PLATINUM METALS REVIEW

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Diesel Emission Control Technology

SYSTEM CONTAINING PLATINUM CATALYST AND FILTER UNIT REMOVES PARTICULATE FROM DIESEL EXHAUST

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Recent concerns over the health effects of particulate emissions from vehicles have focused on diesel engines. While European legislation to limit their emissions is now in place it is expected that future legislation will be more demanding. Using a platinum catalyst it has been possible to demonstrate in various trials the practical application of a novel system for the removal of both the soot and hydrocarbon components from diesel powered vehicle exhaust. The background to the development of this successful technology is described here.

Diesel engines find widespread application as power sources in both mobile and stationary applications. Their innate high efficiency and economy have resulted recently in unprecedented growth in their share of the passenger car market in Western Europe. The durability of the diesel engine has also led to its dominance as a source of motive power for the transport industry.

However, the ubiquity of large diesel-engine vehicles in city environments has persuaded regulatory authorities of the need to control the emitted exhaust pollutants. European legislation limiting the quantities of carbon monoxide, hydrocarbon, oxides of nitrogen and particulate matter were introduced in 1993 and will be strengthened in 1996. However, in spite of the tightening standards, a large fleet of long lived and rather polluting diesel vehicles exists in most cities around the world.

Diesel Exhaust

Diesel exhaust differs from that of petrol engine exhaust in two major characteristics. Firstly, diesel exhaust contains a far higher amount of particulate material, and secondly the exhaust is far “leaner”, that is, it is far more oxidising than the typical exhaust from petrol engines (1).

The health effects of diesel particulate have been a cause of concern for many years, because of both the chemical composition and the particle size spectrum (2). The two major components of particulate are soot and heavy hydrocarbons – the soluble organic fraction, SOF – which condenses on it during its collection. The SOF is known to contain carcinogenic polyaromatic hydrocarbons (3), however, the beneficial effect that oxidation catalysts have on the toxicity of diesel exhaust by removing SOF is well documented (4, 5).

A body of evidence implicating the soot fraction of diesel particulate as damaging to human health has recently begun to emerge. The nature of the effect appears to relate not to the chemical nature of the soot, which is predominantly carbon, but to its particle size (6). A significant quantity of airborne urban particulate is known to derive from the exhaust of diesel engines (7). In studies in the United States, very close correlations have been noted between particulate air pollution and mortality rates (8) and the California Air Resources Board has stated that there is likely to be no threshold limit below which particulate does not represent a finite health risk (9).

The diesel emissions standards for heavy duty vehicles, extant and proposed for the European Union, are shown in Table I. A bus, for example, with a 200 kW engine, which meets the 1993 standards for particulate will, if it conforms to the average emission levels measured in the steady-state test by which its engine is certified for production, emit around 80 grams
Table I

<table>
<thead>
<tr>
<th>Application dates</th>
<th>Mass of CO, g/kW h</th>
<th>Mass of HC, g/kW h</th>
<th>Mass of NOx, g/kW h</th>
<th>Mass of TPM, g/kW h</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 July 1992</td>
<td>4.5 (4.9)</td>
<td>1.1 (1.23)</td>
<td>8.0 (9.0)</td>
<td>0.36* (0.4*)</td>
</tr>
<tr>
<td>new vehicles</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1 Oct. 1993</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>all vehicles</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1 Oct. 1995</td>
<td>4.0 (4.0)</td>
<td>1.1 (1.1)</td>
<td>7.0 (7.0)</td>
<td>0.15* (0.15*)</td>
</tr>
<tr>
<td>new vehicles</td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>1 Oct. 1996</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>all vehicles</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Test Procedures:
1 July 1992 - ECE R49
1 October 1995 - ECE R49

Figures in ( ) refer to conformity of production

* In the case of engines of 85 kW or less, a coefficient of 1.7 is applied to the limit for particulate emissions.
CO is carbon monoxide, HC is polyaromatic hydrocarbons, NOx is nitrogen oxides and TPM is Total Particulate Matter.

of particulate per hour. Therefore, a large fleet of vehicles, which may frequently be older, or may simply not conform to current type-approval standards, will emit a significant mass of particulate into urban environments.

The awareness of the growing concern over these issues has caused Johnson Matthey to reassess the methods by which particulate can be removed from diesel exhaust (10). While the effect of an oxidation catalyst on the polyaromatic hydrocarbons in diesel exhaust is clearly beneficial, it has little or no effect on the quantity of soot. The net particulate mass, which includes SOF, is reduced by an oxidation catalyst, because the hydrocarbons, which co-condense with soot particles, contribute to it.

Filtration is a technique which has been widely studied for the removal of soot from diesel exhaust (11). As soot is collected on a filter placed in the exhaust stream of a diesel engine the pressure drop across the filter increases. The increased engine power which is required to drive the exhaust gases through the filter, causes the exhaust temperature and also the fuel consumption to rise. Soot combusts at 550–600°C, but it is not sufficient to rely on an increased pressure drop to generate the temperatures required in the exhaust gas to initiate the combustion, and damage to the engine under these conditions is a significant risk.

The regeneration of soot filters through soot combustion has been the subject of much work over 20 or more years, and techniques such as in-line fuel burners, catalytic fuel burners and electric heaters have all been examined. Catalyst technology has also been investigated in an attempt to lower the temperature at which the oxidation of soot commences (12). For many years it had been assumed that the mechanism by which such systems began to regenerate the filter traps involved the adsorption of particulate on the catalyst in close proximity to an oxygen activation site.

In the course of experimental work at Johnson Matthey to define the conditions necessary for the catalytic regeneration of traps we uncovered a novel mechanism (13, 14). Carbon, in the form of soot, was being oxidised, not by “activated” oxygen, but by nitrogen dioxide. The diesel combustion process is characterised by higher pressures in the cylinders than occur in spark ignited engines. The rate of formation of nitrogen oxides (NOx) in the combustion process is at least partly a function of the oxygen available, and so the higher pressure and leaner mixture of diesel engines tend to produce
more NOx. The majority of NOx emerges from the engine as nitric oxide, and it is the conversion to nitrogen dioxide, over a catalyst using the excess oxygen present in the exhaust gas, and its subsequent reaction with carbon, which is responsible for the observed depression in the temperature at which a catalysed exhaust filter can be regenerated.

It was also concluded that the nitrogen dioxide required for the reaction could be supplied upstream of a reactor containing a non-catalysed filter trap. The generation of nitrogen dioxide and the oxidation of carbon were observed to be independent processes. Catalyst formulations were investigated and platinum upon alumina was found to be the most active. Since the processes of soot trapping and soot destruction are continuous at temperatures above 275°C, we have chosen to refer to a system based on this technology as a “Continuously Regenerating Trap” or CRT.

It was foreseen at this time that application of this discovery would be problematic because of the high level of sulphur which was then present in diesel fuel. Highly active oxidation catalysts convert sulphur dioxide, formed by the oxidation of fuel-derived sulphur components during combustion, into sulphur trioxide. Sulphur trioxide adsorbs water and condenses on the filter which is used to measure particulate mass. Thus, if a high sulphur fuel is used, a significant increase in particulate mass will be recorded in standard regulatory tests where a catalytically regenerated filter is used to remove soot and SOF.

We have been prompted to re-examine the applicability of this technique as a consequence of a number of changes that have occurred in recent years. The principal changes are the availability of low sulphur diesel fuel and the widespread use of turbocharged diesel engines.

**Construction and Performance of the System**

The systems that have been tested used both ceramic catalyst substrate and ceramic filters. Ceramic filters consist of an extruded ceramic (cordierite) monolith with a low cell density, typically of 100 channels/in², in which alternate channels are blocked at one end. As the exhaust gas enters a channel, it is forced through the channel walls into an adjacent channel to exit

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**Table II**

<table>
<thead>
<tr>
<th>Test cycle</th>
<th>Sulphur content of fuel, per cent</th>
<th>Conversion, per cent</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>TPM</td>
</tr>
<tr>
<td>ECE R49 (13 mode)</td>
<td>0.005</td>
<td>80</td>
</tr>
<tr>
<td>U.S. HDT, catalyst I</td>
<td>0.05</td>
<td>87</td>
</tr>
<tr>
<td>U.S. HDT, catalyst II</td>
<td>0.05</td>
<td>92</td>
</tr>
<tr>
<td>Braunschweig (bus)</td>
<td>0.005</td>
<td>92</td>
</tr>
</tbody>
</table>

*Platinum Metals Rev., 1995, 39, (1)*
the filter. For this reason these devices are often referred to as "wall-flow" filters. The separate catalyst substrate, shown in Figure 1, had a cell density of 400 cells/in² and was coated with a layer of washcoat having a platinum loading equivalent to 50 g/ft². Extruded ceramic monoliths were chosen for these tests because of their well characterised filtration capabilities and because there is substantial experience on their application to diesel exhaust purification (15, 16). Catalyst and filter parts were separately wrapped with a mat of insulating material and welded into steel skins. These were then located in a cylindrical steel shell with appropriate inlet and exit gas distribution configurations, designed and constructed by Eminox Ltd. of Gainsborough. The degree of sound attenuation of this type of device adequately reproduces that of a conventional silencer. Thus, when mounting such a system on a vehicle, the filter system is able to be fitted as a replacement unit with great simplicity, provided that the existing unit is not located too far from the exhaust manifold of the engine.

In order to assess the performance of the system it was first mounted on a laboratory engine bench, and tests were conducted using both ECE R49 and U.S. Heavy Duty Transient (U.S. HDT) cycles on a 6 litre, 6 cylinder engine. The pollutant reductions measured in these two regulatory cycles are shown in Table II. In the case of the Heavy Duty Transient test two catalyst variants were used, the first (catalyst I) was of a slightly higher activity and showed a superior hydrocarbon conversion. The slightly lower net particulate conversion is almost certainly due to a small conversion of sulphur dioxide to sulphur trioxide in the hottest mode of the cycle.

The durability of the system was first examined in laboratory tests using an engine of the same type. A "semi transient" ageing cycle was developed to mimic the long continuous operation of an engine under rather cool conditions. The cycle is shown in Figure 2. The pressure

Fig. 3 Back pressure shown over a period of almost 6 months for a mail truck fitted with a CRT
Temperature, Maximum, °C per cent
99
89
88

Minimum, Average, per cent per cent
96
94
87
83

Pressure drop across the filter was measured over an ageing period of 1000 hours during which no increase was observed.

Practical Trials
The results of these tests were extremely encouraging and several systems have been fitted to vehicles in normal use. The stainless steel filter systems were placed in the same location on the vehicles as the original equipment silencers. This was achieved without significant alteration to the vehicle, as the systems are dimensionally similar to the conventional silencers. In one trial, a unit which had been aged for 1000 hours in the laboratory was fitted to a mail delivery truck which had an engine capacity of 7 litres (245 hp). Pressure drop measurements taken on the vehicle in service over a period of almost six months, during which it travelled a total distance of 58,000 km, are shown in Figure 3. The data shows a remarkably consistent level of pressure drop with no increase observed during the trial. At the end of the period shown the unit was removed from the vehicle and again tested on the laboratory engine. The results are shown in Table III.

In another example, a system was fitted to a city bus having a 10 litre engine (285 hp). The results of this whole-vehicle test are shown in Figure 4. After running for several weeks the bus was tested on a chassis dynamometer using the so-called Braunschweig driving cycle. This cycle has been designed to reproduce, using a complete vehicle, the type of driving experi-

<table>
<thead>
<tr>
<th>Temperature, °C</th>
<th>Maximum, per cent</th>
<th>Minimum, per cent</th>
<th>Average, per cent</th>
</tr>
</thead>
<tbody>
<tr>
<td>250</td>
<td>99</td>
<td>98</td>
<td>98</td>
</tr>
<tr>
<td>380</td>
<td>96</td>
<td>94</td>
<td>95</td>
</tr>
<tr>
<td>450</td>
<td>73</td>
<td>33</td>
<td>51</td>
</tr>
</tbody>
</table>

Table III
Particulate Conversions
(Mail truck CRT after 1000 hours ageing and 58,000 km)

![Fig. 4 Tests performed using the Braunschweig cycle on a Volvo bus fitted with a CRT system. Relative cycle emissions are shown for a normal silencer (100 per cent) and with a CRT installed. Bsfc is the brake specific fuel consumption.](image-url)
enced by a bus in a typical urban application. Normal regulatory tests involve removing the engine from the vehicle and so do not reflect its true on-road dynamic emissions behaviour. Conversions of 98 per cent carbon monoxide, 96 per cent hydrocarbons, 6 per cent NOx and 92 per cent particulate were observed in the cycle. A small increase in carbon dioxide emissions was also noted. This derives from the oxidation of carbon monoxide, hydrocarbons and soot as well as from a 1 to 2 per cent increase in fuel consumption.

To-date some 23 systems have been fitted to heavy duty vehicles in Sweden including buses, delivery trucks and refuse collection trucks. The observed back-pressure behaviour for a refuse truck which covered only 10,000 km over a period of seven months' heavy operation is shown in Figure 5. This is a particularly difficult duty cycle for a filter system since the engine spends much of its time operating with rather a cool exhaust, see Figure 6 which shows a typical temperature trace. All these systems have demonstrated a similar lack of pressure drop build-up as those described above.

**Discussion**

The original work on filter regeneration temperatures suggested that a temperature of below 300°C was achievable, and this work confirms that regeneration is occurring at or below 275°C. This is important because it must be possible to regenerate the filter at temperatures routinely reached in the exhaust of a vehicle operating under normal conditions.

