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Progress in Platinum Group Metal Coating Technology, ACT™

COATED COMPONENTS IMPROVE THE GLASS INDUSTRY

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Refractory ceramics have long formed a vital part of the glass making and glass processing industries. Due to market pressures these industries are moving towards increasingly higher quality products and progressively improved plant efficiency. However, significant improvements to the refractory ceramics are difficult because of the range of properties which they are required to have. This second paper on ACT™ (Advanced Coating Technology) using platinum group metals, describes the latest developments and advantages conferred by ACT™ coatings to the various ceramic forehearth components.

An earlier paper on ACT™ coating technology explained the principles of its application and its potential uses for the glass manufacturing industry (1). It described the protection that could be achieved by using platinum coatings on nickel-based alloys, and gave details of the very earliest service performance of ACT™ platinum-coated tri-level thermocouples on ceramic substrates. The latest progress in ACT™ technology for ceramic thermocouples and for the very diverse refractory ceramic substrates which are used in the forming end of glass making furnaces, are presented here (2–5).

Materials in the Glass Industry

The glass industry provides a rigorous test for any potential containment material for molten glass. Ceramics perform the bulk of this service, and even though manufacturers of ceramics have been successful in progressively developing ceramics with improved properties they suffer limitations in use, so opportunities exist for materials that have higher levels of corrosion and erosion resistance; these are properties which the platinum group metals can enhance.

Platinum is relatively non-reactive with most glass melts and glass vapours at temperatures of up to approximately 1450°C. At the higher temperatures, however, the life of conventionally fabricated sheet metal platinum can be limited by grain growth, and therefore alloying with other platinum group metals may be beneficial. Alternatively, the use of grain stabilised materials substantially reduces the problems caused by grain growth. Johnson Matthey was the first to develop platinum group metals and alloys containing very fine, uniform dispersions of oxide particulates (6). The alloys, designated ZGS (Zirconia Grain Stabilised), are subjected to special processing during manufacture which, in combination with the oxide dispersion, promotes the formation of a high aspect ratio grain structure. Thus these alloys are extremely stable structurally, even at very high temperatures, and exhibit the highest tensile strengths, creep properties and general levels of durability of all comparable platinum group metals and alloys. Therefore ZGS alloys are eminently suitable for glass industry applications (7).

Cladding of Materials

By using sheets of platinum or platinum alloys, it is quite possible to fabricate furnaces, channels and consumables for glass processing (8).
Indeed, for the highest quality glass products, such as optical and lens glasses, this is already done. However, capital cost is high because of the thickness of sheet that is needed, and may only be justified for the highest added-value products. A less costly method is to clad ceramic or molybdenum substrates with sheets of platinum group metals. In this way the amount of

Fig. 1 Standard assembly design for an ACT™ coated tri-level thermocouple assembly; the assembly length, coating length, coating thickness and coating material are selected according to customer requirements.

Fig. 2(a) ACT™ 10 per cent rhodium-platinum coated mullite thermocouple sheath after being in service for 27 months in container glass. The coating has provided excellent protection to the underlying ceramic substrate.
(b) A traditional 10 per cent rhodium-platinum clad tri-level thermocouple sheath after service in container glass.
the platinum group metal employed is significantly reduced, while the strength and corrosion resistance of the component is maintained. However, there are limits beyond which the thickness of the platinum cladding metal cannot be reduced, without hindering fabrication or service requirements. To overcome this restriction Johnson Matthey introduced its ACT™ coating technology which allows coating thicknesses as low as 175 μm to be used.

**Thermocouple Assembly Design with ACT™ Coating Technology**

The first exploitation of ACT™ technology was for the protection of thermocouples used in the arduous service environments associated with the intrusive monitoring of glass temperatures in forehearths, or in melting furnaces (9). The early ACT™ system had been extensively investigated and analysed in tested and untested conditions before field trials on thermocouple assemblies were undertaken. Early field trials were performed in a forehearth for container making where the components were subjected to temperatures of up to 1200°C in flint, amber and green glasses successively, at times up to 1000 hours.

The first commercial products were sheaths for tri-level thermocouples used for measuring temperatures at various depths in molten glass as it flowed down the forehearth. The advantage in using Johnson Matthey ACT™ for thermocouple sheaths, compared with conventional cladding, is that the standardised basic assembly design can be customised for assembly length, coating length, coating thickness and coating material, according to customer requirements, see Figure 1.

Mullite thermocouple sheaths should be used at temperatures below about 1400°C, primarily because they have better thermal shock properties than alumina. Although mullite may be used at temperatures as high as 1700°C, the environmental conditions in the melting zones of glass furnaces (where these temperatures may be approached) are often extreme. Therefore, for temperatures above approximately 1400°C an alumina substrate should be selected.

**Present Status of ACT™ Forehearth Thermocouples**

Forehearth thermocouples, and in particular tri-levels, are used to measure the glass temperature profile both across the width of the forehearth and in the glass depth. This allows total control over forehearth firing cycles, and thus provides controlled viscosity of the glass gob leaving the furnace. Control of viscosity is

<table>
<thead>
<tr>
<th>Country</th>
<th>ACT™ coating type</th>
<th>Glass type</th>
<th>Service life in months</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Australia</td>
<td>10%Rh-Pt</td>
<td>Amber</td>
<td>6</td>
<td>Failure of uncoated Ni-Cr substrate</td>
</tr>
<tr>
<td>Britain</td>
<td>10%Rh-Pt</td>
<td>Flint</td>
<td>27</td>
<td>Mechanically damaged; removed for examination</td>
</tr>
<tr>
<td>Scandinavia</td>
<td>10%Rh-Pt</td>
<td>Amber</td>
<td>32</td>
<td>Still operating</td>
</tr>
<tr>
<td>Scandinavia</td>
<td>10%Rh-Pt</td>
<td>Fibre</td>
<td>28</td>
<td>Still operating</td>
</tr>
<tr>
<td>Holland</td>
<td>10%Rh-Pt</td>
<td>Amber</td>
<td>23</td>
<td>Still operating</td>
</tr>
<tr>
<td>U.S.A.</td>
<td>10%Rh-Pt</td>
<td>Amber</td>
<td>12</td>
<td>Removed as planned for examination</td>
</tr>
<tr>
<td>U.S.A.</td>
<td>Platinum</td>
<td>Flint or amber</td>
<td>20</td>
<td>Still operating</td>
</tr>
<tr>
<td>U.S.A.</td>
<td>Platinum</td>
<td>Flint &amp; amber</td>
<td>19</td>
<td>Still operating</td>
</tr>
<tr>
<td>Britain</td>
<td>Platinum</td>
<td>Flint &amp; amber</td>
<td>18</td>
<td>Still operating</td>
</tr>
<tr>
<td>U.S.A.</td>
<td>Platinum</td>
<td>Amber</td>
<td>17–19</td>
<td>Still operating</td>
</tr>
</tbody>
</table>
essential to ensure that the gob weight may be maintained within the tight tolerance band required, for example, in the production of glass containers by the NNPB (narrow neck press and blow) process.

ACT™ coated sheaths are already installed worldwide in numerous plants in full scale production. The success of the coating technology is demonstrated by the service lives, now in excess of 2.5 years, shown in the Table.

Comparison between ACT™ Coated and Traditional Sheet-Clad Assemblies

The second thermocouple assembly referred to in the Table entered service in May 1992 at PLM Redfearn’s Barnsley plant. Approximately 200 mm of its mullite sheath was coated with ACT™ 10 per cent rhodium-platinum to a thickness of about 200 µm, thickening to 250 µm at the glass line. The thermocouple ran continuously until its removal following mechanical damage during forehearth repair work in September 1994. It had been fractured during the repair work in the uncoated ceramic where it had rested within the forehearth roof.

The thermocouple assembly was visually examined, evaluated, fully destructively analysed and compared to a traditional clad tri-level thermocouple sheath with a cemented ZGS 10 per cent rhodium-platinum cladding that had been in service for several years in a forehearth at the same container manufacturer (10, 11). The cladding had an original thickness of at least 500 µm.

On visual examination the ACT™ 10 per cent rhodium-platinum coating, and particularly the portion that had been submerged in the molten glass, was found to be in excellent condition, see Figure 2(a). The traditional clad product also appeared to be good, Figure 2(b). However, further examination of the clad thermocouple assembly revealed a significant amount of pore development within the structure of the cladding, Figure 3. This degradation is serious since it would be expected to promote considerable mechanical weakening.

Alloy claddings are essentially separate structures from the underlying ceramic sheathing and are expected to have inherent mechanical strength. When the strength is compromised, as happened here, the integrity of the whole assembly must be at risk. A reduction in the mechanical strength of the component could result in thimble failure and loss, with consequential damage to the thermocouple element.

In comparison, ACT™ coated thermocouple sheaths are simple composite structures. They do not lose integrity in the same way as clad products since the mechanical strength of the platinum group metal coating derives from its intimate contact with the substrate sheath. The ACT™ coating had fully protected the underlying ceramic sheath from glass corrosion, even at the critical air/glass interface. It had performed successfully for 27 months in a molten glass environment, and could have continued in service.

The maximum service life of an ACT™ coated thermocouple assembly is therefore still
unknown, currently being 32 months operating in a forehearth in Scandinavia, as shown in the Table. Ultimately service life will be dictated by specific operating and environmental conditions.

Development of ACT™ Technology for Forehearth Consumables

The natural development of ACT™ coating technology was into forehearth consumables and these applications are achieving major success, as the following case studies illustrate.

Glass composition and chemical homogeneity are largely determined by control at the melting stage and during conditioning of the glass. However, the feeder of the forehearth is crucial for the effective manufacture of components and dictates the shape, weight, thermal homogeneity and compositional homogeneity of the glass gob from which the products are made. The introduction of foreign material or defects at this stage in the manufacture will almost certainly have a discernable and detrimental effect.
on the final product. Thus, the performance of the forming end components: spout bowl, plunger, tube and orifice ring, requires careful control.

For the more expensive and difficult glasses, the quality of the glass in the forming end has often been achieved by the use of components made of massive amounts of platinum group metals, and ACT™ coating technology is unlikely to replace all of this use. However ACT™ technology will enable manufacturers who presently produce lower quality optical and heat resistant glasses to upgrade their products and develop into other markets. For container makers the opportunities presented by ACT™ platinum coatings for forehearth consumables are described below.

**Spout Bowls**

The spout bowl is located at the end of the forehearth, see Figures 4 to 6. The glass flowing down the forehearth, which may be 1200 mm wide and 150 mm deep, is funnelled through a hole in the spout bowl into the orifice ring. Therefore the ceramic bowl, especially the leading edges of the basal hole, is subjected to extremely erosive and corrosive conditions due to the passage of high volumes of molten glass.

If erosion takes place it has a detrimental effect on the maintenance of gob weight control and in some product types defects, such as cord and stones, may be formed. Erosion can also make it impossible to close off the glass flow to allow the orifice ring to be changed, so the whole spout bowl has to be removed and replaced.

Changing the spout bowl is a major operation, requiring the glass in the forehearth to be “frozen off” while the old bowl is removed. Installing a new bowl takes the major part of a shift, and re-establishment of a flow of high quality glass may take several hours.

Thus, changing the spout bowl causes major downtime and production loss, and while it may be possible to schedule changes to coincide with other downtimes, the true cost can be very high. Clearly anything which can extend the intervals between changes, or improve the coincidence with other downtimes, must be beneficial. The following service experience of PLM Redfearn, Barnsley, illustrates that a spout bowl ACT™ coated with platinum can provide these benefits.

The alumino-silicate bowl, installed in May 1993, was in a forehearth used for green glass production. As can be seen in Figure 7, the bowl was partially coated only in the most critical region, that is, around the exit hole. No problems were reported at any time throughout its service, although by December 1993 there were concerns about cracks which had developed in the refractory substrate. While not causing leakage, under normal circumstances the cracks would have been sufficiently serious to indicate that the bowl might not survive until the next scheduled break for maintenance. In fact the ACT™ coating sustained the bowl for a further full year.

When the bowl was finally removed at a planned shutdown it had been in service for
20 months. The area of the bowl carrying the ACT™ platinum coating was separated from the bulk of the ceramic and returned for examination.

The ACT™ coating was found to be intact over the major portion of the original surface, see Figure 8. The refractory substrate was in two pieces, resulting from cracks in the ceramic which had developed after only a few months of service. The regions of the coating that were not associated with any ceramic substrate cracking appeared to have performed superbly. In the areas where the ceramic had cracked the platinum coating had even maintained the profile of the original substrate surface, allowing the glass flow to be shut off.

The ACT™ platinum coating on the critical section of the spout bowl had performed effectively. A very significant extension to its life had been achieved, and downtime, from one or more component changes, had been eliminated. The weakness, if any, lay with the refractory ceramic. The cracking could have presented a problem if the ACT™ coating had not been so stable and effective. In non-ACT™ coated ceramics, cracked areas usually erode more rapidly than the surrounding ceramic, and this accelerated erosion/corrosion would traditionally have

Fig. 7 ACT™ platinum coated spout bowl, partially coated only in the area around the exit hole. Protection of this critical region improves maintenance of gob weight control and allows the glass flow to be consistently closed off during orifice ring changes

Fig. 8 ACT™ platinum coated spout bowl after service of 20 months in container glass. The platinum is still intact and throughout the service life of the bowl the ACT™ coating maintained the profile of the original ceramic substrate
caused extreme variations in both flow and thermal distribution within the glass.

Investigations of the bowl have been undertaken and have provided guidelines for the selection of ceramic substrates.

**ACT™ Coated Feeder Tubes**

Unless protected, all ceramics used in glass making will begin to change dimensionally, due to erosion and corrosion, from the moment they come into contact with the glass. Stable components can be created by ACT™ coating with platinum or platinum alloys.

ACT™ coating of a tube requires a considerable quantity of platinum and in many circumstances, although full coatings are desirable, partial coatings can be satisfactory. A short coating over the bottom edge, terminating below the glass surface is very effective in maintaining efficient stirring and permitting closure to allow orifice ring changes. Some corrosion of the tube may occur at the glass/air interface, but in low corrosion glasses this may be tolerable. A partial coating may thus be very cost effective for many applications.

Several ACT™ coated tubes are currently in service and have been operating for long periods, in a variety of glass types. One stirring tube, examined after it had been in service in TV screen and tube glass for 12 months, was found to have edges which were as well defined as when it entered service.

From this observation and from destructive examinations, there are strong indications that the life of ACT™ coated tubes is as long as those expected for other forming-end components.

**ACT™ Coated Plungers**

Ceramic plungers are the easiest forehearth component to change, but are second only to the orifice ring in their contribution to the control of the final quality of the glass gob. Unprotected ceramic plungers change dimensionally due to the erosion and corrosion caused by the flowing glass. This progressive change must be monitored continuously to allow the plunger movement to be adjusted and so control the weight of the glass gob. While the newer continuous gob monitoring and feedback control systems significantly improve the gob weight control, an ACT™ coated plunger would enable even better control to be achieved.

**ACT™ Coated Orifice Rings**

The orifice ring is the final contact surface for the glass before the gob slides down the chute into the mould for forming. The orifice ring controls the dimensions and shape of the gob, and with the plunger and the tube it controls the weight of the gob. Ceramic orifice rings are made of alumino-silicate or zircon-mullite compositions. They provide adequate performance with respect to thermal shock resistance and erosion resistance, but only for limited periods of perhaps a few days to a few weeks. All unprotected ceramics suffer an initial major erosion followed by a steady state change, which causes the gob diameter and hence the gob weight to vary quite dramatically during service if almost-continuous adjustment of tube and plunger is not made.

However, users of ACT™ platinum-coated orifice rings report that both initial erosion and progressive erosion during use are totally eliminated, even for periods of operation lasting in excess of six months. One of the partially coated triple gob orifice rings shown in Figure 9 operated for over four months without any sign of dimensional change, and provided trouble-free operation limited only by loss of sealing against the underside of the spout bowl. The area of failure was not ACT™ coated, and replacements have been totally coated with an optimum amount of platinum. Many examples of ACT™ coated double gob orifice rings are in operation in the U.K. today. One container manufacturer has successfully operated these fully coated components for over six months.

It has also been found that an ACT™ platinum coated orifice ring of one diameter size can be used to produce a range of gob weights. Normally with unprotected ceramic orifice rings a number of diameters are required. One ACT™ coated diameter can effectively cover a range of diameters, which is explained by its stability. By careful selection of the median diameter and
production scheduling, ACT™ platinum coating technology can be used for orifice rings in forehearths where both different sized containers and continuous runs of the same sized container are produced.

Operational benefits include improved control of the gob weight and a reduction in downtimes caused by the need to change the ceramic orifice ring. Being able to maintain the glass flow between different sized containers also avoids the need to re-establish flow, which otherwise can often result in defects in the glass.

**Refractory Ceramics as Substrates**

While many refractory ceramics are available, current usage tends to limit the range employed within each zone of the glass melting furnace. At the forming end, for example, the choice is dominated by variants of alumino-silicate and zircon-mullite. The one selected is generally a compromise to provide the most appropriate combination of strength, thermal shock properties and corrosion resistance.

ACT™ technology creates a special relationship with the ceramic substrate; the coatings are enhanced by high quality refractory substrates, but can be diminished by poor substrates. At the forming end, the ACT™ coating beneficially modifies the corrosion resistance of the composite structure. Thus, the choice of refractory substrate becomes easier, particularly when fully coated, and selection based on mechanical strength and thermal shock resistance becomes possible, and the compromises needed to select a ceramic are reduced.

In fact ceramic substrates can now be reassessed, perhaps enabling alternative ceramics which have some inherently valuable property, but which have been unusable for reasons such as coloration, to be chosen. Optimised refractory ceramic substrates, compatible with ACT™ coating technology will yield composites having far higher capabilities, such as longer service lives, than currently used materials. Such issues are now being studied.

The quality of the surface finish of the refractories used for ACT™ coating is important. It is not unusual to find pores and gas holes on the surface of a ceramic. In order to develop a surface coating with high interfacial integrity, a pre-coating preparatory stage may be required if the initial quality is poor. This pre-processing is clearly undesirable and refractory ceramic manufacturers must be encouraged to supply materials with the improved quality of surface finish that is now needed.

**Conclusions**

Current trends require glass manufacturers to produce better quality products, and are forcing them to improve efficiency. With brittleness, poor thermal shock resistance, high porosity and poor corrosion/erosion resistance inherent in primary refractory ceramic containment
materials this could present insurmountable difficulties. While cladding, relying on metal strength achieved by using sheets of platinum group metals over refractories has been beneficial for long periods of service, the metal requirement is high and therefore expensive.

New ACT™ coatings effectively combine the best features and properties of both ceramics and platinum group metals, and give the operational durability and efficiency required by the glass industry. ACT™ platinum coating of forming-end ceramics has demonstrated major potential for improving glass making operating practices. It has highlighted the benefits possible in control of gob diameter, shape and weight, and has brought stability to the forehearth operation. Major reductions in downtime now provide higher productivity and lower manufacturing costs.

ACT™ platinum coating for tri-level thermocouple sheaths is now a major world-wide product. Trials that have been undertaken on forehearth forming-end consumables have demonstrated the wider applicability of ACT™ coating technology, from which glass makers are now benefiting. It is anticipated that ACT™ coatings will find increased use in glass furnaces as the best combined features and properties of ceramics and metals are sought. These developments will require the integration of technologies, notably those of the ceramicist, the metallurgist, the glass technologist and the furnace builder to ensure that the maximum benefit is gained by customers and manufacturers.

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Ruthenium Improves Corrosion of Stainless Steel

Duplex stainless steels containing typically chromium, nickel, molybdenum and nitrogen, and having approximately equal volume fractions of austenitic and ferritic phases in their microstructure, are used in aggressive chemical and marine environments where high corrosion resistance is required, such as in heat exchangers, desalination plants, food pickling and mine waters. However, there is always a demand for improved corrosion resistance in these steels to cope with increasingly severe environmental conditions, and much work has been done to meet this. In particular, it is known that small additions of the platinum group metals improve corrosion resistance in stainless steel (1). Similar improvements have been observed after adding platinum group metals to duplex stainless steels with low-chromium contents, but no research had been done on the effects of adding platinum group metals to high-chromium duplex alloys.

Now, research from South Africa, involving immersion in sulphuric acid and electrochemical measurements, has shown that the addition of just 0.28 per cent of ruthenium to duplex stainless steel: iron-29 per cent chromium-14 per cent nickel-3 per cent molybdenum can increase the corrosion resistance of the base alloy by improving the hydrogen evolution efficiency and by inhibiting anodic dissolution (2). Adding ruthenium moved the corrosion potential towards more noble values. As the nitrogen content in these alloys was extremely low, in order to obtain the desired microstructure the nickel content was higher than usual; this additionally benefited the observed corrosion resistance.

