particle size 1–100 nm)</td>
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<tr>
<td>H₂O oxidation with elimination of O₂</td>
<td>Polynuclear Ru complexes on Dianion CR-10</td>
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<tr>
<td>Fischer-Tropsch reactions</td>
<td>Ru₃(CO)₁₂, H₂FeO₅(CO)₁₃ on polymers with chelate units</td>
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<tr>
<td>Di-isobutylene hydroformylation</td>
<td>Rh₂(CO)₆Cl₂ on copolymers with N,O-chelate units</td>
</tr>
<tr>
<td>Hexene-1 hydroformylation</td>
<td>Rh₆(CO)₁₆ on polymers</td>
</tr>
<tr>
<td>Oxidation of 2-olefins to alcohols</td>
<td>Co₂Rh₂(CO)₁₂, RuOs₃ on polymers</td>
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<tr>
<td></td>
<td>A mixture of Co₄(CO)₁₂, Rh₆(CO)₁₂ on amino-containing resins</td>
</tr>
<tr>
<td>The water-gas shift reaction</td>
<td>Os₅(CO)₁₂ on P4VPy, clusters of Rh₂, Rh₄, Rh₆ on aminated polystyrene</td>
</tr>
<tr>
<td>Hydrogen transfer</td>
<td>Rh₆(OCOCH₃)₆ on polymers with imidazole groups</td>
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</table>

It may be that such an approach will soon become widely spread and that new classes of polymer-immobilised noble metal clusters can be prepared with its help. This also applies to polymer-immobilised clusters of noble metals prepared by polycondensation of cluster-containing compounds, which is not as yet known.

**PCNM in Catalysis**

Although a role for polymer-immobilised clusters of noble metals in catalysis has only just begun to develop, some publications and reviews have appeared (3, 40). The most important applications of PCNM in catalysis, in our opinion, are summarised in Table II.

Such catalysts can be used as powders, beads, balls, thin membranes (of thickness up to 7 nm), swelling gels, and sometimes in solutions. Kinetic parameters have many features in common with catalysis using immobilised mononuclear complexes. For instance, the rate for ethylene hydrogenation using polymer-immobilised noble metal clusters is ten times higher than for cyclohexene hydrogenation, and the ratio between the rates for cyclohexene and benzene hydrogenation is 25 to 50. The rate of reaction decreases with the accumulation of phosphine ligands in the cluster. The Mₘ particles, where M is the noble metal, formed by reduction of the polymer-immobilised noble metal clusters, for example by hydrogen, differ in their sizes and activities in olefin hydrogenation and isomerisation. This isomerisation is promoted by hydrogen and occurs on the co-ordinated unsaturated active centres. The enlargement of the produced metal particles depends on both the method.
of preparing the catalysts and the conditions of catalysis.

By comparison with homogeneous systems the polymeric carrier substantially suppresses the integration of particles, and the small dimensions, 1 to 2 nm, of the particles produced do not allow them to act as metallic objects. There are probably multinuclear associations, and the dynamics of their formation is very complex. It is important that such processes will be accompanied by saving the co-ordination vacancies after the activation of the catalysts. In many cases the centres, arranged on borders of clusters and stabilised by their electronic systems, are responsible for the catalyst activity. Such co-operative interactions increase the stability and activity of the PCNM and allow them to carry out repeated reactivation and regeneration as well as preventing the precipitation of catalyst from solution, including that on the reactor walls.

The conditions for immobilisation of the clusters and subsequent processes determine the evolutionary transformations of the clusters from being fixed mononuclear complexes to cluster-type structures with a polymeric carrier as macroligand. However it is very difficult to find correlations between the catalytic activity of the PCNM and their nuclearity. We note only that the rate of the water-gas shift reaction increases for complexes immobilised on polymeric amines (23) as: \( \text{Rh}_{12}(\text{CO})_{22} \cdot \text{Cl} \) < \( \text{Rh}_{6}(\text{CO})_{18} \) < \( \text{Ru}_{3}(\text{CO})_{12} \) < \( \text{RhCl(PPh)}_{3} \). Additional possibilities for controlling the catalytic properties by changing the nuclearity of the immobilised complex could be created.

There is a series of processes which are catalysed by clusters, including immobilised clusters. For example, polynuclear clusters are the active elements of transport chains in enzyme photo systems (photo systems II of natural photosynthesis) and/or the catalytic centres responsible for redox transformations; natural polymer peptides are their carriers. Immobilised metalloclusters in heterogenised catalysts are used as catalysts for the water-gas shift reaction, see Table II; here the processes proceed under milder conditions.

The immobilisation of metalloclusters is very useful for investigating the mechanism of catalytic reactions, since in many cases it permits the isolation and thus identification of the intermediates. Immobilised \( \text{RuO}_2(\text{OCCH}_3)_5 \cdot \text{L}^+ \) particles, for example, have been identified during the hydrogenation of cyclooctene by ruthenium complexes fixed on carboxylate matrices (41). Some researchers (23) think that the two cluster anions \( \text{Rh}_{12}(\text{CO})_{22}^+ \) and \( \text{Rh}_{6}\text{H}(\text{CO})_{18}^+ \) are active forms in the water-gas shift reaction when catalysed by \( \text{Rh}_{6}(\text{CO})_{18} \cdot \text{Cl}_2 \) on aminated polystyrene.

There are numerous examples of the higher catalytic activity achieved when using polymer-immobilised bimetallic clusters than when using monometallic clusters; in particular the use of cobalt-rhodium and cobalt-ruthenium in hydroformylation reactions. The observed synergism is probably connected with a matrix effect due to the second metal, which isolates the rhodium or ruthenium atoms, respectively, as well as stabilises the intermediates and improves the introduction of carbonyl into the metal-alkyl bond. Other reasons can be linked to a decrease in the charge density on the atom in the active centre of the heterometallic clusters, for example cobalt-rhodium or iron-rhodium, as well as cobalt and iron acting as a ligand for rhodium since the formation of direct bonds rhodium-cobalt-oxygen and possibly rhodium-iron-oxygen prevents caking of the rhodium and of the catalyst (42).

Several examples of the occurrence of segregation of immobilised heterometallic clusters during the catalytic reaction are known. Thus, \( (\mu-\text{H})_2\text{RhOs}_6(\text{CO})_{10}(\text{acac})\cdot \text{PPh}_3 \) on \( \Phi\text{-PPh}_2 \) fractures during ethylene hydrogenation at 100°C and butene isomerisation, to form a cluster with an osmium-osmium bond (which explains the isomerisation activity) and a mononuclear rhodium complex, which is transformed into rhodium particles of diameter 1 nm, which is active in the hydrogenation (43).

**Conclusions**

The examples listed above testify to the intensive development which is going on for PCNM in catalysis; including effective methods for
im mobilising homo- and heterometallic clusters of the noble metals and identifying their structure. Approaches based on the polymerisation and copolymerisation of cluster-containing monomers are just being developed. However, data on non-carbonyl polymer-immobilised noble metal clusters, such as halides and sulphides are not yet available. This is also true for data on the immobilisation of trimetallic-type clusters and giant clusters.

The quest for effective methods to construct such PCNM is one of the important directions in catalysis. Reviews have recently been published containing data on the immobilisation of noble metal clusters by natural polymers, for example Rh, (44), Os, and Ru, (45) by biopolymers.

In ending it should be noted that the search for methods of improving the properties of polymers may be at the expense of immobilising the metalloclusters. However, increasing the stability of polystyrene, is a possible way to create metallopolymers of uniform structure as new types of construction materials.

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Platinum Assists in Coal Flue Gas Desulphurisation

The flue gas from coal-fired power stations contains particulates, nitrogen oxides and sulphur dioxide. The latter is generally held to be a major contributor to acid rain, a cause of much environmental damage, and thus its elimination from such flue gas is highly desirable. Various methods remove sulphur dioxide by a limestone scrubbing process. Savings are predicted when between 0.5 and 500 \( \text{Nm}^2 \) are applied to the lithium nickel oxide electrodes to achieve a reduction in sulphur dioxide content of 90 per cent is achieved with almost 100 per cent electric current efficiency.

The advantages of this method are that the electrodes remain stable during operation, no reagents are necessary, other than 0.5 to 2 per cent of the electric power output from the plant, the process occurs at flue gas temperatures so that reheating is not required, and the operation is continuous and totally enclosed. In addition there is no emitted waste, no liquids are pumped and oleum is produced.

While commercial and economic evaluations are still required, a full-scale design has been planned using a single set of stacks operating at 500 \( \text{A/m}^2 \) to achieve a 90 per cent reduction in sulphur dioxide. Savings are predicted when compared with conventional limestone scrubbing and using the new electrode material has led to an increase in cell lifetime.

Ruthenium Oxide Anode Coatings

Coatings containing platinum metals oxides have replaced many of the anode materials previously used by the electrochemical industry. The addition of various non-noble metal oxides to ruthenium oxide coatings is known to improve their selectivity and stability, and hence their performance. Now researchers at the Central Electrochemical Research Institute Karaikudi, India, have reported the effects of gradually replacing the titanium oxide in ruthenium-titanium oxide coatings with tin oxide (S. Pushpavanam and K. C. Narasimham, *J. Mater. Sci.*, 1994, 29, (4), 939–942). With constant ruthenium content, the morphology and porosity are determined largely by the ratio of titanium oxide to tin oxide.
Fuel Cell Technology in Action

BRINGING FUEL CELLS DOWN TO EARTH IN CALIFORNIA

Southern California, which has a close association with the space programme and a continuing need to explore new and innovative approaches to improve its air quality, provided a timely venue for a recent conference entitled, "Bringing Fuel Cells Down to Earth". The conference which was organised by the South Coast Air Quality Management District (SCAQMD), and hosted and chaired by H. W. Wedaa, the Chairman of its Governing Board, was held in Long Beach from 23rd to 25th February 1994, and attracted some 200 people, including representatives from Europe and Japan.

California, and notably the Los Angeles basin, was the first area to be recognised as suffering from the deleterious effects resulting from photochemical reactions on a polluted environment and was the first to take positive steps, including legislation forcing the development of technology to overcome the problems. While it is generally recognised that much progress has been made in reducing emissions from motor vehicles, industrial sources and power generation in California, more remains to be achieved.

"The World’s First Fuel Cell Powered ZEV Bus"

People attending the recent "Bringing Fuel Cells Down to Earth" conference had an opportunity to take a tour around Long Beach, California, in a zero emission vehicle powered by twenty-four of Ballard Power System’s proton exchange membrane fuel cell stacks, incorporating platinum metals catalysts. This prototype bus, which is fuelled with compressed hydrogen gas and air, is intended to demonstrate that fuel cell/ electric buses can provide, at least, the same performance as the corresponding diesel equivalent, while satisfying the requirements of the California Air resources Board for zero emission vehicles. Based upon a commercial thirty-two foot long bus chassis, this Phase 1 demonstration vehicle accommodates twenty seated passengers and is fitted with a wheelchair lift. Full load specifications include a range of 100 miles, acceleration from 0 to 30 mph in 20 seconds, and a top speed of 45 mph, while a 20 mph speed can be maintained on an 8 per cent gradient.
For example the vehicle population and the number of miles driven continues to rise, despite restrictions on single person occupancy of motor vehicles and an expansion in public transport networks. SCAQMD estimate that there are now 9 million vehicles which travel one third of a billion miles per day in the Southern California area. It is for these reasons that “Zero Emission” technology is now being sought, not only for motor vehicles, for which legislation starts to take effect from 1998, but also for power plants, factories, offices, homes and all forms of public transport.

It is the view of the SCAQMD that fuel cell technology cannot be developed fast enough, and they therefore hosted this conference to obtain a practical and commercial overview of the subject, to review the role of government and venture capitalists in accelerating its use and to explore opportunities for job creation in a new industry.

Fuel Cells Now Operating

Progress in demonstrating the performance of PC25 units manufactured by International Fuel Cells was presented by W. Lueckel. These commercially available phosphoric acid fuel cell (PAFC) units using platinum metal catalysed anodes and cathodes are installed in a range of on-site locations in North America, Japan and Europe. Performance and durability data from the 40 units in the field is impressive with uninterrupted operation and on-line availability superior to established power generating plant including base load units. PC25 plants which will have reduced weight and volume are being developed, and will lead to a financially attractive, wholly competitive 200 kW unit with combined heat and power capabilities, by 1996.

Progress in the development of platinum metal catalysed proton exchange membrane (PEM) systems is significant, with Ballard making their PEM, hydrogen-fuelled bus shown on the previous page available for conference attendees to take a tour around Long Beach.

The development of compact PEM cells for use in transportable consumer electronic products was described by J. Maceda of H Power, in an enthusiastic presentation. His solution to the fuel challenge is to provide the user with hydrogen storage capsules that are discarded when exhausted and replaced. While this does not directly contribute to the quality of Californian air, the technical challenge presented and the potential market for these products support the overall aims.

Westinghouse, who manufacture 20 kW solid oxide fuel cell (SOFC) units, which now display significant durability, and MC Power who have plans to build two 250 kW molten carbonate fuel cell (MCFC) demonstration units in 1994/95, confirmed that progress is being made with these second generation systems.

The Government Role in Commercialising Fuel Cells

While there is already financial support from government for fuel cell R&D, several new initiatives were announced. L. Edgerton, of the California Air Resources Board, outlined how the Low Emission Vehicle (LEV) programme is expected to operate and lead to significant numbers of fuel cell powered vehicles being used in California by the year 2003. L. Paulitz, and L. Berg, from SCAQMD, described, respectively, plans for having one hundred fuel cell powered buses in operation by 1997 to 1998, and the use of emission credits to encourage the use of fuel cell powered vehicles.