From the work undertaken so far it is clear that this technology is applicable to situations where three basic criteria have to be met, namely:
- There should be a reasonable balance between the levels of NOx and particulate emitted by the engine
- The duty cycle of the vehicle should regularly give rise to an exhaust temperature above 275°C
- The engine should be run on low sulphur fuel.
In our tests of normally operating vehicles we have found that a fuel sulphur level of below 100 ppm will give rise to a very satisfactory performance. Our laboratory data suggest that we will be able to extend this level of confidence to diesel fuel containing 500 ppm in the near future. This is a key level, since diesel fuel will have a legislated maximum sulphur content of 500 ppm in the U.S.A. and the E.C. by the year 1996.

However, the technology cannot be applied as a panacea to old and dirty engines. In particular it has been noted that old fashioned heavy-duty engines which have pre-chamber combustion systems and are not turbocharged frequently give rise to smoky exhausts. The balance of NOx and particulate in such exhausts does not make this a suitable system for them.

The experiments we have performed to-date indicate that filter performance has remained remarkably invariant during the trials. This contrasts to much of the previous experience with filters, and especially experience with wall-flow ceramic filters. With this new technology, the low temperature of filter regeneration, and the fact that regeneration is a continuous process, leads to a significant reduction of thermal and physical stress on the filter units. These considerations would seem to indicate that the filters will have a long lifetime. However, this system does not excuse poor engine maintenance, and in the event of the failure of, for example, a turbocharger, the balance of particulate and NOx may be significantly altered so as to prevent effective regeneration. In order to take account of such servicing needs it is envisaged that the system will be of modular construction. The filter unit can then be removed from the vehicle and exchanged without needing to demount the whole assembly.

Conclusions

Diesel engines of recent manufacture, and engines which have been designed to meet the current and future emission limits, will continue to emit substantial quantities of particulate into the urban environment. The advent of readily available low sulphur diesel fuel in 1996 brings with it the possibility of using a novel form of exhaust filter regeneration technology which has shown great promise in early trials. To-date more than 20 vehicles have been fitted with systems that have been shown to remove a substantial proportion of the hydrocarbons and particulates in the exhaust gas which are the cause of growing concern amongst health experts.

Further work is being undertaken to characterise and develop the performance of the system. The apparent simplicity of the technology, totally without any moving parts or complex control systems, is an added feature which will appeal to operators and owners of vehicles alike.

References

9 "Health Risk Assessment for Diesel Exhaust", Preliminary Draft, Office of Environmental Hazard Assessment, California EPA, June 1994
11 See various authors in "Diesel Exhaust After-treatment", SAE Tech. Paper Series, SP-943, 1993
14 B. J. Cooper, H. J. Jung and J. E. Thoss, U.S. Patent 4,902,487; *European Appl.* 341,832A
Demonstrating the Benefits of Fuel Cells
FURTHER SIGNIFICANT PROGRESS TOWARDS COMMERCIALISATION

The continuing worldwide growth of interest in fuel cells, used for power generation in a variety of applications, was reflected by the record attendance of 700 delegates from 20 countries at the fourteenth Fuel Cell Seminar, held in San Diego, California, U.S.A. from 28th November to 1st December 1994. The theme “Demonstrating the Benefits” was chosen to reflect the view that fuel cells are now on the threshold of commercialisation. The exploitation of this high efficiency, low pollution technology is currently dominated by the low operating temperature, platinum-catalysed fuel cells.

Fuel cell owners from North America reported positively on their experiences with the first commercial phosphoric acid fuel cell (PAFC) cogeneration plants. Clear evidence was presented that these units are showing the necessary reliability to compete with the existing mature natural gas-fuelled engine and turbine technologies. In the next generation 200 kW fuel-cell system, to be launched in 1995 by ONSI, a subsidiary of International Fuel Cells (IFC), manufacturing costs have been reduced by over a half.

The conference also heard from Ballard Power Systems and Dow Chemical Company of their joint plan to enter the market with a compact product based on the rapidly emerging proton exchange membrane fuel cell (PEMFC) technology.

The development of fuel cells as the primary power source in a variety of transport applications is now being spurred on not only by the

Fig. 1 ONSI's 200 kW PC25C phosphoric acid fuel cell production prototype during assembly, showing the three major subsystems, from left to right, the fuel processor, cell stack and power conditioner
impending zero emission standards, due to be enacted in California from 1998, but also by the U.S. Government programme – "Partnership for a New Generation Vehicle" – aimed at producing an 80 miles per gallon vehicle. This has led to the instigation of PEMFC programmes at General Motors, Ford and Chrysler. However, fuel cell powered heavy-duty vehicles are likely to be commercialised before cars and vans. This was demonstrated by the impressive H Power Corporation/U.S. Department of Energy methanol-fuelled, PAFC powered, 30-foot long transit bus displayed at the conference.

Stationary Applications
The PAFC remains the fuel cell closest to widespread commercial exploitation. Over the past two years the ONSI fleet of fifty-six PC25A 200 kW co-generation power plants has provided fuel cell owners around the world with valuable operating experience. Around 50 per cent of the fleet has now been operated for over 10,000 hours, with 17,000 hours being the longest operation. The average fleet availability has been 96 per cent. The views of the users, particularly those of the North American Fuel Cell Owners Group, representing thirteen gas and electric utility companies, was very encouraging. The results have demonstrated that service personnel could operate and maintain these fuel cells to a high degree of reliability. Over the past two years the mean interval between plant power down time has increased from 1010 to 3290 hours. This compares to 507 hours for comparable natural gas co-generation engines rated at over 80 kW.

However, the PC25A units are still too costly for large volume commercial sales. On-going developments at IFC and ONSI have resulted in the recent installation of a more compact PC25 Model C manufacturing prototype plant, see Figure 1. At 1800 ft$^3$ and 40,000 lbs, this is one third smaller and lighter than the PC25A and costs half as much to manufacture. A 25 per cent reduction in the number of mechanical parts is predicted to improve further the system reliability. Production units will be available for delivery in 1995. The user groups indicated that with the benefit of proven reliability, the PC25C could be cost competitive in the premium quality power markets, such as data and communications centres and healthcare facilities. However, unless the significant environmental advantages of fuel cells can be economically accounted for, it will be necessary to reduce capital costs further to enable the fuel cell to compete head-on with current generating technologies. This point was noted by T. Page of the San Diego Gas and Electric Company in his keynote address opening the conference. He emphasised that with the likely future deregulation of electricity generating businesses in the U.S.A., a key priority for fuel cells in this application was the need to be a low cost energy supplier. A further reduction in selling price of approximately 50 per cent for the ONSI PC25 plants is being targeted for 1998, if sufficient production volumes are achieved.

Operation of the PAFC plant at around 200°C provides an opportunity to produce useful heat for co-generation applications. The lower operating temperature of PEMFCs, typically below 100°C, has resulted in transportation being their principal use. However, Dow Chemical Company and Ballard Power Systems reported on progress to develop and commercialise jointly...
Fig. 3 The first methanol-fuelled, phosphoric acid fuel cell powered transit bus, produced by H Power Corporation in the U.S. Department of Energy sponsored programme. This meets all the required performance criteria but with improved fuel efficiency and significantly reduced exhaust emissions and noise pollution.

PEMFC power plants for stationary power markets. A grid-connected 30 kW hydrogen-fuelled plant and the first of several 10 kW natural-gas fuelled plants are already in operation (Figure 2). They plan to launch a prototype 250 kW system in 1996 and enter low-volume production of power plants in 1998. The size and weight specification of the plant are 1184 ft³ and 27,600 lbs, respectively, and it is designed to be cost competitive with conventional power generation technology. Heat at a temperature of 74°C will be available at 810 MBTU/h.

The Japanese PAFC-Technology Research Association is co-ordinating programmes to develop and commercialise larger stationary power plants. The building of 1 MW and 5 MW plants for large scale on-site co-generation and dispersed utility power, respectively, are nearing completion. These plants are due to become operational in 1995. However, in the longer term, the intrinsically more efficient high-temperature fuel cell systems are also being developed for multi-megawatt power generation. Energy Research Corporation and M-C Power Corporation in the U.S. are currently constructing a 2-MW plant and 250-kW plants, respectively, based on the molten carbonate fuel cell. However, significant movement towards commercialisation of this technology is not expected before the end of the 1990s.

Transportation Applications

Urban transit buses represent the earliest and technically least demanding entry point for fuel cells in the transportation market. Consequently there are several programmes which have reached the demonstration stage. The first of three fuel cell powered buses to be built during Phase II of a programme managed by H Power Corporation and co-sponsored by the U.S. Departments of Energy and Transportation and the South Coast Air Quality Management District (SCAQMD) was on show (Figure 3). It provided clean, quiet and smooth rides for the conference delegates. The power system employs a methanol steam reformer and a Fuji 50 kW PAFC engine, with necessary control equipment and ancillaries, including a nickel-cadmium surge battery for hill climbing and acceleration. Toxic emissions from the hydrocarbon-fuelled vehicle are orders of magnitude lower than demanded by 1998 U.S. Federal Standards. To-date it has demonstrated over 1000 hours of operation. It is planned that the
programme will eventually set the stage for the production of fuel cell powered transit buses towards the end of this decade. Significant weight and volume reductions, together with cost reductions across the board, are planned.

Most transportation programmes are focusing on the PEMFC because of its rapid start-up from room temperature and the significantly higher power densities that can be achieved. Ballard Power Systems have already demonstrated a prototype 32-foot long transit bus, fuelled on compressed hydrogen and meeting the zero emission vehicle (ZEV) standards. However, if PEMFCs are to take advantage of the California ZEV mandate, which requires 2 per cent of all vehicles to be ZEV in 1998 and 10 per cent in 2003, there are several crucial technical issues that have to be resolved.

For all light-duty vehicles, on-board reforming of a hydrocarbon fuel appears to be the preferred fuelling option. This is one of the most challenging technical hurdles. General Motors and the Los Alamos National Laboratories (LANL), in a U.S. Department of Energy sponsored project, have demonstrated the feasibility of integrating a compact methanol steam reformer with two 5 kW Ballard PEMFC stacks. The steam reformer has three beds, consisting of the primary reformer, water-gas shift reactor and preferential oxidation reactor. Under steady state conditions the output from the fuel processor is less than 10 ppm carbon monoxide, a level which is considered tolerable for the platinum-based anode catalyst. Transient levels of around 100 ppm carbon monoxide are not tolerable.

Vickers Shipbuilding and Engineering Ltd. and CJB Developments have also developed a prototype methanol reformer based on a similar concept, but the 15 minute start-up time needs to be improved in the next phase of the programme. While methanol steam reforming is favoured in the above programmes, others, including Arthur D. Little, Argonne National Laboratories and Chrysler Corporation, favour partial oxidation with its advantage of fuel flexibility. This technology is less well developed than the steam reformers which are themselves at an embryonic stage. Thus there is still a significant technical challenge to be met in developing compact, rapid start-up and responsive reformer technology. It appears likely that to cope with transient behaviour, the fuel cell anode will have to display significantly greater tolerance to trace levels of carbon monoxide than current stacks possess. This provides an opportunity to develop improved platinum-based catalyst materials, and promising results with low loading carbon-supported platinum-ruthenium alloy catalysts were reported by the groups from General Motors, LANL and Johnson Matthey.

In addition to reformer developments there are other important technical issues concerning the PEMFC stack itself. At present the demonstration stacks are too costly and also need to show improved performance (higher power density), even on pure hydrogen/air operation. Savings in cost through the development of component manufacturing processes and reductions in the cost of materials by using lower platinum cell loadings, cheaper membrane materials and cheaper bipolar plate materials, were emphasised frequently during the conference.

Considerable progress in these areas has been shown in single cell studies. Dow Chemical Company, LANL, Johnson Matthey, ECN and General Motors all showed single cell performance at electrode platinum loadings close to 0.1 mg/cm² comparable to the performance of the 4.0 mg/cm² of unsupported platinum black used in current stacks. Dow showed single cell data on the recently developed membrane material, XUS13204.20, of resistance 0.04 Ω cm², which is approximately 50 per cent lower than the earlier developmental material. This has a large impact on performance, particularly at higher current densities. Dow also believe that a membrane material of ohmic resistance 0.02 Ω cm² could be developed.

ECN have demonstrated that it is possible to run cells using stainless steel bipolar plates, instead of graphite, without severe degradation due to membrane contamination by impurities in the plate. Cell voltages are lower, however, probably because of higher contact resistances.

There is also a resurgence of interest in direct methanol oxidation fuel cells, particularly with
regard to their operation in a PEMFC environment. Siemans reported a performance of 400 mA/cm² and LANL quoted 300 mA/cm², both at 0.5 V, with Nafion 117 electrolyte and platinum/ruthenium anode catalysts. While these performances are considerably higher than those achieved in the past using systems based on a liquid sulphuric acid electrolyte, there is still a need for major catalyst development to reduce the anode overpotential and increase the current density. A further significant problem in this system is methanol permeation through the polymer electrolyte membrane to the cathode.

**Other Applications**

Fuel cells continue to be developed for numerous military related applications. Analytic Power Corporation reported on portable hydrogen-fuelled PEMFC units, rated from 50 to 500 W, for applications such as powering backpack microclimate cooling systems. Studies show that the units can effectively replace batteries on performance and cost, in situations involving long mission times. Direct methanol fuel cells are also being developed for these applications under U.S. Government Advanced Research Projects Agency contracts.

Ballard PEMFC systems are being developed as power sources for submarines. A one-tenth scale 40 kW technology demonstrator, fuelled on reformed methanol with liquid oxygen as the oxidant, is due to be developed by 1996. Design studies on an 850 kW PEMFC for application as the service generators of ships are also being undertaken. A particularly challenging target in this programme is to develop a multi-fuel reformer, which can operate on logistic fuels. IFC have also demonstrated a high power-density 10 kW prototype of a 20 kW PEMFC system, designed to be installed in a 44-inch unmanned undersea vehicle, as a higher energy-density replacement for the currently used silver-zinc batteries. IFC believe that this power plant will have high reliability, durability and mission duration. This is due to design features in which the hydrogen side of the power plant is dead-ended, and on the cathode side a passive water removal system is used, thereby avoiding the circulation of gaseous reactants.