References
Recent Developments in Methodologies Using Platinum Group Metal Catalysts

By D. T. Thompson
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Although most catalytic chemical production processes use heterogeneous gas or liquid phase systems, there are a significant number of industrial processes which depend upon the use of soluble platinum group metal catalysts. Separation of catalysts from the products has been a principal hindrance to more widespread use of these systems.

However, recently developed approaches to the use of soluble platinum group metal catalysts are helping to overcome this problem and to provide useful new routes to organic products with significant market potential, particularly for pharmaceuticals. On the other hand, modification of heterogeneous catalysts via adsorption of certain organic species onto their surfaces is making them more selective, and is promoting investigation of their use into areas, such as stereospecific organic synthesis, which to date have been predominantly the province of homogeneous catalysis.

The principal commercial uses of homogeneous catalysts have been recently reviewed (1). These include the carboxylation of methanol (the Monsanto acetic acid process), hydroformylation for n-butyaldehyde and 2-ethylhexanol production (the Johnson Matthey/Union Carbide/Davy McKee process), the Wacker process for the oxidation of alkenes, the Dupont process for the hydrocyanation of butadiene, the oxidation of saturated hydrocarbons and alkylbenzenes, for example, cyclohexane to cyclohexanone and cyclohexanol, and lastly, the Shell Higher Olefins Process (SHOP) which involves catalytic oligomerisation of ethene, followed by isomerisation and alkene metathesis.

A process for the production of ethylene glycol from synthesis gas has been developed by a consortium of four Japanese companies, and the catalyst system that is used is based on either ruthenium or rhodium with a complex collection of additives in a mixed solvent system.

Many of these processes involve platinum group metal catalysts, and their success, at least in part, is due to their efficient use of the catalyst, single catalyst charges having long lifetimes. If it were easier to separate catalysts from substrates, many more applications might be possible for homogeneous systems. Attempts to anchor complexes onto polymeric supports, such as polystyrene and silica are reported to have been only partially successful (2-4). Some new approaches which may lead to significant industrial developments are considered below.

Ligand-Enhanced Biphasic Rhodium Catalyst System

Catalysis at the interface between phases in a biphasic aqueous/organic system can be enhanced using a ‘promoter ligand’. This ligand is soluble in the organic phase but insoluble in the aqueous phase, and will bind to the water-soluble organometallic catalyst, thereby increasing the catalyst concentration at the interface between the phases.

In a recent example, the hydroformylation of 1-octene was studied using a water soluble catalyst system, [Rh(COD)Cl]2/tppts (where COD is cycloocta-1,5-diene and tppts is triphenylphosphine trisulphonate) in a biphasic system:

$$\text{C}_8\text{H}_{17}\text{CH} = \text{CH}_2 \rightarrow \text{C}_8\text{H}_{17}\text{CH}_2\text{CH}_2\text{CHO}$$

$1$-octene $n$-nonaldehyde

$$+ \text{C}_8\text{H}_{17}\text{CH} (\text{CHO}) \text{CH}_3$$

$\text{i$s$o$- nonaldehyde}$

When a ‘promoter ligand’, triphenylphosphine, is added to this system, it binds to the water-soluble organometallic catalyst, thus functioning as an enabling agent. Using this technique, the catalyst concentration is increased at the
interface between the two phases and as a result promotes an enhancement in the reaction rate of between 10 and 50 times (5, 6).

**Polymer-Supported Catalyst Systems**

Ever since the 1970s polymer-supported metal complex catalysts have been investigated, as their use would facilitate the separation of catalysts from products at the end of the reaction. Such materials were hailed as a third generation of catalysts (3), after heterogeneous and homogeneous systems. Polymer-supported metal complex catalyst systems combine reasonable activity with selectivity, specificity and the easy separation of the catalyst. Although activities are usually reduced compared with homogeneous systems, every metal atom is used in the catalysis, and this gives a potential advantage over heterogeneous systems where only a small percentage of the metal atoms (those at the surface) are exposed to the reactants. This last factor can be significant when selecting the platinum metals catalyst systems. As the structures of homogeneous and polymer-supported systems are well defined, their activities can be modified systematically by changing the chemical environment of the active site much more easily than in heterogeneous systems.

Work on polymer-supported catalyst systems is continuing and there are recent reports of interesting selectivities. One such report describes the remarkable synergistic effect of polymer-anchored bimetallic palladium-ruthenium catalysts in the selective hydrogenation of p-chloronitrobenzene, see Scheme I (7). When PVP-PdCl$_2$-RuCl$_3$ (I) (PVP = poly(N-vinyl-2-pyrrolidone)) is used as the catalyst for the hydrogenation of p-chloronitrobenzene in the presence of 0.01 per cent of sodium acetate, and with a palladium:ruthenium ratio of 1:1 or 1:2, selectivities of 94.1 and 94.9 of p-chloroaniline are obtained, respectively. When PVP-PdCl$_2$ (II) was used as the catalyst in the presence of sodium acetate, the normal dehydrohalogenation to aniline took place, giving selectivities of up to 97.8 aniline. Although ruthenium species are not active both for the hydrodechlorination and the reduction of the nitro group of the nitrochloroaniline, the ruthenium species that are formed *in situ* may inhibit the oxidative addition of the carbon-chlorine bond to the active palladium centres.

**Use of Glass Micro-Beads with a Chiral Ruthenium Catalyst**

Stimulated by the demands of the regulatory agencies, there is an increasing market for enantiomerically pure pharmaceuticals and for
insecticides (1, 8, 9). Recent work by Wan and Davis (10, 11) indicates the use of glass microbeads, with controlled pore size for the absorption of a polar liquid (ethylene glycol), together with a chiral ruthenium complex to form a catalyst phase. This catalyst system has been used in synthesis to give a high enantiomeric excess of the important anti-inflammatory agent (S)-naproxen (IV) from 2(6'-methoxy-2'-naphthyl)acrylic acid (III), using hydrogen reduction at a pressure of 94 to 101 MPa and a temperature of 276 to 297 K and a 1:1 mixture of chloroform and cyclohexane as solvent, see Scheme 11.

The ruthenium complex used was [Ru(BINAP)-4SO₃Na(C₆H₅)Cl]Cl and the controlled-pore glass (CPG-240) had an average pore size of 242Å and 120/200 mesh size. At 276 K the enantiomeric excess at 100 per cent conversion of (III) was 96 per cent, and the initial turnover frequency for this system at 297 K was 41/hour compared with 131/hour for the homogeneous system in neat methanol. The high reaction rate and enantiomeric excess for this new homogeneous catalyst are accomplished without loss of ruthenium to the organic phase at a detection limit of 32 ppb.

The success of this new catalyst system is basically the same as the homogeneous system from which it derives, leading to only a small reduction in activity while retaining high enantioselectivity.

**Greater Optical Yield with Platinum Modified by Dihydrocinchonidine**

There have been reports of useful optical yields resulting from the reduction of methyl pyruvate with platinum in the presence of the alkaloid, cinchonidine (9). Recent work, in which the hydrogenation of ethyl pyruvate over dihydrocinchonidine-modified platinum was studied, has indicated a distinct trend of increasing optical yield with increasing conversion, ultimately reaching a plateau of 54 to 58 per cent enantiomeric excess at conversions over 50 per cent (12), see Scheme III.

This trend occurred over a wide range of reaction temperatures where the reaction time to reach the conversion varied from 2 minutes to 2 hours.

It has been concluded that the dynamic adsorption/desorption processes which occur early on in the reaction ultimately establish an equilibrated surface environment, thus allowing the full potential of this system for chiral hydrogenation to be realised.

A second conclusion drawn from this work was a suppression of optical yield for reactions carried out under diffusion limitations. This suggests that the formation of the R(+) -ethyl lactate has a strong positive dependence on the hydrogen concentration. Development of
an overall kinetic model of this reaction is helping to contribute to a greater understanding of chiral heterogeneous catalysis.

**Rhodium Catalysed Rearrangement of 1,2-Diphenylhydrazine**

The complexation behaviour of 1,2-diphenylhydrazine to metals has not been widely studied, but its reactions with samarium and tungsten complexes have resulted in either the formation of hydrazido complexes or cleavage of the N-N bond; no rearrangement of the aromatic hydrazine has been observed. It has been reported recently that 1,2-diphenylhydrazine rearranges exclusively to o-semidine in the presence of square planar rhodium(1) complexes and this reaction is catalytic when there are two cis-sites in the square plane which are occupied by labile ligands (13), see Scheme IV.

Treatment of a dichloromethane solution of [Rh(PPh₃)₂(nbd)]ClO₄ (nbd = norbornadiene = bicyclo[2,2,1]hepta-2,5-diene) containing an equimolar amount of 1,2-diphenylhydrazine with hydrogen gas (with caution, bearing in mind the possible explosion hazard) gives a deep red solution of [Rh(o-semidine)(PPh₃)₂]ClO₄ which contains a bidentate ligand bonded to rhodium.

It is proposed that the rearrangement involves the initial co-ordination of the 1,2-diphenylhydrazine as a bidentate ligand to rhodium(I). Steric constraints then place the phenyl rings of the co-ordinated ligand in a perfect position to allow the exclusive formation of o-semidine via a similar mechanism to that which occurs in the acid-catalysed benzidine rearrangement.

**References**


**Conference on Chemistry of the Platinum Group Metals**

The Sixth International Conference on the Chemistry of the Platinum Group Metals will be held at York University, England, from 21st to 26th July 1996. The conference, organised by the Dalton Division of the Royal Society of Chemistry, is convened by Professor R. N. Perutz. Keynote speakers are H. Takaya, M. Brookhart, P. Sadler, M. Grätzel, O. Eisenstein and G. Ertl. Both oral and poster contributions will be welcome. For further information contact Dr John F. Gibson, R.S.C., Burlington House, Piccadilly, London W1V 0BN, UK; Fax: 0171-734-1227.
European Precious Metals Conference

NEW TECHNOLOGY AND ADVANCES IN AUTOMOTIVE APPLICATIONS

The Second Eurometaux Precious Metals Conference, organised by members of the European precious metals industry, was held in Lisbon from 10th to 12th May, 1995. The industry is seeing the spread of environmental legislation which is imposing new constraints on it, but at the same time is also creating opportunities for the development of new technologies and uses. Around 200 representatives from European and other noble metals industries attended the conference. Here we present a selective review of some of the platiniferous work reported at the sessions on advances in precious metals applications, and especially on recent innovation in automotive applications.

Precious Metals Applications

A paper by H. H. Beyer of Degussa reported on a method for surface hardening platinum, by the use of boron for jewellery applications. A hardened layer suitable for polishing is produced when a boriding agent diffuses into platinum during heating for three hours at 600°C. Beyer also outlined the use of electroforming for the production of thinner, hollow, intricate jewellery. A system where platinum is electroformed using titanium electrodes at 75°C is now being tested and is expected to become commercially available soon.

Palladium in Contact Bonding

The use of palladium and palladium alloys for contact and bonding applications was discussed by J. Wachter of W. C. Heraeus. For many years palladium has been used in the manufacture of switch contacts. When palladium only is used, a brown powder is formed during operation in an organic gas environment.

The substitution of silver to form a 70 per cent palladium-30 per cent silver alloy significantly reduces the powder formation, and more recently the introduction of copper to form a three-way alloy has increased the tensile properties of the alloy. If palladium-only contacts are required, the formation of brown powder can be reduced to minimal levels by the introduction of a gold film. This also serves to increase the wear resistance of the contact.

Palladium Powders in Microelectronics

A paper describing the use of palladium metal powders for microelectronics was presented by E. M. Meyer of Metalor. Palladium used in the electronics industry accounts for around 47 per cent of the total demand. Palladium is used in bonding applications via ultrasonic friction or press welding, and one of the largest bonding applications is in the production of microelectronic devices. Here layers of palladium powder are sandwiched between barium titanate to form a circuit.

Advances over the years have resulted in smaller devices requiring a continuous layer of palladium powder, which must be free of lumps. With the constant demand for yet smaller electrical devices, new methods will be required to produce finer palladium powders.

Deposition Processes

Various methods of deposition of the platinum group metals, and the components formed using these processes, were discussed by D. A. Toenshoff and R. D. Lanam, Engelhard, (EI). While salt plating is inexpensive, it is difficult to vary the substrate, and the deposit has to be relatively thick. Sputter coatings, however, which need to be only half as thick, retain the same properties as salt coatings, and can utilise many different substrates. New applications for sputter coatings include power tools coated with platinum, platinum on tungsten for the lighting industry and platinum coated wires for pacemakers.

A second process, known as the “PDC” process, described enhanced plasma and high velocity oxygen fuel coating techniques, which are used to deposit fine layers of precious metals. Such techniques are being developed towards
the fabrication of finished forms. Coatings that were mentioned included platinum, iridium and platinum/rhodium.

Electroforming technology can purify the platinum group metals, as well as form complex shapes of platinum group alloys and refractory metals and has been used by EI to produce iridium crucibles. The electrolyte is a complex salt of the metals with halogenoids of alkaline metals. Electroforming takes place from the halogenoid melt under inert gas at elevated temperature, using an anode of the metal to be deposited and a shaped mandrel which determines the geometry of the final component. The advantage of this method is that it produces extremely pure metal. EI are developing this process for ruthenium and iridium products.

**Iridium**

A paper by D. Lupton of W. C. Heraeus and B. Fischer of Jena Polytechnic reported on the difficulties in processing iridium, due to its high rate of work hardening and the deleterious effects of small levels of contaminants segregating strongly to grain boundaries. It pointed, however, to the excellent high temperature strength of iridium, and showed its stress rupture properties at 1800°C to be comparable to those of platinum-rhodium or dispersion strengthened alloys operating at much lower temperatures.

**Advanced Coating Technology**

A paper by P. N. Duncan and W. G. Hall of Johnson Matthey discussed the recent development of a process for thermally depositing platinum onto a wide range of ceramic and metal substrates. This process of advanced coating technology, known as ACT™ has progressed dramatically beyond the development phase to find wide-scale applications notably in the glass industry. The process, which is described elsewhere in this journal, enables the best use of the surface properties of platinum, providing corrosion protection, and the mechanical strength of the substrate materials. Complex shapes can be coated, taking platinum into new areas of application where traditional cladding processes have proved impossible. The benefits to end users in the glass industry are a substantial reduction in downtime and an increased product yield, two factors which are expected to cause the ACT™ technology to grow rapidly in this field. A wide range of examples were given, showing ACT™ products before and after use in different glass types.

**Automotive Applications**

The session on innovation in automotive applications looked at the role of the noble metals, particularly the platinum group metals, in motor vehicles. Emission standards for motor vehicles are being set at increasingly stringent levels in a growing number of countries, and all new motor vehicles are now designed with platinum group metal catalysts to control the emissions of carbon monoxide, hydrocarbons and nitrogen oxides to these legislated levels.

The increasing growth in the use of diesel engines for passenger transport, and especially for cars in Europe, has drawn attention to the ultra fine particulates with a mean diameter of less than 10 μm, PM10s, which are emitted by diesel engines. Platinum group metals assist in the regeneration of self-cleaning particulate traps and filters to control these emissions. While carbon dioxide is not a legislated pollutant, it is the major “greenhouse” gas contributing to global warming, and increasingly more countries are encouraging the development of fuel-efficient cars, which limit the production of carbon dioxide. The growth in electronic systems designed for fuel efficiency, safety and comfort in new cars all involve precious metals for contacts, capacitors and circuitry.

**Legislation and Metal Consumption**

The first paper by R. A. Searles of Johnson Matthey reviewed emission standards around the world and the accelerating rate at which countries are adopting standards requiring platinum group metal catalysts for emission control. While only North America and Japan used platinum group metal catalysts between 1975 to 1985, by the end of the century all the major established and developing car markets of the world are expected to require the use of...
platinum group metal catalysts. This he ascribed to the growing problems caused by transport-related pollution, and the fact that the markets that develop new engines and models have tough emission limits to which all new cars are required to comply.

The new standards set in California and the Northeastern States are actively being considered for the rest of the U.S.A. and for the European Union, and these would require greater dependence on catalyst technology and more platinum group metals in each car. The technology required to satisfy these tighter regulations includes additional starter or light-off catalysts, faster acting catalysts (from a cold start) and catalysts with auxiliary heating (either electrical or by injecting a small amount of fuel).

In May 1995 it was exactly 21 years since Johnson Matthey and other manufacturers had delivered the first production quantities of autocatalysts to the U.S.A. and Japan, and 1995 is the first year in which the majority of cars in the world have catalysts. Johnson Matthey has estimated that there are now 255 million platinum group metal catalyst-equipped cars in the world, out of a total of 491 million cars, and by the year 2000 56 per cent of the car population, or 310 million cars, are expected to have catalysts.

While total demand for new platinum group metals has doubled between 1975 and 1995, their use in autocatalysts during this period has increased more than 7-fold and presently accounts for 36 per cent (3,750 thousand ounces) of all new platinum group metals produced. By 2000 the gross demand for platinum group metals for autocatalysts is predicted to increase to 5,170 thousand ounces, of which 46 per cent will be new metal.

Diesel Emissions Control

The role of platinum group metal catalysis in the control of diesel emissions was reviewed by G. Smedler of Johnson Matthey. He described the differences between petrol and diesel fuels and emphasised the twin challenge of low temperatures and lean operation for the catalyst engineer, with excess air making it impossible to apply classical three-way catalysis. However, the popularity of diesel engines has increased due to their better fuel economy and improved power and performance, and catalyst technology is being developed and applied to enhance their environmental performance.

Smedler reviewed oxidation catalysts, lean NOx and four-way catalysts and particulate filters (with catalytic regeneration). Oxidation catalysts control carbon monoxide, hydrocarbons and some of the particulates, by oxidising the volatile organic fraction. It is necessary to avoid increases in the level of sulphur trioxide in the exhaust since sulphate formation can contribute to particulate levels. Sulphate formation is minimised at exhaust temperatures of less than 400°C, but there is still a problem for engines with exhaust temperatures above 500°C and in these cases the use of the low sulphur level diesel fuels, now becoming widely available, can alleviate any environmental problems.

However, lean NOx control of the diesel engine emissions is still required. Smedler reported that a most elegant method for the decomposition of nitric oxide and other nitrogen oxides (NOx) to nitrogen and oxygen without the formation of by-products had been demonstrated on pre-reduced precious metal, particularly rhodium. However, to maintain the pre-reduced state requires the addition of selective reduction agents. Ammonia, urea and diesel fuel had been tried. Results from several systems, including platinum on alumina and copper on zeolite, were reported; these had achieved NOx conversions of 30 to 45 per cent. Progress towards overcoming the disadvantages of both systems were described.

The concept of the four-way diesel catalyst for controlling emissions of carbon monoxide, hydrocarbons, NOx and particulate was introduced. Limited ageing on experimental catalysts had shown conversions of 92 per cent, 88 per cent, 17 per cent and 37 per cent, respectively. Finally Smedler reviewed systems for filtering and destroying particulate emissions. These systems can be either active or intermittent, using burners or heaters or be passive continuous systems. Ceramic honeycomb wall flow filters are best for meeting the requirements.
The collected particulate must be destroyed by burning.

One system which had demonstrated high levels of particulate removal (and carbon monoxide and hydrocarbon oxidation) with reliable regeneration was the Johnson Matthey continuously regenerating trap, CRT. This system increases the level of nitrogen dioxide in the exhaust by oxidation of nitric oxide using a platinum catalyst. Soot is trapped on a following ceramic wall flow filter. Nitrogen dioxide, which is a powerful oxidising agent, lowers the soot/particulate oxidation temperature from 600 to 250°C. Field trials have demonstrated conversion levels for carbon monoxide, hydrocarbons and particulate of well over 90 per cent and reliable operation on a variety of engines, provided that the inlet temperature to the CRT only exceeds 250°C occasionally and that sulphur levels in the fuel are less than 100 ppm.

Three-Way Catalysts

The role of noble metals in modern three-way catalysts was reviewed by J. Mooney of EI, with respect to emissions standards, the effect on fuel quality as the level of lead is reduced and reformulated gasoline in California which contains reduced sulphur levels. He described how three-way catalyst design in North America is moving away from the original platinum/rhodium catalyst towards the use of palladium/rhodium and palladium-only systems, while in Europe platinum/rhodium and platinum/palladium/rhodium systems are mostly preferred. He said that in emerging world markets, where there was less high quality fuel, use of the platinum/rhodium three-way catalyst systems would be preferred.

After describing the operation of a three-way catalyst and the functions of the platinum and palladium as oxidation catalysts, and rhodium as a NOX reduction catalyst, he went on to discuss the mechanisms occurring on the catalyst surface. These include the role of base metal components, such as cerium, which by an oxygen storage mechanism, widened the operating window. Improved performance was achieved by separating the platinum group metals into different layers in the washcoat. He also described a unique proprietary palladium-only catalyst which could only function with the quality of fuel available in the U.S.A.