So far only Californian legislation requires Zero Emission Vehicles (ZEV), and therefore, the potential market, though significant, may not be sufficient to warrant investment in manufacture by the major motor producers. However in this context, two notable developments were announced. First, a U.S. Court ruling which will allow New York and the associated twelve eastern states to adopt Californian vehicle legislation; second, SCAQMD and the province of British Columbia announced the setting up of a formal working agreement to co-ordinate their air quality management activities, including the LEV legislation.

Electric vehicles are already being produced on a limited scale by some motor manufacturers, but it is unlikely that this will result in
sufficient numbers to meet even the 1998 requirements of California. With this in mind, therefore, California believes that if the manufacture of electric vehicles is established in their state it will be a way to overcome an obvious shortcoming, and will create jobs for their declining defense industry.

**Technical Advances**

No significant advances in PAFC technology were disclosed at this conference, other than those concerned primarily with the systems engineering. However, significant developments were announced in PEM and direct methanol fuel cell (DMFC) technologies.

Progress in their work on PEM fuel cell materials and stacks was outlined by S. Gottesfeld, from the Los Alamos National Laboratory. A 20 kW stack with a 40 kW peak power capability for use in vehicles has been built and endurance tested for 4000 hours. Possible shortcomings in the application of this system to vehicles, such as freeze/melt cycles, have been evaluated and found not to be deleterious. Improvements to the cell and stack power outputs have been obtained using microporous gas distribution plates in preference to ribbed graphite. A 2 per cent oxygen bleed to the hydrogen fuel stream was found to be beneficial in reducing carbon monoxide poisoning effects at the anode.

Confirmation of an improved proton exchange material, which has been developed and manufactured by DuPont was also discussed. This improved polymer electrolyte, used with existing catalyst and electrode technology, enables significantly higher power densities to be achieved. J. Maceda of H Power reported that they had obtained a 100 mV improvement in cell potential using this new membrane.

If there was further development, the use of direct methanol fuel cells would provide an attractive alternative to hydrogen fuelled alkaline, phosphoric or PEM systems. However, to date power densities required for mobile applications using DMFC have not been achieved, despite extensive work in Europe and America in the last 10 years. Thus, work described by G. Halpert, Jet Propulsion Laboratory, to develop a cell system with power densities compatible with vehicle applications was therefore particularly noteworthy. Unfortunately, no details are yet available of the catalyst and electrode materials or the system that is used.

Fuel cells provide clean technology, and apart from being used in space vehicles and some special niche applications, such as "breathalyser" units, have so far promised a great deal but have not yet achieved acceptable commercial status. This conference, organised by SCAQMD with the determination to utilise innovative approaches to improve air quality, was therefore particularly timely in the ongoing development of fuel cell applications. As it is intended that this conference should become a biannual event, the next conference scheduled for 1996, with the stimulus of demonstrations of further stationary and mobile fuel cell units, will be of considerable interest not only to those who have supported fuel cell development, but more particularly to those who will directly benefit from its application.

G.J.K.A.

**Platinum Metals in Commercial Glassmaking**

**Metals in Glassmaking**, Glass Science and Technology 13


The history of the significant contribution made by the platinum metals to the development of high quality glass is presented later in this issue. Coincidently, an English language edition of a book giving the most relevant information about the many metals used in glassmaking has just been published. One twenty-three page section is concerned with the properties of the platinum metals that establish their suitability for specific applications in the glass industry. This includes a list of guidelines indicating how to ensure the most advantageous use of the platinum metals for this purpose. The literature cited covers the period up to the late 1980s, therefore no mention is made of the benefits that can accrue from the use of innovative A.C.T.™ technology, recently made available by Johnson Matthey, see *Platinum Metals Rev.*, 1993, 37, (1), 62–70.
Platinum for Glass Making at Jena

A REPUTATION FOR EXCELLENCE WAS BUILT UPON EARLY RESEARCH BY DÖBEREINER, SCHOTT AND ABBE

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The use of platinum for the preparation of optical glass can be traced back to Michael Faraday who, in 1824, investigated ways of improving the manufacture of optical glass. During this work he began to use platinum for containment vessels, stirrers and ladles. Prior to this Johann Wolfgang Döbereiner had been appointed Professor of Chemistry at the University of Jena and was later supplied with platinum crucibles by his patrons. Crucibles and stirrers made from platinum were also used when Otto Schott was collaborating with Ernst Abbe on the development of new optical glasses. Their work led to a revolutionary upsurge in the optical industry in Jena and, following the involvement of Carl and Roderich Zeiss, the establishment of a reputation for optical-mechanical excellence which has been maintained ever since.

In the early years of the nineteenth century Joseph von Fraunhofer (1787–1826), and Pierre Louis Guinand (1748–1824) succeeded in producing optical glasses of a higher quality than had been attained previously, by utilising a more effective technique which they had developed for stirring molten glass. This was the principal reason why England lost its leading role in the production of telescopes to Germany and France during the first quarter of the nineteenth century. One result of this was the work undertaken by Michael Faraday (1791–1867), funded by the British government through the Royal Society, to improve the quality of optical glasses, especially of flint glasses.

At that time it was extremely difficult to produce optical glasses that were sufficiently homogeneous, uncoloured, and with only a low concentration of schlieren and bubbles, all of which were necessary for the production of a high yield of material suitable for optical purposes. Faraday must have deduced that the uptake of impurities from the ceramic melting pots by the molten glass could be a reason for defects in the glass produced, and he was the first to employ platinum crucibles and stirrers for the production of optical glass. In the 1829 Bakerian lecture to the Royal Society, Faraday reported that he had succeeded in producing a series of new optical glasses of exceptional purity (1–3).

Shortly after, in 1834, the English pastor and natural philosopher W. V. Harcourt (1789–1871) commenced a systematic investigation aimed at developing improved optical glasses. His work lasted for 35 years during which time he tested a wide variety of chemicals for their glass forming properties, introducing no fewer than 29 new substances into glass making. In order to ensure homogeneous heating during his melting experiments Harcourt used a piece of apparatus which he had made himself. This consisted of a platinum crucible suspended by wires in the flame of an oxygen-hydrogen torch, the crucible being rotated around its axis by a clockwork mechanism (4).

Since homogenisation of the molten glass was still not satisfactorily achieved, the experiments of Faraday and Harcourt did not in fact result...
in a decisive improvement in the production of optical glass. Furthermore the new glasses produced by Harcourt were so unstable in the normal atmosphere that polished lenses made from them could be used for only a short time (5).

**Platinum Crucibles at the Time of Goethe and Döbereiner**

In 1810 Carl August von Sachsen-Weimar, the Grand Duke of Sachsen-Weimar-Eisenach, together with his Minister of State with responsibility for science and the arts – the famous German poet Johann Wolfgang von Goethe – had appointed Johann Wolfgang Döbereiner (1780–1849) as Professor of Chemistry at the University of Jena. His scientific and technological capability combined with the support that he received from both the Grand Duke and the Minister accounted for the rapid surge in chemical research in Jena (6, 7). Indeed, Goethe later achieved world fame not only as a poet but also as a promoter of the arts, science and industry, as a result of his untiring efforts as a government minister and head of “Unmittelbaren Anstalten für Wissenschaft und Kunst”, a department at the Court of the Grand Duchess Sachsen-Weimar responsible in some way for research and development.

Döbereiner was provided with a laboratory at the castle in Jena and an auditorium where he could lecture and carry out experiments, with state assistance. In a report dated 7th November, 1811, Goethe recorded that “The chemical institution developed quite successfully due to the diligence and efforts of Professor Döbereiner.” (8)

With untiring attention to detail Goethe made sure that Döbereiner got the equipment he needed for his laboratory. This included platinum pieces obtained from Paris and a silver evaporating dish. His extremely careful and conscientious handling of the situation is documented in a volume concerned with the procurement of physical and chemical instruments (9) and in his diary.

These records show that several meetings took place to consider the equipment needed for the chemical laboratory. In fact Goethe frequently went to Jena to discuss purchases and to check on the work being carried out. As well as having discussions with Döbereiner, Goethe sought the advice of specialists living in the area. Among these was his friend Thomas Johann Seebeck (1770–1831), noted for his discovery of thermoelectricity, who lived as a private lecturer in Jena between 1802 and 1811. Others involved in these meetings included the Jena Court coppersmith, Christoph Gottlieb Pflug (1747–1825) and two Court mechanics, Alexander Franz Joseph Otteny (?–1820) and Johann Christian Friedrich Körner (1778–1847), the latter also being a teacher of Carl Zeiss – founder of the world famous mechanical-optical factory at Jena.

A list was compiled of all the equipment and its accessories, and what it was used for. Descriptions given in various chemical journals were noted and information about supply houses provided. Where Körner, Otteny and Pflug were able to make the instruments required for the chemical laboratory, they had to supply drawings and give prices. If equipment had to be obtained from outside sources the reasons why had to be given.

Financing the purchase of equipment for Döbereiner's chemical laboratory caused problems for Goethe. Valuable assistance was, however, provided by the Grand Duchess Maria Paulowna (1786–1859) a daughter of Tsar Paul I of Russia, who had in 1804 married Carl Friedrich von Sachsen-Weimar the son of Döbereiner's patron. From her own considerable resources she provided Goethe with 1000 Thaler, for which he ordered a separate account to be opened and from which physical and chemical requirements could be satisfied. Over the years Maria Paulowna provided Goethe with appreciable sums of money “as a contribution to the needs of science and the arts”. These enabled him to satisfy the requirements of the laboratory, which far exceeded the normal budget of his ministry. In 1828 Goethe wrote to Johann Peter Eckermann (1792–1854):

“She has been a good angel for our country, and becomes even more so the longer she is connected with it. She is one of the most imposing ladies of our time and would be so even if she were not a Duchess” (10).

When Goethe travelled to Karlsbad in April 1812, as he did regularly during the latter years
of his life in order to improve his health, he stayed in Jena for several days checking up on things before continuing on to Bohemia. Finally he transferred the responsibility for the Döbereiner laboratory to his son Julius August Walter von Goethe (1789–1830), who had studied law at Heidelberg and Jena, and who became an indispensable assistant to his father. Part of the detailed instructions written to the son on 28th April, 1812, states:

“If the equipment arrives from Paris, the Court commissioner Ulmann has orders to send them to Prof. Döbereiner in Jena and hand the bill for them – which may be near 70 Rthlr [Reichsthaler] – to His Excellency der Geheime Rath von Voigt asking him to be so kind as to authorise it with the addition of the separate account.”

In a report to the main control agency dated November 22nd, Goethe gives a summary of the supplies and purchases for the year 1812. Item six on this list relates to platinum equipment costing a total of 113 Reichsthaler, 2 Groschen and 8 Denar, a Denar being equivalent to a Pfennig.

It is clear from the documents that have been examined by the authors during the preparation of this article that Goethe contributed much more than might have been expected of a poet and state minister. Despite his gigantic efforts on behalf of the arts and science he still found the energy to consider carefully and conscientiously the smallest details of the tasks given to him. In the first decades of the 19th century it was very difficult to obtain good quality glass for use in optical instruments. The Fraunhofer Glass Works in Benediktbeuren, which had been founded in 1804 in Munich by G. v. Reichenbach, J. v. Utzschneider and J. Liebherr, did produce excellent glass at that time but this was supplied almost exclusively to the optical shops of the “Mathematical-Mechanical Institute” which formed part of the Glass Works. As a result Jena had to obtain supplies from France and England. This material was not only expensive but the quality was often poor; quite frequently makers of optical instruments found it to be totally useless (5–7).

These problems caused Körner, the Jena Court mechanic, to realise a long planned idea, which was to build a small glass shop where melts could be tested, and where later optical glass was produced. In this endeavour he was supported by both the Grand Duke Carl August von Sachsen-Weimar and by Goethe. The Grand Duke, as Head of State, was personally interested in the development of the glass melting experiment. For example, he sought the opinion of Fraunhofer on the glass samples made by Körner, as is shown by his letter to Goethe dated July 24th, 1825. The work was also of great interest to the latter who mentioned it frequently in his diary as well as in correspondence with Carl August. The export of top quality optical glass and optical precision instruments would have been of utmost economic importance to the German “Mini-State”, especially since Körner used only indigenous raw materials.

Although Körner first tried to prepare flint glass, he began to melt crown glass in 1828. When sending a sample to Goethe he wrote:

“Continuing in the spirit and sense of our most saintly master we began to melt crown glass and, in order to be capable to present most humbly your Most Honourable Excellency with a sample – before taking out the big glass pot – I scooped out with a platinum crucible a piece and let it solidify immediately....”

In all probability the beginning of Döbereiner’s participation in Körner’s glass melting experiments would have been initiated by Goethe. While Körner tried to improve the procedures used for the production of optical glass, Döbereiner tended to put the experiments on a sound scientific basis. He changed the mixing ratios of the raw materials keeping stoichiometric considerations in mind, introduced new components into the melts and studied their influence on the properties of the glasses. Further clues to the use of platinum in the glass chemical laboratories of both Döbereiner and Körner are not known. Otherwise platinum crucibles were mostly used for the decomposition of substances for analytical purposes.

The experiments of Döbereiner and Körner failed, at least in part, because of technical difficulties and incomplete physical evaluation of their results. On several occasions Goethe suggested that systematic measurements should be made

Platinum Metals Rev., 1994, 38, (2)
Otto Schott  
1851–1935

Shown here in his study at the age of 70, Schott pioneered important developments in optical and technical glasses which had properties superior to those previously attainable. The quality of these glasses was largely responsible for the “Jenaer Glaswerk Schott & Gen.” becoming a world renowned industrial corporation. In addition, the new Schott glasses contributed significantly to the world reputation of Jena as the home of precision optical instrument production. Schott presided over the Company as chief manager until after his 75th birthday.

Photograph by A. Bischoff of Jena

Pioneering Work by Otto Schott and Ernst Abbe

Otto Schott was born in Witten, Ruhr, on 17th December, 1851, the son of an owner of a plate glass factory. From childhood onward, therefore, he had an opportunity to obtain a detailed practical knowledge of glass making and the problems associated with it. After finishing his studies at Aachen, Würzburg and Leipzig he obtained his doctorate in 1875 at Jena for a thesis on a “Contribution to the Theory and Practice of Glassmaking”. After working in various factories, in 1878 he began to carry out glass melting experiments in his parents' house, while at the same time looking for a permanent position.