**Conclusions**

The 1990s will be the most significant period in the long development of fuel-cell power generation systems. The first PAFC co-generation plants are proving to be highly efficient and reliable generators, but further developments of the fuel cell, or the emergence of PEMFC stationary plants, are required before a fully commercial, cost effective product is available, near the end of the decade. Opportunities for using fuel cells in transportation have been provided by the impending legislation in the U.S.A. and the U.S. Government programme to improve vehicle fuel economy. Rapid progress is being made in overcoming technical and economic hurdles in the development of PEMFC based systems, and the late 1990s should see the start of a large scale use of this clean, efficient technology for powering vehicles – with the first markets likely to be heavy-duty transit buses.

G.A.H., T.R.R.

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**Nanocatalysis Uses Platinum-Rhodium Tip**

Studying the atomic structures involved in catalysis under catalytic conditions is possible using the recently developed scanning tunnelling microscope (STM) that operates inside a reactor cell. This equipment has enabled the STM tip to pattern a surface and manipulate atoms. Researchers at the University of California, Berkeley, have suggested that the tip can be made to act catalytically to produce investigable surface reactions (B. J. McIntyre, M. Salmeron and G. A. Somorjai, Science, 1994, 265, (5177), 1415-1418).

With a platinum-rhodium STM tip in a reactor cell and a propylene atmosphere ordered propylidyne structures were formed on the platinum surface. Carbon monoxide and propylene-hydrogen mixtures were introduced into the cell to observe the reaction, and characteristic clusters were seen after activation of the tip by short electric pulses. The catalytic action caused by the tip may be atomisation of hydrogen from the gas phase and hydrogenation of the carbon bonds of the clusters under it.

This method provides possible insights into atomic-scale structures and the kinetics of local catalytic activity, which presently is only studied in an average way by more conventional tools.
Ruthenium Phthalocyanines

NOVEL WATER SOLUBLE AGENTS FOR PHOTOdynamic CANCER THERAPY

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Photodynamic therapy is a clinical technique employing the combination of light, oxygen and a sensitising compound to induce the photochemical destruction of unwanted tissue. Light therapy has been known for some time, but it was not until the earlier part of this century that the first clinical work was performed using sensitisers and light. More recently a sensitising compound of a complex mixture of porphyrins has been tested on various cancers, and been awarded regulatory approval for its use. In this paper the synthesis and properties of some novel and easily prepared water soluble ruthenium phthalocyanine complexes are reported. One of these complexes, JM 2929, has been extensively studied and has photosensitising properties which when used in combination with light and oxygen in vitro and in vivo during photodynamic therapy displays remarkable cytotoxic effects.

Although photodynamic therapy (PDT) as an innovative cancer treatment has received much attention recently, the basic concept is not new. The healing aspects of light were described by the Greek historian Herodotus in the 5th Century BC, and the first use of a combination of a sensitiser (eosin) and light to treat skin cancer took place in 1903 (1). In recent years, clinical work in PDT has been focused on Photofrin™, a complex mixture of porphyrins. Photofrin™ has been extensively studied in the treatment of bladder, oesophageal and lung cancers and has recently received regulatory approvals in Canada, Japan and also the Netherlands.

However, there is great interest in the development of “second-generation” PDT agents to overcome some of the drawbacks of treatment with Photofrin™. Some of the issues which need to be considered in the development of new PDT agents include:

[a] The need for a pure compound: the heterogeneous nature of Photofrin™ makes its production and analysis very difficult. Additionally, the use of a mixture renders preclinical and clinical results harder to interpret.

[b] Reduction of normal skin photosensitivity: patients receiving Photofrin™ must stay out of bright sunlight for many weeks.

[c] Light penetration into tumours can be improved by using photosensitisers that have their maximal light absorption in the 650–750 nm range of the spectrum.

Fig. 1 General structure of a six-co-ordinate ruthenium phthalocyanine complex
As a class of dyes, phthalocyanines (Pcs) and metallophthalocyanines (MPcs) generally have strong Q-absorption bands in the 600–750 nm range. Therefore, Pcs and MPcs have been extensively studied as potential PDT agents, but unfortunately, many of these compounds are insoluble in water (2). Water soluble derivatives of Pcs and MPcs have been prepared by the addition of sulphonic acid or carboxylate moieties to the periphery of the macrocyclic ring, often giving complex isomeric mixtures.

An alternative approach is to confer improved solubility to an MPc via axial co-ordination of solubilising groups to the central metal atom, see Figure 1. Since six-co-ordinate ruthenium(II) Pcs are well established in the literature (3) we synthesised a variety of water soluble ruthenium phthalocyanine derivatives with the goal of studying their photosensitising properties.

**Synthesis**

In order to prepare a variety of water soluble ruthenium phthalocyanine, RuPc, complexes, a general starting material was needed of the type PcRuL₂, where L is an easily replaced ligand. Previous syntheses of pure RuPcs have been difficult, tedious and suffered from low yields (4, 5). The synthetic pathway that we developed for the RuPcs is summarised here in Figure 2. A template reaction for the formation of ruthenium phthalocyanine occurred in pentanol in the presence of a base. Under these conditions, but without a metal, phthalocyanine did not form. Using RuCl₃·xH₂O directly as the metal template resulted in low yields of highly contaminated products.

When an anhydrous “ruthenium blue” solution, (made by boiling hydrated ruthenium chloride, RuCl₃·xH₂O, in pentanol until it was completely blue and no water remained) was used as the ruthenium source, the reactions for the formation of phthalocyanine were essentially quantitative. Insoluble RuCl₃(phthalonitrile), A, was formed initially when the “ruthenium blue” solution was treated with phthalonitrile, and could be isolated in good yield. This was then converted into a RuPc over a period of several days.

The base used in these reactions was often co-ordinated to the ruthenium in the final product. With ammonia this resulted in the formation of the previously unreported bis(amine) complex, (Pc)Ru(NH)₂, as a blue insoluble solid. The formation of this insoluble (Pc)Ru(NH)₂ was an essential ingredient to the success of the reaction shown in Figure 2. It allowed the bulk of the impurities to be easily washed away after the formation of RuPc.
reaction of (Pc)Ru(NH$_3$)$_2$ with neat benzonitrile at reflux temperature gave the new complex (Pc)Ru(PhCN)$_2$, B, in high yield. The high solubility, high purity, and the relative lability of the axial ligands of (Pc)Ru(PhCN)$_2$ made it particularly suitable as a starting material for the synthesis of water soluble (Pc)RuL$_2$ complexes.

The first water soluble RuPc complex which was synthesised employed the water soluble phosphe ligand, triphenylphosphinomonosulphonate (TPPMS). The reaction of the tetrabutylammonium (TBA) salt of TPPMS with (Pc)Ru(PhCN)$_2$ resulted in a high yield of (TBA)$_2$[(Pc)Ru(TPPMS)$_2$], which was converted to water soluble K$_2$[(Pc)Ru(TPPMS)$_2$], JM 2929.

JM 2929 has a typical optical metal phthalo-cyanine spectrum, which is shown in Figure 3. The Q-band absorbance, important for PDT work, is at 652 nm with an extinction coefficient of 9.0 x 10$^4$/M cm. The compound has been characterised by elemental analysis, 'H and $^3$P NMR spectroscopies, field desorption mass spectroscopy and high-performance liquid chromatography (6).

Solution studies of JM 2929 have shown that the complex forms a five-co-ordinate species, [(Pc)Ru(TPPMS)$_2$], in aqueous solution. Thus a wide variety of different water solubilising ligands, including those of sulphonate and carboxylate substituted pyridines, nitriles, amino acids and other water soluble phosphines, have subsequently been evaluated (6).

**Biological Studies**

Our first indication that JM 2929 possessed interesting photosensitising properties came from a study in which its cytotoxicity, in the absence of light, was compared with its phototoxicity to HeLa (HeLa cells are a standard tumour cell line commonly used in cancer research) cells in vitro (7), as shown in Figure 4. Whereas concentrations of more than 10$^{-4}$ M of JM 2929 are non-toxic to HeLa cells, a 10$^{-6}$ M concentration of the compound, in combination with light of wavelength 650 nm killed 50 per cent of the cells. Identical results were obtained with the isolated five-co-ordinate complex.

Subsequent studies showed that the light mediated cytotoxic effects of JM 2929 were dependent upon the presence of oxygen, as is the case with most PDT agents. Preliminary studies of the toxicity indicated that the compound could be safely administered to animals at a sufficiently high dose to ensure a photodynamic effect on the cancerous irradiated tissue. Moreover, using the RIF-1 tumour model in mice, biodistribution studies showed ratios for the tumour: surrounding muscle of approximately 7, indicating there is selective uptake in the target tissue.
Actual PDT experiments were conducted using the RIF-1 tumour model in mice. It was found that a dose of 20 mg/kg of JM 2929 administered intraperitoneally, followed by 150 J/cm² of 650 nm laser irradiation at 4, 24, 72 or 168 hours after treatment with the drug resulted in the complete destruction of the tumour, with no regrowth, see Figure 5. Neither light nor drug alone had any effect on the tumour. Preliminary experiments indicate that the photosensitivity of skin due to JM 2929 is much less pronounced than it is due to Photofrin™.

**Mechanism of the Action**

The mechanism by which PDT agents cause tumour destruction is most likely to be a combination of the direct killing of tumour cells and a shut-down in the vascular supply to the tumour (8). Cytotoxicity resulting from PDT treatment is most probably the result of photo-oxidation reactions. The excited sensitiser can induce photochemical damage by two major pathways (9). Type I photo-oxidation involves the reaction of photoexcited sensitiser with a substrate molecule, by a mechanism which involves hydrogen or electron transfer, to yield radical species that react further with oxygen. In the Type II photo-oxidation reaction the triplet excited state of the sensitiser transfers energy to molecular oxygen to produce singlet oxygen, 'O₂, which is a highly reactive species that can oxidise biological molecules. Recent work has shown that JM 2929 does not produce singlet oxygen upon irradiation in aqueous solution (10). This is in contrast
to the large number of Pc and MPE PDT agents studied to date, all of which produce 'O, in solution. JM 2929 is, to our knowledge, the first transition metal MPE to show PDT activity. The exact nature of the Type I reaction which is involved in the JM 2929 mediated phototoxicity is currently being investigated.

Conclusions

Novel water soluble RuPcs sensitisers have been synthesised using the versatile precursor (Pc)Ru(PhCN). These new complexes can be easily prepared in high yield as non-isomeric pure compounds. The biological properties of one of these complexes, JM 2929, have been extensively studied and it has been found to be a potent PDT agent both in vitro and in vivo. The development of JM 2929 and other ruthenium based sensitisers is continuing towards clinical evaluation.

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References


The Published Platinum Metal Alloy Systems

Phase Diagrams of Precious Metal Alloys, First Supplement

Compiled by He Chunxiao, Zou Yuehua and Wang WenNa


Some ten years ago, an important compilation of phase diagrams of precious metals alloy systems which had been published prior to 1976, was brought to the attention of readers (Platinum Metals Rev., 1984, 28, (3), 108). During the years 1976 to 1985 there were significant developments in the study of precious metal alloy phase diagrams, and by the end of 1985 the number of known systems had reached 754, mainly ternary and quaternary systems. In order to meet the needs of researchers, a First Supplement to the former book - which was published in 1983 - has now been compiled (mainly in Chinese but supported where necessary in English). This supplement collects together information on 380 systems of 641 phase diagrams published from 1976 to 1985, including 150 binary, 212 ternary and 15 quaternary systems that contain a precious metal. Of these over 85 binary, 160 ternary and eight quaternary systems involve the platinum group metals.

It is worth noting that the systems occurring in both the earlier book and this supplement are listed in the contents section of the latter. In addition to over 1765 binary and ternary compounds of the precious metals, their structures and crystal lattice constants are given, together with supporting references.

This First Supplement will be a valuable reference book for people working in the field of precious metal alloys. Both it and the earlier 1983 publication can be purchased from The Metallurgical Industry Press, Mr. Zhang Wei, Beijing 100009, People's Republic of China, or contact direct Prof. He Chunxiao, Institute of Precious Metals, Kunming 650221, People's Republic of China.

L.G.-F.
Structure Reconstruction in Palladium Alloy Catchment Gauzes

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The changes of topography and structure in palladium-5 per cent nickel alloy catchment gauzes, which are used to capture the platinum lost from the catalyst gauzes employed in the ammonia oxidation reaction to produce nitric acid, have been studied by scanning electron microscopy, electron probe microarea analysis, X-ray diffraction and other techniques. The structure of the palladium-5 per cent nickel alloy gauze is reconstructed by recrystallisation and this is controlled by vapour deposition (adsorption) and diffusion re-alloying. The initial solid solution of palladium(nickel) changed into palladium(platinum) solid solution, the nickel being gradually oxidised to nickel oxide until no nickel remained. The lattice constants of the palladium(platinum) solid solution increased with the ratio of platinum:palladium. Ladder-like (layered) growth was a main mechanism in the formation of new lattice planes and crystals, while screw-type growth played an important role in the formation of new crystals.

In the preparation of nitric acid by ammonia oxidation platinum-rhodium or platinum-palladium-rhodium alloy gauzes are used as the catalysts. Under typical operating conditions for the process of temperatures from 750 to 950°C and pressures of 1 to 10 atmospheres, platinum oxide, PtO\textsubscript{2}, which is volatile, is formed on the catalyst surfaces (1-7) and this can cause a loss in platinum of between 0.05 and 0.5 grammes per ton of nitric acid produced. In order to recover the lost platinum, catchment gauzes made of palladium-gold alloy have been introduced into the ammonia oxidation reaction chamber and installed directly beneath the catalyst gauzes (8-10). In recent years, metals from Groups VIII and IB have been suggested as substitutes for the gold, to economise on its use (11), and as a result, catchment gauzes comprised of a high palladium content alloy containing copper or nickel or other metal have been developed (12, 13).