Other Automotive Uses of Platinum Group Metals

The application of precious metal contacts in automotive applications was discussed by R. Schnabl of Heraeus who reported on the significant increase in electrical systems utilising electrical contact materials in modern cars. These systems, important for reliability and safety, increasingly depend on precious metals in the contacts. Typical service requirements for robust contact materials used to switch currents of up to 100 amps and for carrying electrical signals in the milliamp and millivolt ranges are: 2.5 million switches/lifetime at temperatures up to 180°C in the presence of corrosive pollutants, with vibrations in the kilocycle range and accelerations up to 100 g. Schnabl described the use of silver/nickel and palladium/copper contacts in headlamp relays, copper contacts plated with gold or palladium/silver alloy for critical systems like airbags and brake controls. Increasingly potentiometers are used to monitor the position of throttle pedals, chokes, mirrors and seats, and require palladium-silver alloy wiper or slide contacts alloys. More demanding applications using sliding contacts in servo motors require gold or platinum alloys with copper or nickel to meet greater resistance to welding and erosion.

Recycling Catalytic Converters

The final paper in the session was presented by C. Hagelüken of Degussa, who reviewed the recycling of automotive catalyst converters. Recycled platinum, palladium and rhodium from autocatalysts already account for 18, 14 and 9 per cent, respectively, of gross demand, with most recycled platinum group metals coming from North America – an estimated 6,000 to 8,000 tons/year of autocatalyst substrate (containing 7 ton platinum, 2 ton palladium and 0.6 ton rhodium), and Japan, estimated at 1,500 to 2,000 tons/year (containing 1.7 ton platinum, 0.5 ton palladium and 0.15 ton rhodium). In Europe in 1994 only 250 tons of autocatalyst
substrate were available for recycling; this contained 400 kg of platinum and 70 kg of rhodium. In Germany the number of cars sold with catalytic converters has risen from 50,000 in 1985 to 3.3 million in 1992. Hageluken estimated that by the end of 1994 there were 40 million catalyst-equipped vehicles in Europe and this would increase by 10 million cars during 1995. At present some 8 million cars are scrapped each year, but very few are fitted with converters.

Hageluken reviewed the system of returning scrap catalytic converters to the precious metal refiner as well as the hydrometallurgical and pyrometallurgical methods of platinum group metal recovery and separation. By the year 2000 it is anticipated that 3,500 to 4,000 tons of autocatalyst substrate should be available annually for platinum group metal recovery.

In conclusion, continuing advances in the precious metals industries, even since the first Eurometaux conference was held in 1993, together with the driving force of legislation to cope with levels of pollutants in the environment, will ensure that the interest in innovation within the European refining and fabrication industries for noble metals, remains at a high level. The Proceedings of the Conference will not be published, but papers may be obtained from Eurometaux, Av. de Broqueville, Brussels, Belgium.

A Comprehensive Commentary on the Platinum Metals

The Platinum Group Metals: A Global Perspective


Frank Vermaak, a prominent South African geologist, has undertaken the daunting task of writing a comprehensive overview of the geology, production and consumption of the platinum group metals. His aim is to provide a down-to-earth review, accessible to a wide audience, of all aspects on the platinum group metals and to suggest future developments.

With his long experience in the platinum industry, Dr Vermaak is ideally placed to provide a thorough review of world resources and production of platinum group metals; and he devotes the first half of the book to this, outlining the occurrence of these metals in deposits across the world. He then considers output by producer, and concludes with a discussion of the technical issues involved in mining, beneficiation and refining. Much of this section concentrates upon South Africa, but there is also extensive information on platinum group metal resources and production in the U.S.A., Canada, China and Australia. This section performs a valuable service in bringing together information on smaller producers which, because of their relative insignificance in terms of total world supply, are not often reviewed elsewhere. He also includes a long discussion of platinum group metals deposits and output in Russia, although he admits that "vital data on tonnage and grade remain pretty much guesswork".

One chapter examines the marketing, distribution, trading and pricing of platinum group metals, especially up to 1992, with graphs showing the long-term price trends. Dr Vermaak also discusses trends in world consumption of platinum group metals between 1981 and 1992, providing detailed tables of usage by region and by application.

The latter part of the book provides an introduction to the many applications of the platinum group metals. One chapter discusses catalysis, and covers development and manufacture of autocatalysts and reviews environmental legislation. However, due to the extended timescale required for the production of such an ambitious treatise, Stage II European Union emissions standards and the improvements in catalyst technology which have permitted increased use of palladium in autocatalysts are not mentioned. Another chapter deals with chemical, glass and electronic applications.

Finally, Dr Vermaak examines future demand and supply of the platinum group metals. He devotes a chapter to the prospects for significant platinum usage in fuel cells; there is detailed discussion of the different types of cell, their potential applications, and progress towards commercialisation. The book ends with an examination of the social, political and economic factors influencing the outlook for demand and supply, concentrating upon the impact of the political changes in South Africa and Russia.

"The Platinum Group Metals" is a valuable addition to the literature on this subject. It should prove particularly useful for the reader seeking an expert overview of the background, geology and resources, and the uses to which the platinum group metals are put.

A.J.C.
Palladium Alloy Pinning Wires for Gas Turbine Blade Investment Casting

By D. C. Power
Johnson Matthey Noble Metals, Royston

Turbine blades in aero-engine and land-based power generation gas turbines are complex components manufactured to precise geometric, structural and mechanical property tolerances. High pressure turbine blades used in the hottest, most hostile and demanding sections of gas turbines often contain integral cooling channels. The production of such cooling channels has been a significant advance in gas turbine efficiency and emission control. Pinning wires are used during mould preparation and investment casting of the blades for reliable manufacture of the cooling channels. Traditional platinum-based materials and new palladium-refractory alloys for use as pinning wire are discussed here.

Gas turbine engines find widespread use for aircraft and marine propulsion and for land-based power generation. The engines consist of an inlet duct followed in sequence by a compressor section, combustion chambers, high and low pressure turbine sections and an exhaust duct. Gas turbine engines operate on the simple principle of converting heat energy into mechanical work, by taking a large volume of air, compressing it to high pressure, mixing the compressed air with fuel and then igniting it. Propulsion or power generation is obtained by the very rapid expansion of this ignited fuel-air mixture through the turbine blades.

Thermodynamic efficiency is an important consideration in gas turbine engine design, most particularly for those turbines destined for the aerospace market where the power:weight ratio and fuel efficiency are of major concern. A significant parameter in the equations which describe thermodynamic efficiency is the temperature difference that can be achieved across the engine. Designers of turbine engines try to maximise the operating temperature of the turbine section of the engine, or more specifically, the high pressure turbine section. However, there are limitations. A turbine is composed of hundreds of turbine blades which rotate at very high speed on a series of coaxial disks. Operating stresses and temperatures are therefore very high and further increases in operating temperature, even if only marginal, can profoundly reduce the service life of these blades.

Over the years, designers have actually been able to achieve higher operating temperatures at the same time as improving the service life of
Fig. 2 A section through a 2-inch long high-pressure turbine blade exposing the internal network of air cooling channels

The technology of incorporating cooling channels within turbine blades has traditionally been applied to aircraft propulsion plant. More recently designers of land-based gas turbines are showing interest in applying this technology to create cleaner, more efficient power generating plant. The higher operating temperatures that are possible using cored turbine blades improve thermodynamic efficiency and, significantly, reduce nitrous oxide emissions.

The cooling channels are produced by placing ceramic cores within the mould cavity in which the turbine blade is cast. These ceramic cores are subsequently dissolved out of the cast turbine blade, leaving behind the required network of cooling channels. Precise positioning of the ceramic cores within the mould cavity, and maintenance of that position throughout an elaborate series of mould preparations, firing and blade-casting processes are vital for achieving blade dimensional stability/tolerances. However, the ceramic cores have a very high length to diameter ratio and are only poorly supported within the mould cavity. To overcome this difficulty pinning wires are anchored in the mould cavity wall and butt against the ceramic cores. The pinning wires are used to maintain core position.

Platinum-based materials have traditionally been used for ceramic core pinning. Seven to ten pins, each of 5 to 10 mm long are typically required for a 2 inch high-pressure aero-engine turbine blade. Platinum-based materials are
used because of their proven ability to maintain ceramic core position and subsequently dissolve into the turbine blade without any deleterious effects on the structure or properties of the blade material. Oxide dispersion strengthened platinum and, more recently, pure platinum have seen extensive application in this area.

A drawback to the more widespread use of platinum-based pinning wires is the cost of the raw material. Recognising this, Johnson Matthey Technology Centre embarked on a programme of work to develop novel pinning wire materials (1). This paper discusses some of the functional requirements of pinning wires and shows how these have been met by alloy design. So far, this work has led to the development of a range of commercial, novel pinning wire alloys based on palladium and specific refractory metals (2) and the acceptance of one alloy by Rolls-Royce plc. This alloy is cheaper than platinum and has been shown to give comparable performance.

**Turbine Blade Manufacture**

Turbine blades have a complex geometry and contain many areas of double curvature. Therefore the blades have to be precisely manufactured by the precision casting process of investment casting, also known as the 'lost wax process'. Ceramic cores for the cooling channels are positioned within a master mould pattern. Wax is then injected into the mould cavity to produce a preform of the turbine blade. Pinning wires are then pressed through the wax to butt against the ceramic cores within the preform. Next, the preform is coated with multiple layers of ceramic, ultimately forming a thick casing around the preform with the pinning wires embedded in it. The assembly is heated to melt out the wax and then fired to strengthen the ceramic. The result is a ceramic shell mould containing a complex ceramic core pattern which is held in position by pinning wires anchored in the ceramic shell, see Figure 3. Finally, the mould assembly is preheated prior to casting the turbine blade.

Turbine blade manufacture crucially requires the nucleation and growth of precisely controlled microstructures. The grain structure within the turbine-blade superalloy material is frequently described by terms such as ‘equi-axed’, ‘directionally solidified’ and ‘single crystal’. These characterise the grain boundary length and thus
ultimately the performance of the turbine blade.

Equi-axed blades contain many small grains of similar size having no preferential orientation. These types of blades are widely used in the cooler parts of an engine. Directionally solidified blades offer significant advantages in mechanical performance over equi-axed blades, due to the preferred crystallographic orientation of the grains and the avoidance of transverse grain boundaries. Such blades are used in the hottest parts of the engine where service conditions are the most arduous. The very best performance is given by the single crystal turbine blade, but unfortunately these are very expensive and therefore not as widely employed as directionally solidified blades, though their use is increasing.

Pinning Wire Alloy Design and Functional Requirements

The primary function of the pinning wires is to maintain the position of the ceramic cores during mould preparation and casting. While doing this the pinning wires must be able to survive exposure to the mould preparation conditions and must not have any deleterious effects on the mechanical properties or integrity of the turbine blade. Mould preparation conditions differ from one blade manufacturer to another and are also dependent upon the type of turbine blade being cast. The highest usage of pinning wire is currently in the manufacture of directionally solidified aero-engine blades — although there is an increasing amount of interest from manufacturers of land-based turbines. The alloy development programme therefore concentrated on directionally solidified blades for aero engines.

Typical mould preparation conditions include air firing (sometimes in oxygen-rich air) at temperatures up to 1100°C, followed by preheating and casting under vacuum at temperatures of about 1500°C. Processing times for each of these stages can vary from between 20 minutes to many hours. These conditions mean that the pinning wire must be resistant to oxidation, and have high temperature stability under vacuum.

Precise control of the grain structure of a turbine blade is necessary during its manufacture if the blade is to perform reliably during service. However, pinning wire oxidation and the subsequent entrapment of oxide within the molten superalloy can lead to the nucleation and growth of undesirable grains. This must be avoided, particularly in directly solidified and single crystal blades. Since most metals survive exposure to air at high temperatures by the formation of a stable oxide layer then clearly there are significant constraints on the design of a pinning wire alloy.

The pinning wire must be able to maintain its primary function of core pinning at temperatures up to the melting point of the superalloy.

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It must subsequently disperse quickly and completely within the superalloy, and the effects of these small additions of metal from the pinning wires must not poison the precipitation hardening reactions or compromise the mechanical properties of the superalloy.

**Alloy Design**

Several types of materials were examined as pinning wires before a selection was made. Superalloys were considered because of their compatibility with the turbine blade material. However, superalloys might present problems resulting from oxidation during initial firing of the mould. This would probably lead to adverse grain nucleation. Clearly the pinning wire needs to possess good oxidation resistance, and in this platinum is exceptional. Oxidation is a surface phenomenon and hence a platinum coating over a base metal substrate could suffice, with the platinum providing the necessary oxidation resistance and the base metal core providing the stiffness and mechanical strength needed at high temperatures.

Structures utilising a platinum coating over a base metal have many potential engineering applications. However, there is a drawback for this present use, in that the cut ends of the pinning wire could expose the vulnerable base metal core and ultimately undermine the structural integrity of the pinning wire.

Materials and alloys possessing high thermal expansion were also considered as pinning alloys. The length of a typical 8 mm long oxide dispersion strengthened platinum pinning wire increases by about 0.12 mm (0.005 inches) between temperatures of 20 and 1400°C. If pinning wire with a higher thermal expansion were used then it would exert an even greater pinning force on the ceramic cores during mould preparation. The use of such materials appears practical until both the heating and cooling cycles are considered: cooling nullifies any beneficial effects gained from having a high thermal expansion. However, there is merit in using these materials if high thermal expansion is achieved only during the final preheat stage of the mould preparation process (that is, there is no subsequent cooling) following an order-disorder transformation.

Palladium was finally chosen as the most promising material for pinning wires as it offers comparable oxidation resistance to platinum at temperatures up to about 900°C (3). Being half as dense as platinum and currently costing around $155 per ounce, compared with around $440 per ounce for platinum, it offers potential savings in materials. Previous work had demonstrated that palladium behaved in a similar manner to platinum when dissolved in a nickel-based superalloy (4, 5). However, it was considered that palladium by itself was unlikely to be able to meet the service conditions as well as platinum; the principal reason being that its melting temperature, 1554°C, is far too close to the final mould preheat temperatures involved in turbine blade casting. Development work therefore concentrated on improving the high temperature capability of palladium by alloying with refractory metals.

**Development and Experimental Work**

When the development programme commenced, no information was available on the length of time that a pinning wire was required

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to survive within the molten superalloy during casting of directionally solidified aero-engine blades. In the first experiments the recession rates in molten superalloys of a number of different platinum and refractory metal wires, including oxide dispersion strengthened platinum (the standard pinning wire material) were compared.

The experiments revealed that when oxide dispersion strengthened platinum wire of diameter 1.4 mm (more than four times the cross-sectional area of standard pinning wire) was dipped into molten nickel-based superalloy to a depth of about 20 mm for three seconds, the wire completely dissolved, see Figure 4. By comparison, smaller diameter platinum-rhodium and platinum-iridium wires suffered significant dissolution and reduction in their length. While a platinum-8 per cent tungsten alloy also suffered dissolution, this was at a much slower rate than for the other alloys, and it still retained its original length. Full results of these investigations are shown in Table I. Clearly there is a relationship between the melting temperature and the dissolution rate. It may also be suggested that the dissolution rates of the platinum alloys are more related to the melting temperature of the alloying element, rather than to the melting temperature of the alloy itself.

This initial work demonstrated that prospective new pinning wire materials do not need to survive in the molten superalloy for very long to be successful. In fact, it emphasised the importance of rapid dissolution in order to ensure that no concentration of pinning wire material exists anywhere within the turbine blade.

Following these melt exposure tests, the experimental programme next examined the oxidation properties of samples and evaluated their high temperature stability under vacuum. Temperatures and times of exposure were selected following consultation with major aero engine manufacturers. Oxidation tests to simulate different ranges of mould firing conditions were performed at 850°C for 18 hours and at 1075°C for 8 hours. The same samples were then placed under vacuum at 1475°C for up to one hour. Tests were also conducted in air at 950°C for 70 minutes followed by 30 minutes under vacuum at temperatures of 1500 to 1550°C. Results are shown in Tables II, III and IV. Samples were assessed by weight change,
### Table III
**Assessment after 8 hours at 1075°C in Air (Stage 1) and 30 minutes at 1475°C under Vacuum (Stage 2)**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Weight change after Stage 1, per cent</th>
<th>Weight change after Stage 2, per cent</th>
<th>Observations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd-20%W</td>
<td>+0.8</td>
<td>-17.4</td>
<td>Very minor surface blistering after Stage 1, oxide penetration to 0.3 mm; no deterioration in surface condition after Stage 2 but all oxide vaporised to leave Pd-rich surface</td>
</tr>
<tr>
<td>Pd-15%Mo</td>
<td>-11.2</td>
<td>-28.2</td>
<td>Internal delamination and oxide penetration to 0.5–0.6 mm after Stage 1; oxide was vaporised during Stage 2 but delamination increased</td>
</tr>
<tr>
<td>Pd-16%W-4%Ir</td>
<td>+0.1</td>
<td>-9.9</td>
<td>Surface blistering after Stage 1, oxide penetration to 0.2–0.3 mm; most oxide vaporised during Stage 2</td>
</tr>
<tr>
<td>Pd-11%Mo-4%Ir</td>
<td>-1.9</td>
<td>-10.3</td>
<td>Slight surface discoloration after Stage 1, oxide penetration to 0.2 mm; substantial removal of oxide after Stage 2</td>
</tr>
<tr>
<td>Pd-15%W-5%Pt</td>
<td>+0.7</td>
<td>-7.5</td>
<td>Obvious surface blistering after Stage 1, oxide penetration to 0.2–0.4 mm; blistering disappeared after Stage 2, leaving behind an intermittent oxide layer to a depth of 0.1–0.3 mm</td>
</tr>
<tr>
<td>Pd-10%Mo-5%Pt</td>
<td>0</td>
<td>-2.9</td>
<td>Surface condition perfect after both Stages; oxide penetration to 0.13 mm was substantially stable during Stage 2</td>
</tr>
<tr>
<td>Pd-10%Mo-5%Ta</td>
<td>-2.1</td>
<td>-4.0</td>
<td>Surface condition perfect after both Stages; oxide penetration to 0.3 mm substantially stable during Stage 2</td>
</tr>
<tr>
<td>Pd-15%W-10%Au</td>
<td>+1.1</td>
<td>-5.1</td>
<td>Very good surface condition after Stage 1, oxide penetration to 0.25 mm; substantial loss of oxide from near surface regions after Stage 2</td>
</tr>
<tr>
<td>Pd-20%W-10%Au</td>
<td>+1.2</td>
<td>-11.3</td>
<td>Severe surface oxidation to depth of 0.34 mm evident after Stage 1; blistering disappeared after Stage 2, leaving an intermittent oxide layer</td>
</tr>
</tbody>
</table>

### Table IV
**Assessment after 70 minutes at 950°C in Air (Stage 1) and 30 minutes at 1500 to 1550°C under Vacuum (Stage 2)**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Observations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd-15%Mo</td>
<td>Oxidation to 0.04 mm depth after Stage 1; complete removal of oxide layer by vaporisation after Stage 2, leaving behind a Pd-rich surface region</td>
</tr>
</tbody>
</table>
Table V
Pinning Wire Dissolution in Nickel-Based Superalloys
(Analysis of Investment Cast Turbine Blades)

<table>
<thead>
<tr>
<th>Pinning wire alloy</th>
<th>Nominal concentration in turbine blade</th>
<th>Analysis site</th>
<th>Dispersion within turbine blade</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Platinum, per cent</td>
<td>Palladium, per cent</td>
<td>Platinum, per cent ± 0.05</td>
</tr>
<tr>
<td>Pd-15%Mo</td>
<td>-</td>
<td>0.21</td>
<td>Root</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Blade</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Tip</td>
</tr>
<tr>
<td>Pd-20%W (Pt coated)</td>
<td>0.01</td>
<td>0.19</td>
<td>Root</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Blade</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Tip</td>
</tr>
<tr>
<td>Pt</td>
<td>0.25</td>
<td>-</td>
<td>Root</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Blade</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Tip</td>
</tr>
</tbody>
</table>

appearance and by metallographic examination.