In this way he obtained skills and knowledge of refractive indices and the optical dispersion of the glasses. In most cases the small size of the test melts resulted in schlieren-containing glasses, so that optical values could not be determined. Apparently Döbereiner and Körner did not pursue this task far enough, although they did get close to their aim of producing optical glass of a high quality. But glass research can be proud of the fact that such a genius as Goethe took an interest in it.

which far exceeded those necessary for the routine running of a glass melting factory. His aim was to establish the “chemistry of the fiery fluxes” (5, 12, 13). It was only later that he became interested in the optical properties of glasses and their application. Even before this Schott had introduced compounds of new chemical elements into glass, the effects of which on glass making had not been investigated previously. Apparently his investigations were carried out to satisfy his scientific curiosity and determine if glasses with useful properties could be produced by new chemical compositions.

After Schott succeeded in melting a lithium glass, which he expected to have improved optical properties, he wrote to Ernst Abbe (1840–1905), who was Professor of Physics and Director of the observatory at the University of Jena, asking him to study the properties of this glass (5, 12, 14). The first letter sent from Witten on 27th May, 1871, begins:

“A short time ago I produced a glass which contained an appreciable amount of lithium. It had a fairly low specific gravity. I guess that this glass shows excellent optical properties in one or other direction and in this letter I dare to ask you if it would be possible for you to test these or ask one of your associates to test it for refractive or diffractionary in so far as it may confirm or contradict my earlier surmise.” (12)

This was the start of a very fruitful collaboration. Fortunately Schott was not discouraged by early failures. The problem of excessively high schlieren concentrations in the new glass, the
difficulty that defeated Harcourt after over 30 years’ work, was finally solved by Schott who stirred the melt intensively until it became homogeneous.

In a letter dated 3rd August, 1879, Ernst Abbe wrote to Schott:

“I consider it a tremendous success that you succeeded in making test melts in small crucibles in such quality that a complete optical investigation of the product becomes possible. . . . For the progress in the production of optical glass it looks to me however as if the most essential presupposition to have a possibility to generate useful (optically measurable) test glass melts, since this is the only way in which methodical testing can be carried out.” (14)

Schott did not give up when his new lithium-containing glass did not prove to be as successful for optical purposes as he had hoped. At that time the flourishing German optical industry depended upon glass imported from a few factories in France and England, and there was an obvious desire to change this situation. In addition, Ernst Abbe had already observed that the construction of top quality optical instruments was dependent upon the development of glasses having improved optical properties. It was perceived to be especially important to develop optical glasses which were superior to the existing crown and flint glasses, by having a rather low refractive index at a high dispersion, or vice versa, or glasses which when used in combination would compensate for the individual defects that were then unavoidable, such as chromatic and spherical aberration, and astigmatism (15).

In response to this situation, Otto Schott in 1881, first working at home in Witten, began a series of careful and systematic melting experiments set up jointly with Ernst Abbe. Schott’s aim was to investigate the dependence of the optical properties of a glass on its chemical composition. In the course of his work he intended to select from all the compounds available to him — and which dissolved in glass — those which might improve optical glasses. He saw this as the way to produce deliberately, on a sound scientific basis, top quality glasses with the required optical properties. For the very first experiments Abbe provided Schott with platinum crucibles, at his own cost, and he immediately began optical measurements on Schott’s test melts. At first both scientists worked to establish the formulations of the glasses to be prepared so that the attack on the crucible walls by the glass melt was minimised, and contamination by the crucible material avoided (15). In general, dissolution of the ceramic refractories worsened the optical properties of the glass. For example, discolouration reduced transmission and schlieren formation resulted from local differences in the composition of the melt. Abbe and Schott tried to avoid such defects by using platinum as the crucible material. In this connection, Abbe wrote to Schott on 3rd October 1881:

“Concerning the prisms presently under investigation, I may preliminary remark that No.XC1 (cryolite) does not permit a determination of the dispersion, since the piece consists totally of schlieren. In view of the greatest interest in this sample . . . you should prepare a new melt in platinum crucibles. First do a melt in your small crucible; today I ordered in Frankfurt a larger sized crucible — 50-60 ccm volume, with lid and a piece of thick wire for stirring . . . .” (14).

Another letter from Abbe to Schott states:

“A platinum crucible of about 60 ccm volume, with lid and a thick platinum rod for stirring — the whole for about 100 Mark — I do hope to receive in the next few days — possibly this crucible may provide you some help in your next melts.” (14).

A letter of reply sent at about this time gives the important results of the first 100 test melts:

“We succeeded in preparing from boric acid and strontium oxide, as well as from boric acid and thallium oxide, glasses which can be used practically to obtain complete achromaticeity in field glass objectives, which means that the up to now unavoidable colour diffraction can be avoided and images result which do not contain any coloured edges.”

This success encouraged both scientists to continue their investigations. Schott later summarises his feelings:

“One year after the start of our work we obtained enough material to predict with certainty that a purposeful continuation of our researches in our field of interest must lead to a widening of our knowledge and research in practical optics.” (15)

Schott and Abbe went on to establish their own private laboratory in Jena, where they formulated the technical basis for a continuation.
of their experiments on a wide basis. In addition to furnaces this involved a steam engine and bellows in order to obtain high melting temperatures. In January 1882 Schott moved his residence from Witten to Jena. As well as the help provided by Abbe, during the build-up and operation of his laboratory Schott received support from Carl Zeiss and his son Roderich, the owners of the Jena optical works who urgently needed indigenous sources of glasses with improved properties for the development of new top quality optical instruments.

During extensive melting tests Schott investigated a total of 28 chemical elements in addition to seven glass forming oxides. By his extraordinary experimental skill he succeeded in producing on a small laboratory-scale glass samples having excellent homogeneity, thus enabling their optical values to be determined completely. In this way Schott raised glass chemical work from a trial-and-error basis to the level of scientific experimentation. The results convinced him that the refractive index and dispersion of glasses could be varied significantly by changing their chemical composition.

In order to avoid contamination of the melt by dissolution of the crucible walls, Schott often used crucibles and stirrers made from platinum and in this way he obtained glass of a higher quality. In his laboratory notebooks and his correspondence we find extensive reference to this. For example, Schott's

These excerpts from Schott's laboratory notebooks are a limited selection of the instances where he recorded his use of platinum: (top) By the use of a platinum crucible he tried to avoid bubble formation in melt No.478 as it was cooled; (middle) A barytes-zinc-borate glass which had been melted in a platinum crucible was found to have a refractive index of 1.65 to 1.66, and an Abbe number of 50 to 52. Schott also records that a platinum crucible was ordered from Heraeus in Hanau; (bottom) A particular large platinum crucible contained 4 litres if filled to overflowing, but generally it was used for only 3.25 litres, 9 kilogrammes, of flint glass or 3 litres, 6 kilogrammes, of glass composition 645
notebook No. II contains an entry indicating the need to determine if bubble formation during cooling could be avoided by melting a glass sample in a platinum crucible. In another place we find "ordering a platinum crucible with Heraeus in Hanau". Heraeus was, of course, Wilhelm-Carl Heraeus (1827-1904), founder of the leading special metals firm. Here, and in other places, optical data of glass melted in platinum were listed ("barytes-zinc-borate in platinum crucibles"). In his laboratory diary, Schott gives the wall thickness of a crucible as 3/4 to 1 mm. From his notes we can deduce that he used platinum containers inside graphite heaters (16).

Concerning the supply of platinum equipment, on 28th October 1883, Abbe wrote to Schott who was in Witten for his mother's birthday:

"found here on my desk a platinum crucible from Heraeus (326 gr. billed at 345 Mark). Apparently quite close to the specification, only it looks thicker (scrap platinum at 800 Mark per kilo taken back). Was told from London by 26th (as mailed): crucible 716 gr. stirrer 1098 gr. 1814 gr. to 2267.5 frs..." (16).

Again on Schott's notebook No.II we find among other entries from the same time: "volume of a small platinum crucible (filled) – 720 ccm, usable filled 600 ccm" and "volume of the large platinum crucible: 1) before flowing over 4 litres, 2) usable filled 3.25 litres 9 kg flint"; see also (16) page 358.

The comments on the large platinum crucible are contained in the above illustration. From a note in a letter by Abbe to Schott dated 29th October 1883, the dimensions of this crucible can be estimated to be 15 cm diameter at the bottom, 16 cm diameter at the upper rim and with a height of 22 cm (16).

It is not the purpose of this paper to examine in detail the continuation of the work by Schott with glass melts of varying compositions and the influence of individual constituents on the optical properties of the glass, nor to give a full report of his life and works. From his many investigations we will consider only those which involved the use of platinum.

Schott observed that the introduction of fluorine into glass would be very important for optical use since for crown glasses it made possible an advantageous reduction in optical dispersion. In many tests he succeeded in forming colourless glasses with high fluorine content, bound to lithium, barium, cadmium and aluminium with phosphoric acid. Due to the strong chemical attack by the fluorine compounds on silicate-containing crucible materials, and the decomposition of the fluorides as gaseous compounds developed, Schott processed such materials using crucibles and stirrers made from platinum. Even in platinum equipment, however, reactions with oxygen and moisture in the air as the glass melts were being stirred resulted in the formation of gaseous fluorine compounds. As the volatile constituents of the glass evaporated inhomogeneities (schlieren) were generated in the glass, ruining it. Schott therefore considered it necessary to experiment further on a larger scale, although this would be very expensive because of the need for even larger platinum crucibles (15).

Despite the attention given to the stirring of the melts, at first Schott did not succeed in producing homogeneous pieces of glass sufficiently large to be used for telescope objective lenses from the borate, borosilicate and phosphate glasses he had developed. As he remarked in a lecture entitled "on melting glass for optical and other scientific purposes", the dissolution of the porcelain crucible material was the reason why small agglomerates of schlieren occurred in the whole melt, dispersing when the molten glass was poured. Therefore only small pieces of homogeneous glass could be obtained. Schott hoped to solve this problem by the use of platinum apparatus. In his lecture he talked of:

"expecting to produce something perfect in spite of this problem we decided to replace the soluble porcelain wall and the porcelain stirrer, regardless of the cost, by a platinum crucible of 3 litre volume and a platinum stirrer weighing 1.5 kg" (15).

Initially, the use of a platinum crucible proved to be unsuccessful. Where the molten glass was in contact with the platinum excessive bubble formation was observed, the glass became useless and the platinum brittle, with the crucible
cracking after three or four melts. Schott reported in his lecture that further experiments using a smaller, thicker-walled crucible avoided bubble and crack formation, so demonstrating that platinum could be used for the production of optical glasses, the constituents of which when molten strongly attacked ceramic refractories. He subsequently restricted the use of platinum to the melting of borate glasses. With phosphate glasses, however, the dissolution of metallic platinum, and its subsequent precipitation as a greyish substance on cooling, was observed (15).

We now know more accurately why Schott had problems with the use of platinum apparatus. At that time the furnaces used for heating the containment vessels were fuelled by coal gas, and this caused some reduction of the constituents of the glass, which was one of the reasons for the damage that then occurred to platinum containers. It was only in the second half of this century when glass melting units heated by electricity became available that platinum crucibles and stirrers were applied on a large scale in the glass industry. Now nearly all top quality optical glass is melted in platinum crucibles.

The use of gas for heating Schott’s furnaces explains not only the formation of gas bubbles but also the embrittlement and cracking of the platinum. Many of the chemicals present in glass compositions are harmless to platinum as long as they remain in the melt in the form of compounds, generally as oxides. If, however, they are reduced to their elementary form by the action of agents from outside the melt, then these elements may react and diffuse into the platinum along grain boundaries. Furthermore, platinum may catalyse reactions in the melt. In addition such “foreign” elements can form low melting compounds and eutectics of platinum alloys and these reactions are the cause of the embrittlement of platinum by intercrystalline cracking and corrosion. Elements detrimental to platinum in this way include phosphorus, lead, arsenic, antimony, boron, bismuth and even silicon.

Schott later summarised the wide ranging experiments he had carried out in the glass technical laboratory, claiming that after two-and-a-half years’ work the main scientific foundations of optical glass technology had been established (15). The expenses for platinum equipment for melting experiments carried out between the Spring of 1881 and the end of 1883 amounted to 4000 Mark (16).

The next problem was to transfer the results obtained into usable products for practical optics. This required the establishment of a facility which could produce on an industrial scale, and with the same high quality properties, the glasses developed in the laboratory. It was anticipated that an expensive and time consuming experimental development programme would be required to scale-up production from a laboratory-to-a-factory-process. To achieve this Otto Schott, Ernst Abbe, Carl Zeiss and Roderich
July
Zeiss decided to establish a factory in Jena at their own expense. The fire in the first furnace was lit on September 1884 and this can be regarded as the birth of the Jenaer Glaswerk. The company first appeared in the Trade Register at the official Court of Jena on 22nd July 1884 as “Glastechnisches Laboratorium Schott & Gen. in Jena” and due to the great importance of this project to the optical industry in Germany, the four partners succeeded in obtaining a large subsidy of 60,000 Mark from the State of Prussia. This enabled them to fund a large part of the running costs of the factory during the first two years.

Within four years they had successfully developed their production processes and the company was able to supply the total German demand for optical glass. In addition strong interest was shown by the optical industries in other countries. In these early years, the company consisted of fourteen workers, one chemical assistant and two clerks. So began the organisation that has grown to become the world famous company “Jenaer Glaswerk Schott & Gen.”, which was registered on 11th October, 1920, in the Trade Register of the Court in Jena.