Changes in the constituents and surface states have been reported for catchment gauzes made of palladium-5 per cent nickel, when used at high pressures of 7 to 9 atmospheres and high temperature of 920 to 940°C, and at medium pressures of 3 to 4 atmospheres and temperatures of 800 to 850°C (13, 14). However, the re-alloying and recrystallisation processes that take place in palladium-gold and palladium-nickel alloy catchment gauzes have been little reported on. In this paper, therefore, the structure reconstruction and recrystallisation processes occurring in palladium-5 per cent nickel catchment gauzes will be discussed, based on the topographic and structural changes observed under conditions of medium pressure and temperature.

Experimental Procedure

Samples of catchment gauzes were removed from a medium pressure ammonia oxidation apparatus which operated at a pressure of 0.35 MPa and temperature of 850°C. The ammonia concentration in the ammonia-air gas mixture was 10.5 to 11.5 per cent, and the catalyst gauze consisted of three sheets of platinum-4 per cent palladium-3.5 per cent rhodium alloy of 1024 mesh/cm\textsuperscript{2}.

The platinum recovery packages, which were installed underneath the catalyst gauzes, were made of two sheets of palladium-5 per cent nickel catchment gauze separated and supported
by three sheets of iron-22 per cent chromium-5 per cent aluminium alloy gauze.

The recovery packages were operated for 5 months – the (G-5) gauze, and for 8 months – the (G-8) gauze. Samples for study were taken from the top and bottom gauzes. In the downstream direction, the surfaces of the samples were marked as [a] on the front surface of the first gauze through [b] and [c], to [d], on the back surface of the second gauze.

The topography of the samples and a quantitative analysis of the surface constituents were observed by electron probe and also scanning electron microscopy with an energy spectrometer, and the lattice parameters of the gauzes were determined by X-ray diffractometry.

**Experimental Results**

**Topography and Structure of New Catchment Gauzes**

New catchment gauzes were woven from clean smooth palladium-5 per cent nickel alloy wire of diameter 0.09 mm which had been previously annealed in an argon atmosphere. Although there were some defects on the surface of the wire, no contrasts in crystallisation were observed on SEM photographs. The alloy had a single-phase solid-solution structure with fine crystal grains, see Figure 1(a) and 1(b). X-ray photo-electron spectroscopic analysis (XPS) indicated that the surface of new catchment gauzes was mainly palladium without any palladium oxide, PdO, being present (14).

**Topography of Used Catchment Gauzes**

During the ammonia oxidation process the platinum-palladium-rhodium catalyst gauzes produced the volatile oxides: platinum oxide, PtO₂, and palladium oxide, PdO, and the non-volatile rhodium oxide, Rh₂O₃. The weight loss in the catalyst gauzes resulted mainly from volatilisation of platinum as PtO₂, since the concentrations of palladium and rhodium, and thus of PdO and Rh₂O₃, in the catalyst alloy were low. The PtO₂ vapour was transported by the gas stream to the surface of the palladium alloy catchment gauze where it was reduced to plat-

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*Fig. 1 Fresh palladium-5 per cent nickel catchment gauzes showing: (a) the surface topography, the scale line is 100 μm (b) the crystal structure, and (c) the surface topography of (G-5) gauze, after being used for 5 months; the line is 10 μm long.*
Platinum and immediately deposited onto the surface of the bright palladium metal (14). The platinum dissolved into the palladium matrix and was alloyed by diffusion, thus causing changes in the structure, topography and constituents of the palladium alloy catchment gauzes.

The process of change is called structure reconstruction or recrystallisation. These structural changes in the catchment gauzes depend upon the position of the gauzes and on how long they are in operation.

The topographies of surfaces [a], [b], [c] and [d] of the (G-5) gauze, are shown in Figures 1(c) and 2. The skeletal construction of the (G-5) [d] surface contains up to 90 per cent palladium, which corresponds to the amount of palladium in molecular PdO. XPS analysis indicated that the (G-5) [d] surface was covered by PdO film. The catkin-like matter around the skeleton was mainly made of nickel oxide, NiO, with additional small amounts of the oxides of palladium, platinum, iron, chromium and aluminium (14). The NiO, which formed on the surface of the catchment gauzes, grew outwards from the surface by nickel diffusion and volatilisation, and accumulated there after transportation by the gas stream. This led to the formation of the catkin-like matter.

On the (G-5)[c] surface, the skeletal construction is obviously swollen, and the NiO catkins have essentially disappeared. On the (G-5)[b] surface the layered structure can be clearly seen and facets of the recrystallised crystals have appeared on the (G-5)[a] surface.

The topographies of various surfaces of (G-8) gauzes, which were used for 8 months, are shown in Figure 3, and some differences can be seen between the (G-8) and (G-5) gauzes.

First, the [d] and [c] surfaces of (G-8) gauze have become porous sponges, evolved from the skeletal construction of the [d] and [c] surfaces of (G-5) gauze. The layered structure which
Fig. 3 Topography of (G-8) gauzes: (a) is the front face, (G-8)[a] and (b) is the back face, (G-8)[b], of the first gauze; (c) is the front face, (G-8)[c] and (d) is the back face, (G-8)[d] of the second gauze.

occurred in the sponge of [d] surface has developed further on the [c] surface of (G-8) gauze. The formation of the holes may be linked to the oxygen that is released during the reduction of PtO₂ on the surface of the catchment gauzes. The wiry substance seen on the (G-8) [d] surface, in Figure 3(d), is the remnants of wire of the iron-22 per cent chromium-5 per cent aluminium alloy support gauze. Facets of the recrystallised crystals have developed on the (G-8) [b] surface, and whole recrystallised crystals have formed, or are forming, on the (G-8) [a] surface, as shown in Figure 3(a).

Careful observation has indicated that the whole crystals are of tetrakaidecahedron structure, (a 14-faced body) made up of quadrilaterals and hexagons, and are grains ranging in size from several micrometres to tens of micrometres, which are visible to the naked eye.

Second, no NiO catkins were visible on the various surfaces of the (G-8) gauzes. Chemical analysis has indicated that the content of the nickel in used (G-5) catchment gauzes is 0.18 weight per cent in the first sheet and 1.17 weight per cent in the second sheet, but only 20 to 40 ppm in the two sheets of (G-8) gauzes. During operation, the nickel solute in the catchment gauzes is gradually oxidised until it is all reacted.

Structure of Used Catchment Gauze

Palladium-5 per cent nickel alloy exists as a single-phase solid solution with lattice parameter \( a = 0.3858 \) nm, which is smaller than the lattice parameter of palladium, \( a = 0.3890 \) nm. This results from the atomic radius of nickel, 0.125 nm, being smaller than that of palladium, 0.137 nm.

The (G-5) and (G-8) gauzes also exist as single-phase solid solutions. Figure 4 shows the X-ray diffraction pattern of (G-8) gauze and Figure 5 shows the lattice parameters for (G-5) and (G-8) gauzes and the platinum:palladium ratios on the gauze surfaces. The lattice parameters
of (G-5) and (G-8) gauzes are larger than those of palladium-5 per cent nickel alloy and pure palladium. Thus, the solid solubility of platinum, which has a larger atomic radius (0.139 nm) than palladium (0.137 nm), increased in the palladium matrix, while the solid solubility of nickel in palladium decreased. That is to say, the initial solid solution of palladium(nickel) has transformed gradually into a palladium(platinum) solid solution, while the catchment gauzes were in use.

The trends in the changes of the lattice parameters on various surfaces of (G-5) and (G-8) gauzes are the same as for the values of their respective platinum:palladium ratios, which are found from weight per cent measurements, see Figure 5. For (G-5) gauzes, the lattice parameters and the values of the platinum:palladium ratio decrease from the [a] to the [d] surface. For (G-8) gauzes, both the lattice parameters and the size of the platinum:palladium ratios are generally higher than for the (G-5) gauzes, and for both measurements the values of the front faces of the gauzes, namely the [a] and [c] surfaces, are higher than for the back faces, the [b] and [d] surfaces, respectively. This indicates that more platinum is dissolved in the (G-8) gauzes, which were used for 8 months, than in the (G-5) gauzes, used for 5 months, and that more platinum dissolved in the front faces of the gauzes than in the back faces.

On the other hand, it can be seen in Figure 4,
that the X-ray diffraction intensity on the (200) crystal plane of the [a] surface of (G-8) gauze is clearly higher than on the (111) crystal plane, but the intensities of the diffraction on the (111) and (200) crystal planes are reversed for other surfaces of (G-8) gauze, and this is also true for various surfaces of (G-5) and new gauzes. This is because the [a] surface of (G-8) gauze is the most completely recrystallised surface, which indicates that the orientations of the crystals must have changed during the recrystallisation process in the gauzes.

The Growth Pattern of Recrystallised Crystals

The key to the recrystallisation process in the palladium-nickel alloy catchment gauze is the substitution of palladium(platinum) solid solution for palladium(nickel) solid solution. This process can be divided into two stages: the formation and the growth of recrystallised crystals, namely new palladium(platinum) solid solution crystals.

The structures of the [c], [b] and [a] surfaces of (G-5) gauzes and the [c] surface of (G-8) gauze, shown in Figure 6, illustrate to a certain extent the formation process of crystal recrystallisation. This process includes the deposition of platinum and the alloying of platinum with palladium Figure 6(a), ladder-like growth Figures 6(b) and 6(c) and the formation of the layered structure, and new facets and crystals Figure 6(d).

In other words, the ladder-like growth mechanism controls the formation of recrystallised crystals. The structures of the [c], [b] and [a] surfaces of (G-8) gauze, shown in Figure 7, illustrate the growth process of the recrystallised crystals. On the [c] surface, Figure 7(a), new facets and small crystal nuclei can be seen. On the [b] and [a] surfaces of the (G-8) gauze, screw-type growth and screw cones are visible on the faces and crystal planes in addition to the
layered structure. This indicates that the screw growth mechanism plays an important part in the growth process of recrystallised crystals.

**Discussion and Conclusions**

The basis of the structure reconstruction in palladium-5 per cent nickel alloy catchment gauges during the platinum recovery process is that the initial palladium(nickel) solid solution is replaced by new palladium(platinum) solid solution. It is a re-alloying or recrystallisation process in the palladium-nickel alloy. The recrystallisation process can be divided into two stages: the formation of new crystals controlled by a ladder-like growth mechanism and further growth controlled by both a ladder-like and a screw growth mechanism. A simple discussion is given here, based on Figure 8.

When a platinum atom is absorbed onto the lattice of the palladium matrix, it deposits preferentially into position '1' where there is a trirectangular “concave” structure, Figure 8(a).

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**Fig. 7** Screw growth and screw cones occurring during recrystallised crystal growth: (a) the (G-8)[c] surface; (b) the (G-8)[b] surface, showing screw-type growth and screw cones; (c) the (G-8)[b] surface, showing ladder-like structure and small screw cones on the crystal face, and (d) the (G-8)[a] surface for (G-8) gauges.
This position has the strongest attractive force for platinum atoms, which deposit there until the line containing position '1' is fully filled. Then a platinum atom deposits on position '2', where there are two-rectangular "concaves", and immediately forms a tri-rectangular "concave", similar to position '1'. The deposition process of position '1' is repeated until the plane is fully filled. When a platinum atom deposits onto position '3', it immediately creates two-rectangular and then tri-rectangular "concaves", and the above deposition processes are repeated until the adjacent plane is fully filled. This gradual and parallel deposition and evolution results in the formation of a layered structure.

The palladium(platinum) solid solution lattice, facets and crystals are formed by mutual diffusion and alloying. The completely recrystallised crystals are tetrakaidecahedron, each made up of quadrilaterals and hexagons. During the formation of new facets and crystals, ladder-like growth is the main mechanism, while screw-type growth is hardly observed. The increasing solid solubility of platinum in the palladium matrix expands the palladium lattice and produces internal stress. Through the action of the internal and thermal stress, a relative shear displacement can easily occur along some crystal planes, thereby forming a screw dislocation, and creating the tri-rectangular "concave" shown in Figure 8(b). The tri-rectangular "concaves", are the preferred places for the deposition of platinum atoms. The deposition along the screw dislocations produces the screw-type growth and the formation of screw cones. Thus, in the growth process for crystals of palladium(platinum) solid solution, the screw-type growth mechanism plays an important role.

In summary, the recovery of platinum by palladium-nickel catchment gauzes is a re-alloying and recrystallisation process of the palladium-nickel alloy. The reduced platinum atoms deposit on the surfaces of the catchment gauzes and are alloyed with the palladium matrix, changing the topography and structure of the gauzes. The bright smooth palladium-nickel alloy wires gradually acquire a porous sponge and layered structure, and faces and crystals of new palladium(platinum) solid solution form. The growth of the new crystals finally produces a tetrakaidecahedron structure and the initial solid solution of palladium(nickel) with lattice parameter \(a = 0.3856 \text{ nm}\) turns gradually into palladium(platinum) solid solution. The lattice parameters of the palladium(platinum) solid solution increase with the increasing platinum:palladium ratio. The nickel solute in the initial palladium(nickel) solid solution is completely oxidised to NiO. In the early stages of recrystallisation, that is during the formation of new crystals of palladium(platinum) solid solution, ladder-like growth is the main mechanism; while in the later stages, during the growth of new crystals, screw-type growth plays an important role.