Collaboration with Rolls-Royce plc enabled an in situ assessment to be made of prototype alloys for pinning wire, using commercial production equipment and techniques, and the materials typically utilised in the manufacture of directionally solidified blades. The assessment included grain nucleation testing, evaluation of pinning wire dissolution within turbine blades, see Table V, stress rupture testing, see Table VI, and statistical evaluation of core drift under production conditions. Finally the

Table VI
Longitudinal Stress Rupture Properties

<table>
<thead>
<tr>
<th>Nickel-based superalloy</th>
<th>Pinning wire used</th>
<th>Amount of pinning wire in superalloy, wt. %</th>
<th>Test temperature, °C</th>
<th>Applied stress, MPa</th>
<th>Sample size</th>
<th>Average life, hours</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>none</td>
<td>-</td>
<td>1040</td>
<td>145</td>
<td>3</td>
<td>52</td>
</tr>
<tr>
<td>&quot; X</td>
<td>0.25</td>
<td>&quot;</td>
<td>145</td>
<td>4</td>
<td>48</td>
<td></td>
</tr>
<tr>
<td>&quot; Y</td>
<td>0.25</td>
<td>&quot;</td>
<td>5</td>
<td>39</td>
<td></td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>none</td>
<td>-</td>
<td>850</td>
<td>500</td>
<td>3</td>
<td>79</td>
</tr>
<tr>
<td>&quot; X</td>
<td>0.25</td>
<td>&quot;</td>
<td>5</td>
<td>69</td>
<td></td>
<td></td>
</tr>
<tr>
<td>&quot; Y</td>
<td>0.25</td>
<td>&quot;</td>
<td>5</td>
<td>75</td>
<td></td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>Pt</td>
<td>0.25</td>
<td>1040</td>
<td>145</td>
<td>3</td>
<td>56</td>
</tr>
<tr>
<td>&quot; X</td>
<td>0.13</td>
<td>&quot;</td>
<td>3</td>
<td>60</td>
<td></td>
<td></td>
</tr>
<tr>
<td>&quot; Y</td>
<td>0.15</td>
<td>&quot;</td>
<td>3</td>
<td>62</td>
<td></td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>Pt</td>
<td>0.25</td>
<td>850</td>
<td>500</td>
<td>3</td>
<td>84</td>
</tr>
<tr>
<td>&quot; X</td>
<td>0.13</td>
<td>&quot;</td>
<td>3</td>
<td>87</td>
<td></td>
<td></td>
</tr>
<tr>
<td>&quot; Y</td>
<td>0.15</td>
<td>&quot;</td>
<td>3</td>
<td>92</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

A is a proprietary Ni-based superalloy used for directionally solidified turbine blades
X = Pd-15%Mo pinning wire
Y = Pd-20%W pinning wire with 5 μm Pt coating
The proposed new pinning wire alloy was batch tested alongside platinum pinning wire and subjected to stringent production control tests.

**Discussion**

Oxidation testing and high temperature stability testing clearly demonstrated the ability of platinum to survive unscathed in these arduous environments. In comparison, palladium almost disappeared when exposed to high temperatures under vacuum. However, there was a profound improvement in the high temperature stability of palladium when it was alloyed with particular refractory metals. Molybdenum and tungsten additions to palladium, at levels of 15 per cent and 20 per cent, respectively, were most notable in this aspect. Furthermore, additions of refractory metals to palladium promoted a higher degree of grain stabilisation than could be achieved in platinum, palladium or palladium-platinum-refractory metal alloys. Exposure of palladium-molybdenum and palladium-tungsten alloys to temperatures of 850 and 975°C in air caused far less surface oxidation than was expected. Unalloyed tungsten, and especially molybdenum, undergo rapid, if not catastrophic, oxidation when exposed to these temperatures. The behaviour of palladium-molybdenum was particularly interesting; exposure to temperatures of 850 and 975°C in air resulted in surface oxidation and the formation of voids close to the surface. These voids are thought to be the result of molybdenum oxide formation and volatilisation following oxide migration to the surface of the metal. Subsequent exposure to vacuum at high temperatures ensured the complete removal of any remaining oxide by volatilisation, leaving behind a pure palladium outer layer with a core of palladium-molybdenum.

Cleaning up the surface of the alloy by volatilisation of the oxide avoids adverse grain nucleation in the superalloy through oxide entrapment, and the material becomes very suitable for use as pinning wire for directionally solidified and single crystal blades. Rolls-Royce plc have now accepted palladium-15 per cent molybdenum alloy pinning wire for use in the production of directionally solidified turbine blades.

The behaviour of palladium-tungsten alloy was slightly different to that of palladium-molybdenum alloy. Tungsten oxide is far more stable at high temperatures than molybdenum oxide.

This means that palladium-tungsten alloys are better able to survive high mould firing temperatures, such as 1075°C. It also means that tungsten oxide is not as easily removed as molybdenum oxide is during high temperature vacuum treatment. Nevertheless, test results clearly show that samples of oxidised palladium-tungsten alloy exposed to temperatures of 1475°C under vacuum for only 30 minutes developed a palladium-rich near-surface region with a palladium-tungsten core.

An improvement to the oxidation resistance of palladium-molybdenum and palladium-tungsten alloys can be achieved by making ternary additions to the alloy. Oxidation is a diffusion process which is primarily controlled by temperature and exposure time, temperature being by far the more significant variable. Tests conducted for 8 hours at 1075°C in air showed that the palladium-molybdenum alloy which performed so well at temperatures of 850 and 975°C suffered extensive oxidation at 1075°C. When the palladium-molybdenum was alloyed with a small amount of platinum, however, the oxidation resistance was much improved. Platinum additions to the palladium-molybdenum alloy clearly impart higher temperature stability to what is otherwise a very unstable, volatile oxide. A similar improvement in oxide stability occurs on adding platinum to palladium-tungsten alloy, a feature which should result in an extension to the potential applications of this alloy to even higher processing temperatures.

**Conclusion**

A range of alloys have been developed for use as pinning wire during turbine blade casting. The alloys are based on the addition of the refractory metals molybdenum and tungsten to palladium, possibly also with some additions of platinum to enhance the properties further, offering significant cost savings over traditional pinning materials without sacrificing performance.
References
2 D. R. Coupland and M. L. Doyle, European Appl., 533,385; 1993
3 H. Jehn, J. Less Common Met., 1984, 100, 321

Bibliography

Platinum Group Metals in Catalysis
The 14th North American Meeting of the Catalysis Society was held in Snowbird, Utah, from June 11th to 16th, 1995. This prestigious meeting attracted some 1000 participants from industry and universities predominantly from North America. The four parallel sessions for each of the 5 days meant that it was impossible to do more than sample the wide range of catalytic topics covered. The meeting had a special emphasis on environmental catalysis, with 31 oral papers being presented, and as usual in this area the noble metals, such as platinum, featured prominently. The low temperature carbon monoxide oxidation activity of platinum/ceria combinations was discussed by J. C. Frost from Johnson Matthey and L. Murrell from ABB Lummus Crest/Engelhard, while M. Prairie from Sandia National Laboratories emphasised the dominant role of platinum/gold/titania as a photocatalyst for treating air and water pollutants.

A slightly disappointing aspect of the meeting was the lack of presentations on genuinely new catalytic materials. Many of the most interesting presentations reviewed new techniques such as NMR studies of molecules in zeolites to probe acidity (J. Haw from Texas A & M University) or electron holoigraphy in electron microscopes which allows the 3-dimensional interior structure of nanoscale particles to be examined; this was discussed by A. Daye and L. Allard from the University of New Mexico. Other developments of note included the detailed work on membrane reactors and particularly the use of membranes to control the rate and position of mixing of reactants in hydrocarbon selective oxidation, reviewed by M. Harold from Du Pont.

There were sessions on surface science, catalyst characterisation, sulphide catalysts, hydrocarbon conversion, acid catalysts, zeolites, the evergreen topic of syngas formation and reactions, selective oxidation (with only a few presentations on methane coupling), residual oil upgrading, catalyst deactivation and reaction engineering. An unusual but refreshing feature of the meeting was the number of high quality presentations by industrial organisations. Conspicuously absent were discussions on homogeneous catalysis, polymerisation catalysis, biomimetics and other topics which normally attract considerable interest worldwide.

While new applications of the platinum group metals were not much in evidence, almost a third of the papers dealt with some aspect of platinum group metal catalyst performance and the continuing importance of these materials in heterogeneous catalysis came across very clearly throughout the meeting.

J.C.F.

Palladium Shape Memory Alloys
High-temperature shape memory alloys, especially titanium-nickel-based alloys, are used in industrial and medical applications because of their unique combination of perfect shape memory and ductility. However, their use is restricted to temperatures around 373 K, the temperature of the thermoelastic martensitic transformation. There is now a need for shape memory engineering alloys with higher temperatures for use as actuators in motor vehicles, aircraft engine and pipe couplings, and titanium-palladium alloys with a martensite start temperature of 823 K may be suitable.

Now, researchers from Japan have studied the means to improve the characteristics of these alloys (D. Golberg, Y. Xu, Y. Murakami, K. Otsuka, T. Ueki and H. Horikawa, Mater. Lett., 1995, 22, (5, 6), 241-248). Using Ti, Pd, Ni (x = 10, 15, 20) alloy high temperature tensile tests at 293–858 K were carried out. They found that reversibly transforming the as-rolled martensitic phase and annealing it below the recrystallisation temperature improved the shape memory characteristics of this system.
First International Workshop on Diffusion and Stresses

STRESS/STRAIN EFFECTS OF HYDROGEN PERMEATING THROUGH PALLADIUM ALLOY MEMBRANES

An increasing general appreciation of the importance of stress and accompanying strain factor involvement in solid state physicochemical processes has resulted recently in the formation of the First International Workshop on Stress and Diffusion, organised by Professor D. L. Beke of L. Kossuth University, Debrecen, Hungary and held in Balatonfüred, from 26th to 29th May, 1995.

The consequences of stress involvement were reported by internationally well-recognised authorities, in plenary contributions which covered a wide range of topics, including phase relationships, internal friction, precipitate growth and thermodynamic features. In the general study area of thin film interdiffusion and multilayer growth processes, a review by F. M. d’Heurle, I.B.M. Research Center, Yorktown Heights, U.S.A., and O. Thomas of MATOP, URA CNRS, Marseilles, France, of stresses developed during silicide formation included a specific platinum group element participation in terms of the compositions Pd,Si and Pt,Si.

The influence of stresses which develop in reaction zones as a result of the relatively higher mobility of one of the components, such as platinum in a platinum/silicon carbide diffusion couple, was considered to be a probable controlling source of layer distortions. This was reported in a paper on periodic layer formation in ternary diffusion couples by M. R. Rijnders, A. A. Kodentsov and F. J. van Loo, Laboratory of Solid State Chemistry and Materials Science, Eindhoven and C. Cserháti of L. Kossuth University.

A study of solid state interactions in successively deposited components of thin films, reported by F. B. Barna, G. Zsigmond, A. Csanády and Zs. Radi, Research Institute for Technical Physics, Hungarian Academy of Sciences, Budapest, considered the levels of importance of stresses concurrently developed in platinum films which were grown upon aluminium film substrates.

Uphill Hydrogen Diffusion Effects

Evidence of stress/strain factor influences noted during studies of hydrogen permeation through palladium and palladium-alloy membranes has been centred on observations of Uphill Effects. Uphill Effects are broadly indicative of the presence of membrane cross-sectional regions of hydrogen flux, which are acting in opposition to the concentration gradient, and are “self-produced” by the Gorsky-Diffusion-Elastic Effect strain gradients, the latter being associated with expansions of the interstitial sites effected by permeating hydrogen. Uphill Effect observations in sheet and tubular diffusion membranes, which were recorded using measurements of hydrogen gas pressures and of electrode potentials at catalytically active surfaces, have been substantially extended recently by experimental studies from the research groups of B. Baranowski, Institute of Physical Chemistry, Polish Academy of Sciences, Warsaw, and Y. Sakamoto, University of Nagasaki.

In addition, previous results have also been extended by increased variations of temperature, membrane thickness and other constructional geometries, in further series of measurements that have now also been obtained over a wider range of membrane compositions. Overall progress in such recent experimental and complementary theoretical aspects were outlined in a workshop contribution entitled “Gorsky-Diffusion-Elastic Effects of Hydrogen Interstitial Strain Gradients in Palladium and Palladium Alloys”, presented by F. A. Lewis, Queen’s University, Belfast, Y. Sakamoto, University of Nagasaki, K. Kandasamy, University of Jaffna and X. Q. Tong, University of Birmingham.
Uphill Effect research studies, using a tubular form of membrane having a composition similar to that of the initially investigated, and subsequently well-characterised Pd$_x$Pt$_{1-x}$ alloy have been extended recently by employing a wider range of temperature, in combination with accurately correlated results from corresponding isothermal equilibrium pressure-hydrogen content (p-n) relationships, by Professor Baranowski and colleagues. A survey of consolidated results and current research progress was comprehensively outlined in a contribution to the Workshop by D. Dudek and B. Baranowski concerning strain gradient influences on hydrogen diffusion coefficients in the Pd$_x$Pt$_{1-x}$-H system.

A total of some fifty participants in the Workshop drawn from 12 different countries, contributed to a programme of approximately twenty-five verbal and fifteen poster presentations. Corresponding refereed articles prepared from these contributions are planned to be published in a forthcoming issue of the journal Defect and Diffusion Forum.

Platinum 1995
DEMAND FOR PLATINUM A RECORD HIGH

Since 1985 Johnson Matthey has been publishing an annual survey of the commercial aspects of the platinum group metals, with particular emphasis on platinum. Following tradition, the launch of "Platinum 1995" took place in London during Platinum Week and was well received by the analysts, financial journalists, mining engineers and industrialists who attended. Based, in essence, on information gathered from numerous sources worldwide and well supported by statistical data, "Platinum 1995" details the progress of the platinum metals during 1994 and the events which affected both supply and demand, with forecasts for the coming year.

The price of platinum during the year averaged $405.25 per ounce, an eight per cent increase over 1993, peaking to $427.50 in July. This was upheld by factors such as economic recovery, speculation and spasmodic uncertainty over supply. However, prices began a further climb in late March 1995 and soared to reach a four year high of $459 per ounce on 4th April 1995, following the announcement of a new platinum-based technology for the reduction of ozone and carbon monoxide.

Supplies of platinum during 1994 rose by three per cent to 4.53 million ounces. A fall in output from South Africa was offset by a significant increase in exports from Russia. Supply and demand were closely matched.

The motor industry again led the way in the consumption of platinum, chiefly for the manufacture of autocatalysts, with the U.S.A. consuming an increased 32 per cent bringing the total for 1994 to 1.86 million ounces. This was followed closely by the Japanese jewellery industry with its eleventh consecutive year of growth. An increase in the fabrication of Platinum 1000 jewellery resulted in escalating demand with sales spiralling by 100,000 ounces to reach 1.45 million ounces. Growing appreciation of platinum jewellery in North America has encouraged established manufacturers to step-up production and also new participants to develop products.

In addition to dealing with industrial and investment demand, "Platinum 1995" has devoted a chapter to mining and exploration, principally in South Africa. It also contains special features covering mining the platinum group metals in Russia, worldwide coverage of emissions legislation and the use of platinum in the car. On a lesser scale, there are also surveys of the other platinum group metals markets, in particular palladium.

This fifty-two page analysis of trends in the platinum group metals market worldwide is regarded as the authoritative source of such information and is highly respected throughout the financial world. If you would like to receive your free copy of "Platinum 1995" or be added to its distribution list, please contact Alison Cowley, Johnson Matthey PLC, 78 Hatton Garden, London EC1N 8JP, England; Fax: 0171-269-8389.
Some Observations on Laser Trimming Platinum Thin Films

By D. A. Dimitrov

Institute of Solid State Physics, Bulgarian Academy of Sciences, Sofia, Bulgaria

Platinum resistance thermometers have been selected for use as the basic instrument to define and reproduce the International Temperature Scale (ITS-90) (1, 2). The upper limit of the temperature region which they define has increased by some 300°C when compared to the previous International Temperature Scale, IPTS-68. On the ITS-90 scale the upper limit is defined by the freezing point of silver, 961.78°C. Thin film platinum sensors have demonstrated that they are able to meet the requirements of industrial operation, but ITS-90 has underlined their shortcomings, and improvements to production processes are required in order to enhance their performance, if ITS-90 is to be approached.

Thin Film Preparation

Thin film sensors are usually produced by the deposition of platinum onto a suitable substrate. In order to avoid any problems that might arise at the interface between the platinum layer and the substrate, the following criteria have to be taken into account (3):

[a] Mismatch between the lattices must be less than ±0.2 per cent
[b] Differences in the coefficients of thermal expansion must be less than 20 per cent
[c] There must be stability at the chemical interface. This means that the material which is selected for the substrate must not react chemically with the platinum layer.

Since the coefficients of thermal expansion of platinum and polycrystalline alumina are almost equal, being $7 \times 10^{-6}$ /K over the temperature range 50 to 300 K (4), alumina was chosen as the substrate for these sensors.

The production technology has been described elsewhere (5). Platinum layers were deposited, at 580 K, by magnetron sputtering of a platinum target onto alumina substrates. The meaner shape was then drawn by laser evaporation of the layer, using a pulsed Q-modulated Nd:YAG laser ($\lambda = 1.06 \mu m$) with pulse repetition rate of 20 Hz and train energy (for 10 pulses in a train) of 50 to 60 mJ. This technique is faster and more cost effective, and avoids the mask writing and chemical treatment that are necessary for lithographic patterning.

However, laser treatment of the layer parameters is not controllable, and so the final characteristics of the layer cannot be predicted.

Temperature/Resistance Values of the Layer

An assessment of the purity of the platinum target was made in accordance with ITS-90. It was found that the resistance ratio at the boiling point of water, $W(H_2O \text{ b.p.}) > 1.3927$ ($W = R_{0.785}/R_0$ where R is the electrical resistance of the platinum layer). However, contrary to this, the sensors that were produced had a resistance ratio $W(H_2O \text{ b.p.}) = 1.385$. In addition the resistance ratio at 4.2 K, $W = R_{4.2K}/R_{0.785}$ was about $10^{-1}$, which is two orders of magnitude greater than that proposed by ITS-90 for the most accurate thermometers.

An earlier investigation with this type of sensor showed that they required individual calibration in order to achieve an accuracy of ±10 mK (6). The results for the percentage variation of the resistance with temperature for two typical sputtered platinum/alumina sensors, prepared by the same method, serial numbers 023 and 028, are presented in the Table. Their behaviour is characteristic of this type of sensor.

The sensors show significant differences in their values for resistance below 50 K. This can be explained (via Matthiessen’s rule) by any
Resistance/Temperature Dependence from 5 to 270 K for Two Sputtered Laser Treated Sensors and Percentage Variation of their Resistance

<table>
<thead>
<tr>
<th>Temperature, K ± 3 mK</th>
<th>Resistance, ohms</th>
<th>ΔR, per cent</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>023</td>
<td>028</td>
</tr>
<tr>
<td>5.010</td>
<td>0.6456</td>
<td>1.6468</td>
</tr>
<tr>
<td>9.911</td>
<td>0.6788</td>
<td>1.6797</td>
</tr>
<tr>
<td>14.994</td>
<td>0.8048</td>
<td>1.8141</td>
</tr>
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<td>1.0989</td>
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<td>86.4281</td>
<td>86.6378</td>
</tr>
<tr>
<td>270.017</td>
<td>98.2334</td>
<td>98.3117</td>
</tr>
</tbody>
</table>

residual relative resistance. However, there is no reason to suppose that there are any impurities present in the layer during the platinum deposition process.

Eleven sensors of the same type were repeatedly subjected to thermal cycling between 60 to 320 K, and measurements of resistance were taken at 48 temperature points during every cycle. A visible shift in the temperature/resistance, T(R), function was observed up to the sixteenth cycle and only after 20 cycles was saturation achieved. These results may be due to both the laser processing of the layer during fabrication of the meander shape and/or to interaction between the layer and the substrate. The effects of the laser processing can be observed by scanning electron microscopy (SEM).

Effects of the Laser Treatment

A SEM micrograph of a part of sensor 028 is shown in Figure 1(a). The sensor was covered with a glass frit to isolate the layer electrically. However, where the glass frit acted as an electrical isolator the SEM micrographs of the platinum layer were spoilt. Therefore the cover was removed, but small amounts of glass frit which had been deposited in the laser-drawn lines still remained. For this reason, in Figures 1(a) to (d), lighter (white) lines appear on part of the sensor.

Thus laser treatment of the sensors appears to create some problems. First, the rough edges of the treated layer are clearly visible; these cause a reduction in the cross-sectional area of the platinum film. In Figure 1(b), which has twice the resolution of Figure 1(a), it can be seen that in some places the dimensions of the vertical cross section have become too small. Any mechanical tensions which have arisen as a result of the high temperature laser treatment will be increased in these cross-sectional areas and affect the temperature/resistance ratio.