Thus it can be claimed that Carl Zeiss, Ernst Abbe and Otto Schott together established the worldwide reputation of the German mechanical-optical industry for precision and excellence. To maintain this position, continuing research and development is required. Indeed recurring problems of corrosion and the relatively limited life of platinum crucibles used in the Jena Glassworks were among reasons for the founding of the technology section of the Friedrich-Schiller-University in Jena, in 1973. Since that time systematic investigations have been carried out on the use of platinum in the glass industry.

From 1992 collaborative work has been undertaken with the newly founded Jena Polytechnic Institution, and with W. C. Heraeus G.m.b.H. in Hanau, on stress rupture versus time data for both platinum and iridium at extremely high temperatures.

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ABSTRACTS

of current literature on the platinum metals and their alloys

PROPERTIES

Platinum Etching and Plasma Characteristics in RF Magnetron and Electron Cyclotron Resonance Plasmas


Pt etching was examined using r.f. magnetron plasma (1) and electron cyclotron resonance (ECR) plasma at 0.4–50 Torr in Cl₂ plasmas. For (1) the etch rate of Pt was constant at substrate temperature 20–160°C. The etch rate and plasma electron density increased with decreasing gas pressure from 50 to 5 mTorr. In ECR plasma for r.f. power of 300 W, the etch rate of Pt was almost constant at ~100 nm/min at gas pressure of 5–0.4 Torr, while the plasma electron density was gradually increased with decreasing gas pressure. Highly accurate sub-micron patterning of 0.5 μm lines and spaces of Pt masked with photoresist was achieved using Cl₂ plasmas in ECR discharges.

Effect of Diamond Facet on the Electrical Properties of Pt/BF₄⁻ Ion Implanted Polycrystalline Diamond Contacts


The effect of the diamond facet on the electrical properties of Pt/poly crystalline diamond contacts grown on Si(100) substrates at different positions of the plasma ball in a microwave plasma enhanced CVD chamber was examined. The Pt/BF₄⁻ ion implanted polycrystalline diamond contacts showed Schottky behaviour for diamond film with major facet (100) whereas Pt/BF₄⁻ ion implanted polycrystalline diamond contacts exhibited ohmic behaviour for the diamond film with major facet (111).

Electrocristallization of Cobalt/Platinum Multilayers

Y. JYOKO, S. KASHIWABARA and Y. HAYASHI, Mater. Trans. JIM, 1993, 34, (10), 946–951

Co electrocrystallisation on Pt(111) surfaces was examined in order to produce Co/Pt superlattices of comparable structure and magnetic properties to those prepared by vapour phase deposition. REM-RHEED studies carried out under potential control showed that simultaneous multinuclear multilayer growth up to 10 monolayer coverage could be obtained. Room temperature magnetic measurements were made on the electrodeposited [Co(2 nm)/Pt(4 nm)]ₘ multilayers. Their magnetic properties tend to exhibit in-plane anisotropy, but remnant perpendicular magnetisation for the multilayer with a rougher interface electrodeposited under a higher overpotential.

Catalytic Role of Nickel, Palladium, and Platinum in the Formation of Carbon Nanoclusters


Carbon clusters were prepared by arc discharge from graphite anodes containing Pt, Pd or Ni under nanotube production conditions. No nanotubes and very few nanoparticles were found to be encapsulated. With Pt in the anode the highest density of nanotubes was formed in the cathode deposit, while Pd-filled anodes produced the lowest density of nanotubes. The Pt-produced cathode deposit has columnar structure, while the Pd-produced cathode deposit is like molten clay, of laminar structure, having lower nanotube density.

TEM and AES Characterization of Thin Films of Au, Pt and Pd Deposited on Mica


Highly pure Pt, Pd and Au were thermally evaporated as ~ 200 nm films of f.c.c. structure on mica under high vacuum conditions. Layer by layer AES showed contamination of the film surfaces with S and preferentially with C decreasing inside the film with distance from the surface. Oxygen in the film tends to diffuse into the Pd especially at the metal/mica region. At the Pt/mica and Au/mica interfaces are K and traces of Si, respectively. The films are polycrystalline with preferential <111> orientation.

Magnetic Properties of ErPt₃Si₂


Susceptibility measurements and magnetisation measurements were carried out on ErPt₃Si₂ at 1.5–300 K using a SHE-SQUID magnetometer or an Oxford Faraday balance, giving magnetic fields up to 50 kOe. The compound crystallises with the CaBe₂Ge₂ type structure, and remains paramagnetic down to 1.5 K. It is concluded that the Er moment associated with the ground state amounts to 8.25(20)μ₅ for Er³⁺ ions.

Carbon Monoxide Adsorption on a Pt₃Fe₃(111) Single-Crystal Alloy


HREELS measurements of CO adsorption on the Pt₃Fe₃(111) single crystal alloy at 120 K showed that CO was adsorbed mainly on the top layer although bridge-bonded CO also occurred near saturation. CO adsorption on Pt-rich surface of Pt₃Fe₃(111) exhibits significant differences compared to CO on Pt(111). The presence of Fe atoms in the sub-surface induces the observed decrease in the CO binding energy.
Solid State Reactions between Pd and Si and Recovery Induced by High Energy Ball Milling

The phases resulting from diffusion during high energy ball milling between Pd and Si depend on the amount of Si present. At 19 % Si, an amorphous phase forms and becomes Pd₅Si₂ and Pd₃Si on continued milling. At Si contents ≥ 33 at.%, Pd₅Si phase was produced but no amorphous phases. For powder compositions corresponding to the stoichiometric compound Pd₅Si at 33 at.% Si, Pd₃Si forms and remains stable during further milling. At Si contents of ≥ 50 at.% the Pd₅Si is destabilised by a reaction with Si to form Pd₃Si, which is metastable at the temperature of ball milling.

Reliability and Microstructure of Al-Si-V-Pd Alloy Films for Use in Ultralarge Scale Integration

Highly reliable Al-based quaternary Al-Si-V-Pd films were studied and compared to conventional ternary Al-Si-Cu alloy films. The Al-Si-V-Pd films containing 0.1 at.% V and 0.1 at.% Pd displayed excellent plasma etchability together with good corrosion resistance. Electromigration tests of Al-Si-V-Pd films showed a high stability at 180°C. Highly stable microstructure is due to the presence of finely dispersed, small precipitates of both (Al,V) and (Al,Pd) phases.

Plastic Deformation in Icosahedral Al-Pd-Mn Alloys

Deformation in the face-centred icosahedral phase in Al-Pd-Mn alloys at high temperatures and 23.6–47.3 MPa was investigated by TEM after preparation from the high purity metals of nominal composition Al₇Pd₃Mn₄. At 730–780°C, deformation was controlled by dislocation glide with activation energy of 210 ± 30 kJ/mole and stress exponent of 1.2 ± 0.2. At 780–810°C, microstructures were characteristic of deformation controlled by dislocation glide and climb, with activation energy of 1700 ± 80 kJ/mole and stress exponent 2.9 ± 0.3. Deformed samples were ~ 10 % harder than as-cast samples.

Dislocation-Enhanced Hydrogen Solubilities in Pd-Ni, Pd-Ag and Pd-Ni-Ag Alloys

The solubility enhancements for cold-worked Pd-Ni alloys were determined for a series of homogeneous ternary PdₓNi₃₋ₓAgₓ alloys with x = 0–0.2 at 273–348 K. Substitutional Ag in Pd increases the lattice size, but substitutional Ni decreases the Pd lattice. Pd-Ni forms a series of f.c.c. solid solution alloys over the entire composition range. A mechanism is suggested where the larger Ag and the smaller Ni substitutional solute atoms segregate to or leave the tensile stress fields, respectively, during cold working of the binary alloys.

Structural Phase Transformation and Shape Memory Effect in ZrRh and ZrIr

Crystal structure investigations of ZrRh and ZrIr compounds have shown a B19′-type phase at room temperatures, a B2-type phase at 670 and 1050°C, respectively and a b.c.c. phase for ZrRh in the temperature range 1455°C to melting point. For a ZrRh specimen of 0.8 × 2 × 20 mm³ in size at a load of 400 gf, a shape memory effect caused by the structural transformation on cooling of B2 ↔ B19′ with a transformation hysteresis width of ~ 200°C was found. Full shape restoration took place after ≥ 20 heating/cooling cycles. A similar shape memory effect is expected for ZrIr.

Fracture Behaviour of Polycrystalline Iridium under Tension in the Temperature Range 20–1500°C

The fracture behaviour under tension of dangerous-impurity-free polycrystalline Ir and alloy Ir-0.3 wt.% Re-2 wt.% Ru was studied at 20–1500°C. The wire specimens were made from a single crystal rod without any annealing and stretched at 1 mm/min for 15 min. The fracture mode of the single crystals and polycrystalline Ir, both C-free, was brittle transgranular (BTF), in the latter BTF was seen in the neck region after plastic deformation. Transition from BTF to brittle intercrystalline fracture (BIF) in the alloy at temperatures > 1250°C may be connected to C and other contaminants. BIF is environmentally induced fracture without prior specimen deformation.

High-Temperature Stability of Heteroepitaxial Ir-Silicide/SiGe Layers Co-deposited on Si(100) under Ultra-High Vacuum

Heteroepitaxial Ir-silicide/SiGe layers were grown on top of p-Si(100) at a substrate temperature of 450°C under UHV. A critical transition temperature existed at 550–750°C; epitaxial IrₓSiᵧ/SiGe layers were stable when annealed at 550°C, but unstable during rapid thermal annealing at ≥ 750°C for 20 s. The IrₓSiᵧ layer became a mixture of dual Ir-silicide phases containing Ge atoms as the instability occurred.

Grain Boundary Scattering in Ruthenium Dioxide Thin Films

Studies of RuO₂ thin films with an average grain size of 12–50 nm deposited by reactive sputtering showed that the factors correlated to the resistivity of the films also govern the average grain size of the films. The grain boundary reflection coefficient for electrons in RuO₂ was 0.785. The total resistivity of RuO₂ polycrystalline films was affected by electron scattering due to the grain boundary. The resistivity of RuO₂ thin films could be 10 times higher than that of the bulk material and still have metallic behaviour.
Surface Structure of Semiconducting Ruthenium Pyrite (RuS₂) Investigated by LEED and STM


Atomic resolution scanning tunnelling microscopy images of (100) cleavage planes of semiconducting RuS₂ are presented. RuS₂ has a remarkable stability against reactions under ambient conditions and its surface appears to be essentially unreconstructed. This may be due to the pronounced low energy of electronic surface states of pyrite-type compounds which is known for FeS₂.

CHEMICAL COMPOUNDS

Giant Pd Clusters Observed by High Resolution Electron Microscopy


Giant cationic Pd clusters of approximate formula Pd₆₋₉L₃(OAc)₉, where L is Diph or Phen, obtained by reduction from Pd(OAc)₉ with Hz in acetic acid solution at 30°C. At low overpotentials Tafel slopes of -0.060 V/decade were observed. At high overpotentials in 1.0 M H₂SO₄ acid + K₂SO₄ solution at 30°C. At low overpotentials Tafel slopes of -0.060 V/decade were obtained for all three electrodes; at high overpotentials in 1.0 M H₂SO₄ the usual Tafel slope of -0.12 V/decade was observed for (1) and (PC), but -0.165 V/decade on (2). The behaviour of surface properties of RuₓPtₓ, RuₓPtₓOₓ, RuₓTiₓOₓ, RuₓTiₓOₓ(DSA) and PtₓTeₓOₓ electrodes has been compared electrochemically and by UHV (oxides containing Pt have variable stoichiometry). Adding Pt to RuO₂ + TiO₂ electrodes changes their morphology with an increase in charge. Ru and Ti are in the +4 oxidation state, and Pt is in the +2 oxidation state. The high oxidation state of Pt may be linked to decomposition occurring in aqueous solution, and tends to decrease with potential cycling. The surface concentration of Pt in freshly prepared mixed oxides is higher than the nominal one.

Comparison of Lead Zirconate Titanate Thin Films on Ruthenium Oxide and Platinum Electrodes


The interfaces and microstructures in two PZT/RuO₂/SiO₂/Si and PZT/Pt/Ti/SiO₂/Si (1) ferroelectric thin films were examined by HRTEM to compare the improved fatigue characteristics of PZT thin films with RuO₂ electrodes. A nanocrystalline pyro-chlore phase Pb₂ZrTiO₇, where x = 1 was found on the top surface of the PZT layer. Thin film (1) was well crystallised with sharp interfaces throughout.

CO Electrooxidation on Well-Characterised Pt-Ru Alloys


The electrocatalytic activity of Pt-Ru alloy electrodes for CO electrooxidation in acidic electrolyte at room temperature was measured on UHV-prepared alloy surfaces. CO stripping voltammetry and the potentiostatic oxidation of adsorbed CO showed maximum activity in alloys of surface composition ~50 at.% Ru, which corresponds to a surface with a maximum number of Pt-Ru pairs. Sputter-cleaned Pt-Ru alloy electrodes showed synergistic properties not observed in annealed Pt-Ru electrodes. This is attributed to a uniquely active state of OH⁺ on Pt-Ru pair sites. The different electrode electrocatalytic activities are explained by Ru clustering during annealing, creating Ru nano-electrodes embedded in a Pt electrode.

UHV and Electrochemical Studies of the Surface Properties of Ru + Pt + Ti Mixed Oxide Electrodes


The behaviour of surface properties of RuₓPtₓ, RuₓTiₓOₓ, RuₓTiₓOₓ(DSA) and PtₓTeₓOₓ electrodes has been compared electrochemically and by UHV (oxides containing Pt have variable stoichiometry). Adding Pt to RuO₂ + TiO₂ electrodes changes their morphology with an increase in charge. Ru and Ti are in the +4 oxidation state, and Pt is in the +2 oxidation state. The high oxidation state of Pt may be linked to decomposition occurring in aqueous solution, and tends to decrease with potential cycling. The surface concentration of Pt in freshly prepared mixed oxides is higher than the nominal one.