Acknowledgement

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Continued Importance of Platinum Metals Catalyst Systems

Catalytic Naphtha Reforming, Science and Technology

Catalytic reforming is used in oil refineries to improve the octane number of naphthas or light distillates to convert them into the motor fuel required for high compression ratio internal combustion engines. It is also a major source of aromatics for the petrochemicals industry. In this book the editors have collected together fifteen useful contributions on this important area of catalytic processing technology, based on the use of supported platinum on alumina catalysts. The net effect of catalytic reforming the naphtha feedstock is to convert the paraffins and naphthenes into aromatic hydrocarbons.

The first section of the book deals with the chemistry and processing of petroleum and the chemical reactions which take place in the presence of reforming catalysts. The relationships between chemical composition of the fuel, its octane number, and its performance are indicated, and the various petroleum conversion processes outlined.

The second part of the book gives methods for the preparation and characterisation of the various bi- and multimetallic platinum catalysts used in reforming processes. Preparative techniques for multimetallic catalyst systems include successive impregnation, co-impregnation, successive ion exchanges, and use of metals in alumina sols. Although platinum catalyst technology was first used commercially in the late 1940s, much research and development has been performed since that time. This has resulted, for example, in the introduction of bimetallic catalyst systems, such as those involving platinum/rhenium, platinum/tin, platinum/iridium and platinum/germanium combinations. It is thought, however, that improvements in catalyst formulation and preparation procedures are still possible and that more fundamental studies are required in order to achieve better control of the individual preparative steps. The acidity of the high surface area alumina support is normally promoted with halogen, usually chlorine. There is still a perceived need for new preparation routes which would lead to highly tuned multimetallic catalysts and also for entirely new formulations. Some less well established patented bi- and multimetallic catalysts are listed in a useful Table.

For characterisation, both the acidic and metallic functions of these bifunctional catalyst systems must be considered. Methods to determine the characteristics of the alumina supports are given, including surface area, porosity and acidity. The chemical state of the metal in platinum on alumina catalysts may be assessed using numerous techniques, such as dispersion, XRD, TEM and chemisorption. The application of various aspects of these techniques to the characterisation of supported platinum/rhenium, platinum/tin and other bimetallic catalysts and platinum on alkaline L zeolites is also considered. The relationships between the method used for preparation and the structure of the resulting catalyst are discussed.

For a commercial plant, the pre-treatment and operation procedures appear to produce a catalyst having a high platinum dispersion. The combination of high dispersion and low metal loading does, however, mean that most of the experimental characterisation techniques have only limited value for commercial catalysts. One useful indicator is that the hydrogen:platinum ratio for chemisorption of hydrogen should closely approach or exceed unity. The relationships between catalyst composition and structure and its performance receive detailed consideration in two chapters. In view of the large volume of naphtha throughput in reforming plants, the characteristics of the catalyst performance can have very big implications on the economic returns.
In a third section of the book, catalyst deactivation and regeneration during use in commercial processes is discussed. The mode of operation during manufacturing procedures is considered in detail and processes such as coking, poisoning, and sintering are described. Methods used to regenerate and re-activate the catalysts are given. For optimum performance of the catalyst it is crucial that a proper balance between metal and acid function is maintained. If the metal function is too strong, excessive hydrogenolysis to produce C₁ to C₄ gases and dehydrogenation to give polyolefinic coke precursors can occur; but if it is too weak then excessive coking also takes place and the catalyst deactivates rapidly. An acid function which is too strong leads to excessive hydrocracking and coke laydown on the catalyst; but if it is too weak the rate-determining carbonium ion reactions involved in dehydroisomerisation and dehydrocyclisation do not proceed fast enough, and this in turn leads to an increase in C₅ to C₁₀ gas production and a decrease in the yield of liquid product. Recovery of platinum and rhenium from spent reforming catalysts is also an important part of the total economic picture and a chapter on the methods used is included.

In a final section of the book the plant aspects of catalytic reforming processes are discussed. The main elements of reforming process technology include operating strategy and steady-state optimisation, process control, catalyst selectivity and stability, environmental control, integration with other refinery units and refinery energy balance. The reforming process continues to satisfy changing gasoline pool requirements, but refiners and catalyst manufacturers must seek means to improve catalyst performance to enhance the selectivity to aromatics and high octane reformate.

Several commercial reforming processes are available for licensing worldwide, these include UOP-Platforming, IFP Reforming, Engelhard Magnaforming, Exxon Powerforming, Chevron Rheniforming, Amoco Ultraforming, and Houdriforming; and the similarities and differences between these various processes are considered. Catalytic reforming enjoys a virtual monopoly of supplying aromatics to the petrochemical industry.

Changes in process design are frequently accompanied by modification of the catalyst for improved performance to achieve one of the following objectives:
- Higher reformate octane yields
- More efficient catalyst regeneration
- Longer catalyst life and enhanced surface stability
- Lower-pressure operation and less hydrogen recycle

A chapter in this section discusses modelling commercial reformers, and a final chapter describes recent developments in reforming. The increasing world demand for unleaded and higher octane gasoline as well as for aromatics will continue to spur the development of more efficient catalysts and processes. The implementation of clean air regulations, which restrict the benzene and aromatics content of gasoline will also have an effect on reforming. Catalysts which isomerise the lighter C₅ and C₆ hydrocarbons to the branched isomers with higher octane numbers will be much in demand. Vapour pressure constraints will result in the elimination of butane from gasoline. The use of cleaner alternative fuels, such as oxygenates, may reduce the demand for aromatics in gasoline, but the increased demand for aromatics from the petrochemicals industry means that processes which result in high aromatics will continue to be important.

This book contains some interesting articles on various aspects of catalytic naphtha reforming, and has a useful subject index. The authors are from industry, universities and research institutes in a number of countries, but the picture presented is reasonably unified; however, there is repetition as most writers introduce the topic in a general way. Many chapters in books and review articles in journals are available on aspects of this subject, but it is still useful to have a one-volume up-to-date collection of contributions on this very significant aspect of catalytic processing which affects important facets of our daily lives, and to have pointers to likely future developments.

D.T.T.
International Conference on “Noble and Rare Metals”

METALLURGICAL AND MINERALOGICAL STUDIES OF THE PLATINUM GROUP ELEMENTS AND COMPOUNDS IN THE CIS

Academic, technological and economic aspects of platinum group elements were quite comprehensively included in the programme of the NRM-94 (Noble and Rare Metals) conference held from 19th to 22nd September 1994 in the State University of Donetsk, Ukraine, under the Chairmanship of Professor V. A. Goltsov. Contributions to the programme were divided into three main sections, each comprising some forty oral and forty poster items. Significant numbers of reports within each section emphasised the depth of resources and breadth of investigations involving platinum metals by scientists from the Commonwealth of Independent States, with most of the papers originating from Russia and Ukraine. There were 296 participants, mostly from Ukraine and Russia; other attendees came from Uzbekistan, Belorussia and Kazakhstan, Great Britain, Germany, Japan, and the U.S.A. These participants represented various research institutes, universities, industrial firms and government bodies.

Mineralogical and Other Platinum Metals Sources and Their Recovery

Section 1 of the Conference was centrally concerned with sources of mineral concentrations and the abstraction and recovery of the platinum group metals. With regard to mineralogical sources, a general survey and overall assessment of the mineral wealth of Ukraine was presented by B. S. Panov, (State Technological Institute, Donetsk). Contributions more specifically dealing with the isolation of the platinum metals from non-traditional shales, and from wider deposits in the Aldan Shield area, were presented, respectively, by A. F. Korobeinikov and colleagues (Polytechnic Institute, Tomsk, Russia) and V. V. Stogny and colleagues (State University, Yakutsk, Russia); and isolation from waste deposits in the Don Basin coal mines was discussed by A. F. Gorovoi and colleagues, (Mining and Metallurgical Institute, Alchevsk, Ukraine).

Papers concerned with the abstraction of platinum metals from various industrial wastes included one discussing the treatment of Chineisk dissolved wastes (B. I. Gongal’sky and colleagues, Institute of Natural Resources, Chita, Russia); while the abstraction of platinum metals from general and from secondary scrap was discussed, respectively, by A. A. Mazhan and colleagues (State Alloy Institute, Donetsk) and S. I. Pechenyuck and colleagues (Institute of Chemistry and Technology of Rare Metals and Minerals, Apatity, Russia). Techniques of abstracting platinum metals from sulphuric acid solutions with thiourea derivatives were described by Yu. A. Mirgorod (State Institute, Sumy, Ukraine) and ways of separating platinum metals from nuclear fuel wastes were described in papers by Yu. A. Sidorenko and colleagues (Alloy Company, Krasnoyarsk, Russia), V. I. Volk and colleagues, and E. V. Renard (all of the A. A. Bochvar Institute of Inorganic Materials, Moscow).

Platinum Metals Chemistry and Electrochemistry

Various aspects of the general and complex chemistry of platinum metals were discussed in Section 2 of the Conference, including: the redox properties of 4-valent rhodium, by A. V. Khaperskaya and colleagues (All-Russia Science Research Institute, Moscow); properties of rhodium and platinum complex compounds with phosphorus and silicon, by V. N. Nazmutdinova and colleagues (Institute for General and Physical Chemistry, Kazan, Russia); and studies of the phosphides of platinum, by V. B. Chernogorenko and colleagues (Institute for Problems of Materials Science, Kiev). Studies
of ruthenium and osmium complexes were reported by O. Ya. Borovaya and colleagues (Lvov Polytechnic Institute, Ukraine).

Several presentations were concerned with the precipitation, deposition and other electrochemical problems of the platinum group metals; these included studies of anodic processes on platinum anodes by N. M. Barbin (Institute of High Temperature Electrochemistry, Ekaterinburg, Russia); and the electrochemical behaviour of palladium ions in a melted eutectic mixture of sodium and caesium chlorides, by N. P. Borodina and colleagues (also from the Institute of High Temperature Electrochemistry). The electrodeposition of iridium was discussed by N. V. Grushina and colleagues (Institute of Organic Chemistry, Catalysis and Electrochemistry, Almaty, Kazakhstan); and new methods for refining iridium were described by A. A. Omel'chuck (Institute of General and Inorganic Chemistry, Kiev). The mechanical behaviour of iridium and ruthenium was described by P. E. Panfilov and colleagues (Ural State University, Ekaterinburg) and osmium extractions from sulphuric acid solutions was discussed by I. D. Troshkina and colleagues (Russian Chemical and Technological Institute, Moscow).

Other topics discussed were palladium alloy electrodeposition and utilisation by S. N. Vinogradov and colleague (State Technical University of Penza, Russia); electrodeposition of palladium based alloys in preference to palladium and gold by T. V. Silysarskaya and colleagues (State Educational Institute, Kharkov, Ukraine); and rhodium plating by electrodeposition by A. V. Boiko and colleagues (also from the State Educational Institute).

**Techniques of Platinum Metal Analysis**

A contribution from M. K. Nauryzbaev and colleagues (State National Institute, Almaty) on methods for the determination of palladium in alloys and catalysts, presented a general review of available techniques. In analytical papers, centred on more specific methods, A. A. Valter and colleagues (Institute of Geochemistry, Mineralogy and Ore Production, Kiev, Institute of Applied Physics, Sumy, and Physico-Chemical Institute, Kharkov), reported on nuclear physical methods for noble metal analysis; Kh. Kh. Turaev (State Institute of Termez, Uzbekistan) reported on the radiometric determination of palladium and N. A. Kolpakova and colleagues (Polytechnic Institute, Tomsk) reported on the inversion voltammetric determination of platinum metal composition. Two papers concerned with analysis of platinum metals sorbed on porous media were introduced by A. S. Karasick and colleagues (Engineering and Technological Centre of Powder Metallurgy, Perm, Russia) and I. P. Bakhvalova and colleagues (Research Engineering Centre, Krasnoyarsk). S. I. Degtyarev and colleagues (State University, Yakutsk) reported on γ-ray methods for the analysis of noble metals.

**Physical and Technological Aspects of Platinum Metals and Alloys**

Contributions which concentrated mainly on physical and technological aspects were the basis of Section 3 of the conference programme. Production of palladium powders was discussed in a paper by D. R. Shul'gin and colleagues (Institute for Non-Ferrous Metals, Krasnoyarsk) and the production and use of artiris of noble metal alloys was reviewed by D. S. Tykochnisky (Scientific Production Complex, “Supermetal”, Moscow). The advantages of reduced corrosion of platinum metals in molten oxides was reported by V. P. Kochergin and colleagues (Ural State University, Ekaterinburg); while the loss of platinum metals from catalysts employed in nitric acid production was discussed by A. Yu. Chernyshev and colleagues (State Institute of Nitrogen Industry, Moscow) and the regeneration of catalysts based on platinum alloys was the subject of a contribution from A. S. Savenkov and colleagues (Polytechnic Institute, Kharkov). The influence of the platinum metals on martensite transformations was discussed by E. L. Semenova and colleagues (Institute for Problems of Materials Science, Kiev) and a review on the casting of noble metals and noble metal alloys was presented by S. P. Doroshenko (Polytechnic Institute, Kiev).

An account of phase transitions in palladium-
rich palladium-rare earth alloys was presented by Y. Sakamoto (University of Nagasaki, Japan) and an account of interdiffusion in the gold-platinum system was given by M. Onishi and colleagues (Kyushu Institute of Technology, Japan). Two papers about the palladium-gold-iron system alloys were presented by authors from the Ural State Technical Institute, Ekaterinburg; one, by Yu. K. Serdyuk and colleagues, covered the influence of ordering on physical properties, while the other, by I. I. Piratinskaya and colleagues, was on the effect of melt heat treatment on magnetic state.

Stepwise ordering in alloys of iron-palladium-gold was discussed by S. Yu. Zaginaichenko and colleagues (Metallurgical Institute, Dnepropetrovsk, Ukraine) and a study by computer engineering of equilibria in ternary alloy systems was reviewed by O. M. Irbelkhaeva and colleagues (Buryat Institute of Natural Science, Ulan-Ude, Russia). A review of the scandium-ruthenium system was presented by V. G. Khoruzhaya and colleagues (Institute for Problems of Materials Science, Kiev).