During laser patterning evaporated material is redeposited onto the nearby film; this is shown by the spots in Figure 1(c). Some of these drops have dimensions equal to the width of the meander line layer, see Figure 1(d). It is therefore important to know both the structure and the
composition of the drops, but this analysis is made difficult by the narrowness of the layers. If the drop is predominantly composed of alumina the stress will be larger, since alumina vaporises at a higher temperature than platinum. However, as a result of the large temperature difference between each drop and the layer on which it is deposited, strong mechanical tensions will occur in the cross section, causing the platinum lattice to become overstrained. It is suggested therefore that the electrical properties of the layer in this section become the determining ones for the sensor.

Some of these defects could be avoided if techniques used in the preparation of high transition temperature superconducting films (7) were employed. The film could, for example, be covered with photoresist prior to laser treatment and any redeposited material can then be removed by dissolving the resist in ethanol.

To sum up, we have found that the $T(R)$ function in thin film platinum sensors used for temperature measurement is affected in an uncontrollable manner by laser treatment of the layer. Changes in the meander shape are caused by laser processing.

For this reason sensors fabricated by this method display a non-uniform temperature/resistance dependence. It is also suggested that due to the diffusion of aluminium atoms into the platinum lattice, changes in the electrical properties of the layer may also take place.

Acknowledgements
This work was completed with the financial support of the National Foundation for Science Investigations under contract number TH-265. The author wishes to thank Professor N. Kirov and Dr. E. Nazarova for their valuable discussion during preparation of this manuscript.

The sensors used in this investigation were manufactured by Pribor Ltd, Bulgaria.
Iridium Microelectrode for Testing Water Quality

The lack of sound environmental management of our natural resources is of growing concern, and increasingly legislation is setting standards for the pollutants which can be released into the environment. Pollution in river water, however, is now routinely checked, and improving the quality of the water into which industrial and domestic effluent may be discharged is one aim of the national River Authorities.

Water is tested for the presence and quantity of many different types of pollutants, including organic pollutants, such as pesticides and insecticides, nitrates and nitrates, and the elements, such as the heavy metals: lead, cadmium and copper. A number of analytical techniques are presently used to measure the amounts of around 6000 individual pollutants, mainly by laboratory analysis from collected samples.

However, an advance on the technique for monitoring lead and cadmium using an improved mercury-based iridium microelectrode is suggested in a paper from the University of Geneva (M.-L. Tercier, N. Parthasarathy and J. Buffle, *Electroanalysis*, 1995, 7, (1), 55–63).

The drawbacks to using microelectrodes for water analysis have been a lack of reproducibility in their fabrication and the difficulty in characterising them, and since complete reliability is necessary in the analysis of water contaminants, microelectrodes have not been used. However, based on prior research on ultramicroelectrodes, the researchers have produced a sturdily constructed, reliable mercury-plated iridium-based microelectrode, having a central iridium electrode of radius 62 µm, which gives reproducible results. This has been achieved by thorough attention to all aspects of the fabrication process, in particular, since the electrode is built within a glass pipette, to the iridium-glass sealing, and to the iridium-copper soldering in order to obtain perfect electrical contact. The morphology of the iridium disk is very important and strongly depends on using a reproducible standard polishing procedure.

Optimal polishing procedures and conditions are given to achieve this. The build up of electrostatic charge on the tip of the microelectrode is avoided by shielding the glass pipette with an outer layer of palladium.

To date the system has achieved near 100 per cent reproducibility and reliability for the measurement of trace metals by differential pulse anodic stripping voltammetry and square wave anodic stripping voltammetry (SWASV). Electrodes have been used continuously for several days without requiring a renewal of the mercury layer.

When tested using SWASV in river water, which contained a high level of suspended particle content, trace amounts of free cadmium and lead were able to be measured in concentrations as low as 0.5 nM and 0.1 nM, respectively. Direct SWASV measurements using such a microelectrode were the best for routine analysis of dissolved trace metals in fresh water, since problems caused by contamination and/or adsorption are minimised. This method allowed the free and total metal concentrations to be rapidly determined. These are the most important trace metal speciation parameters. Sample pretreatment is not required. At present the lifetime of these state-of-the-art microelectrodes is more than 2 years.

If dissolved organic matter in low concentrations of 1 to 2 mg/litre, relative to particle load, is present then trace metals at levels of 50 pm can be detected, although high levels of particles do not hinder SWASV measurements. To avoid problems in water with higher dissolved organic content and to extend the use of the sensor for *in situ* measurements of any type of natural water, a membrane coated microsensor is being developed. Other uses suggested for this sensor include an *in situ* automatic quality control system for industrial application, the measurements of samples of small volume, being used in still waters and as part of other routine detection systems.
ABSTRACTS
of current literature on the platinum metals and their alloys

PROPERTIES

Short-Range Order in Ni-Pt Alloys
The existence and shape of the diffuse intensity in Ni-Pt alloys with x = 0.25, 0.35, 0.44 and 0.50 were studied. The dependence on composition of the diffuse intensity was observed where the shape of diffuse intensity changed with Pt content, and was similar to that for Cu-Au alloy. The change in shape from disc-like for the 100 position for the x = 0.25 to spherical for x = 0.5 can be explained using a linearised correlation function.

A technique for obtaining p-c(T) relationships at near 25°C involving derivations from electrode potential measurements in the Pd-Pt-H system, where sensitive changes of electrical resistance can be measured, was used to examine hysteretic differences between forms of relationships in the Pd alloy-H system. Size of alloying element is a guide to change of form in p-n.

Kinetics of Hydrogen Desorption from Palladium and Ruthenium-Palladium Foils
Studies of absorption of H and CO at room temperature by Pd and 5% Ru-Pd foils showed that H readily diffused into the Pd and desorbed as one broad peak at ≈ 650 K. The 5% Ru-Pd is less effective than pure Pd for the absorption and transport of H but can withstand more H absorption-desorption cycles. Activation energies for bulk diffusion obtained from H uptake measurements corresponded to 4.4 and 4.9 kcal/mol for Pd foil and Ru-Pd alloy, respectively.

Microstructural Development, Electrical Properties and Oxygen Permeation of Zirconia-Palladium Composites
Studies of Y2O3-stabilised cubic ZrO2 (YSZ)-Pd dual phase composites showed a larger O permeability in the percolative composite containing 40 vol.% Pd (ZYPd40) than that of the non-percolative composite containing 40 vol.% Pd (ZYPd30). It is concluded that the transport of the O ions through the YSZ phase in the percolative system is the rate limiting step.

Submicronic Ag-Pd powders containing 70:30 and 75:25 wt.% Ag-Pd, prepared by precipitation in aqueous solution, were studied for use in the multilayer ceramic capacitor industry. The powders consisted of submicron spherically shaped particles with a narrow size distribution and very little agglomeration. They were made into a paste by blending with an organic binder, screen printed, fired and sintered into a conductive layer of resistivity, 15-30 μΩcm for 2 μm thickness, with only a few remaining voids. Thermal measurements showed that alloying was achieved below 960°C.

Hydrogen-Induced Ordering in a Pd0.81Au0.19 Alloy
Ordering in Pd0.81Au0.19 alloy proceeded under the effect of large amounts of dissolved H2, which stabilised the ordered structure as the alloy reverted to the disordered state upon annealing in vacuo, at the same temperature used for ordering the alloy by H2 heat treatment. The present results showed that the alloy does not order because it is not thermodynamically stable in the absence of H2.

Magnetization and FMR Linewidth in Annealed Co-Pd-Si Amorphous Alloys
The effect of the annealing on the magnetic polarisation and FMR linewidth of the amorphous alloys Co0.75Pd0.25Si and Co0.75Pd0.25Si0.19 was studied at room temperature. A small maximum polarisation was observed at the annealing temperature of ≈ 400°C, which corresponds to the crystallisation region. A comparison between the saturation magnetic polarisation and the effective value obtained from FMR showed that the maximum volume of Co clusters occurs for materials annealed at 700-800°C. The possible contribution of magnetic inhomogeneities to the linewidth is discussed.

New Heavy-Electron System Ce3Pd20Si6
Studies of magnetic and transport properties of Ce3Pd20Si6 showed that this compound is a Kondo material with a strongly enhanced C/T value of 24 J/mole K² at 0.2 K. This suggests that Ce3Pd20Si6 is one of the heaviest-electron systems.
Mössbauer studies of magnetic properties of the ferromagnetic lattice CrO₂ doped with Ir(IV), which has a high value for the spin-orbit coupling constant, showed that Ir(IV) in CrO₂ is mainly stabilised in such a lattice. However, after very high O₂ pressure treatment, Ir(V) was found close to the surface. The orbital contribution to the spin only magnetic moment is 8 times larger for Ir than for Cr.

Electrical and Optical Properties of Ruthenium-Related Defects in Silicon


The electrical and optical properties of defects due to ion implantation of Ru in Si were studied by using junction space-charge techniques. Two energy levels were observed with energy positions at \( E_1 = -0.184 \, \text{eV (A-level)} \) and \( E_2 = 0.265 \, \text{eV (B-level)} \), respectively, at 77 K. The changes in enthalpy resulting from the capture of electrons and holes were \(-8 \, \text{meV (A-level)}\) and \(-1 \, \text{meV (B-level)}\), respectively. Gibb's free energies at different temperatures were calculated for both levels. A model for the origin of the observed defects is discussed.

Conduction Mechanisms in RuO₂-Glass Composites


The correlation between microstructure and electrical transport in RuO₂-glass composites with metal oxide volume fractions 0.01–0.4 was studied by SEM, HREM and temperature, frequency and electric field dependent conductivity studies. At high RuO₂ fractions \( > 20 \% \) a metallic conduction mechanism was identified, but at low RuO₂ contents \( \leq 5 \% \) ionic transport dominated. A quantitative description of electrical transport in RuO₂-glass composites is presented.

CHEMICAL COMPOUNDS

Highly Reactive Platinum(0) Carbene Intermediates in the Reactions of Diazocarbonyl Compounds. A Fast Atom Bombardment Mass Spectrometric Study


A direct reaction of \( [\text{Pt}(\text{CH}_2=\text{CH})_2](\text{PPh}_3)_2 \) (1) with \( \text{N}_2\text{CHCO}_2\text{Et} \) under a fast atom bombardment matrix, yielded molecular ions corresponding to the species \( [\text{Pt}(\text{N},\text{C}(\text{H})\text{CO}_2\text{Et})(\text{PPh}_3)_2]_1 \), \( [\text{Pt}(\text{C}(\text{H})\text{CO}_2\text{Et})(\text{PPh}_3)_2]_2 \) and \( [\text{Pt}(\text{C}(\text{H})\text{CO}_2\text{Et})(\text{PPh}_3)_3]_3 \), which are intermediates in the formation of the fumarate Pt(0) derivative \( [\text{Pt}(\text{trans}-\text{C}(\text{H})\text{CO}_2\text{Et})(\text{C}(\text{H})\text{CO}_2\text{Et})(\text{PPh}_3)_3]_3 \) which was active in the cyrclopropanation of styrene in the presence of \( \text{N}_2\text{CHCO}_2\text{Et} \).

The Cossee Mechanism: Migratory Insertion Reactions in Palladium Phosphine-Phosphinite Complexes


Methyl Pd complexes containing phosphine-phosphinite bidentate ligands containing two P atoms which are only slightly inequivalent undergo stepwise insertions of CO and norbornadiene. The \(^1\)P NMR spectra showed that a true migration pathway is the main mechanism in this reaction. The large chemical shift difference between the two P atoms allows studies of the intimate mechanism of multiple migratory insertions in 4-co-ordinate complexes.

Synthesis and Properties of Cationic Organopalladium Complexes. Remarkable Rate Enhancement in Olefin Insertion into the Palladium-Aryl Bond by the Generation of a Cationic Palladium Complex from trans-[PdBr₂(Ph)(PMe₃)₂]


Pd complexes trans-[PdPh₂(py)(PMe₃)]BF₄, and trans-[PdPh₂(solvent)(PMe₃)]BF₄, were obtained by removing the bromide ligand in trans-[PdBr₂(Ph)(PMe₃)]BF₄ by AgBF₄, in the presence and absence of pyridine, pyridine-co-ordinated and solvent-co-ordinated cationic complexes. The cationic phenyl Pd complexes have greater reactivities than the parent neutral complex (1) toward olefins to give phenylated olefins by insertion followed by \( \beta \)-H elimination processes. A cationic aryl Pd complex is generated with a vacant site for olefin insertions.

A Novel Route to Dinuclear Heteroleptic Rhodium(II) Complexes of 1,4,7-Trithiaacyclononane


A novel route to dinuclear Rh(III) complex cations with \( 1,4,7 \)-trithiaacyclononane (9S₃): \([\text{Rh}(\mu\text{-SPh})(\text{MCp})_2]_1 \), where M = Rh, Ir; Cp* = \( C_{(11)} \text{H}_{10} \), is described using \([\text{Rh}(9S₃)(\text{CO})(\text{PPh}_3)]_1 \)' as a synthron. (1) is reactive toward oxidative decarbonylation reactions forming a new oxidative addition product with \( \text{I}_2 [\text{Rh}(\text{9S₃})(\text{PPh}_3)](\text{I})_1 \)', in good yield. In the presence of excess benzenethiol and \( \text{NEt}_3 \), the reaction gives an insoluble red neutral solid \( \text{Rh}(\text{9S₃})(\text{PPh}_3)(\text{I})_1 \) in good yield. In the presence of excess benzenethiol and \( \text{NEt}_3 \), the reaction gives an insoluble red neutral solid \( \text{Rh}(\text{9S₃})(\text{PPh}_3)(\text{I})_1 \) in good yield. In the presence of excess benzenethiol and \( \text{NEt}_3 \), the reaction gives an insoluble red neutral solid \( \text{Rh}(\text{9S₃})(\text{PPh}_3)(\text{I})_1 \) in good yield. In the presence of excess benzenethiol and \( \text{NEt}_3 \), the reaction gives an insoluble red neutral solid \( \text{Rh}(\text{9S₃})(\text{PPh}_3)(\text{I})_1 \) in good yield.
High Oxygen Pressure and the Preparation of New Iridium (VI) Oxides with Perovskite Structure: Sr$_2$M$_x$IrO$_6$ (M = Ca, Mg)


Ir(VI) in an octahedral co-ordination was stabilised in Sr$_2$M$_x$IrO$_6$ (M = Ca, Mg) oxides with an ordered perovskite structure by use of high O pressure. The structure of Sr$_2$CaIrO$_6$ depends strongly on the O pressure and reversibly returns to the original structure according to the heat treatment applied. The oxidation state of Ir is determined and correlated with the structural factors and the covalency of M-O bonds. The electronic configuration of Ir(VI) leads to a high Néel temperature with 55 K (Ca) and 80 K (Mg).

Trans-Cis Isomerization in [Os(tpy)(Cl)]$_2$(N)]$^+$


The Os complex trans-[Os(tpy)(Cl)]$_2$(N)]$^+$ (1) was synthesised by adding 2.2′,6′,2″-terpyridine (tpy) to [NBu$_4$][Os(N)(Cl)$_2$] in dichloromethane and trans-[Os(tpy)]$_2$(Cl)]$_2$(PF$_6$) by addition of [NH$_4$]$_2$[PF$_6$] to a methanolic solution of (1). When dissolved in MeOH in the presence of added chloride, (1) slowly isomerised to cis-[Os(tpy)]$_2$(Cl)]$_2$(N)]$^+$, which was isolated as its PF$_6$ salt. With added chloride, an equilibrium was achieved in the solution between the trans and cis isomers. Isomerisation did not occur in dichloromethane. A mechanism for isomerisation and isomerisation substitution is proposed involving associative attack of methanol to form seven-co-ordinate, solvent-bound intermediates, which undergo solvolyis.

A Dihydrogen Complex, [Os(η$^2$-H$_2$)(CO)(quS)(PPh$_3$)$_2$]$^+$, in Equilibrium with Its Coordinated Thiol Tautomer (quS = quinoline-8-thiolate)


The mixture of two isomers of the new Os complex Os(η$^2$-H$_2$)(CO)(quS)(PPh$_3$)$_2$, reacted with HBF$_4$.Et$_2$O at –80°C to produce the Os complexes [Os(η$^2$-H$_2$)(CO)(quS)(PPh$_3$)$_2$]$^+$ with dihydrogen trans to sulphur or nitrogen along with tautomeric thiol complexes [Os(η$^2$-H$_2$)(CO)(quS)]$^+$ (PPh$_3$)$_3$. The tautomeric equilibria shifted with temperature.

Vertically Linked Ruthenium(II) Porphyrin Oligomers


A novel porphyrin trimer linked vertically, of formula Ru(OEP)/(H$_2$PyP)$_3$, was synthesised and characterised. The porphyrin ligands with pyridyl groups in these oligomers are perpendicularly co-ordinated to the metal centres of Ru(II) porphyrins. Porphyrin oligomers, Ru(OEP)(CO)(H$_2$PyP)$_3$, Ru(OEP)(CO)(ZnPyP)$_3$P and [Ru(OEP)(CO)]$_2$(trans-H$_2$PyP)$_3$P were also prepared. This gives a systematic route for constructing perpendicularly linked porphyrin oligomers and polymers and studies of their potential functions are currently in progress.

Synthesis of a [60]Fullerene Derivative Covalently Linked to a Ruthenium(II) Tris(bipyridine) Complex


The synthesis of a [60]fullerene derivative containing the transition metal complex Ru(bpy)$_3$" is described. Its UV-VIS spectrum showed absorptions typical of the two independent chromophores.

ELECTROCHEMISTRY

High Efficiency Electrochemical Reduction of Carbon Dioxide under High Pressure on a Gas Diffusion Electrode Containing Pt Catalysts


The electrochemical reduction of gas phase CO$_2$ under high pressure (<50 atm) was performed on a gas diffusion electrode containing Pt electrocatalyst at high current densities. The faradaic efficiency for CO$_2$ reduction reached 46% at a current density of 900 mA/cm$^2$. CH$_4$ was produced at 35% efficiency.

Fabrication of Highly Dispersed Pt Coated Carbon Electrodes by a Combination of Partial Thermal Decomposition and Electrolytic Reduction of Pt Complex


A Pt electrocatalyst electrode was made, using a combination of partial thermal decomposition of Pt(NO$_3$)$_2$(NH$_3$)$_2$ on C paper at 350°C and electrochemical reduction of the Pt complex at 0 V (vs. Ag/AgCl) in a mixed solution of 1 M MeOH and 0.5 M H$_2$SO$_4$ at 60°C. The specific surface area and activity of Pt on this electrode was higher than those obtained with H,PtCl$_4$.

Electrochemical Sulphur Dioxide Oxidation with Platinum-Aluminium Electrocatalsysts


Pt-Al electrocatalysts supported on C black were studied for electrocatalytic SO$_2$ oxidation in hybrid type, liquid-phase SO$_3$/O$_2$/SO$_2$ cells. When 1–30 at.% Al was incorporated with Pt electrocatalysts on C, electrocatalytic activity increased for SO$_2$ oxidation. Even a small amount of Al ~ 1 at.% incorporated in the Pt produced a significant synergistic effect.

Kinetic Properties of a Pt/Lambda-MnO$_2$ Electrode for the Electroinsertion of Lithium Ions in an Aqueous Phase


Kinetic properties of a Pt/β-MnO$_2$ electrode for the electrochemical insertion of Li ions were studied in the aqueous phase. The electrochemical insertion reaction of Li ions proceeded in two steps at 0.6–0.98 V (vs. S.C.E.). The chemical diffusion coefficients of Li ions in the MnO$_2$ were 6.6 × 10$^{-6}$–1.4 × 10$^{-8}$ cm$^2$/s.
Preparation of Microparticle Palladium Incorporating Poly[N-(5-hydroxypentyl)-pyrrole] Film-Coated Electrode
A new conducting polymer catalytic electrode incorporating Pd microparticles into poly[N-(5-hydroxypentyl)-pyrrole] film-coated electrode was prepared by immersion treatment in NaPdCl₄ solution, followed by electrochemical reduction of permeated PdCl₄²⁻ ions in the films. The electrode exhibited catalytic activity for the hydrogenation of acetylene compound.

PHOTOCONVERSION

Effects of H⁺, Cl⁻ and CH₃COOH on the Photocatalytic Conversion of PtCl₆²⁻ in Aqueous TiO₂ Dispersion
Studies of the effects of H⁺, Cl⁻ and CH₃COOH (1) on the photocatalytic conversion of PtCl₆²⁻ in an aqueous TiO₂ dispersion showed that the hydrolysis product of PtCl₆²⁻ is photocatalytically converted into a solid deposit on the TiO₂ surface which changes with the degree of the PtCl₆²⁻ hydrolysis. No deposit was observed on the TiO₂ when both H⁺ and Cl⁻ concentrations were high enough to depress the hydrolysis. The effect of (1) on the composition of the photocatalytic product of PtCl₆²⁻ on TiO₂ is closely related to the degree of its ionisation.