Lignin Augmented Hydrogen Absorption by Palladium Cathode


Cyclic voltammetry and H permeation studies carried out at the Pd/0.1 M NaOH interface showed that lignin enhances H adsorption on Pd during the cathodic polarisation. The kinetics of the cathodic reaction is controlled by H adsorption on the electrode surface for the Pd/NaOH interface but by mass transfer control for the Pt/NaOH interface.
Reproducible Tritium Generation in Electrochemical Cells Employing Palladium Cathodes with High Deuterium Loading
Reproducible T generation has been observed in tightly closed D₂SO₄ containing cells in four Pd wire cathodes. No T generation was observed in four identical Pd cathodes in H₂SO₄ cells under the same conditions. A cyclic loading/unloading regime used with low current density showed that D/Pd loadings of > 0.8±0.05 are needed to generate T. The most T generated in 7 days of continuous electrolysis was 2.1×10¹¹ T atoms, compared with a background of 4×10⁸ T atoms.

Electrochemical Hydrogen Discharge Characteristics of Pd and Pd-Ni-Rh Alloy Hydride Electrodes Catalysed by Pd/Pt-Black Coatings
The electrochemical H discharge characteristics of pure Pd and Pd-Ni-Rh alloy hydride electrode, activated by a superimposed electrodeposited film of Pd/Pt-black, were studied as the negative electrode for Ni oxide-metal hydride battery. The best discharge characteristics were obtained for Pd-7.5 at.% Rh and/or Pd-2.5 at.% Ni-7.5 at.% Rh alloy hydride. The electrode surfaces were first activated with ~1-2 mg/cm² of Pd black and then with Pt black.

Electrochemical Copolymerization of Aniline and para-Phenylenediamine on IrO₂-Coated Titanium Electrode
Cyclic voltammetry studies of the copolymerisation of aniline and p-phenylenediamine (1) on IrO₂-coated Ti electrodes in 0.5M H₂SO₄ showed a peak at about 580 mV corresponding to the p-aminophenol/benzoquinoneimine redox couple and cross-linking sites. The mass of polymer deposited on the IrO₂-coated Ti electrode is correlated with the polymer anodic peak current at various concentrations of (1). The morphology of the polymer film depends greatly on concentration of (1).

In-situ Twin-Electrode Spectroelectrochemical Voltammetry with a Cell Composed of a Pair of Naftion-Coated Indium Tin Oxide Electrodes Each Incorporating Ru(bpy)₃²⁺ and Methylviologen
Electrochemical redox reactions in a cell composed of two Naftion-coated indium tin oxide electrode (ITO) electrodes were analysed. The cell system ITO/Nafion[Ru(bpy)₃²⁺]/aqueous electrolyte/Nafion [MV⁺]ITO showed changes in the visible absorption spectra induced by cyclic scanning of the potential difference between the two ITO electrodes. The spectral changes were attributed to the redox reaction of the Ru and MV, showing multicolour electrochromism.

Thermoanalytical Investigation of the Formation of RuO₂-Based Mixed-Oxide Electrodes
Formation of RuO₂/TiO₂ film coatings from precursor salts dissolved in isopropanol was studied. For pyrolysis of Ru and Ti salt mixtures, the final decomposition temperature was reduced by > 10⁰°C due to the catalytic effect of the Ru addition. The highest rate of decomposition and heat release, and the maximum charge-storage capacity were observed for a coating composition of 10-30 mol% of Ru.

PHOTOCONVERSION
XPS-Characterization of Hydrogen-Evolving Platinum-Coated p-Silicon Photocathodes
The photoelectrochemical behaviour of homogeneous Pt films and microscopic Pt islands on top of doped Si were studied on Pt samples deposited on monocrystalline Si by physical vapour deposition and a photoassisted electrochemical technique. Crystalline p-Si covered with Pt layers on the atomic scale operate as stable H-evolving photocathode. Only ultra-thin Pt submonolayers or microscopic islands can affect the H evolution at the photocathodes during long-term operation in various electrolytes.

Laser Flash Photolysis and Pulse Radiolysis Studies of Ruthenium Complexes
Laser flash photolysis and pulse radiolysis techniques were used to obtain the absorption spectra of charge-transfer excited states and one-electron-reduced states of a number of mono- and binuclear Ru complexes in H₂O. Bimolecular rate constants for the reaction of e⁻ with the above complexes and with the mixed-ligand complexes Ru(bpy)₃dpp²⁺ and Ru(bpy)₃dhp²⁻ were also determined.

ELECTODEPOSITION AND SURFACE COATINGS
Covalent Binding of Pd Catalysts to Ligating Self-Assembled Monolayer Films for Selective Electroless Metal Deposition
Selective electroless (EL) metallisation of surfaces is described; surfaces are modified with a ligand-bearing organosilane film then catalysed with chloride-containing Pd(II) solutions buffered at pH 5.0-6.4. Oligomeric chloro and/or hydroxo-bridged Pd(II) complexes act as the catalytic species at the surface. A minimum surface concentration of ~10¹⁰ Pd atom/cm² is needed to start EL metallisation of a substrate.
Reductive Deposition of Pd on Porous Silicon from Aqueous Solutions of PdCl₂: An X-ray Absorption Fine Structure Study


Pd was successfully deposited on the large surface of porous Si from aqueous solutions of PdCl₂. The reductive deposition of Pd metal from PdCl₂(aq) occurred at specific surface sites by an oxidation-reduction reaction. Thus porous Si deposits Pd reducibly on its surface from Pd(II) ions and so could be a suitable substrate for the deposition of noble metal and bimetallic catalysts.

Chemical Vapor Deposition of Ruthenium and Osmium Thin Films Using (Hexafluoro-2-butyne)tetrafluororuthenium and -Osmium


Reflective pure polycrystalline Ru thin films can be produced by CVD from Ru(hfb)(CO)₉, where hfb is hexafluoro-2-butyne, by H₂ carrier gas, with a growth rate of 21 nm/min at 500°C. The resistivity of the film is 22 μΩ cm for a grain size of 60 nm. Polycrystalline thin Os films can be produced from Os(hfb)(CO)₉, using H₂ carrier gas, at a growth rate of 14 nm/min, resistivity of 81 μΩ cm, and grain size of 20 nm. The film consists of 84 % Os, 7 % O and 9 % C.

APPARATUS AND TECHNIQUE

Iridium-Based Ultramicroelectrode Array Fabricated by Microlithography


The microlithographic fabrication of an Ir-based Hg ultramicroelectrode (UME) is described. The Hg was stable on the Ir without degradation or dissolution of the Ir pads after several days of use. The array has 19 interconnected 10 μm diameter UMEs and multiplies the signal current in proportion to the number of UMEs in the array, without overlap of the diffusion fields. The Hg UME can analyse Cd(II), Pb(II) and Cu(II) in spring water.


A luminescent pH sensor based on p-t-butylcalix[4]arene-linked trisbipyridyl Ru(II) complexes has been developed. The trisbipyridyl Ru(II) moiety (the luminophore) and the free phenolic units of the calix[4]arene acting as the acid-base sites, were coupled by a methylene spacer to maximise the electron transfer rate and to buffer the units. Photo-induced intramolecular electron transfer was caused by the formation of phenolate anions, thus quenching the luminescence. The sensor works in 50% aqueous MeOH by this photoinduced electron transfer.

HETEROGENEOUS CATALYSIS

From CH₄ Reforming with CO₂ to Pyrolysis over a Platinum Catalyst


At temperatures up to 1100°C CH₄ and CO₂ react over a Pt wire to give CO, even at a CH₄:CO₂ ratio of 4:3. But if coke is on the wire the dominant reaction becomes the pyrolysis of CH₄ to give mainly acetylene and benzene. Higher temperatures and larger CH₄:O₂ ratios favour the formation of coke and the pyrolysis. The O₂ and H₂O have the opposite effect.

Structure Characterization of Platinum/Alumina, Ruthenium/Alumina, and Platinum-Rhenium/Alumina Catalysts


The structures of Pt/Al₂O₃, Re/Al₂O₃ and Pt-Re/Al₂O₃ catalysts were studied during the impregnation, calcination and reduction stages of preparation. Both Pt and Re reacted strongly with the support after calcination. The Pt species reacted more strongly with TiO₂ than with Al₂O₃, PtO, ReO and Pt-Re coexisted in the reduced Pt-Re/Al₂O₃ catalyst. H adsorption at a high temperature increased with increasing Pt-Re ratio.

Preparation, Activity and Durability of Promoted Platinum Catalysts for Automotive Exhaust Control


The effects of the additions of CaO, CeO₂ and La₂O₃ to Al₂O₃ supported Pt catalysts on the simultaneous control of HC, CO and NOx automobile emissions were analysed. The activity of the samples was determined with steady-state, reducing and oxidising, simulated feedstreams, etc. The catalysts had better resistance to accelerated ageing, with catalysts modified with CeO₂ being the best. The catalysts had lower light-off temperatures than the known Pt/Al₂O₃ catalysts, but not as low as with Pt-Rh/Al₂O₃.

Chemical Vapor Deposition of Platinum Hexafluoroacetylacetonate inside KL Zeolite: A New Route to Nonacidic Platinum-in-Zeolite Catalysts


Pt/KL catalysts were prepared by selective introduction of Pt hexafluoroacetylacetonate inside KL zeolite channels via CVD in a flow of Ar at 70°C. In situ DRIFTS and EXAFS studies of the metal particles formed via removal of the volatile organic ligands under H₂ at 350°C showed very small Pt clusters with a nucleophilic character. The nonacidic Pt/KL catalysts show high activity and selectivity in the conversion of methycyclopentane to C₂H₆ at 500°C, and long life due to reduced coke formation.
Characteristics of Electron Migration in Oxide Catalysts. I. Formation of Paramagnetic Palladium Ions in Pd/Y₂O₃ and Pd/La₂O₃ Systems


The ionic state of a Pd compound stabilised in the oxide matrices of Y₂O₃ and La₂O₃ was characterised. Promoting Y₂O₃ and La₂O₃ with Pd was found to be similar to stabilisation by a large amount of paramagnetic Pd⁺ and Pd⁰, which are usually found in the bulk and on the surface. Additionally, all Pd ions appeared to be co-ordinate-absorbed on the surface, thus resulting in extremely unstable reductive-reaction processes.

The Promotion Effects of Iron and Lithium on Ethanol Synthesis from Syngas over Rhodium-Based Catalysts


The addition of Fe to Rh/SiO₂ catalyst used during Rhodium-Based Catalysts


The adsorption of CH₃CHO, CH₃COOH and crotonaldehyde was studied by FTIR on Rh/SiO₂ catalysts which were either unpromoted or promoted with CeO₂ and ZrO₂. Acetyl species were identified on the promoted catalysts. The role of the promoter is to stabilise the acetyl species. The Rh/SiO₂ produces almost pure CH₃CHO from the CO + H₂ reaction at atmospheric pressure. CH₃CHO is only physisorbed and heating gives CH₃CO without intermediates.

Hydrocarbons from Synthesis Gas: Selectivity Changes Induced by the Zeolite Matrix on the Metallic Function in Rh/Y Catalysts


RhNaY and RhHY zeolites were prepared either by ion exchange with RhCl₃, giving very small Rh aggregates within the supercages of faujasitic zeolite, or by Rh₄(CO)₁₂ sublimation under vacuum. The clusters became aggregated during reduction or on-stream mainly at the outer zeolite surface irrespective of the degree of protonation of the zeolite. The RhNaY catalyst was used for the conversion of CO/H₂ mixtures to low C alkenes and alkanes, mostly butenes/butanes.

Catalytic Properties of RhCl₃.3H₂O Immobilized on the Modified Poly(styrene-divinylbenzene) Copolymer in Aqueous Phase Hydroformylation of Propylene


RhCl₃.3H₂O and RhCl(CO)(PPh₃)₃ immobilised on the poly(styrene-divinylbenzene) copolymer containing -CH₂(C₆H₅)₂O(H), groups, Rh(III)/SPPS and Rh(I)/SPPS, respectively, were active and stable hydroformylation catalysts in aqueous phase. ¹H NMR and FTIR studies showed that Rh(III)/SPPS and Rh(I)/SPPS have a similar structure and the Rh complexes are covalently anchored on the polymer. Their activity and selectivity increased with the increase of H₂ pressure. The rate increased with the increase of P₀ below 10 atm and decreased above 10 atm.

Oxidative Methane Conversion to Carbon Monoxide and Hydrogen at Low Reactor Wall Temperatures over Ruthenium Supported on Silica


Oxidative CH₄ conversion to CO and H₂ was catalysed over Ru/SiO₂ at reactor wall temperatures as low as 400°C, when reactant flow rate is significantly high. The conversion of CH₄ and the yields of CO and H₂ increase with increase in the flow rate of reactants, while O₂ is always completely consumed. Addition of CO₂ to the reactant flow can increase the CO yield, which suggests that CO₂ acts as an oxidant and the catalyst surface temperature is high enough to allow thermal conversion of CH₄ via CO₂ and H₂O to occur.

HOMOGENEOUS CATALYSIS

Hydrogenation of Unsaturated Compounds in the Complex System Palladium-1,2-Diene. I. Catalytic Properties of Compounds Formed in the Pd(II)-Alene System


Complexes PdCl₂, K₂PdCl₆, Pd(AcAc)₂ with allene, 1,1-dimethyllallene, trimethylene cyclohexane, isoprene in alcohol containing H₂O and in toluene, were found to be catalytically active during hydrogenation of unsaturated hydrocarbons, especially in isoprene. The highest hydrogenation rate of 1.5 × 10⁻¹ mol/min was obtained in the presence of dimethylallene ligands containing complex catalyst.