Studies with electronic and biological interest were presented in papers concerning radio modifiers based on palladium alloys by I. A. Efimenko and colleagues (Kurnakov Institute of General and Inorganic Chemistry, Moscow), and in papers which discussed the uses of platinum compounds in chemotherapy. These included platinum complexes which display antitumour properties, discussed by A. L. Konovalova and colleagues (Oncology Science Centre, Moscow and Chemico-Pharmaceutical Institute, St Petersburg); and acetylene complexes of platinum potentially exhibiting biological activity presented by L. L. Sichinava and colleagues from the V. I. Nikitin Institute of Chemistry, Dushanbe, Tadzhikistan.

Hydrides: Hydrogen Permeation Membranes

The research involvement of Professor Goltsov’s Donetsk group in studies of hydrogen in metals has been emphasised by the regular appearances of their extensive Russian-English translations database in the International Journal of Hydrogen Energy. The database is a compilation of Russian hydrogen energy and metal-hydrogen publications. This high level of involvement was reflected at the conference by the inclusion of a special section on contributions involved with metal/hydrogen interactions, most importantly concentrated on aspects of the palladium-hydrogen and allied systems. In this section a general review of phase relationships and thermodynamic aspects of metal-hydrogen systems, with emphasis on statistical thermodynamic correlations, was presented by H. Brodowsky and colleagues (University of Kiel, Germany and the University of Sendai, Japan). Further information concerning the phase relationships and related structures of palladium-rare earth alloy-hydrogen systems was presented in relation to recent extensive series of allied contributions in this field of study, by Y. Sakamoto and colleagues (University of Nagasaki).

Two papers, containing information of further research into possibilities of technologically attractive evidence of cold fusion in hydrogen isotopes discharged electrolytically at palladium surfaces, but with different perspectives and representations of experimental results, were contributed by J. S. Cantrell (Miami University, Ohio, U.S.A.) and T. Matsumoto (Hokkaido University, Sapporo, Japan). Interrelationships between lattice hardening and strengthening effects of interstitial hydrogen in relation to phase (p-c(n)-T) relationships in the palladium-hydrogen system, were subjects of a wide ranging review of progress in regard to these factors by Professor Goltsov.

This review served as a background for several related oral and poster presentations by members of the Donetsk group, including contributions by R. V. Kotelva and Goltsov, and by Yu. A. Artemenko and M. V. Goltsova. An important concern with the use of palladium alloys as hydrogen permeation membranes, was the basis of a contribution presented by Goltsov, A. P. Kuzin and colleagues.

Hydrogen permeation through palladium alloy membranes was also a central topic of contributions from other centres with allied interests.
Thus the influences of palladium membrane coating on hydrogen permeation through iron were discussed by Y. Hayashi and colleagues (University of Fukuoka, Japan) and comparisons of hydrogen permeabilities in palladium-yttrium-(gadolinium)-silver and palladium-yttrium-indium(tin, lead) alloys were reported by Y. Sakamoto and colleagues (University of Nagasaki). Evidence from observations of 'uphill' hydrogen permeation effects, originating from self induced strain gradients, and consequent Gorsky effect hydrogen migration, that result from the lattice expansive nature of hydrogen interstitials, was reviewed by F. A. Lewis (University of Belfast). A survey of potential applications and general prospects for the development of palladium alloy membranes for hydrogen purification and catalytic utilisation was presented by V. G. Sorokin (“Lenneftekhim”, St Petersburg), and the application of mathematical modelling to clarify the process mechanisms of hydrogen permeation in palladium alloys was outlined by A. M. Dobrovitskovey and colleagues (also of “Lenneftekhim”). A broader general assessment of the prospects for utilising palladium and palladium alloys in future hydrogen research was presented by P. G. Berezhko (Scientific Research Institute of Experimental Physics, Arzamas, Russia).

Substantial details of the contents of the papers were available in books of abstracts, most of which were in Russian, the remainder being in English. The location of the next conference in this series has yet to be finalised, and enquiries should be addressed to Professor V. A. Goltsov in Donetsk.

F.A.L.

A Copper-Free Ruthenium Perovskite Superconductor

In recent years layered perovskite structures exhibiting superconductivity at low temperatures have been synthesised. Work on these compositions, with various substitutions, has resulted in materials which display significantly higher transition temperatures, and hence are superconducting at relatively higher temperatures. These increases in transition temperature are sufficiently large to suggest that a market for such materials is likely to develop during the last few years of this century.

Materials developed to-date are based upon systems, such as La$_{2-x}$Ba$_x$CuO$_y$, where the copper is present in layers, together with oxygen. This layering is necessary to induce superconductivity, as are the barium substitutions into the basic perovskite structure. However, work is now reported on the evaluation of a perovskite compound based on Sr$_{2}$RuO$_{4}$ (Y. Maeno, H. Hashimoto, K. Yoshida, S. Nishizaki, T. Fujita, J. G. Bednorz and F. Lichtenberg, Nature, 1994, 372, (6506), 532–534). When $n=1$ Sr$_2$RuO$_4$ is formed, having crystal structure isostructural with La$_{2}$-Ba$_x$CuO$_y$.

Single crystals of Sr$_2$RuO$_4$ were cleaved, and measurements made which revealed superconductivity below about 1 K. The transition temperature, $T_c$, was 0.93 ± 0.03 K. Critical current density measurements were made at 0.32 K.

A Palladium Source of Protons

The use of very bright gaseous sources for lithographic purposes has been suggested, but no practical ion sources have been found. Now, however, researchers from the Muroran Institute of Technology in Japan, have made a preliminary proton ion source using palladium (T. Teraoka, H. Nakane and H. Adachi, Jpn. J. Appl. Phys., Part 2 Lett., 1994, 33, (8A), L1110-L1112), making use of the fact that palladium has the highest hydrogen permeability of all metals. The needle-shaped palladium allows hydrogen diffusion at the same rate as it permeates in bulk palladium. The ion source must be operated so as to avoid a phase transition which occurs at 100–200°C in the palladium. The ion source is expected to be useful for future microfabrication technology.
New Large Molecules Contain Ruthenium

By J. R. Moss
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Of all the platinum group metals, rhodium is, perhaps, the most notable. It is the most expensive, costing about $2000 per ounce in 1992, though today it is typically around $700 per ounce. This price is largely a result of its scarcity, but also because of its important catalytic applications. Rhodium is an excellent catalyst for so many processes, from the Monsanto acetic acid synthesis to the selective hydrogenation of alkenes, and in such reactions rhodium is superior to most other catalysts.

By comparison, ruthenium, which is one of

\[ \begin{align*}
2, 2' \text{-bipyridine (bpy)} \\
2, 3' \text{-bis(2-pyridyl)-pyrazine (2,3-dpp)}
\end{align*} \]

Fig. 1 A dendritic co-ordination complex held together by 22 ruthenium atoms. (Structure adapted from Ref. (2))
its nearest neighbours in the Periodic Table, is a much cheaper metal, costing around $27 per ounce today, and in the past this metal has been overlooked. Ruthenium does, however, have good catalytic properties, for instance for the hydrogenation of carbon monoxide in the Fischer-Tropsch reaction, although iron is the metal that is commonly utilised for this reaction. Iron performs well catalytically and is very much cheaper than ruthenium; it is therefore used in preference to ruthenium in commercial plants, such as the giant SASOL plants in South Africa.
Africa. Nevertheless, ruthenium is thought by many to be a better catalyst than iron for the process.

Rhodium is a good catalyst, partly because it forms labile complexes. Compared with rhodium, ruthenium often forms more stable metal-ligand bonds, which is not good for catalytic reactions but is essential for building up large molecules, where it is important to have thermodynamically strong bonds and kinetically inert complexes. Indeed, ruthenium is particularly well-suited to this task, the ruthenium-ligand environment having the capacity to withstand the conditions necessary to build up big molecules.

Thus, it may not be too surprising to learn that four independent research groups in Italy, England, the U.S.A. and South Africa, have obtained similar results.
recently prepared some of the largest metal complexes known and that all of these very large metal complexes contain ruthenium. For this and other reasons, ruthenium is now becoming much more important.

In 1992 a group in Bologna, Italy, reported an elegant synthesis of a novel dendrimer that is held together by 22 ruthenium atoms and is believed to be the largest co-ordination complex ever made, Figure 1, (1). This complex may well have novel properties and applications, for instance for use in new light harvesting devices for solar energy conversion (1, 2).

At the University of North Carolina the search for artificial photosynthetic reagents is one of the main driving forces of a research group at Chapel Hill, who have recently prepared polymer supported ruthenium complexes (3). These materials are not unimolecular but they are believed to contain about 30 ruthenium atoms co-ordinated through functionalised bipyridyl ligands to a polymer backbone, see Figure 2.

One of the founders of dendrimer research is George R. Newkome, of the University of South Florida, who has synthesised many organic dendrimers by the divergent approach (4). Dendrimers are highly branched polymers and can be considered to be molecular fractals. Collaboration between the group run by Newkome in the U.S.A. with a co-ordination chemistry group headed by E. C. Constable which was based at Cambridge University, U.K., has resulted in the development of a new type of dendritic co-ordination complex containing 12 ruthenium atoms, see Figure 3, (5). More recently, at the University of Cape Town, we have used a convergent approach to prepare the first organotransition metal dendrimers containing ruthenium-carbon σ-bonds (6). Here, the synthesis of discrete molecules each containing up to 12 ruthenium atoms, see Figure 4, was performed in a stepwise process, with the metal atoms being bonded exclusively to the surface of the growing macromolecules. This approach has now been taken further and we have built bigger organometallic dendrimers, up to the 3rd and 4th generations (7).

Attaching a 4th generation dendritic wedge to a trifunctional core has now resulted in a molecule with 48 ruthenium atoms – all in the same molecule, and all being close to the surface of the molecule. While this is probably the largest organometallic complex ever prepared, having a molecular mass of 18,438, it is readily soluble in organic solvents and can be fully characterised by various spectroscopic techniques including NMR and infrared spectroscopy.

**Future Applications**

The solubility of these organoruthenium dendrimers may be the key to possible applications, since large metal cluster compounds are often insoluble. Thus, for example, these organometallic dendrimers may find use in the preparation of thin metallic films. In the unique molecular architecture of the ruthenium dendrimer the ruthenium atoms all lie close to the molecular surface, and this has resulted in a new type of polymer-supported complex which might find application as a novel catalyst, functioning at the interface between homogeneous and heterogeneous catalysts.

Thus, if these recent reports are typical of what can be expected, there will be many more new and exciting complexes which could soon be discovered. The future does indeed look very promising for bigger, and maybe even better, ruthenium complexes.

**References**

ABSTRACTS

of current literature on the platinum metals and their alloys

PROPERTIES

Desorption and Dissociation of Oxygen Admolecules on a Stepped Platinum (533) Surface
The desorption and dissociation of O
admolecules were studied on a stepped Pt(533) surface by using thermal desorption combined with an isotope tracer. The desorption from the molecular adsorption state yielded two main peaks at 145 and 225 K, the latter peak being assigned to desorption from step sites. Most of the admolecules on step sites dissociate into adatoms in the subsequent heating at 150-250 K, but admolecules on terraces desorb without dissociation.

Superconductivity in PtSi Ultrathin Films
Studies of normal and superconducting properties of PtSi films of thickness d = 2-20 nm showed the superconducting transition on the thin films down to d = 4 nm. The systematic reduction of the transition temperature with decreasing d was explained by the localisation and Coulomb interaction effects on superconductivity. The temperature dependence of the upper critical field shows that the PtSi films behave as homogeneous superconductors.

The Pt-Sn Binary System
The Pt-Sn binary system has been examined over the concentration range 1-2 at. % Sn. The five stoichiometric intermediate phases had generally higher melting points than previously indicated, for Pt and Sn. The five stoichiometric intermediate phases had generally higher melting points than previously indicated, for Pt-Sn and PtSn

Molecular Dynamics Simulations of Consolidation Processes during Fabrication of Nanophase Palladium
Dynamic consolidation processes which occur during fabrication of nanophase Pd from atom clusters have been simulated. Several phenomena, such as surface rounding, "neck" formation, void formation and shrinking, and cluster extrusion, were observed. The grain boundary structures are all very narrow and show only localised disorder. The effect of applied compressive pressures on the final structures of the nanophase materials during consolidation was shown.

Synthesis of Pd-doped SnO, Films on Silicon and Interaction with Ethanol and CO
Pure and Pd-doped polycrystalline SnO, films were prepared by a modified CVD method on oxidised Si using the pyrolysis of an aerosol generated by ultrahigh frequency spraying of a volatile precursor solution. The deposition at 460-560°C controlled the growth rate, microstructure and composition of the films, and the moisture of the carrier gas. At low temperature the moisture increases the growth rate of SnO; but not of Pd. The heat treatments induce an increase of O and C concentration. Adding Pd to the films largely increases the gaseous adsorption, showing a maximum at low temperature.

Formation of Pd Silicides and Periodicity in Sputtered Pd/Si Nanometric Multilayers
Studies of the formation of Pd silicides and the periodicity in sputtered Pd/Si nanometric multilayers showed both Pd, Si and PdSi in as-deposited Pd/Si multilayers with small periods of 1-5 nm, but only PdSi for large periods. It is concluded that the roughness of the Pd/Si interfaces can reach about 2.0 nm and is related to the formation of the Pd silicides.

Ferromagnetism in an Intermetallic Compound Containing Palladium, Titanium and Aluminium
Ferromagnetism was observed in a ternary intermetallic Pd,TiAl (1) compound in which the constituent elements do not order magnetically. The stoichiometric compound Pd,TiAl has the cubic Heusler L2, structure and a lattice parameter of 6.322 Å. The presence of a hysteresis in the magnetisation process confirms the existence of a spontaneous ferromagnetic moment. The ferromagnetism reported in (1) contrasts with the apparent antiferromagnetism in Pd,TiIn and the small moment system, 0.005µ, observed for Pd,TiSn.