Photoinduced Addition of Dioxogen Molecules in the Unsaturated Sites of the Pd₃(dpmm)₃(CO)₂⁺ Catalyst
The photoinduced addition of O₂ onto the unsaturated cluster Pd₃(dpmm)₃(CO)₂⁺ (as a CF₃CO₂ salt) in acetonitrile is reported. The final product Pd₃(dpmm)₃(O₂)₂⁺ is formed in a multi-step in which two photochemical intermediates are observed, such as Pd₃(dpmm)₃(O₂)⁺ and Pd₃(dpmm)₃(O₂)⁺. Studies showed that O₂ binds the Pd₃ centre as a peroxo-O₂, and acts as a two electron donor that triply bridges the metal atoms, forming a 44-electron cluster.

Photochemistry and C-H Bond Activation Reactivity of (HBPz⁺)(Rh(CO)₃) (Pz* = 3,5-Dimethylpyrazolyl) in Hydrocarbon Solution
The solution photochemistry of (HBPz⁺)(Rh(CO)₃) was studied and the absolute quantum efficiencies for intermolecular C-H bond activation at several excitation wavelengths were determined. The C-H bond activation reaction proceeded well and cleanly in room-temperature solutions after photolyses in either the near-UV or visible region. Quantum efficiency data revealed that the C-H bond activation is strongly dependent on the wavelength of light excitation, and that high conversion efficiencies can be obtained.

Electronic Energy Transfer in a Supramolecular Species Containing the [Ru(bpy)₃]²⁺, [Os(bpy)₃]²⁺ and Anthracene Chromophoric Units
A very fast and efficient energy transfer of 9.7 × 10⁻⁹ s was observed from the Ru- to the Os-based moiety in the reaction of the above components. In O₂, a photo-reaction occurred which gave a strong decrease, ~80 times, in the rate of the energy transfer process.

Dramatic Increase of 3MLCT State Lifetime of a Ruthenium(II) Polypyridine Complex upon Entrapment within Y-Zeolite Superstructures
Entrapment of Ru(bpy)₃(daf)²⁺, where daf is diazafluorene, in zeolite Y supercages induced a dramatic increase in the excited-state lifetime and emission intensity compared to solutions of the complex. The observed temperature dependence of the excited-state lifetime was modelled by a kinetic equation with two thermal terms corresponding to the so-called fourth 3MLCT state and ligand field (LF) state, respectively. The increased lifetime of the entrapped complex was found to result from zeolite-induced destabilisation of the LF state.

Photoadduct between Tris(1,4,5,8-tetraazaphenanthrene)ruthenium (II) and Guanosine Monophosphate—a Model for a New Mode of Covalent Binding of Metal Complexes to DNA
Ru(TAP)₃(2-TAP-G)²⁺ (TAP = 1,4,5,8-tetraazaphenanthrene), in which the guanine moiety is bound via visible light irradiation of [Ru(TAP)₃]²⁻ in aqueous solutions containing 5'-guanosine-monophosphate (GMP) and subsequent treatment with HCl. The reaction is said to proceed by initial oxidation of the guanine by the Ru complex excited state, subsequent proton transfer (both processes were verified by laser flash photolysis) and subsequent coupling of the radicals that were formed.

ELECTRODEPOSITION AND SURFACE COATINGS

Fabrication of Ultrathin Metallic Membranes on Ceramic Supports by Sputter Deposition
Ultrathin Pd films (< 500 nm) grown on porous ceramic supports were prepared by sputter deposition. Fairly gas-tight Pd films with good adhesion could be coated on sol-gel derived fine pore γ-Al₂O₃ supports but not on coarse α-Al₂O₃. Both coating temperature and substrate type affect the grain size, N gas-tightness and the adhesion of the deposited metallic films. The optimum coating temperature is 400°C.
Effect of KCl Concentration on Activation Using Pd-Sn(I1) Chloride Solutions

Formation of Pd nuclei on the surface of plastics using colloidal activating solutions strongly acidified with HCl is compared with results obtained using weak HCl with a KCl based activator. The effect of temperature increase and modification of the HCl and KCl concentration on the activation performance are examined. The greatest Pd adsorption was obtained using solutions with concentrated HCl. Results were obtained by measurement of surface tension, contact angle, and radiochemical and SEM-based methods.

Electrodeposition of Ru-Sn Coatings

Ru-Sn plating solutions containing RuCl3 and SnCl2. 5H2O dissolved in H2SO4 were prepared and electrodeposition was carried out at room temperature using a Pt mesh anode surrounding a Ti cathode, at a constant current density of 30 mA/cm2, for various times. Coatings were deposited onto a Ti strip, previously etched in oxalic acid. A dramatic increase in durability was observed after heating the deposits from a solution containing Ru 0.009 mol/dm3 and Sn 0.19 mol/dm3, in air for 1 h at 500°C. This method is fast and the deposits become more stable by heating in air.

APPARATUS AND TECHNIQUE

A Method for Preparation of Pt-Ir Tips for the Scanning Tunneling Microscope

Pt-Ir tips for STM were prepared by AC etching of Pt-Ir specimens, using Pt, Ir, wire of diameter 0.25 mm, in 1–2 M NaOH + saturated NaOCN distilled H2O solution. The optimal frequency was ~ 400 Hz and the etching duration was about 30 min. This method is simple, relatively fast, taking ~ 35–40 min per tip, and produces tips with a small opening angle.

Application of Redox Cycling Enhanced Current at an Interdigitated Array Electrode for Iron-Trace Determination in Ultrapure Spectral Carbon

Vertically arranged interdigitated array (IDA) electrodes, containing a continuous Pt-film base and a 0.5 μm thick insulation layer in the middle separating the upper Pt-IDA electrodes from the Pt-base, were used for Fe trace analysis in ultrapure spectral C. The spiked samples were used during tests and the results were compared with those obtained by AAS. The redox cycling enhanced the electrochemical signal of the IDA microelectrode, and the IDA signal was obtained for 1 x 10–3–1.5 x 10–6 wt.% Fe. The method is a less expensive alternative to the AAS determination of Fe pollutants in ultrapure carbon.

Electrochemical Removal of Both NO and CH, under Lean-Burn Conditions

An electrochemical cell Pd/YSZ/Pd of simple structure and small size was placed in a flow of NO and CH, mixture at 650–750°C with direct current. Both NO and CH, were removed, even in the presence of excess O2. No deterioration of activity was found in the presence of H2O and CO2. NO was reduced to N2 at the cathode, and CH, was oxidised to CO2 at both the anode and cathode. At the cathode, the reduction of NO and the oxidation of CH, proceeded with the removal of chemisorbed O species from the Pd surface, and at the anode, the oxidation of CH, was increased by forming an active O atom.

Characterization of Nanocrystalline Palladium for Solid State Gas Sensor Applications

Nanocrystalline Pd was prepared by the inert gas condensation technique, consolidated into pellets, and characterised. The H gas absorption/desorption properties of the nanocrystalline Pd were studied to show their application to solid state gas sensor development. The nanocrystalline materials exhibited fast response to H, and complete recovery up to an exposure to several % of H. Studies showed that the dissociative chemisorption of H on the surface of the Pd is the rate controlling step for absorption, while desorption was controlled by diffusion of H out of the Pd metal.

Highly Selective Biosensing of Lactate at Lactate Oxidase Containing Rhodium-Dispersed Carbon Paste Electrodes

A highly selective lactate biosensor based on the immobilisation of lactate oxidase within a Rh-dispersed C paste is presented. The amperometric biosensing of lactate can be performed at low operating potentials. The effective catalytic action of the Rh microparticles towards the generated H2O2, or consumed O2 allows tuning of the operating potential to a region which prevents unwanted reactions. The detection limit was 1.5 x 10–3 M and the response time 8 s. A fast and sensitive flow injection operation is obtained.

Design and Optimization of a Selective Subcutaneously Implantable Glucose Electrode Based on “Wired” Glucose Oxidase

An implantable 0.29 mm wide flexible wire electrode for glucose monitoring contains 3 layers with no leachable components: a “wired” glucose oxidase (GOX) sensing layer formed by cross-linking [poly{((1–vinylimidazolyl)Os(4,4'-dimethylpyridine)2}]2* and GOX with poly(ethylene glycol) diglycidyl ether, a mass transport limiting layer, and a non-fouling biocompatible layer. When poised at +200 mV vs S.C.E. and at 37°C, the electrode had in vitro sensitivity of 1–2.5 nA/mM.
JOINING
Thin Multilayer Palladium Coatings for Semiconductor Packaging Applications. Part I: Solderability
Physical and chemical characteristics of Pd and Pd alloy electrodeposits were studied to find their performance as solderable and wire-bondable materials. The most stringent soldering requirements were met by combining layers with limiting porosity, inhibiting thermal diffusion and increasing wetting speeds. Combinations of Pd and Pd alloys with thin Au flash showed good solderability and wire bonding. Pd finishes have superior bond strength than Sn-Pb ones.

HETEROGENEOUS CATALYSIS
Investigation of Methane Oxidation on Pt/Al₂O₃ Catalysts under Transient Reaction Conditions
The oxidation of CH₄ on Pt/Al₂O₃ catalysts was studied using various gas mixtures as a function of the state of oxidation or reduction of the Pt surface. The activity for CH₄ oxidation increased sharply after addition of the reactants to either a pre-reduced or a pre-oxidised catalyst. Even after re-oxidation at 300°C, the Pt particles had a strong “memory” of previous reduction treatments, and the position of the maximum activity was reproducible for pre-reduced catalysts.

A New Class of Chiral Modifiers for the Enantioselective Hydrogenation of α-Ketoesters with Pt/Al₂O₃
A series of enantiomERICALLY pure chiral amino alcohols was prepared and applied as modifiers in the enantioselective hydrogenation of ethyl pyruvate over Pt/Al₂O₃ catalysts. Their use allowed an enantiomeric excess of ≤ 75% to be obtained. A molecular model of the modifiers and reactant on a Pt(111) surface explained the observed enantiodifferentiation.

Increased Aromatization in the Reforming of Mixtures of n-Hexane, Methylcyclohexane and Methylcyclohexane over Composites of Pt/BaKL Zeolite with Pt/β or Pt/USY Zeolites
The performance of the individual L, β and USY zeolites supporting Pt and of composites of Pt/BaKL with either Pt/β or Pt/USY was studied during reforming of n-hexane, methylcyclohexane, or methycyclohexane. The increase of the Pt loading increased the aromatic selectivity for the hydrocarbons. Reactions over the composites gave increased selectivities for C ≥ 7 aromatics. This is attributed to the synergism caused by the components of the composites in combination with components of the feed mixture.

The Preparation of High-Surface-Area Pt/SiO₂ Catalysts with Well-Defined Pore Size Distributions
Thermally stable supported Pt catalysts were prepared by matching the metal particle size to the average pore diameter. In the 3–8 nm range, blank SiO₂ gels prepared using tetraethoxysilane (TEOS) had BET surface areas of 350–800 m²/g and mesoporous structures with an average pore diameter of 4–25 nm at a constant H₂O:TEOS ratio of 10. The use of Pt(AcAc)₂ resulted in average pore diameters of 4–20 nm by adjusting the H₂O:TEOS ratio during synthesis. Catalytic activities were found to be comparable or slightly superior to supported metal catalysts prepared by traditional methods.

Synthesis of a Highly Active Supercacid of Platinum-Supported Zirconia for Reaction of Butane
A highly active superacid of 8 wt. % Pt/ZrO₂ was obtained for the skeletal isomerisation of butane to isobutane by impregnating ZrO₂ gel with 0.5 mol/dm³ H₂SO₄, followed by drying. The sulphated gel was impregnated with H₂PtCl₆ solution and calcined in air at 600°C. The catalytic activity achieved was the greatest of any solid catalyst yet reported for the acid-catalysed isomerisation of butane without reducing the catalyst before use or in the absence of H₂.

Effects of Modification of Pd/SiO₂ with Rh on Catalytic Activity for Ethene Hydroformylation
The catalytic activity of Pd/SiO₂ catalysts modified with Rh was studied during ethene hydroformylation using Pd catalysts with high (1) or low dispersions. The activity for propionaldehyde formation on (1) catalyst modified with Rh(CH₂CO₂)₃ at Rh:Pd = 1.0 was very high, being about 4 times that on unmodified (1) or more than 50 times that on Rh/SiO₂ containing the same amount of Rh alone. This remarkable increase in activity is probably due to the formation of a Rh-Pd bimetallic structure at the surfaces of metal particles.

Catalytic Properties of Nanocrystalline WO₃, Pt/WO₃ and Pd/WO₃ Particles
Nanocrystalline (NC) WO₃, Pt/WO₃, and Pd/WO₃ catalysts showed good interfacial bonding between NC Pt or Pd and WO₃ particles. The nanocrystals WO₃, Pt/WO₃, and Pd/WO₃ grew into needle shapes with a plate structure inside after sintering at 900°C, to form a network structure. However, the mean particle size of nanophase Pt and Pd increases only from < 10 nm to 30 nm and 50 nm, respectively. The results of CO oxidation show that nanophase Pt/WO₃ powders have better catalytic effects on converting CO to CO₂ than nanophase WO₃, and Pd/WO₃ powders.
Selective Hydrogenation of Phenylacetylene on Pumice-Supported Palladium Catalysts


The behaviour of Pd/pumice catalysts during the above reaction in the liquid phase, was studied for a large range of metal dispersions. The hydrogenation was “structure insensitive”. Pd/pumice catalysts show high activity and selectivity at high metal dispersions, so they can be used in industrial applications.

New Catalyst Precursors Constituted of AsPh₃ and Palladium on Carbon or Palladium(II) Acetate as Efficient Promoters of Selective Cross-Coupling Reactions between Functionalized Alkenyl Halides and Aryl- or 1-Alkynylzinc Chlorides


Catalyst precursor containing a mixture of Pd/C and AsPh₃ and also that obtained by treatment of Pd(OAc)₂ with AsPh₃ in THF at 60°C were found to promote efficient cross-coupling reactions between aryl- or 1-alkynylzinc chlorides and arylalkynyl halides. The latter contain an electron-withdrawing substituent linked to their C–C double bond.

One-Step Synthesis of PdSAPO-5 Catalysts and Their Structure


PdSAPO-5 bifunctional catalysts were prepared by direct addition of Pd to the reactant gel mixture of silicoaluminophosphate followed by their modification. The addition of H₂PdCl₆ did not depress the yield of SAPO-5 and the Pd could be evenly dispersed in the channels of PdSAPO-5(5Cl). The dispersion of Pd in PdSAPO-5 was much better than that in PdSAPO-5 prepared by impregnation.

[Ru₄(CO)₁₈]⁻ in NaX Zeolite Cages: Characterization by EXAFS and FTIR Spectroscopy


Ru²⁺(NH₃)₆ in the cages of NaX zeolite was converted into the Ru carbonyl cluster dianion [Ru₄(CO)₁₈]⁻ in the presence of CO + H₂, which was reversibly fragmented and reconstructed under oxidative and reductive conditions, respectively. The structure of this Ru cluster was very sensitive to O₂.

New Supported [Ru₅N] Clusters as a Potential Transition Metal Nitride Catalyst


[Ru₅N] cluster catalysts were prepared by reacting [Ru₅N(CO)₁₀] clusters with MgO, K⁺-doped MgO or Cs⁺-doped MgO. The [Ru₅N] unit remained in reaction conditions and showed higher activities in NH₃ synthesis than conventional Ru catalysts or Ru clusters prepared from [Ru₅(CO)₁₀]Me or [Ru₅(CO)₁₀] complexes.

HOMOGENEOUS CATALYSIS

Highly Stereoselective Allylation of Benzaldehyde: Generation of a Sterechemically Defined Allylzinc Species from a 2-Allylpalladium Intermediate and Diethylzinc


The stereoselective addition of 2-cyclohexenylzinc species, generated by the Pd⁺-catalysed reaction of 2-cyclohexenyl esters and diethylzinc, to benzaldehyde using Pd(PPh₃)₃ catalyst is reported. The Pd⁺-catalysed allylation had the excellent stereoselectivity of syn addition with inversion of the allylic stereocentre for 2-cyclohexenyl substrates and (Z)-anti addition for acyclic 1,3-disubstituted allylic substrates. This technique can be applied to a range of allylic substrates prepared from allylic alcohols and α,β-unsaturated aldehydes.

Homogeneous Multimetallic Catalysts. 11. Carboxylation of Aryl Iodides with HSiEt₃ Catalyzed by Pd-Co Bimetallic Systems

Y. MISUMI, Y. ISHII and M. HIDAI, Organometallics, 1995, 14, (4), 1770–1775

The bimetallic catalysts PdCl₂(PPh₃)₂-Ru(CO)₃ or PdCl₂(PPh₃)₂-Co₂(CO)₅ were found to be effective for carboxylation of aryl iodides and HSiEt₃ to yield benzyl silyl ether as the main product, although they were not active individually. Addition of NEt₃ to the Pd-Co mixed-metal-catalysed carboxylation greatly changed the selectivity of the products giving 1,2-diaryl-1,2-diisoxethane as the major product. Detailed mechanisms are proposed for this reaction.

A Simple, Effective, New, Palladium-Catalyzed Conversion of Enol Silanes to Enones and Enals


Enol silanes obtained from aldehydes and ketones were easily converted to the corresponding α,β-unsaturated carbonyl compounds by 10% Pd(OAc)₂ in the presence of 1 atm O₂ in dimethylsulphoxide as the solvent. The process requires no additional reagents or reoxidants for Pd, so it is environmentally attractive and should therefore find widespread use.

 Palladium-Catalysed Carboxylation of Halogenoalkynes to Alkynylcarboxylic Acid Esters under Mild Conditions


Alkynylcarboxylic acid esters were formed by Pd-catalysed carboxylation of bromoalkynes, iodoalkynes and α-alkynyl Pd(II) complexes under CO at atmospheric pressure. Et₃N or NaOAc may be added to the methanol solution of PdX₂-LiX (X = Br, I) catalyst. Esters were produced in high yield and under mild reaction conditions at 40°C. Ester formation must occur from iodoalkyne as an intermediate product.
Novel Palladium-Catalyzed Cyclodimerization of Butadiene in the Presence of Carbon Dioxide and Water

A Pd-catalysed cyclodimerisation of butadiene to 2-vinylmethylene cyclopentane occurring in catalytic turnovers and giving yields much superior to those of the Ni-based systems, which are specific for cyclodimerisation reactions, is reported. The system used Pd(O)L₆ (L = Ph₃P, (o-tolyl)P), CO, and H₂O.

Hydroesterification of Olefins Catalyzed by Pd(OAc)₂ Immobilized on Montmorillonite

Pd acetate immobilised on montmorillonite was found to be an efficient catalyst for the hydroesterification of olefins with CO and CH₃OH, in the presence of an acid promoter, giving branched chain esters in good yields and selectivities. The reaction was regiospecific for aryl olefins and vinyl benzoate, and regioselective for aliphatic olefins.

Palladium(0)-Catalyzed Phenylation of Imidazo[4,5-b]pyridines

Coupling of benzenoboronic acid with 2-chloro, 6-bromo, and 2-bromo-6-chloro derivatives of 1- and 3-methylimidazo[4,5-b]pyridines was catalysed by Pd(PPh₃)₄ to novel 2-phenyl-, 6-phenyl- and 2,6-diphenylimidazo[4,5-b]pyridines. The phenylation of imidazo[4,5-b]pyridines containing labile H was unsuccessful.

Rhodium-Catalyzed Intramolecular Silylformylation of Acetylenes: A Vehicle for Complete Regio- and Stereoselectivity in the Formylation of Acetylenic Bonds

Regio- and stereospecific intramolecular silylformylation of acetylenic bonds was studied in the presence of a Rh complex catalyst. Reaction of pent-4-ynylmethylphenylsilane with CO and a catalytic amount of either the zwitterionic Rh complex \( \text{Rh}(\text{dppc})\text{NBD}^\text{--}\text{PF}_6^\text{--} \) (1) (NBD = bicyclo[2.2.1]-hepta-2,5-diene, dppc = 1,1-bis(diphenylphosphino)cobaltocene) is reported. (1) reacts in both states of charge with H₂ in acetone to give [Rh(dppc)- (acetoacetate)]²⁺ (2). Studies of the effect of changes in the ligand state of charge on catalytic activity showed that between the two states of charge of (2), (2)₆ is the faster and more durable hydrosilation catalyst, while (2)₆ is the faster hydrogenation catalyst.