Palladium(0)-Catalyzed Conversion of Vinyl Trifluoromethanesulphonates into α, β-Unsaturated Nitriles


Vinyl triflates were converted by a new general method into the corresponding α, β-un saturated nitriles in good to excellent yields on treatment of each vinyl trifluoromethanesulphonate with dry LiCN in the presence of catalytic amounts of (Ph₃P)rPd and the crown ether 12-crown-4. Additional Pd improved the conversion.

Platinum Metals Rev., 1994, 38, (2)
Stereospecific Palladium/Copper Cocatalyzed Cross-Coupling of α-Alkoxy- and α-Aminostannanes with Acyl Chlorides


Stereospecific PalladidCopper Cocatalyzed Cross-Coupling of a-Alkoxy- and acylstannanes, proceeds with likely obtainable by BINALH asymmetric reduction of α-ether-substituted ketones in moderate to good yields. Coupling of chiral α-alkoxystannanes, which are easily obtainable by BINALH asymmetric reduction of acylstannanes, proceeds with ~ 98% retention of configuration. Aromatic acid chlorides gave the best yield.

Dehydrogenative Silylation of 1,5-Dienes with Hydrosilanes Catalyzed by RhCl(PPh3),


Studies of the effect of the chelating substrate in catalytic reactions showed that reaction of 1,5-dienes with hydrosilanes involves dehydrogenative silylation in the presence of RhCl(PPh3), catalyst, yielding 1-silyl-1,5-dienes instead of the usual hydroisilylation products. The vinylsilane formation seems to be specific to 1,5-dienes. The RhCl(PPh3), catalysed reaction of 1,4-pentadiene or 1,6-heptadiene with HSiEt2Me under identical conditions did not result in exclusive formation of similar 1-silyl 1,6-dienes.

Stereoselective Reduction of Disubstituted Aromatics on Colloidal Rhodium


Hydrogenation of disubstituted aromatic rings was achieved under mild conditions in a two-phase system in the presence of RhCl, and an amine phase transfer agent. The system was optimised for the 2-methylanisole reduction, with very small colloidal Rh particles stabilised by a suitable amine:Rh ratio. High chemoselectivity and high stereoselectivity to the Z isomer are obtained. α-Cresol derivatives were enantioselectively reduced with colloidal Rh stabilised and modified by chiral amines. Additionally, diastereoselective reduction was obtained with chiral auxiliaries bound to the substrate.

Selective Rhodium-Catalysed Oxidation of Alkanes to Alkyl Esters with Peracids


Treating saturated hydrocarbons with H2O2 in trifluoroacetic acid in the presence of Rh salts at room temperature resulted in their selective transformation to the corresponding alkyl trifluoroacetates in good yields. [Rh(OAc)3(H2O2)]OAc was the most effective catalyst, followed by various Rh compounds such as [Rh(acac)3], [RhCl(CO)3I3], Wilkinson’s complex [RhCl(PPh3)3] and the Rh acetate dimer [Rh2(OAc)4]. A reaction pathway is proposed which uses the results from the reactivity order tertiary > secondary > primary, and the reaction’s ionic nature.

Kinetic and Spectroscopic Study of the Hydrogen-Transfer Reaction from 2-Propanol to Cyclohexanone Catalysed by [IrH2(pz)(Hpz)(PPh3)2] (Hpz = pyrazole)


A kinetic and spectroscopic investigation of the H transfer reaction from 2-propanol to cyclohexanone at 60°C catalysed by the title complex is discussed. Air was excluded from the reaction. The concentration of the catalyst has a linear relationship with the initial rate of the reduction. The rate of cyclohexanol formation was inhibited by the addition of pyrazole.

Concomitant Catalytic Transformations of Geminal Ethynyl and Hydroxy Groups of Steroids into Acetyl and Ester Functions with Retention of Configuration by [Ru(μ-CH2(OH))(CO)2(PPh3)2].


Steroids containing both hydroxy and ethynyl groups at C(17) have been selectively transformed by reaction with carboxylic acids, in the presence of [Ru(μ-O,CH)(CO)2(PPh3)2], complex catalyst, into β-oxopropyl esters which retain the configuration at C(17). The retention of configuration can be explained by addition of carboxylic acid to the Ru(II) activated C=C bond, followed by intramolecular transestersification, according to a proposed catalytic cycle.

Selective Electrooxidative Transformations of Alkylaromatics Using a Polypyridyl Complex of Ruthenium(IV)


Alkylaromatics were electrocatalytically oxidised with [Ru2O(bpy)(trpy)2ClO4] on toluene, p-methoxytoluene, ethylbenzene, o-, m-, and p-xylenes. Toluene and p-methoxytoluene yielded their respective carboxylic acids, but ethylbenzene produced acetophenone, without bond cleavage, in 66.5% yield. The xylenes were oxidised to their mono and diacids, o-toluic and phthalic acid, m-toluic and isophthalic acid, and p-toluic and terephthalic acid, respectively.

FUEL CELLS

Hydrous Oxide Species as Inhibitors of Oxygen Reduction at Platinum Activated Fuel Cell Cathodes


MeOH/Air fuel cells require optimum performance of the air/oxygen cathode at ~0.8 V vs RHE, due to the inhibition, at above 0.8 V, of O2 reduction on finely divided Pt deposits prepared by chemical reduction from aqueous solution. Thermally prepared Pt/C electrodes were more active in this region than those prepared by wet techniques. Hydrous oxide films which may be produced on Pt in 3.0 M H2SO4 at 60°C are quite stable on open circuit in the hot acid.
On the Role of Surface Functional Groups in Pt Carbon Interaction


The interaction between Pt crystallites and C surface functional groups in Pt/C catalysts for PAFC has been studied. The area of the Pt surface depends on the amount of oxygenated groups on the C support. XPS shows the effect of the presence of O=C complexes on the Pt dispersion. The binding energy shifts in the XPS Pt 4f signals reflect the electron withdrawing nature of the neighbouring oxygenated C support.

Effect of Platinum Particle Size on the Performance of PAFC O₂ Reduction Electro catalysts


The effects of mass activity on Pt surface area and the behaviour of some catalysts for PAFC in short-term endurance tests have been examined under controlled simulated conditions. Strictly controlled preparation of Pt/C materials, including functionalisation of the support, are needed for good activity and stability. Electro catalyst activity increases as Pt particle size decreases.

Advances In Direct Oxidation Methanol Fuel Cells


A liquid feed direct MeOH fuel cell has been developed based on a proton-exchange membrane electrolyte and Pt/Ru and Pt-catalysed fuel and air/O₂ electrodes, respectively. The cell can deliver significant power outputs at 60–90°C. At operating temperatures < 88°C outputs in excess of 250 mA/cm² current density at cell voltage is ~0.5 V. Performance can be further improved by minimising the MeOH crossover rate.

CORROSION PROTECTION

Adsorbate-Catalyzed Dissolution in Inert Electrolyte: Layer-by-Layer Corrosion of Pd(100)-c(2 × 2)-I


The anodic dissolution of Pd in halide-free sulphuric acid, catalysed by a single adsorbed layer of I, was studied using a Pd(100) single crystal electrode having an ordered c(2 × 2) I adlayer. Pd dissolution only occurred on surfaces pretreated with I. The surface coverage and structure of the iodine adlayer were not affected by the corrosion reaction, which shows that anodic dissolution occurs on one interfacial metal-layer at a time. Layer-by-layer dissolution was also shown at the more closely packed Pd(111) electrode surface. The ordered I₃⁻-catalysed corrosion of Pd is independent of the surface crystallographic orientation.

CHEMICAL TECHNOLOGY

Methanation of Carbon Deposited Directly from CO₂ on Rhodium-Bearing Activated Magnetite


The methanation reactivity of surface C deposited from CO₂ on the surface of Rh-bearing activated magnetite was studied, a typical composition being (Rh₆O₁₂)₁₋ₓ(FeOₓ). The most active material contained 0.83 wt. % Rh and was prepared by impregnation at 60°C giving 98% CH₄ conversion at 300°C. Surface C contained elemental C (α-C) and polymerised C (β-C), with ratio depending on the density of C deposited. During the surface reaction the conversions of α-C and β-C to CH₄ was 0.34 and 0.53, respectively. Both forms of C are converted to CH₄ over Rh-bearing activated (α-C) magnetite.

ELECTRICAL AND ELECTRONIC ENGINEERING

A Novel Fabrication Process and Analytical Model for Pt/GaAs Schottky Barrier Mixer Diodes


Pt/GaAs Schottky barrier diodes for millimetre and submillimetre wave mixing applications with near-ideal I/V characteristics were fabricated by application of new processing techniques. The fabrication process is based on the anodic pulse etching technique of GaAs in combination with an electrolytic in situ Pt deposition. The fabricated diodes show nearly ideal I/V and noise characteristics. The current spreading, the current dependent recombination velocity at the metal/semiconductor interface, the barrier lowering due to image forces and n-n' junction voltage were the most important effects encountered during Schottky diode operation in forward bias.

AlGaAs/GaAs Charge Injection Transistor/ Negative Resistance Field-Effect Transistor Fabricated with Shallow Pd/Ge Ohmic Contacts


AlGaAs/GaAs charge injection transistor (CHIP)/negative resistance field effect transistor (NERFET) devices have been fabricated with Pd/Ge ohmic contacts, deposited by e-beam evaporation. The contact metal layers were annealed by rapid thermal annealing at 450–500°C for 1 min, giving a shallow ohmic contact and low specific contact resistivity, of the order of 10⁻⁶ Ωcm². Using Pd/Ge contacts and rapid thermal annealing, the metallisation of CHIP/NERFET becomes less critical, with simplified fabrication. Good device performance under NERFET mode and CHINT mode was achieved.
NEW PATENTS

ELECTROCHEMISTRY

Electrolytic Asymmetric Hydroxylation of Olefins
SEPACOR INC.  World Appl. 93/17,150A
Electrolytic preparation of optically active compounds, such as glycols, more specifically enol ethers or vinyl halides comprises (a) asymmetric hydroxylation of olefins in a protic medium in the presence of a catalytic amount of an OsO₄-chiral ligand complex; and electrolytically regenerating OsO₄, for reuse in (a) from lower valent Os species. The process conditions give molar amounts of optically active compounds.

Catalytic Activation of Cathode for Alkaline Electrolysis of Water
DEUT. AEROSPACE A.G.  German Appl. 4,232,958
Catalytic activation of a cathode for alkaline electrolysis of water involves adding a water soluble Pt metal salt to the electrolyte and electroplating the cathode with metal during cell operation. Activation reduces the over-voltage of the cathode by ~ 200 mV at 80°C, 240 mV at 130°C and 1 N cm² and by 80 mV at 300 mV at 300 mA/cm² compared to a reversible H₂ electrode of a Pt cathode coated with Pt black. A dense deposit can be obtained, which remains active for months or years, and reactivation is simple.

ELECTRODEPOSITION AND SURFACE COATINGS

Electrodeposition of Uniformly Thick Metal Foil
TDK CORP.  European Appl. 554,793A
The electrodeposition of uniformly thick metal foil, especially Cu, on a rotating cathode includes using a concentric anode of multiple arcuate segments of valve metal coated with Pt group metal oxide and releasably secured to a back plate. Anode segments are easily replaced, giving simplified maintenance. The use of multiple segments minimises edge effects and contributes to improved uniformity of foil thickness with extended segment life.

Diffusion Coating for Nickel and Cobalt Superalloy Turbine Engine Components
WALBAR INC.  European Appl. 567,755A
The high temperature oxidation and corrosion resistance of a metal superalloy is improved by applying a thin layer of a Pt group metal (preferably Pt) to the surface, heating to diffuse the metal into the surface and to form a Pt group metal aluminate, followed by packing the superalloy into a diffusion coating container, heating to diffuse Al and Cr into the surface, and removing the superalloy from the container and heating it to its solvus temperature. The resulting superalloy has a microstructure comprising an outer zone of Pt group metal aluminate.

Electrolyte for Platinum Plating Bath
JOHNSON MATTHEY P.L.C.  World Appl. 93/25,733A
An electrolyte for a Pt plating bath comprises a Pt(II) salt present in solution as Pt(H₂O)₄²⁻. A process for electroplating a Pt or a Pt alloy film onto a conductive substrate using a plating bath is also claimed. The anion component of the salt is one or more groups or radicals derived from an organic or inorganic acid. The concentration of Pt in the bath is 0.005–0.015 mol/dm³, and the operating temperature of the bath is preferably 15–60°C. The process operates at a current density of 0.03–10 A/dm² of substrate surface. The electrolyte allows the rapid deposition of high-quality, thick layers of Pt over a wide temperature range, even down to room temperature.

Catalyst for Electroless Plating
HITACHI CHEM. CO. LTD.  Japanese Appl. 5/255,861
A catalyst for electroless plating is made by dipping carrier particles into an aqueous solution containing Pd ions, to precipitate Pd or Pd compounds on the surfaces of the carrier particles, and firing the particles in O₂, to convert Pd into Pd oxide. The catalyst is used for making laminated boards for printed circuit boards.

Platinum Plating Bath
NIPPON ELECTROPLATING ENG. K.K.  Japanese Appl. 5/271,981
A Pt alloy plating bath contains Pt as Pt(OH)₄⁻ complex ion and Sn, Zr or Pd. Sulphuric acid amide, Na- or K sulphuric acid amide is added to the bath, which is used at pH ≥ 11 and ≥ 60°C. The plating is carried out using a pulse power source. The Pt plating provides higher gloss and hardness than pure Pt. A glossy Pt-Zn alloy coating containing 96% Pt was obtained from a plating bath of K₂Pt(OH)₄, 10g Pt/l, ZnO alkali solution with 0.2 g Zn/l and 60 g KOH/l.

Direct Formation of Electrocoating Layer on Non-Conductive Body
OKUNO PHARM. IND. K.K.  Japanese Appl. 5/287,583
A non-conductive body is coated with alkaline permanganate solution, then dipped into a catalyic solution containing Pd, Pt, Au, Ag or Cu, and thiourea, and a N-containing S compound consisting of a thiourea derivative; reduction-treating, activating, and forming the electrolytic layer on the body.