High Field Magnetisation of UPdAl
Studies of the high field magnetisation of antiferromagnetic heavy fermion material UPdAl, at ≤ 50 T showed a clear metamagnetic step at 18 T along the a-axis at 1.3 K. The angular dependence of field-magnetisation shows a large anisotropy in the c-plane. The spin system can be described by the XY-spin model except for very small anisotropy in the c-plane.
Magnetic Ordering in U₃Pd,In and U₃Pd,Sn
Studies of the tetragonal intermetallic compounds U₃Pd,In and U₃Pd,Sn showed them to order antiferromagnetically at 36 and 41 K, respectively, and to have enhanced electronic specific heat coefficients γ of 393 and 203 mJ/mol K², respectively. At low temperature, the nearest-neighbour U-U spacing is along the c axis in both compounds, but in U₃Pd,Sn the in-plane U-U distance was shorter at room temperature. This crossover is due to motion of the U atoms within the cell rather than anisotropy of the thermal contraction. At 10 K, the magnetic moments are (1.6 ± 0.2)μ₃ and (2.0 ± 0.1)μ₃ per U atom in U₃Pd,In and U₃Pd,Sn, respectively.

Electrical Resistivity and Thermopower Studies of Ce(Rh,_,Ru,)Si, Compounds with 0 ≤ x ≤ 0.4
Electrical resistivity (ρ) and thermopower (S) were measured on both LaRh,_,Si, and the heavy fermion compounds Ce(Rh,_,Ru,)Si, at 3.5–300 K. The ρ (T) and S(T) curves for LaRh,_,Si, showed that the thermopower and electrical resistivity in Ce(Rh,_,Ru,)Si, mainly reflect the rather anomalous scattering arising from the Ce ions. Transport properties of isomorphous LaRh,_,Si, were studied for comparison.

Polycrystalline Iridium Silicide Films. Phase Formation, Electrical and Optical Properties
Electrical and optical properties of thin Ir,Si, films (0.25 ≤ x ≤ 0.55) prepared by DC-magnetron co-deposition and annealed at 400–1170 K, were studied as a function of the crystallisation. The dominant phases were Ir,Si, Ir,Si, Ir,Si, and Ir,Si, and films having the semiconducting compound Ir,Si, as main phase showed a large thermopower only in a small composition range depending on the grain size. The optical gap of Ir,Si, was determined to be 1.56 eV.

The Nuclear Magnetic Resonance of "Ru and "Ru in Hexagonal Close-Packed Ruthenium Metal
The NMR of "Ru and "Ru was observed in hexagonal close packed Ru metal and the field spectra show the characteristics of quadrupolar disturbed NMR. The measurement of the spin-lattice relaxation of the isotopes "Ru and "Ru, carried out at 4.2 K, yielded spin-lattice relaxation times of 3.7 ± 0.2 s and 3.1 ± 0.2 s, respectively. The rather high positive isotropic Knight shift is due to the Van Vleck contribution, which is also responsible for the strong anisotropy.

Chemical Compounds
Heterometallic Binuclear Complexes Having the Mercury-Platinum-Rhodium Bond as a Source of a Platinum Carbeneoid in Reactions with Fullerene-60
The cleavage of two σ bonds and the formation of (η¹-C₆H₅)₂Pt(PPh₃)₂, occur in a new reaction between fullerene-60 and binuclear heterometallic compounds, with a Hg-Pt bond. Complex trans-Ph,C₆H₅HgPt(PPh₃),Br reacts much faster than cis-(C₆H₅)₂Pt(PPh₃),H₂, which gives a Pt-centred radical under photolytic conditions. A Pt-fullerenyl radical cis-(C₆H₅)₂Pt(PPh₃) was identified by EPR spectroscopy.
Synthesis and Structure of Li,RhH, – a Ternary Hydride with Isolated [RhH,]+ Octahedra


The ternary Rh hydride Li,RhH, was prepared by reacting Li hydride with Rh under a H, pressure of 80 bar. The atomic arrangement is isotypic to the Na,RhH, structure type. The crystal structure contains isolated [RhH,]+ octahedra, which are separated by the Li ions. X-ray studies on powdered samples and elastic neutron diffraction experiments on the deuterated compound showed that it crystallises in space group Pnma with Z=4.

Crystal Growth and Properties of Novel Ternary Transition Metal Chalcogenide Compounds [Ir,Ru,_,S,](0.005 < x < 0.5)


Pure semiconducting pyrite phases RuS, and IrS, and mixed pyrite phases Ir,S, Ru,S, (0 < x < 1), prepared in powder form, were used to produce single crystals by chemical vapour transport and high temperature solution growth from Bi fluxes. Ir,Ru,S, (0.005 < x < 0.5) crystals were synthetically grown, resulting in a S deficiency. The incorporation of Ir in the RuS matrix induced a degenerate character in these mixed-phase single crystals, at carrier concentration of > 10^19/cm^3. Thus a new class of ternary Ir,Ru-S compounds has been synthesised for the first time. They have potential applications for photovoltaic solar energy use.

The First Ruthenium Carbonyl Derivative of Fullerene: (η-^1-C^60)Ru(CO)


Ru(CO), solution was added in mole ratio 1 : 1 to a toluene solution of C^60 under N2 to yield a 1 : 1 adduct (η-^1-C^60)Ru(CO),. It indicates that (η-^1-C^60)Ru(CO), is more stable then (η-^1-C^60)Fe(CO),, but since Ru has stronger bonding to this fullerene than does Fe. The structures of (1) and (2) are similar and they have very similar IR and ^13C NMR spectra. The synthesis and spectroscopic characterisation of compound (1) is described.

Auration of Ruthenocene: Synthesis and Molecular Structure of Mono- and Diaurated Derivatives


Ruthenocene, like ferrocene, yields the gem-diaurated derivative CpRuC,H,(AuPh,)+BF, (1) when reacted with (Ph,Pu),OF, . Treatment of (1) with PPh, gives CpRuC,H,AuPh,. It is suggested that the order of interaction of Ru-Au and the corresponding order of positively charged transport to Ru is higher than that of Fe-Au. X-ray analysis showed an important interaction between Ru-Au in the diaurated derivative.

Preparation of Ultrafine RuO2-IrO2-TiO2 Oxide Particles by a Sol-Gel Process


Ultrafine RuO2-IrO2-TiO2. ternary oxide particles with different content ratios were prepared by a sol-gel method with metal alkoxides. Only a RuO2-rich sample contained a mixture of rutile-type oxide phase and a metallic phases. However, for Ti-deficient samples, uniform solid solutions with rutile-type oxide were prepared after calcination in air at 450°C, while mixtures of heterophase oxide particles were prepared for the other samples. These powdery oxides can aid development of active catalysts and explain the phase diagram.

ELECTROCHEMISTRY

Chemically Modified Electrodes by Nucleophilic Substitution of Chlorosilylated Platinum Oxide Surfaces


Chlorosilylated Pt oxide electrode surfaces were generated by reaction of SiCl, vapour with an electrochemically prepared monolayer of Pt oxide. Various nucleophilic agents, such as alcohols, amines, thiols, etc., can be used to displace chloride and thus functionalise the metal surface. Electroactive surfaces prepared with ferrocene MeOH as the nucleophile show that derivatisation by small molecules can achieve coverages of the order of a full monolayer.

Electroreduction of Carbon Dioxide on Palladium Electrodes at Potentials Higher than the Reversible Hydrogen Potential


The electroreduction of CO2 was observed on electrodes of dispersed electrodeposited Pd on Pt wire net and on Pt plate at potentials more positive than the reversible H potential, at pH 0–10, with the HCOO current yield close to 100%. The adsorbed H atoms were assumed to participate in the slow stage of the electroreduction of HCOO (CO2) to HCOO.

Stabilization of the Redox Polymer [Os(bipy),,(PVP),,Cl]Cl in Situ Chemical Cross-Linking


The redox polymer [Os(bipy),,(PVP),,Cl]Cl where bipy is 2,2’-bipyridyl and PVP is poly-4-vinylpyridine, was physically stabilised by chemical cross-linking at various levels via the solid-state reaction with the cross-linking agents p-dibromobenzene, 1,5-dibromopentane and 1,10-dibromodecane. The stability of the polymer films was increased, compared to uncross-linked polymer, when under severe hydrodynamic operation, such as in thin-layer flow cells. The charge transport properties of the redox polymer were maintained or improved by cross-linking.

Platinum Metals Rev., 1995, 39, (1)
PHOTOCONVERSION

Photochemical C-H Bond Activation of Methane on a Pt(111) Surface


CH₃ adsorbed on a Pt(111) surface desorbs at ~70 K. However, after the CH₃-precovered surface was irradiated with 193-nm photons, the intensity of the thermal desorption peak decreased and a new CH₃ peak at ~260 K grew with the accumulated number of photons. CH₃ on Pt(111) was photodissociated to yield a chemisorbed CH₃ radical and an adsorbed H product as atoms. The total cross-section of the photochemical process was ~1.5 x 10⁻¹⁶ cm².

The Influence of Conditions on the Yield of an Aldehyde in the Photocatalytic Carbonylation of Pentane in the Presence of the System RhCl₃(CO),+PMe₃


Studies of the photocatalytic carbonylation of pentane in RhCl₃(CO),+PMe₃ displayed a maximum dependence for the aldehyde yield on the CO and PMe₃ concentrations. The increase in aldehyde yield with increasing CO pressure is closely related to the increase in the carbonylation rate and the decrease in aldehyde photodecomposition. The rate of photocatalytic carbonylation of pentane in this system is 20 times higher than that in RhCl₃(PMe₃),CO.

Reductive Quenching of the Excited States of Ruthenium(II) Complexes Containing 2,2'-Bipyridine, 2,2'-Bipyrazine, and 2,2'-Bipyrimidine Ligands


The reductive quenching of the luminescent excited states of Ru(bpy)₂⁺, = (bpm)ₓ(bpz)ₓ⁺ (bpy = 2,2'-bipyridine, bpm = 2,2'-bipyrimidine, bpz = 2,2'-bipyrazine, m = 0, 1, 2, 3 and m + z = 3) by aromatic amines and methoxybenzenes as non-sacrificial electron donors and by C₆O₇⁻, EDTA and TEOA as sacrificial donors in aqueous, acetonitrile, and propylene carbonate solution was studied by laser flash photolysis. An E° for the irreversible oxidation of TEOA (~0.84 ± 0.12 V vs. NHE) in acetonitrile was obtained.

Intramolecular Transfer of MLCT Excitation Energy in [Ru(bpy)₃]²⁺


The rate of MLCT excitation energy transfer between the two crystallographically equivalent ligand units of [Ru(bpy)₃]²⁺ in [Zn(bpy)₂](ClO₄)₂, lattice was measured by time-resolved luminescence line-narrowing studies. At 1.8 K, the transfer rate is ~1 x 10⁻¹⁰ s⁻¹ in the second lowest-excited level II. The slow transfer rate is consistent with a small excitation exchange interaction between the equivalent metal-ligand units.

Semiconductor Sensitization by RuS₃ Colloids on TiO₂ Electrodes


RuS₃ (n-type) colloids, prepared by a new technique using diluted RuS₃ colloidal suspension in sulpholane, displayed green photoluminescence. The RuS₃-coated TiO₂ electrodes showed spectral sensitisation caused by RuS₃ with an increase in the photocurrent response of TiO₂ towards the longer wavelength spectral region. The photocurrent action spectra of these electrodes qualitatively suggests a band gap of ~2.2–2.8 eV for RuS₃, which is wider than that of the bulk material, showing size quantisation effects. A flat-band potential of ~0.15 V (vs. Ag/AgCl) was observed.

ELECTRODEPOSITION AND SURFACE COATINGS

Electrolytic Deposition of Palladium-Iron Alloys


Pd-alloy layers were produced from an ammoniacal bath containing Pd(II) and Fe(III) chlorides, with sulphosalicylic acid as a complexing agent. In the range of the limiting solid solutions of Pd- and Fe-rich alloy, the layers were crystalline, while in the medium concentration range they showed a multiphase structure with at least one phase being exceptionally distorted. Non-metallic impurities were ~10 ppm and H content and coercive force displayed a maximum near 75 wt.% Pd. The coercive forces of the as-deposited alloys were ~100–150 Oe.

Crack-Free Rhodium Deposition on Brass Substrates

M. L. DAS, Metal Finish., 1994, 92, (10), 12.

A Rh plating solution containing 15 g/l Rh was prepared by dissolving concentrated Rh sulphate in distilled H₂O at 30°C and a current density of 7.5 A/dm² was applied. A brass panel was electroplated with Rh for 30 min using a Pt metal sheet as anode. Al, Mg and Se were added to the plating solution to reduce cracks. With selenic acid in the plating bath, the deposit became completely crack-free, but the surface roughened. Roughness could be removed by polishing.

APPARATUS AND TECHNIQUE

Capacitive Air-Fuel Ratio Sensor


Air-fuel ratio in automotive exhaust can be monitored by capacitive measurement of the reversible change in the work function of Pt at stoichiometry. This change, which is as much as 0.7 V, occurs at elevated temperatures when the Pt is alternately exposed to dilute mixtures of oxidising (O) and reducing (HC and related molecules) species that are rich or lean of their stoichiometric ratio. It can be electrically monitored by the Kelvin vibrating capacitor method.
Investigations of Platinized and Rhodinized Carbon Electrodes for Use in Glucose Sensors
Studies of graphite electrodes modified by the electrodeposition of either Pt or Rh showed that platinised C electrodes could directly oxidise glucose at a potential of +350 mV (vs. Ag/AgCl). H2O2 was detected at +400 mV using glucose enzyme electrodes, with glucose oxide immobilised in hydroxyethylcellulose. The sensors had a linear range of 0.1–25 mM glucose and a slope of 8 nA/mM. Glucose sensors using rhodinised electrodes operating at +400 mV, had a linear range of 0.1–2 mM and a slope of 21 nA/mM glucose.