Rhodium Catalysed Asymmetric Hydroformylation with Diphosphite Ligands Based on Sugar Backbones

Chiral diphosphite ligands prepared from (2,2'-biphenyl)-1,1'-diyl, etc., and sugar backbones were used in the Rh catalysed asymmetric hydroformylation of styrene. Enantioselectivities ≤ 64% were obtained with stable 

Hydroisilylation of Phenylacetylene Catalyzed by [Ir(COD)(η²-Pr₂PCH₂CH₂OMe)][BF₄]⁻

The cationic complexes [Ir(diolefin)(η²-Pr₂PCH₂CH₂OMe)][BF₄] (diolefin = 1,5-cyclooctadiene or tetrafluorobenzobarrelene) and [Ir(diolefin)- (η²-Pr₂PCH₂CH₂OMe)][BF₄] catalyse the reaction of phenylacetylene with triethylsilane to give PhCH=CH₂, Ph₂C=CH₂, Ph₂C=CH₂, cis-PhCH=CH₂, trans-PhCH=CH₂, and Ph₃Si=CH₂. Under catalytic conditions both hydridoalkylsilane and hydridoalkylsilane intermediates are formed.

Aromatic Hydrogen Isotope Exchange Reactions Catalysed by Iridium Complexes in Aqueous Solution

Ir chloro complexes in aqueous acetic acid solution are active catalysts for H isotope exchange in aromatic compounds. The optimum conditions for exchange were found at 0.02 M catalyst concentration in a solvent consisting of 50 mol % acetic acid/H₂O, at 160°C when the exchange rate was significant and precipitation of Ir metal was minimised. The active catalyst for both systems is a solvated Ir(III) specie.
Ruthenium-Catalyzed Synthesis of Butenolides and Pentenolides via Contra-Electronic α-Alkylation of Hydroxyalkynes


The addition of alkynes to 4-hydroxy-2-alkynoates in an Alder-ene type mode yielded butenolides in the presence of CpRu(COD)Cl, which was the most effective catalyst, in aqueous DMF or MeOH when the reaction proceeded with excellent chemoselectivity. Ru catalysts changed the rules of selectivity with respect to regioselectivity, when the usual preference for β-alkylation is reversed and α-alkylation becomes predominant. Acetogenin (+)-ancepsenolide was obtained from commercially available 10-undecenal and methyl (S)-lactate in seven steps with 31% overall yield.

Catalytic Addition of Aromatic Carbon-Hydrogen Bonds to Olefins with the Aid of Ruthenium Complexes


Ru(H)(CO)(PPh3)3 catalysed the addition of ortho C-H bonds of aromatic ketones to olefins with a high efficiency and selectivity. 2'-Methylacetophenone reacted with terminal olefins to give 1:1 coupling products in good to excellent yields. Acetylnaphthalenes, cylic aromatic ketones and heteroaromatic ketones also reacted with triethoxyvinylsilane to give 1:1 addition products in nearly quantitative yields.

GLASS TECHNOLOGY

Platinum Tube Feeder Aids Holloware Forming

E. SCHÖTZ, Glass, 1995, 72, (5), 181–182; 185–186

Development in feeder tube technology showed the advantages of using a Pt tube feeder with an agitator chamber, for processing special glasses which are chemically highly homogeneous. The increased demand for quality, and the reduction in cost, is making the use of Pt feeders for mass-produced container or domestic glassware very important.

ELECTRICAL AND ELECTRONIC ENGINEERING

Highly Reproducible Fabrication Technology for Passivated AlGaAs/GaAs Heterojunction Bipolar Transistors with Pt/Ti/Pt/Au Base Electrodes


A highly reproducible fabricaton technology for passivated heterojunction bipolar transistors has been developed using a thermally stable Pt/Ti/Pt/Au base electrode. Metal penetrates through the AlGaAs emitter layer to contact the base layer. A citric acid based selective etchant is used to allow the reproducibility of passivation layer thickness. The excess base leakage current density was reduced to ~1 μA/μm.

Direct Liquid Injection MOCVD of High Quality PLZT Films


High quality La-modified lead zirconate titanate (PLZT) which has excellent ferroelectric properties for non-volatile memory was deposited as films on (111)Pt/Ti/SiO2/Si substrates by direct liquid injection metal-organic chemical vapour deposition. The as-deposited PLZT films had smooth, reflective surfaces. XRD studies showed a single perovskite phase with a-axis oriented PLZT films formed in situ at a substrate temperature of 650°C. Electrical fatigue tests showed 70% of the original switched polarisation still remained after 1×10⁷ cycles.

Magnetoresistance and Interlayer Coupling in Co-Pt/Cu/Permalloy Sandwiches


Addition of a small amount of Pt (~5.5 at.%) greatly improved the magnetic hardness of very thin Co films. Co-Pt/Cu/permalloy sandwiches were prepared by combination of the hard Co94.5Pt5.1 film with a soft permalloy film. The sandwiches exhibited a large magnetoresistance of ≤4.4% without any buffer underlayers, but the magnetisation reversal field of the permalloy layer was increased due to the ferromagnetic interlayer coupling with a Co-Pt layer. This coupling could be decreased by reducing the interfacial roughness in the sandwiches and the magnetisation fluctuations in each magnetic layer.

Field Emission and Atom Probe Field Ion Microscope Studies of Palladium-Silicide-Coated Silicon Emitters


Pd-silicide-coated field emitters were prepared by Pd thermal evaporation onto Si tips, followed by annealing at 675 K. Pulsed laser atom probe analysis showed a clean near stoichiometric, Pd5Si layer with a thin Si-enriched surface, which is converted to an oxidised layer after exposure to air. As the voltage is raised there is a large increase in field emission which corresponds to the disruption of the oxide layer.

MEDICAL USES

Platinum Anticancer Drug Binding to DNA Detected by Thickness-Shear-Mode Acoustic Wave Sensor


Nucleic acid was attached to the electrodes of thickness-shear-mode acoustic waves devices to produce a biosensor for Pt-based drugs. The decreases in series resonant frequency for interactions of DNA with both cis- and transplatin showed two distinct kinetic processes which were explained in terms of nucleic acid binding of the hydrolysis products. Concentration-dependent decreases of series resonant frequency showed the detection limit for the drugs of ~10⁻⁷ M.
NEW PATENTS

METALS AND ALLOYS

Gold-Colour Tarnish Resistant Alloy
N. J. LAMONTAGNE et al. U.S. Patent 5,409,663
An In-free gold-coloured alloy comprises (by wt. %):
≤ 10 Au, 28-35 Cu, 19.5-22.5 Ag, 6-11 Pd, 22-32
Zn, 0.1-1 Al and 0.5-3 Pt. Also claimed is a gold-
coloured alloy containing: 5-11 Au, 28-35 Cu,
19.5-22.5 Ag, 6-11 Pd, 22-32 Zn, 0.1-1 Al, 0.5-3
Pt, 5-8 Ni, 0.1-1 Si and 0.01-0.1 B. The alloy is
tarnish and corrosion resistant.

CHEMICAL COMPOUNDS

Chloropentane Ammine Iridium Dichloride
TANAKA KIKINZOKU KOGYO K.K.
Japanese Appl. 6/298,535
IrCl₃ is dissolved in HCl, added to an autoclave with
NH₃ water at 120°C for 24 h, to form chloropent-
tane ammine Ir dichloride, followed by filtration and
purification by recrystallisation. The process is
simple and efficient and the compound is used as a
catalytic material in vehicles.

ELECTROCHEMISTRY

Electrode Used in Electrolytic Processes
IMPERIAL CHEM. IND. P.L.C.
World Appl. 95/5,498-99A
An electrode with a valve metal (alloy) substrate is
given an outer coating of an electrocatalytically-active
material, that contains ≥ 10 mol % of Ru oxide and
≥ 20 mol % of a non-noble metal oxide, by thermal
spraying or PVD. Also claimed is an electrode, where
the coating has a loading of 5-100 g/m² of nominal
electrode surface. The electrode has long life and is
used in the electrolytic production of Cl₂, etc.

Electrolytic Production of Palladium Deuteride
OSAKA GAS CO. LTD.
Japanese Appl. 6/293,985
Production of Pd deuteride by electrolysis comprises
occluding D into Pd at 10°C lower than normal elec-
 trolytic temperature and raising the temperature to
the normal electrolytic temperature. The Pd deuteride
can initiate normal temperature nuclear fusion. In an
example, a Pd plate cathode, Pt wire anode, and LiOD
0.5 mol/l D₂O solution were used during electrolysis
at 10°C and 200 mA/cm². The D/Pd ratio was 0.95.

Iridium Oxide-Coated Electroplating Electrode
NIPPON STEEL CORP.
Japanese Appl. 6/293,998-294,000
A Ti nitride ceramic layer is on the surface of a Ti
metal base material and an Ir oxide ceramic layer on
the surface of the Ti nitride ceramic layer. Layers of
Ir and Ir oxide may be formed on the surface of the
Ti base. The Ir oxide layer protects the electrode base
from penetrating pin holes, thus preventing corrosion,
and so can be used under severe conditions.

Corrosion Resistant Insoluble Electrode
NIPPON STEEL CORP. Japanese Appl. 6/299,396
The insoluble electrode comprises a conductive metal
electrode mother material, a conductive IrO₂ top layer
and a layered structure of porous non-conductive
material and conductive oxide consisting mainly of
IrO₂ to fill the voids in the porous non-conductive
material between the mother material and the top
layer. The electrode has a high corrosion resistance
even under a high current density.

Electrode for Surface Treating Stainless Steel
DAISO CO. LTD.
Japanese Appl. 6/346,267
The electrode comprises a conductive metal base of
valve metal or its alloy, covered with an electrode active
layer containing Pt group metal oxide prepared by the
sol-gel method and a valve metal or oxide of Group
IVB (not C). The base body is protected from electro-
lyte owing to the dense and strongly adhered thin
wet gel film. In an example, the electrode was used
as the anode in an aqueous Na sulphate using a Pt cath-
ode at 200 A/dm². The electrode is used for electro-
plating of Sn, Zn, Cr or treating stainless steel.

Preparation of Ammonia or Alkali Solution
BASF A.G.
German Appl. 4,326,539-40
Preparation of NH₃ or aqueous alkali solution (1) and
peroxodisulphate (2) from electrolytes containing NH₃,
or alkali sulphate involves electrolysis of dilute or con-
centrated sulphate solution in a cell with cation
exchanger membrane and a smooth Pt anode, using
additive containing C and S and/or N. H₂S₀₄ and/or
H₂SO₄ are also prepared by electrolysis of H₂SO₄ solu-
tion. NH₃ or (1) and (2) are prepared with high cur-
rent yield and the process uses waste liquors.

ELECTRODEPOSITION AND SURFACE COATINGS

Electroless Plating on Palladium Seed Layer
ASTARIX INC.
World Appl. 95/2,900A
A structure comprising Al-Pd alloy with an active cat-
ylatic surface, provided by etching away Al, acts as a
catalytic ‘seed’ layer. Small isolated regions can be
plated at the same rate as larger regions or dense arrays.
Good adhesion of the plated film is obtained. It is use-
ful in electroless plating for forming high-resolution
conductive wiring patterns in semiconductors, etc.

Selective Seeding for Electroless Plating
INT. BUSINESS MACHINES CORP.
U.S. Patent 5,380,560
A polyimide surface of a metal or alloy is selectively
seeded for electroless deposition of a further metal by
treating with an activating solution of PdSO₄,
Pd(CIO₃)₂, Pd(CF₃SO₃)₂, Pd(NO₃)₂ or Pd(BF₄)₂. Pd
is removed from the polyimide by rinsing with deionised
H₂O or aqueous Na citrate and plated further with
metal. The seeding of metal interconnections on Pd(II)
polyimide dielectrics is highly selective.
Electroless plating for multilayer circuits uses a catalyst of reduced noble metal bromo complex with bromide ions. The substrate to be plated is contacted with the bromo Pd solution and the catalyst is then reduced by, for example, a borohydride or an amine borane, and electrolessly plated. A stable electroless plating is achieved. There is high catalytic activity even with a large Br molar excess and no displacement coatings are formed on metallic surfaces.

Platinum Coating with Uniform Thickness
TANAKA KIKINZOKU KOGYO K.K.

Pt coating comprises holding a workpiece with top and bottom clamps coated with insulation material in a Pt coating jig, applying chemical etching as pre-treatment, holding the workpiece with top and bottom clamps uncoated with insulation material in the Pt jig, immersing the workpiece into the Pt coating bath and applying electric current through the uncoated top and bottom clamps. Pt is coated at a uniform thickness around the clamped part.

Palladium-Copper Alloy Plating
TAKAMATSU MEIKI KOGYO K.K.

A Pd-Cu alloy plating coating layer contains 50–95% Pd and 2–50% Cu and is made electropplatting using a solution containing, for example, ethylene diamine Pd complex salt and Cu sulphate. The coating may have a metal plating layer and/or Cu alloy plating layer as a base layer. The Pd-Cu plating coating is used for watch cases or glasses for a white coloured appearance. It has high coating quality and avoids inducing allergies by using Cu instead of Ni.

Electroless Plating Catalyst
ISIHARA YAKUHIN K.K.

Electroless plating for selective coating of Ag base material comprises an aqueous solution containing 0.0001–0.5 mol/l Pd compound and 0.1–10 mol/l of alkali metal halide, sulphate of alkali metal earth, NH₄ halide or NH₄ sulphate. The catalyst solution assures selective electroless plating only on the Cu base material, and eliminates skip-phenomenon on printed wiring board.

Palladium Coating Solution
KOJIMA KAGAKU YAKUHIN K.K.

Pd coating solution comprises: soluble Pd salt 1.0–40.0 g/l as Pd; pyridine sulphonate or its salt, or pyridine carboxylate or its salt 0.1–20.0 g/l; and urea or its salt 1.0–50.0 g/l. The Pd coating solution may also contain an anionic surfactant. This high purity Pd coating solution forms a Pd deposit, preferably > 5 μm, suitable for electronic devices or for ornaments. The obtained Pd deposit has high gloss and high ductility, does not crack under bending or under NH₄ exposure testing, and does not discoulour under bonding at an elevated temperature.

Electroplated White Palladium Coatings
ENTHONE-OMI INC.

A process for depositing white Pd coatings on a substrate comprises immersing the substrate in a Pd electroplating bath containing, as brighteners, special sulphur and special N compounds, such as formyl benzene sulphonic acid and sulphopropyl pyridinium betaine. The process provides a stable electroplating solution which enables the production of white Pd coatings, preferably ≤ 5 μm thick, without using metallic brighteners such as Ni and Co salts. It is used for producing a white finish on jewellery, etc.

APPARATUS AND TECHNIQUE

Gas Vapour Sensor Element
MOTOROLA INC.

A gas vapour sensor element for arsine or phosphine comprises a substrate with a surface and a Au-Pd alloy layer on the substrate. The alloy layer has an as-applied volume Pd concentration of 1–20%. The process of sensing gas vapours comprises exposing an Au-Pd alloy film disposed on the substrate to gas vapour and detecting a change in a work function of the film. The sensing element can detect less than 1 ppb of phosphine and much less than 1 ppb arsine.

Organopolysiloxane Composition
SHINETSU CHEM. IND. CO. LTD.

An organopolysiloxane composition useful as a sealant for optical devices comprises alykenyorganopolysiloxane, silicone compound, Pt catalyst and inorganic filler with a refractive index different from that of the cured product, such as SiO₂-TiO₂ glass. The composition gives cured product, with good moisture and heat resistance, mechanical strength, low thermal expansion coefficient and superior transparency.

HETEROGENEOUS CATALYSIS

Sulphided Platinum Charcoal Catalyst
DEGUSSA A.G.

Sulphided catalyst containing 0.1–5.0 wt.% Pt on activated charcoal and 0.1–2 mole S/mole Pt is obtained by mixing an aqueous Pt compound solution with an aqueous suspension of activated charcoal and heating the mixture at 70–100°C. The solution also contains an oxidant and the charcoal has particle diameter of 10–40 μm, specific surface area of > 500 m²/g and pH > 5. The catalyst is used in the selective hydrogenation of p-aminodiphenyl amine and after partial poisoning by S has improved catalytic activity.

Exhaust Gas Purification Catalyst
NE CHEMCAT CORP.

An exhaust gas purification catalyst comprises crystalline Ir silicate with atomic ratios 50–800 for Si:Ir and ≥ 15 for Si:Al. Also claimed is a catalyst-coated structure comprising a refractory support at least partially coated with catalyst. The catalyst is highly durable to hydrothermal ageing and has high activity for exhaust gas from lean burn I.C.E., boilers or gas turbines.
Catalytic Combustion Device for Purification of Polluted Air
MANNESMANN A.G. European Appl. 633,065A
Device for purification of polluted exhaust air by heterogeneous catalysis consists of a non-metallic, gas-permeable, spiral formed carrier element, that has an adsorbing layer of a coated fibrous material impregnated with Pt by sol-gel deposition, with a heatable metallic woven band. The carrier element for the coating substances is a band of knitted glass-fibre yarn, which with the metallic woven band is formed into an annular spiral disk. The device has high specific surface area and purifies exhaust air/gases from diesel engines, food processing, chemical manufacture and waste processing.

Ozone Decomposition
E. DODUCO DUERRWAECHTER G.m.b.H. & CO. European Appl. 634,205A and 635,685A
An unheated ozone decomposition catalyst consists of a metal or plastic mesh support coated with noble metal, such as Pt, Pd, etc. An air conditioning unit for cooling ambient air has the O3-splitting Pd catalyst in front of the cooling apparatus. The catalyst can decompose O3 in an air stream in air conditioning and ventilating equipment, cars, etc. It is effective at ambient temperature and also at 0°C.

Continuous Dialkyl Carbonate Production
BAYER A.G. European Appl. 634,388A
Continuous production of dialkyl carbonates of formula CO(OR)(l), where R = 1-4C alkyl, is effected by gas-phase reaction of CO with RON0 in the presence of a supported Pt group metal catalyst, an inert gas, ROH and optionally NO, with periodic or continuous addition of a halogen. The reaction is performed at 50-170°C and 0.5-10 bar using RON0:CO volume ratio of 0.1-10.1. The (1) are useful as solvents, carbonylating and acylating agents, intermediates for urethanes, ureas and gasoline octane improvers. Addition of halogen avoids possible corrosion problems associated with HCl gas addition.

Paraffin Dehydrogenation
ENRICERCHI S.p.A. European Appl. 637,578A
Light olefins (especially 2-5C) are dehydrogenated in a reactor at 450-8000°C, 0.1-3 atm and GHSV 100-10,000/hr over a Pt group metal catalyst of 0.1-33.6 wt.% Ga (as Ga2O3); 1-99 ppm Pt; 0-5 wt.% (as oxide) alkali or alkaline earth metal; and 0.08-3 wt.% modifying SiO2 on δ, δ', δ, θ, θ'/α or δ/θ/α Al2O3. Coked catalyst is regenerated at >4000°C.

Production of Phenols
TOSOH CORP. European Appl. 638,536A
Phenol (1) production comprises reacting an aromatic compound with O2 and H2 in the liquid phase in the presence of a supported Group VIII metal catalyst containing Ru, Rh, Ir and particularly Pd and Pt, and in the co-presence of a V compound, such as V(III) acetylacetone, etc. Halogens in the catalyst are ≤0.15 wt.%. (1) are produced with high selectivity. High catalytic activity is achieved over a long time. Phenols are used for resins and alkyl phenols.

Partial Oxidation of Natural Gas
SNAPROGETTI S.p.A. European Appl. 640,559A
Synthesis gas and formaldehyde are obtained by catalytic partial oxidation of natural gas, with a Pt group metal catalyst at ≥300°C. The catalyst is a wire mesh or is deposited on an inorganic carrier. The Pt group metal(s) are 0.1-20 wt.% of the wt. of catalyst plus carrier. Syndgas is obtained at UHSV and lower temperatures than at present. Further reaction can produce MeOH and optionally dimethyl ether, or be used in the Fischer-Tropsch synthesis.

Pristine Alkylsiloxanes
DOW CORNING CORP. European Appl. 641,799A
A pristine alkylsiloxane (A), containing 1-3C alkyl or phenyl, is prepared by reaction of siloxane polymer with olefinic compound in the presence of a supported Pt catalyst. Yield of (A) is >99.9% and consists of <1 ppm SiH, <100 ppm (CH2=CH-) and <ppm Pt. Also claimed is a preparation of (A) by reacting under anhydrous conditions a SiH containing siloxane polymer and an olefinic compound with ≥4C, in the presence of the catalyst and O2. The process produces extremely pure alkylsiloxanes which are clear, colourless and odourless.