Electroless Chemical Production
DAIMLER-BENZ A.G.  German Appl. 4,220,621
Electroless chemical production of a structured metal layer on a glass, quartz or ceramic substrate comprises forming a structured base layer containing SnO₂ on the substrate before deposition of a Pd layer. The substrate surface is treated with a reductant of Cl₂ or Cl-containing medium to convert SnO₂ into SnCl₂. The base layer is produced as an In-Sn layer. The substrate is treated in a gas atmosphere, such as of Cl₂ or HCl vapour, or in a liquid bath, such as HCl.
APPARATUS AND TECHNIQUE

Optical Filter

An optical filter used for absorption of electromagnetic (em) radiation in a narrow wavelength band comprises a transparent host material, such as a polymeric matrix of polycarbonate, and an em radiation absorbing material of 5,10,15,20-tetrakis (4-methoxyphenyl)-21H, 23H porphine Pd(II), and a narrow waveband em radiation absorber of vanadyl phthalocyanine. The filter absorbs em radiation of wavelength 532 × 10⁻⁴ m, while passing other wavelengths.

Alcohol Sensor

FIGARO Giken K.K. Japanese Appl. 5/302,905

A highly alcohol-sensitive sensor comprises a mixture of SnO₂, Y₂O₃, and Pt in atomic ratio Sn:Y:Pt of 0.6–0.5:0.001–0.05. Preferably the amount of Y₂O₃ to be added to SnO₂ is 10–50 mol.%, and the amount of Pt added is 0.2–3 mol.%. The alcohol sensor can detect an alcohol (EtOH) at the 10 ppm level and the interference caused by H₂S or CH₃SH is low, so alcohol exhaled can be detected.

HETEROGENEOUS CATALYSIS

Production of Dimethyl Naphthalene

Mitsubishi Gas Chem. Co. INC. European Appl. 557,722A

Dimethyl naphthalene for use in the manufacture of 2,6-naphthalenedicarboxylic acid is produced by catalytic cyclisation dehydrogenation of 2-methyl-1-(p-tolyl)butene and/or 2-methyl-1-(p-tolyl)butane in the presence of 0.05–20 wt.% of a Pd catalyst such as PdCl₂, Pd(NO₃)₂, Pd acetate, Na₂PdCl₄, H₂PdCl₄, etc., 0.1–20 wt.% of alkali and/or alkali earth metal compound(s), particularly LiCl, LiNO₃, KCl, NaCl, NaNO₃, and KNO₃, on an Al oxide.

Catalyst for Purification of Exhaust Gas

Nippon Shokubai Co. Ltd. European Appl. 558,159A

A catalyst for purifying exhaust gas comprises a monolithic honeycomb carrier with a first coating layer of CeO₂, a first refractory inorganic oxide without noble metal and a secondary refractory inorganic oxide carrying 5–30 wt.% of Pt and/or Pd and/or refractory inorganic oxide with 1–20 wt.% of Rh; or a refractory inorganic oxide carrying 5–30 wt.% of Pt and/or Pd and 1–20 wt.% of Rh. The catalyst has outstanding durability even under harsh conditions.

Dehydrogenation of Saturated Hydrocarbons

Inst. Francais du Petrole European Appl. 559,509A

Dehydrogenation of a saturated aliphatic hydrocarbon charge comprising 3–5C per mole uses a supported catalyst of one or more Pt group metals, a promoter and an alkali or alkaline earth metal and with no H₂. The preheated charge was introduced into one or more reactors for catalytic dehydrogenation. The process gives high conversion rates and high selectivity.

Shell Catalyst Containing Palladium

HOECHST A.G. European Appl. 565,952A

Shell catalysts, for gas phase production of vinyl acetate from C₃H₆O₂, acetic acid and gas containing O₂, are made by dissolving salts of Pd, K and Cd, Ba or Au in a suitable solvent, atomising the solution ultrasonically, impregnating the support one or more times and curing after each impregnation. The catalysts have better selectivity than those impregnated to the core.

Palladium and Copper-Based Supported Catalyst

ITAL. MIN. UNIVERSITA DEI TECNI. European Appl. 567,198A

A Pd and Cu based supported metal catalyst, for selective hydrogenation of polyunsaturated hydrocarbons, is prepared by impregnating a porous support with a Pd and K salt solution, followed by treatment in a flowing H₂ stream; impregnating with a Cu salt solution and followed again by treatment with H₂; and finally drying the resulting solid product. A typical composition is 0.05–0.4% Pd, 0.01–0.06% Cu and 0.01–3% K. The catalyst produces hydrocarbons containing the same number of C atoms but with a higher H:C ratio.

Acetic Acid Production

GHIOUDA CORP. European Appl. 567,331A

Acetic acid production comprises introducing a feed including MeOH, CO, an alkyl iodide and a solvent into a reaction zone containing a solid Rh compound catalyst supported on an insoluble, pyridine-containing resin substrate, at 140–250°C and 15–60 kg/cm² pressure at a partial CO pressure of 7–30 kg/cm². Acetic acid can be obtained in high yield and high selectivity even at relatively low reaction pressures. The high catalytic activity can be maintained for a long time.

Catalyst for Selective Hydrogenation of Unsaturated Compounds

HUELS A.G. European Appl. 576,828A

The catalyst, for use in the chemical and oil industries, contains Pd and/or PdO, with x = 0–1, on an Al₂O₃ support, and may also contain 0.01–3 wt.% Pt, Ir, Ru and Rh (oxide). Fresh catalyst contains crystallites and has a Na content of 0.01–1%. The support contains γ- and/or γ-Al₂O₃, and the noble metal is in an outer zone of thickness 5–200 μm. The catalyst is used to manufacture phenol and acetone. It has high initial selectivity on direct use, without time-consuming start-up procedures.

Separating or Reducing Oxygen, Nitrite and/or Nitrate in Water

Solvay Umweltchemie G.m.b.h. World Appl. 93/17,790A

The process comprises treating H₂O with H₂ and contacting it with a catalyst of Pd and/or Rh or Pd and a metal of the Cu group impregnated in Al₂O₃, carrier of θ and κ modification but with no or little η, γ and δ modifications. The pH is ≤ 8 and the process is repeated until the O₃, nitrite and/or nitrate contents are zero or negligible. The catalyst is abrasion resistant.
Removal of Sulphur and Nitrogen from Hydrocarbon Feedstocks
EXXON RES. & ENG. CO. U.S. Patent 5,252,199
S and N are removed from hydrocarbon feedstock by treatment, in the presence of H₂, with a highly dispersed multimetallic sulphide catalyst of MoS₂ promoted with Pt, Pd, Rh or Ir in amount 0.1-10 wt.%, with the noble metal in an oxidation state > 0 and co-ordinated to M, where M = Pt or Pd; or ML₂ where M = Rh or Ir, and L is dithiocarbamate, dithiophosphates, etc.

Catalytic Production of Hydrogen Cyanide
E. I. DU PONT DE NEMOURS & CO.
U.S. Patent 5,262,145
The production of HCN is effected by feeding a gaseous mixture of N₂ and C compounds to a reactor containing two catalytic superposed piles both containing 33-67 wt.% of Pt group metal, either as mesh or particles. For gauze the mesh size of the first pile is finer than the second. The surface density of the gauzes decreases from the entrance to the exit according to the change in the O₂: NH₃ ratio as the reaction proceeds. A catalyst pack for this reaction contains at least four gauze sheets.

Allylic Chloride Production
DOW CHEM. CO. U.S. Patent 5,262,575
Allylic chloride is produced by contacting an olefin-containing feed stream with a Pt- or Pd-chloride-containing chlorination composition, where the mole ratio of O₂:olefin is 0-1:20, at 200-300°C. The chlorination composition is separated from the feed-stream and regenerated with Cl₂ in a second reactor before recycling for contact with the feedstream. High conversion of olefins and high selectivity to allylic products are achieved.

Reforming Naphtha to Improve Octane Quality
EXXON RES. & ENG. CO. U.S. Patent 5,269,907
The octane quality of a naphtha comprising a mixture of paraffins, aromatics and naphthenes is improved by reforming the feed over a high activity, high yield Sn modified Pt-Ir catalyst at reforming conditions sufficient to produce predominantly dehydrogenation and ring isomerisation reactions, yielding products useful as gasoline blending components. The catalyst comprises 0.1-0.7 wt.% Pt, 0.1-0.7 wt.% Ir and 0.02-0.4 wt.% Sn, with each metal being uniformly dispersed throughout an inorganic oxide support. A reforming unit is also claimed.

Distillate Hydrogenation for Deaomatisation
AMOCO CORP. U.S. Patent 5,271,828
Hydrocarbon feedstock, having a distillate portion with boiling point 150-700°F, is hydrogenated by contact with H₂ at 400-750°F and 300-2000 psig in the presence of 0.1-2.0 wt.% Pd and 0.1-2.0 wt.% Pt on a borsilicate support. The catalyst is durable and resilient with high crush strength.

Catalyst for Decomposing Hydrazine
ISHIKAWAJIMA HARIMA HEAVY IND.
Japanese Appl. 5/261,285
A catalyst to decompose hydrazine, used in a propulsion device for a space rocket, consists of a ceramic cordierite-type honeycomb with a layer of a gibbsite supported with Ir. A propulsion device is also claimed having a reaction part with the rear containing the catalyst and the front containing an Ir loaded granular hydrazine decomposition catalyst. Hydrazine is fed to the front catalyst and an exhaust nozzle jets out decomposition products at the rear.

Catalyst for Nitrous Oxide Decomposition
SAKAI CHEM. IND. CO. LTD. Japanese Appl. 5/317,648
The catalyst comprises at least one of Pt, Pd, Rh, Os, Ir, Ru or Re supported on a hydrophobic material. The catalyst contains preferably 0.3-2 wt.% of Rh or Ru. The hydrophobic material includes SiO₂ gel, activated Al₂O₃ and SiO₂-Al₂O₃. The decomposition of N₂O is performed at 300-500°C. The catalyst can decompose N₂O contained in effluent from factories, refuse and sewage sludge incinerators.

Low Pressure Hydrogenation of Aromatic to Cycloaliphatic Amines
BASF A.G. German Appl. 4,207,314
Catalytic hydrogenation of aromatic amines to cycloaliphatic amines is effected at 120-250°C at 0.1-5 bar in the presence of NH₃ using an alkali- and/or alkaline earth metal-doped catalyst containing supported Ru and Pd or Pt. Total amount of Ru + (Pd or Pt) is preferably 0.2-5 wt.% and the weight ratio Ru:(Pd or Pt) is preferably 0.2-5:1. This low pressure process overcomes catalyst deactivation by NH₃, slow reaction and NH₃ condensation.

HOMOGENEOUS CATALYSIS
Production of Cinnamic Acid Derivatives
BAYER A.G. European Appl. 564,919 A
The production of cinnamic acid derivatives is effected by the reaction of bromo-aromatic compounds with acrylic acid derivatives in the presence of a Pd catalyst, an inorganic base, a phosphine, and an alcohol an/or a phase-transfer catalyst. The phosphine is used in large excess with respect to Pd. Cinnamic acid derivatives, such as 2-ethylhexyl and isoamyl p-methoxycinnamates, are useful as UV absorbers in cosmetics. The process gives high space-time yields without amine and solvent handling problems.

Carbonylation of Olefinically or Acetylenically Unsaturated Hydrocarbons
SHELL INT. RES. Mij. BV. European Appl. 565,199 A
Carbonylation of an olefinically or acetylenically unsaturated hydrocarbon compound is effected by a reaction with CO and a hydroxy compound in a catalyst system of cationic Pd, a phosphine and a protonic acid; the reaction is carried out in the presence of a free radical inhibitor. The initial molar ratio of phenol:Pd is 5-30 and of protonic acid:phosphine is 0.5-10. The consumption of the phosphine is reduced.
Production of Isoprene Derivatives

F. HOFFMANN LA ROCHE & CO. A.G.  
European Appl. 565,975A

Production of both, tri- or tetra-isoprene derivatives comprises asymmetric hydrogenation of an (E)- or (Z)-alkene or alkadiene in the presence of a Ru complex of an optically active atropisomeric diphosphine. The derivatives are intermediates for (R,R,R)-α-tocopherol, vitamin K1 and phytol manufacture.

Stereospecific Production of Olefins  
KURARAY CO. LTD.  
European Appl. 566,030A

Production of olefins with an adjacent optically active C atom is carried out by reaction of Z or E allylic carbonate ester with formic acid or its salt in the presence of a tertiary phosphine and Pd salt catalyst. The olefin contains groups of 1-6C alkyl, H or 14C alkyl, H, OH or an organic group; or a pair of substituents on adjacent C atoms to form a bond, etc. The reaction proceeds stereospecifically to produce an optically active side chain to the ring system X in high yield and high selectivity. The process is industrially applicable and avoids the use of toxic materials.

Asymmetric Hydrogenation Using an Optically Active Ruthenium Complex Catalyst  
F. HOFFMANN LA ROCHE & CO. A.G.  
European Appl. 570,764A

The preparation of 3-carboxy-perhydro-pyrrole, -pyridazine and 1,2-diazacycloheptane derivatives in (S) or (R) form comprises asymmetric hydrogenation of the corresponding 3-carboxy-3-pyrazoline, 3-carboxy-1,2,5,6-tetrahydropyridazine or 3-carboxy-1,2-diaza-3-cyclo-heptene derivatives or their salts in the presence of an optically active Ru diphosphine complex. The derivatives can be prepared with high optical purity.

Preparation of Carbonyl Compounds  
IDEMITSU KOSAN CO. LTD.  
European Appl. 572,036A

Preparation of carbonyl compounds comprises reacting an olefin or O₂ or O₂-containing gas in the presence of a Pd compound and/or metallic Pd, a polyoxoanion compound and an organic P compound in a solvent selected from 2-10C carboxylic acids, and a carboxylic acid at low temperature is increased. The reactions are safe and have excellent selectivity and yield for the compounds which are useful as synthetic intermediates to pharmaceuticals, agrochemicals and artificial sweeteners.