Dibenzylamine Preparation
DSM N.V. European Appl. 644,177A
Dibenzylamine preparation comprises hydrogenation of benzaldehyde in the presence of NH3 and a Pd-containing catalyst, using 3-60% of a solvent or dispersion medium with respect to benzaldehyde. Preferably, the solvent or dispersion medium is H2O in an amount of 5-20 wt.%; the catalyst is Pd/C and the reaction is performed at 80-120°C. High selectivity of >95% with complete conversion is obtained. High production capacities are achieved and simple recovery procedures can be used.

Catalyst for Thermal Decomposition of Nitrogen Oxides
NAT. SCI. COUNCIL European Appl. 645,171A
A catalyst for the thermal decomposition of NO in I.C.E. or industrial exhaust gases comprises an Al2O3, or Mg aluminate support which in an active phase of Pd crystallites on a Pd alloy dispersed on the support. The Pd alloy is Pd crystallites modified by addition of at least one alloying metal of Cu, Ag or Au. The catalyst has high activity especially at ~800°C, is resistant to poisoning by high concentrations of O2 or SO2 in the feed gas and retains high activity over time.

Catalyst for Removing Dioxins
NE CHEM CAT CORP. European Appl. 645,172A
Catalyst (1), for treating exhaust gases containing dioxins comprises Pt, Pd and/or Ir or their oxides on a support (2) of SiO2/B2O3/Al2O3 composite oxide or zeolite, is obtained by spraying or dripping a solution or dispersion of the active components onto a powder of (2). Exhaust gas (3) containing dioxins at concentration below 10 ng/m3 is contacted with (1) at 150-280°C. (1) has long life and reduces dioxin concentration in (3) to below 0.1 ng/m3 and also suppresses additional dioxin formation.
Palladium Three-Way Catalyst

ENGELHARD CORP. World Appl. 95/235A

A layered catalyst composite consisting of 2 similar layers is used as a three-way catalyst to treat automotive exhaust gas. The first layer comprises a first support, a first Pd component, an oxygen storage component, and optionally a Pt group metal component other than Pd, a Zr component, an alkaline component, or PdO (WPd = 1-20%) to form a combustion catalyst. The second layer is then applied in a similar way.

Low Pressure Manufacture of Cyclohexane Dicarboxylate Ester

EASTMAN CHEM. CO. U.S. Patent 5,399,742

Manufacture of dimethyhcyclohexane dicarboxylates in a continuous process comprises feeding H₂ gas with a liquid mixture of the dimethyl cyclohexane dicarboxylate product and the corresponding dimethyl benzene dicarboxylate to a hydrogenation zone containing at least one fixed bed of Pd/Al₂O₃ catalyst. H₂ and a liquid product containing the dimethyl cyclohexane dicarboxylate product are removed.

Hydrogenation of Aromatics and Olefins

UOP U.S. Patent 5,384,038

A hydrocarbon feedstock is reformed to obtain an aromatics-rich product by contacting Pt and Pd on a support of a non-acidic large pore molecular sieve, such as zeolite L₁ and an inorganic oxide binder, such as SiO₂. The specified Pt and Pd metal distribution improves catalyst activity and selectivity to aromatics, and enhances catalyst stability when small amounts of S are in the feed.

Catalyst for Chlorine Dioxide Generation

AMTX INC. U.S. Patent 5,391,533

A catalyst system comprising a porous sintered Al₂O₃ and SiO₂ agglomerate catalyst substrate, with Al₂O₃ particles joined to other Al₂O₃ particles via point bonding silicates, is produced by compressing a particular material at low pressure. The Pt group metal, preferably Pd, is supported on the substrate. The catalyst is useful in CH₂Cl₂ generation. The system creates a unique microstructure with a unique surface area which contributes to maintaining constant conversion efficiency and high chemical activation levels.

Improved Preparation of Acetic Acid

SHOWA DENKO K.K. Japanese Appl. 6/293,695

Preparation of acetic acid (1) comprises reaction of ethylene with O₂ and H₂O in the gaseous phase over Pd-V,H₂PO₄ catalyst prepared by treating supported Pd catalyst containing one or more metals (2) selected from Cr, V, Mo and W with H₂ PO₄. The catalyst is prepared by supporting Pd containing salts and (2)-containing salts on SiO₂, Al₂O₃, etc. The process is performed in the gaseous phase, and (1) is prepared more economically than from liquid phase reactions.

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Purification of Organic Impurities in Inert Gas

SINCO ENG. S.P.A. World Appl. 95/2,446A

O₂ or O₃ containing gas (1) is added to an inert gas containing organic compounds as impurities circulated at 250-600°C on a catalyst bed of Pt optionally with Pd on an inert porous support to purify the gas. Amount of (1) added is stoichiometric with respect to impurities, or in excess, so that gas leaving the bed contains < 10 ppm O₂. Inert gas is N₂; impurities are aldehydes, glycols and glycol oligomers. The process avoids a deoxidation stage with Pt prior to recycling of purified gas.

Combustion Catalyst for CH₄-Type Fuel

DENRYOKU CHUO KENKYUSHO Japanese Appl. 6/296,866

Rh is supported on a catalyst surface containing Pd or PdO (Rh:Pd = 1-25%) to form a combustion catalyst for CH₄ type fuel. The catalyst has good durability. In an example, 12 g/l Pd and γ-Al₂O₃ are supported on a cordierite honeycomb support, immersed in 2.5% Rh nitrate solution, ion exchanged to precipitate Rh and thermally treated at 700°C for 30 min to form catalyst with Rh:Pd of 3%.

Dehydrocyclisation of Paraffins

UOP U.S. Patent 5,384,038

A hydrocarbon feedstock is reformed to obtain an aromatics-rich product by contacting Pt and Pd on a support of a non-acidic large pore molecular sieve, such as zeolite L₁ and an inorganic oxide binder, such as SiO₂. The specified Pt and Pd metal distribution improves catalyst activity and selectivity to aromatics, and enhances catalyst stability when small amounts of S are in the feed.

Purification Catalyst for Exhaust Gas

NISSAN MOTOR CO. LTD. Japanese Appl. 6/296,869

A catalytic component, composed of Pd, activated Al₂O₃, and CeO₂ containing Fe and Zr, Co or Ni, and Li, Na, K, Ba or Sr as additive, is used to purify hydrocarbon, CO and NOx in exhaust gas. In an example, activated Al₂O₃ supporting 2% Pd and CeO₂ containing Fe and Zr, was mixed and wet ground using HNO₃ to form a slurry, coated on a cordierite support, dried and burned at 400°C for 1 h, to form the catalyst.
2,3-Dihydro-1H-indene Derivative

Preparation of optically active 2,3-dihydro-1H-indene derivative (1) and its salts (2) comprises catalytic hydrogenation of 2,3-dihydroindene derivative (3) or its salts in the presence of PtO, or Pd/C catalyst. Preferably, (3) is hydrogenated in suitable solvent such as lower alcohols at -20°C to 100°C under 1-50 atm for 0.5-10 h. A specific optically active stereoisomer (1) and (2) with high optical purity can be prepared selectively by using these catalysts. (1) and (2) are useful as materials for drugs in treating hypoxia, etc.

Preparation of Chloroformic Acid Esters

UBE IND. LTD. Japanese Appl. 6/306,016-17 Preparation of chloroformic acid ester (1) comprises contact reacting Cl,, CO and nitrous acid ester in the presence of a solid catalyst supporting a Pt group metal, such as Pd/Al2O3, and maintaining 0.1-100 moles of nitrous acid ester to 1 mole of Cl,. The esters (2) may also be prepared by reacting CO with nitrite ester and HCl or nitrosyl chloride with a Pt group metal catalyst. (1) and (2) are starting materials for chemical manufacture. The one-step method forms esters selectively. The process may be performed without using toxic phosgene.

Catalytic Reduction of Nitrogen Oxides

AGENCY OF IND. SCI. & TECHN. Japanese Appl. 6/327,980 The catalyst substrate is coated with an undercoat containing 100 pts. wt. of a Pt group metal, such as Pt, Rh, Ir, Pd and Ru, 100-100,000 pts. wt. oxides of Ce, La, Nd, Ge or Ga, and preferably 0.0001-0.1 pts. wt. Au on a support and laminated with a top coat containing Al2O3, TiO2, ZrO2 or H type zeolite. NOx is reduced efficiently and selectively. It can be used for purification of exhaust gases.

Decomposing Organic Halide

SUMITOMO METAL MINING CO. Japanese Appl. 6/335,619 Organic halide is removed from waste gas by contacting it with a Pt or Pt oxide loaded catalyst containing 0.1-5 wt.% Pt. The catalyst support is ZrO2 prepared by reacting zirconyl nitrate with NH4 water in the presence of organic halide containing gas, air and H2O2, followed by heating at 700-850°C. The organic halide, which contains Cl and/or F, such as freon or trichloroethylene, is decomposed. The catalyst is quite stable to concentrated HCl or HF, so it can be used over a long time.

Harmful Volatile Organic Halogen Treatment

KURITA WATER IND. LTD. Japanese Appl. 6/343,983 The treatment comprises contacting a gas containing volatile organic halogen compound with a reducing agent (H2) in the presence of a catalyst supporting a metal, preferably Pd, Pt etc., in an amount of 0.1-10 wt.% based on the carrier, to decompose the gas. The reaction is controlled to 100-250°C. The carrier is preferably Al2O3, TiO2, active C, etc. Compounds, such as trichloroethylene, etc., of boiling point < 150°C, are removed from the gas, making it harmless.

Highly Dispersed Platinum Catalyst

TANAKA KIKINZOKU KOGYO K.K. Japanese Appl. 7/8,807 Highly dispersed Pt catalyst is manufactured by reducing Pt ion using Pt dinitro diamino nitrate solution and ethanol as reducing agents. The catalyst is manufactured without using surfactant, so the process is simple and the cost is low.

Preparation of Cyclopentyltrichlorosilane

SHINETSU CHEM. IND. CO. LTD. Japanese Appl. 7/10,887 Cyclopentyltrichlorosilane is prepared by reacting cyclopentene with trichlorosilane in the presence of a Pt catalyst which includes H2PtCl6H2O, Pt/C, etc., while introducing gaseous inorganic oxygen compounds into the reaction system. When solvent is used, hydrocarbon or chlorinated solvent is used in 0.1-100 times as much as the raw material cyclopentene. Cyclopentyltrichlorosilane, which is useful as high activity base material for organic Si compound and compounds with groups of organic Si, is prepared in markedly high yield > 90%.

Simultaneous NOx Reduction and CO Oxidation

GAS DE FRANCE French Appl. 2,707,075 A catalyst, for the reduction of NOx to N2 by CH4 or any mixture containing CH4 (such as natural gas) in an oxidising atmosphere, comprises a MFI-type zeolite exchanged with 0.3-2.0% of Pd, relative to total catalyst weight. Simultaneous oxidation of CO to CO2 and CH4 to CO2 also occur. The catalyst can be used in an oxidising medium with CH4, natural gas or petrol in the presence of H2O.

HOMOGENEOUS CATALYSIS

Production of Thiophene Compounds

SUMITOMO METAL MINING CO. European Appl. 633,263A Production of thiophene compounds from alkylidene derivatives comprises catalytically reducing them with H2 in a solvent mixture of at least one alcohol and H2O in the presence of a Pd catalyst soluble in organic solvents. Flocculent and adsorbent, to flocculate the Pd catalyst which is removed, are optionally added. High yields of thiophene can be obtained.

Isomerisation of External Olefins

FRANCAIS DU PETROLE European Appl. 636,676-77A Isomerisation of external olefins to more highly substituted and/or internal olefins in diolefin-free or diolefin-containing charge is carried out over a Pd containing catalyst pretreated with a solution of a S compound to give 0.05-10 wt.% S. The catalyst is then activated by treatment in a neutral or reducing atmosphere at 20-300°C, 1-50 bar and 50-600 volume of gas per volume of catalyst per hour and H2 at 20-200°C and 1-50 bar. The catalyst gives 100% removal of diolefin and higher conversion of 1-olefins than untreated catalyst.
Process for Hydrosulphination of Olefins

HORCHST A.G.

European Appl. 641,755A

Hydrosulphination of olefins is carried out in the presence of a Pd(II) salt, such as PdCl₂, PdBr₂, etc., and at a temperature between the ceiling temperature of the SO₂ olefin copolymer system and 160°C. The sulphinic and sulphonylic acids produced are useful as precursors for plant protection agents and pharmaceuticals, and as intermediates for reactive dyestuffs.

Acetic Acid Production

BP CHEM. LTD.

European Appl. 643,034A

Acetic acid production comprises carboxylation of MeOH, or a reactive derivative, using CO in a liquid reaction mixture containing acetic acid, an Ir catalyst soluble in H₂O, such as IrCl₃, Ir₂, etc., MeI, H₂O, methyl acetate, and Ru and/or Os as promoters, such as Os(III) chloride hydrate, OsO₄, etc., Ru(III)- and Ru(IV) chlorides, etc. Increased reaction rates of ≥ 96% higher than prior methods, are obtained at relatively low CO partial pressures. When Ru is the promoter the volatility of Ir catalysts may be reduced, allowing operation at reduced Ir levels, which may reduce by-product formation.

Preparation of N-Vinyl Compounds

BASF A.G.

European Appl. 646,571A

N-vinyl compounds are produced from NH compounds using acetylene at 50-250°C and 1-30 bar in the presence of a Pt group metal compound as catalyst. The acetylene is used with an inert gas in a volume ratio of 6:1-0.5:1. N-vinyl compounds can contain H, 1-20C alkyl, 5-8C cycloalkyl, 7-18C aralkyl or 6-18C aryl, or a saturated, unsaturated or aromatic heterocyclic ring, etc. The vinyl compounds can be used to produce polymers for clarifying liquids, film-formers in hair treating agents or in detergents. The process gives an improved space-time yield and better control of acetylene conversion.

Modified Pyrimidine Derivatives

UNIV. WASHINGTON STATE RES. FOUND.

World Appl. 94/29,279A

Modified pyrimidine derivatives for production of nucleic acid antibodies are prepared by reacting pyrimidine starting material with tetraalkyl Sn compound in the presence of a PdL₃ catalyst, where L may be PPh₃, and isolating the modified pyrimidine. The catalyst is prepared in a solution of Pd(OAc)₂ and PPh₃ in a molar ratio of 3, in THF, MeCN, oxane, aceton, tetrahydropropylene or morpholine. The catalyst improves yields of vinyl and aryl coupling products. The antibodies may have altered structures with increased capacity to bind target molecules.

Ethynically Unsaturated Compounds

SHELL CANADA LTD.

World Appl. 95/5,354A

Hydroformylation of ethynically unsaturated compounds by reaction with CO and H₂ uses a catalyst of Pt group metal cations, anions other than halide and bidentate ligands. Improved conversion rate, linearity of products and suppression of paraffins are obtained even at moderate temperature. Aldehydes and/or alcohols, such as propanol, are produced.

New Polyethers

EASTMAN CHEM. CO.

U.S. Patent 5,393,867

New polyethers, used in the production of surfactants are prepared by polymerising 3,4-epoxy-1-butene in the presence of a Pd(0) catalyst and nucleophilic initiator, or at -40 to +60°C in the presence of a Pd(0) catalyst, 2-4 trihydrocarbonyl-phosphine ligands and an organic hydroxyl initiator. Polymers containing polyether residues can be produced.

Aryl-Aliphatic Carboxylic Acid Derivatives

ALBEMARLE CORP.

U.S. Patent 5,399,747

The preparation of aryl substituted aliphatic carboxylic acid derivatives comprises treating an aryl substituted aliphatic ether or thio ether and H₂O with CO at a pressure of ≥ 1 atm and 25-200°C in the presence of Pd(0) catalyst or a Pd compound where Pd has valence 1 or 2, mixed with a Cu compound, and at least one acid-stable ligand. Ibuprofen can be produced economically.

Chlorobutene Carbonylation Catalyst

DSM N.V.

U.S. Patent 5,399,753

A process for the preparation of 3-pentenoyl chloride (3PC) comprises treating the still gases obtained by the distillation of 3PC with a reaction mixture containing Pd catalyst residue with concentrated HCl acid at 100-120°C. The above products are combined with chlorobutene to form an organic phase and a HCl acid phase containing the Pd catalyst residue; the latter is combined with chlorobutene and distilled to an azeotropic mixture in a CO atmosphere at 70-75°C until only a chlorobutene phase remains, forming crotyl Pd chloride, heating and recovering 3PC by distillation. Pd catalyst is recovered, recycled and re-used.

Fluorine-Containing Surface Active Agent

SHINETSU CHEM. IND. CO. LTD.

Japanese Appl. 7/793

Preparation of the F-containing surface active agent comprises batch-mixing organic Si compound with polyether compound in aprotic solvent in the presence of Pt-based catalyst followed by hydroisolation. The agents are prepared without side reaction and with high reaction efficiency in a short period of time.

Production of Carbonyl Compounds

TOSOH CORP.

Japanese Appl. 7/10,797

Carbonyl compounds are produced quickly and efficiently from cyclic or straight chain olefins using a catalyst containing a Pd compound and a polyoxoanion group compound. At least a part of the counter-cation of the polyoxoanion group compound is greater than selected from Ni, Mn, La, Zn and Ce.

Production of Intermediates for Vitamins

RHONE POULENC NUTRITION ANIMALE

French Appl. 2,706,452

Production of intermediates for synthesis of vitamins A and E and carotenoids comprises: reacting an allylic compound (1) with a vinyl halide compound in a polar solvent in the presence of a base and Pd(OAc)₂, PdCl₂ or a Pd phosphine complex catalyst, and treating the product with a protonic acid. The base may be an alkaline metal carbonate or acetate, or a Ag or Ti salt. (1) is vinyl-β-ionol, methylbutenol, linalool, etc.
Selective Oxidation of Organic Compounds
BAYER A.G. German Appl. 4,331,671
The selective oxidation of organic compounds by $O_2$ is performed in the presence of a Pd and Cu catalyst and CO. The process is useful for oxidizing linear and cyclic 2-5C olefins to epoxides; aromatics to phenols, etc. With $H_2O$ additions, olefins or acids give glycols or glycol esters; and cyclohexanone with NH, etc. With HzO additions, olefins or acids give glycols or glycol esters; and cyclohexanone oxime and/or e-caprolactam; and linear ketones with NH, give azines.

FUEL CELLS
Solid Polymer Electrolyte for Fuel Cell
TANAKA KIKINZOKU KOGYO K.K. European Appl. 631,337A
A solid polymer electrolyte (SPE) composition comprises a solid polymer cation or anion exchange resin and 0.01–80 wt.% metal catalyst. The catalyst is Pt, Pd, Rh, Ir or Au. SPE is used as a fuel cell membrane. It produces $H_2O$ and also retains the $H_2O$ so that it has high ionic conductivity. The membrane depresses the crossover which improves cell performance.

Steam-Reforming Catalyst for Fuel Cells
TONEN CORP. Japanese Appl. 6/339,633
A steam-reforming catalyst for hydrocarbons for fuel cells contains a catalytically active component of a Pt group element in 0.1–10 wt.% with respect to the total amount of catalyst and with a specific surface area of 1–20 m$^2$/g. The fuel cell is preferably molten carbonate and the fuel of LNG, LPG, etc. is reformed directly inside. Contamination by alkali carbonate via a gas phase route is inhibited and catalyst has longer life.

CHEMICAL TECHNOLOGY
Ruthenium Oxide Hydrate Powder
JAPAN ENERGY CORP. Japanese Appl. 6/345,441
Ru oxide hydrate powder is prepared by reducing a solution of Ru salts of valency >4. An aqueous solution of Na$_2$RuO$_4$ and acetone were reacted, and uniform grain size powder was obtained. The powder is used to make thick film resistors. The uniform grain size RuO$_2$, $NH_3$ and RuO$_2$ powder is prepared with low cost materials, and without crushing apparatus.

ELECTRICAL AND ELECTRONIC ENGINEERING
Soft Magnetic Material Composition
READ RITE CORP. European Appl. 642,183A
A soft magnetic alloy contains 82.7–84.7 at.% Ni, 15.3–17.3% Fe and Rh in an at.% defined by Rh = 11.63 (Ni:Fe atomic ratio)−49.53 (1). Also claimed is a magnetoresistive read transducer with a magnetoresistive layer and at least one soft magnetic layer as above. Reduction of the corrosion rate of Ni-Fe alloys while maintaining low magnetic permeability, and high temperature stabilities, ductility, etc.

Use of Gold-Palladium Alloy for Dentistry
DEGUSSA A.G. German Appl. 4,324,738
High gold content Au-Pd alloy comprises 6–5 wt.% Pd, 0–12 wt.% Pt, 0–2 wt.% Ir, Rh and/or Ru, 0.7–5.8 wt.% Sn and remainder Au, for dental cast parts, which are optionally blended with ceramics. The alloys have improved corrosion resistance, good mechanical and high temperature stabilities, ductility, etc.

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