Three-Way Catalyst for Treatment of Exhaust Gas  
ENGELHARD CORP.  
U.S. Patent 5,254,519

A catalyst comprises a carrier with a catalytic coat of rare earth oxide-ZrO₂ support containing a 0.03-1.0 wt.% first Rh component, with respect to total weight of co-formed support, and a first activated Al₂O₃ support with a 0.01-5 wt.% Pt component. The coat also contains a metal oxide, preferably Ni, Cu, Mn and/or Ge, to suppress H₂S emission from the catalyst, a second Rh component dispersed on the first Al₂O₃ support; and a second Al₂O₃ support with a second Rh component. The rare earth oxide is Ce, Nb and/or Y.

Preparation of Aromatic Acetaldehydes  
TAKASAGO PERFUM. CO. LTD.  
Japanese Appl. 5,229,981

Aromatic acetaldehydes are prepared by oxidative decomposition of aromatic compounds with an alkyl group such as propyl benzene, in the presence of Ru and phase transfer catalysts. The oxidising agent for the oxidative decomposition is a periodate. In an example RuCl₃ was used as the catalyst in the room temperature reaction. The reactions are safe and have excellent selectivity and yield for the compounds which are useful as synthetic intermediates to pharmaceuticals, agrochemicals and artificial sweeteners.

Preparation of Cyclic Amines  
KANEBO LTD.  
Japanese Appl. 5,255,285

Optically active cyclic amines having benzyl, benzoyl, p-tolueneasulphonyl or up to 10C alkyl, are prepared stereoselectively, in high yields, in an inert organic solvent in the presence of a Pd complex catalyst, in which an optically active phosphine is co-ordinated, and preferably in the presence of a base. The amine is a raw material for physiologically active substances.

3-Pentenoic Acid Preparation  
E. I. DU PONT DE NEMOURS & CO.  
U.S. Patent 5,250,726

3-Pentenoic acid is prepared from a reaction mixture of butadiene, CO, 1-20 wt.% H₂O, a carboxylic acid solvent selected from 2-10C carboxylic acids, and benzoic acid optionally alkyl-substituted, where the total number of C in the alkyl group is ≤ 3, a homogeneous Rh catalyst, a heterogeneous or homogeneous sulphonic acid catalyst, and an iodide promoter, at CO partial pressure of 50-1000 psi and 50-120°C. The rate of conversion of butadiene to 3-pentenoic acid at low temperature is increased.
High Selectivity Hydrogenation of Acetylenes to Olefins
HENKEL KGAA.  German Appl. 4,211,126
Olefin production by H₂ hydrogenation of acetylenic compounds is effected using a catalyst consisting of a Pd salt, an activator, and also a base to neutralise acid formed by reduction of the Pd salt; and/or H₂O and/or an inert H₂O-immiscible solvent. The catalysts give high conversion rates at 0–150°C and are effective in small amounts for use in tubular reactors.

Production of Long Chain Methyl Alkyl Ethers
HENKEL KGAA.  German Appl. 4,221,099
Methyl alkyl ethers of formula R₁–O–CH₂R₂, where R₁ = 6–22C aliphatic hydrocarbyl with 0–3 double bonds are produced by hydrogenation of R₁–O–CH₂R₂ (1) in the presence of Pd catalysts and H₃PO₄. Hydrogenation is performed at 150–250°C and 10–100 bar, using 0.1–5 wt.% of Pd and 0.1–5% H₃PO₄, with respect to (1) and a Pd/H₃PO₄ ratio of 1:10–10:1. The ethers are raw materials for lubricants.

FUEL CELLS
Hydrogen and Hydrocarbon Gas Storage for Vehicle Fuel
BC LTD.  World Appl. 93/22,236A
Storing H₂ or hydrocarbon gas comprises adsorbing or absorbing the gas with a transition metal dichalcogenide of formula: MX₂, where M = Mo, W or Ti; and X = S or Se; preferably coated with Pt catalyst or H absorbent. A composition of formula: Y-MX₂ is also new, comprising MX₂ coated with Pt, Pd, Ni, Co, Fe, Mg, Zr, Cr, Al, Zn, Mn or their mixtures.

CORROSION PROTECTION
Composite Anticorrosive Material
LIMES K.K.  Japanese Appl. 5/311,402
Composite anticorrosive material, prepared with high energy efficiency at low cost, consists of a metal base with multiple Ni-Ta-Pt coatings containing Pt ≥ 10 at.% content in each layer. The layers are formed by ion beam sputtering or ion beam mixing. In an Ar ion beam sputtering unit a Ti sheet was coated with a 3μm layer of Ni–40at.%Ta–5at.%Pt, at an acceleration voltage of 3 keV, ion current 1.5 A, 5 × 10⁻⁶ Torr.

ELECTRICAL AND ELECTRONIC ENGINEERING
Magneto-Optical Layer and Magneto-Optical Recording Medium
TEIJIN LTD.  European Appl. 576,292A
A magneto-optical layer of a Co-Pt-Ru alloy has composition Co₉Pt₄Ru, where a = 20–70, b = 10–70, c = 10–60 and a + b + c = 100, the magneto-optical layer has an easy magnetisation axis perpendicular to the main surface of the magneto-optical layer. The magneto-optical layer has a magneto-optical effect at a wavelength shorter than currently used.

Cobalt-Platinum Magnetic Film
EASTMAN KODAK CO.  European Appl. 576,376A
A CoPt magnetic film is deposited onto a substrate with a curved surface. Also claimed is a method for depositing the magnetic film by sputtering an underlayer onto a substrate, and sputtering a CoPt film from a CoPt target onto the underlayer in an H₂ and/or Xe atmosphere. The underlayer is preferably Cr or W. The magnetic film is > 300 nm thick with a coercivity > 2300 Oe. Film hardness is > 14 GPa at a depth of 150 nm and a built density for the CoPt film of ≥ 13 g/cm³. The film is used for rotating cylindrical recording surfaces.

Thick Film Resistor Compositions
E.I. DU PONT DE NEMOURS & CO.  World Appl. 93/23,855A
A thick film resistor composition comprises in wt. %: 5–30 of a Ru pyrochlore oxide, namely PbRuO₄, and 10–90 of a glass binder comprising a first glass containing PbO, SiO₂ and B₂O₃. The first glass comprises 5–30 wt.% of the resistor composition. The weight ratio of PbRuO₄ to the first glass is 5:30–60:40. The thick film resistor composition minimises fluctuations and variations of resistance and has a small thermal coefficient of expansion.

Palladium Thick Film Resistor
MOTOROLA INC.  U.S. Patent 5,250,358
A thick film resistor comprises a resistive sintered thick film bonded to a ceramic substrate of sintered Pt matrix, a first dispersed phase of BN and a second dispersed phase of Ta₂O₅. A preferred film comprises in wt. %: 1–15, preferably 2.5–7.5 BN and 2.5–7.5, preferably 4.0–5.0 Ta₂O₅, up to 2.5% Ca oxide borosilicate glass, up to 3% Ag and up to 5% alkaline earth titanate may also be present. The thick film resistor composition can be derived from a paste and is sintered by co-firing with a metal titanate substrate.

Patterning of Conductive Metal Oxide Film on a Substrate
MOTOROLA INC.  U.S. Patent 5,254,217
Fabrication of a semiconductive device involves taking a substrate having a conductive metal oxide film selected from Ru, Rh, Ir or Os disposed on it and etching the oxide film using an O₂ gas plasma. The Ru oxide has a stoichiometric composition of 2.03 atoms of O to every one atom of Ru. The RuO₂ film is sputter deposited from a Ru target in an O₂ ambient. This method is a means for plasma etching to provide a high resolution metal oxide pattern.

Thick Film Resistor Paste
SUMITOMO METAL MINING CO.  Japanese Appl. 5/242,722
The paste comprises conductive particles coated with oxide(s) of Ru, Ir and Rh; a glass frit and an organic vehicle. The coating layer covers part or all of the surface of the particles. In an example, Re₂O₇ powder, RuO₂ and EtOH were mixed, filtered and dried to obtain surface modified powder. The paste, which is used for hybrid IC or thick film chip parts, is printed onto Al₂O₃, and sintered at a maximum of 850°C.
High Density Recording Medium

TOSHIBA K.K.  
*Japanese Appl. 5/282,718*

The medium comprises a laminate of dielectric film, a transition metal group-Pt type perpendicular magnetisation film and a metal reflecting film. When the dielectric film has a refractive index of \( n_1 \) and an attenuation factor of \( k_1 \), and when the metal reflecting film has a refractive index of \( n_2 \) and an attenuation factor of \( k_2 \), then: \( n_s = 2 - 2.5, k_s \leq 0.3; n_t = 1.1 - 1.9, k_t = 1.6 - 2.5 \). The medium is used for high density recording and has an improved C:N ratio.

Photomagnetic Recording Medium

SONY CORP.  
*Japanese Appl. 5/282,721*

A photomagnetic recording medium comprises laminations of a polymer substrate, a dielectric layer, a Co-Pt type artificial lattice film (4 Å thick Co layers and 10 Å thick Pt layers were used in an example) and a UV ray curing type resin layer. The signal is preferably written by a laser of 3~6 mW power at rate of 1~3 m/s of linear speed. The medium has improved write/read characteristics for CD-MO use.

Target for Corrosion-Resistant Magnetic Film

HITACHI LTD.  
*Japanese Appl. 5/290,330*

A target for corrosion-resistant magnetic film comprises (Fe,Co)M(C,N) based alloy (where M is at least one selected from Hf, Zr, Ta, Nb, W, Mo and Ti) with added Cr and Rh and/or Ru. The target is used for depositing ferromagnetic film as a core material of a magnetic head.

Magneto-Optical Recording Medium as Disk, Card or Tape

DAICEL CHEM. IND. LTD  
*Japanese Appl. 5/290,418*

A magneto-optical recording medium has a recording layer based on Pt and Co, made of a composition-modulated multilayer film and an enhance layer made of substance(s) undergoing electron transition in the wavelength range of the laser beam for recording or regenerating information. The layers are laminated to form a single composite film. The enhance layer increases the Kerr rotation angle.

Magneto-Optical Recording Medium with Fewer Regeneration Errors

SANYO ELECTRIC CO.  
*Japanese Appl. 5/290,419*

A recording medium has a magnetic layer made of layers containing a noble metal(s) comprising Pt, Pd, Au, PtN, PtFe and PtCo; and layers containing Fe, Co, Ni, FeCo and CoNi, laminated alternately, on a board as a recording layer. A UV-cured resin film is formed on the recording layer. Heat conduction is perpendicular to the recording layer.

Magneto-Optic Recording Medium

SANYO ELECTRIC CO.  
*Japanese Appl. 5/298,759*

A new magneto-optical recording medium consists of alternating laminate layer film of Pt and transition metal, a transparent board and a transparent under-layer which gives compact lamination of Pt sandwiched between them. The medium has improved crystallinity of Pt resulting in high coercive force of the alternating laminate layer film for high packing density recording.

TEMPERATURE MEASUREMENT

High Temperature Oxidation Resistant Noble Metal-Aluminium Alloy Thermocouple

NAT. AERONAUTICS SPACE ADMIN.  
*U.S. Patent 5,275,670*

A thermocouple has an electropositive leg formed from a noble metal-Al alloy (such as Pt, Pd, Rh, Ir, Ag and Au) and an electronegative leg electrically joined at respective ends thereof to form a thermocouple junction. The electropositive leg comprises a Pt wire with a Pt-Al alloy coating and the electronegative leg comprises a Pt wire sometime coated with Pt-Al. The thermocouple provides accurate and reproducible measurement of high temperatures of 600~1300°C in inert, oxidising, or reducing environments.

MEDICAL USES

New Optically Pure Platinum Anticancer Complex

TANAKA KIKINZOKU KOGYO K.K.  
*European Appl. 567,438A*

An optically active Pt complex compound is resolved by subjecting a solution of a di-isomer and of a 1-isomer of a Pt complex compound to liquid chromatography and recovering the eluted solution of one of the two optically active-isomers. The new optically pure cis-oxalato (trans-1,1,2-cyclohexanediameine)Pt(II) has a melting point of 198.3~199.7°C.

Anticancer Platinum Complex

SEIKAGAKU KOGYO K.K.  
*World Appl. 93/21,193A*

A new Pt complex contains a (3-8C cycloalkanediamine)Pt(II) with co-ordinated carboxyl and/or sulphate groups of a chondroitin-4-sulphate. The complex is electrophoretically homogeneous, with ≤ 5 wt.% Pt and H2O solubility at 20°C of ≥ 10 mg/ml with high selectivity for liver and spleen.

Tetra Valent Platinum Diamine Antitumour Complexes

ROGER LAB BELLON S.A.  
*World Appl. 93/23,410A*

New amino-aminomethyl-cyclic compound Pt(IV) complexes and their enantiomers, racemates, salts and hydrates contain optionally (i) unsaturated 7~12C polycyclic carbocyclic groups or (ii) saturated or partially unsaturated mono-, di- or tricyclic heterocycle containing 5~11 members and a heteroatom. The complexes are effective against colon and pancreatic adenocarcinoma in mice.

Corrosion-Resistant Dental Alloy

C. HAFNER G.m.b.H. & CO.  
*German Appl. 4,211,403*

The dental alloy contains in wt.% 95~95 Au, 2~12 Pt, 0~5 Pd, 0~5 Ag, 0.1~2 Sn and 0.05~0.5 Re. Preferably the alloy also contains 0.05~0.5% of each of Ir, Ru, Rh and Fe. The alloy is corrosion resistant and has an adequate melt-interval and an optimum coefficient of heat expansion.

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