A New Hydrogen Sensor Using a Polycrystalline Diamond-Based Schottky Diode
A new polycrystalline diamond-based H-sensitive Schottky diode using layered Pd-undoped diamond/ p-doped diamond has been fabricated and the H sensing performance was analysed at 27–85°C. The H sensitivity was high, repeatable and reproducible. The study showed that the barrier height of Pd-diamond Schottky diode increases upon H adsorption. This leads to a change in the I-V characteristics from near ohmic to rectifying behaviour. This new H sensing technology should have many applications due to its reproducibility, sensitivity and performance over a wide temperature range, including room temperature.

Screen-Printed Glucose Strip Based on Palladium-Dispersed Carbon Ink
Pd-dispersed graphite ink was used for screen printing a disposable biosensor for glucose. The dispersed Pd particles decreased the overvoltage for the oxidation of the enzymically liberated H2O2 and greatly enhanced sensitivity and selectivity. The electrocatalytic behaviour was characterised, the sensor operation optimised and the analytical performance reported. The possibility of using metallised graphites for mass producing amperometric biosensors is discussed.

Luminescence Lifetime-Based Sensor for Relative Air Humidity
Sensitive coatings were developed for fibre optic sensors based on phosphorescent H2O-soluble Pt- and Pd-porphyrin dyes contained in monomolecular thin solid Langmuir-Blodgett films. These were transferred onto solid supports. The coatings have intense long-decay phosphorescence in ambient air, and are sensitive to the environmental H2O content, such as the relative humidity (RH) of air. The studied coatings have been applied to luminescence lifetime-based sensing of RH, and a highly reproducible prototype fibre-optic device has been produced.

Highly Selective Membrane-Free, Mediator-Free Glucose Biosensor
Highly selective amperometric glucose biosensors were produced by coupling the catalytic action of Rh microparticles with C paste/glucose oxidase probes. The dispersed Rh particles displayed efficient and preferential electrocatalytic activity toward the liberated H2O2 species and allowed cathodic detection of the glucose substrate at −0.10 V, with no interference from easily oxidisable constituents.

HETEROGENEOUS CATALYSIS

A Model for the Enantioselective Hydrogenation of Pyruvate Catalysed by Alkaloid-Modified Platinum
Molecular modelling studies for the above reaction showed that a highly specific 1:1 interaction between cinchonidine and pyruvate explains the observed enantioselectivity, and the product of this 1:1 interaction is a suitable precursor to the H-bonded state required for the increased rate which accompanies enantioselective reaction over cinchona-modified Pt. Catalysts modified and used only under anaerobic conditions showed little activity and enantioselectivity showing the crucial role of O in successful catalyst preparation. Various configurations of ephedrine, D- and L-histidine, etc., were studied as modifiers for supported Pt.

Influence of Operational Variables on the Catalytic Behavior of Pt/Alumina in the Slurry-Phase Hydrogenation of Phenol
Hydrogenation of phenol in the liquid phase was studied in a stirred tank reactor with highly dispersed Pt/Al2O3 catalyst prepared by adsorption from an aqueous solution of H2PtCl6, which was suspended as a slurry. Stirring rates > 9 Hz, catalyst particle size < 50 μm, and catalyst weight < 0.5 g ensures a chemically-controlled regime during catalysis. Increasing the total pressure resulted in an almost linear increase in activity and decrease in selectivity.

Effects of Metal Accessibility on Catalytic Performance for Pt/H-Mordenite
When calcined precursors of 0.5% Pt/H-mordenite catalysts were exposed to H2O vapour before reduction, they displayed enhanced catalytic activity for methylcyclopentane conversion and larger Pt particles were formed after reduction. Hydrated Pt ions are mobile and are formed near the mouth of the zeolite pores where the concentration of precursor ions is high.
The Role of Rh on Pt-Based Catalysts: Structure Sensitive NO + \text{H}_2 Reaction on Pt(110) and Pt(100) and Structure Insensitive Reaction on Rh/Pt(110) and Rh/Pt(100)


The catalytic activity of the Pt(110) surface for the NO + \text{H}_2 reaction was less than that of the Pt(100) surface, but the catalytic activity of the Rh deposited Pt(110) surface was almost equal to that of the Rh deposited Pt(100) surface. The reaction of NO + \text{H}_2 on Pt(110) and Pt(100) surfaces is highly structure sensitive, but becomes structure insensitive on deposition of Rh atoms. The formation of the Rh-O/Pt overlayer during catalysis was responsible for the structure insensitive catalysis of Rh on Pt-based catalysts. This active overlayer is responsible for the catalytic activity of Pt-Rh three-way catalysts.

Enhancement of Pt-Sn/Al,O_3 Catalyst Stability for Butane Dehydrogenation by Modification with Sm and Li


Studies of the effects of modification, by Sm and Li, on the stability of Pt-Sn/Al,O_3 catalysts showed that Pt crystallite dispersion on the support can be promoted by both Sm and Li. When Sm was incorporated into the Pt-Sn/Al,O_3 catalyst carbonisation was inhibited and the catalyst lifetime was prolonged.

Effect of Dispersion of Palladium on the Selective Hydrogenation of Acetylene in Ethane-Ethylene Fraction


The effect of dispersion of Pd particles in 1.0-0.03\% Pd/Al,O_3 catalysts on the activity and selectivity of the catalyst was studied during acetylene hydrogenation in ethane-ethylene fractions. The majority (70-90\%) of Pd particles used in the catalysts were 9; 15; 25; or 75 Å in diameter. Catalysts with Pd particles of 75 Å in diameter have many properties of the metal, so are capable of H diffusion. It is shown that an increase in Pd particle size led to a decrease in selectivity of catalyst during the above reaction.

Stabilisation of Palladium Metal Function of Ozone Supported Palladium Catalyst during the Hydrogenolysis of Chlorofluorocarbons


Pd/ZnO catalysts supported on γ-Al,O_3 showed enhanced catalytic activity and stability towards deactivation by halogen adsorption during the hydrogenolysis of 1,1,2-trichlorotrifluoroethane, when compared to Pd/C and Pd/γ-Al,O_3 systems. Catalysts with Pd/ZnO ratios of 0.25, 0.5, 1.0 and 2.0 were tested. The catalytic activity and selectivity of the Pd/ZnO catalyst towards complete dechlorination of the chlorofluorocarbon substrate is dependent on an optimum stoichiometric ratio of the two catalyst components.

Pd\text{Ni}_{100}, Pd\text{Ni}_{100}, and Pd\text{Ni}_{100}; Pd Surface Segregation and Reactivity for the Hydrogenation of 1,3-Butadiene


Pd was found to segregate on Pd\text{Ni}_{100} and Pd\text{Ni}_{100}. After annealing and stabilising at 870 K, the external Pd concentration reached 20 and 50 at.\%, respectively. On both solids, the Pd segregation displayed quite steep concentration profiles. The study of activities for 1,3-butadiene hydrogenation showed that the alloys were either equivalent or more active than pure Pd, while the selectivities for butenes remained close to unity. “Active sites” of small ensembles of Pd atoms electronically modified by the surrounding Ni atoms is proposed.

A Polymer-Bound Bidentate-Phosphine-Palladium Complex as a Catalyst in the Heck Arylation


Polymer-supported 1,2-bis(diisopropylphosphino)benzene Pd(II) complex catalyst was developed for a Heck arylation by incorporating a bidentate phosphine ligand onto a polystyrene backbone. The catalyst displayed high turnover number, ease of recycling without loss of activity, moderate efficiency with reaction rate being slightly slower than with Pd(OAc)_2/PhH, easy separation of product from the catalyst and stability for handling in air. Dimerisation of the reactive Pd(0) sites, which may occur during coupling under homogeneous conditions, is suppressed with this Pd catalyst.

Mechanism of the Wacker Oxidation of Alkenes over Cu-Pd-Exchanged Y Zeolites


The catalytic potential of CuPd zeolites with faujasite topology in the Wacker oxidation of 1-alkenes with dioxygen is reported and compared to that of a homogeneous PdCl\text{CuCl} salt solution. From in situ spectroscopy measurements an active site is proposed, consisting of a trinuclear Cu-O-Pd-O-Cu cationic complex, and also a catalytic cycle for the Wacker oxidation in which the reoxidation of Cu’ by dioxygen or of Pd’ by zeolite Cu++ is rate determining.

Preparation and Catalytic Properties of NR,-Stabilized Palladium Colloids


NR,-stabilized Pd colloids with mean particle diameter of 1.8-4.0 nm, which can be isolated totally dispersed, and are easily handled in unusually high concentrations, were prepared as both heterogeneous and homogeneous catalysts. The standard activity of a charcoal catalyst with 5\% colloidal Pd considerably exceeded the activity of the conventional catalyst. The lifetime of these catalysts, isolated from the reduction of [N(octyl)]_2PdCl_2Br, with H, was superior to conventionally prepared Pd charcoal catalysts.
The Promoter Function of Molybdenum in Rh/Mo/SiO, Catalysts for CO Hydrogenation
FT-IR, chemisorption and CO hydrogenation of a number of Rh/Mo/SiO2 catalysts with fixed Rh and varying Mo contents showed that the addition of Mo to Rh/SiO2 suppresses the linear and bridged CO species, but promotes the twin CO species. The Mo promoter appears to work via stabilisation of Rh ions and the coverage of Rh sites by forming oxygenates and shifting the selectivity from HC to oxygenates.

Hydrogenation of Carbon Monoxide on Polymetallic Ruthenium Containing Catalysts
Studies of the relationship of the surface of Ru-Cr-Mn/Al2O3 catalysts and their adsorption and catalytic properties during CO hydrogenation showed independent action between system components and substrate, forming a disordered structure. The nature of the structure depended on the behaviour of adsorbed oxides of C and H, and determines the activity and selectivity of the catalysts.

Hydrogenation and CO Intrapellet Diffusion Effects in Ruthenium-Catalyzed Hydrocarbon Synthesis
Intrapellet H2 and CO concentration gradients within Ru-based catalyst pellets during Fischer-Tropsch (FT) synthesis lead to lighter and more paraffinic hydrocarbon products than when intrapellet diffusion limitations are negligible. Extreme intrapellet diffusion restrictions totally deplete CO near the pellet centre and restore the hydrogenolysis activity of Ru which is usually strongly inhibited by CO during FT synthesis. In the absence of CO, large hydrocarbons that are removed slowly from liquid-filled catalyst pores undergo extensive hydrogenolysis on Ru sites close to the centre of the pellets, leading to lower wax yields and to higher methane and light paraffin selectivity.

HOMOGENEOUS CATALYSIS

Palladium-Catalyzed Syntheses of 2-Arylbenzothiazoles
R. J. PERRY and D. D. WILSON, Organometallics, 1994, 13, (8), 3346–3350
A new synthetic route for the preparation of 2-arylbenzothiazoles is described consisting of the reaction of a haloaromatic compound with an o-aminothiol. Good yields of products can be obtained through the proper choice of base, which suppresses unwanted amide thioester as well as benzamide and 2-methylbenzothiazole formation. This method is tolerant of a variety of functional groups and offers a route to 2-arylbenzothiazoles complementary to those that normally employ acid chlorides.

Synthesis of Novel Mono- and Diaryl-Substituted [2.2]Paracyclophanes
Studies of the activity of various Pd and Ni complexes during the cross-coupling reaction of 4-bromo-[2.2]paracyclophane with p-tolyl Mg bromide showed that (1,1'-bis(diphenylphosphinoferrocene) palladium dichloride (PdCl2(dppf)) catalyst was most active for this reaction. A series of new monon- and diaryl [2.2]paracyclophane derivatives with various substituents in the arene ring were prepared with this PdCl2(dppf) catalyst. It is concluded that the cross-coupling of organozinc [2.2]paracyclophane derivatives with aromatic bromides could occur. The composition and structure of the compounds were established. Some correlations between the structure and spectral parameters of mono- and diaryl-substituted [2.2]paracyclophanes were discovered.

Hydrogenation of Heptene-1 in the Presence of Palladium(II) Complexes with Cyclic Aminomethyl Phosphines
Studies of the liquid-phase hydrogenation of heptene-1 by the Pd(II) complex with 1,5,3,7-diazadiphosphophyclocloctane and 1,3,5-diazaphosphorinane in a mixture of ethanol and benzole are reported. The results showed the dependence of the activity and selectivity of the reaction on the substitutes for N atoms in the complex, and on the chosen solvents.

H. KAGA, Z. AHMED, K. GOTOH and K. ORITO, Synlett, 1994, (8), 607–608
An efficient one-pot method for the synthesis of conjugated dien- and enamides by the Pd-catalysed coupling reaction of (E)-β-bromoacrylamides, using Pd(OAc)2/PPh3/Na2CO3 or PdCl2(dppf)/K2CO3 catalysts, with alkenyl- and alkylboronates is reported. This route provide some biologically active, naturally occurring unsaturated amides, and is the first synthesis of dehydrodiisopropynaline and pipernonaline.

Oxidation of Methanol Catalysed with Giant Palladium Clusters
Studies of the kinetics of MeOH oxidation by O2 in the presence of giant Pd clusters of formula Pd20-(Phen)3(OAc)6 showed that the rate of formation of metal formate is proportional to cluster and MeOH concentrations. The kinetic data and the value of the kinetic isotopic effect agreed with the reaction mechanism. The presence of the C-H bond in the coordinated MeOH cluster limits the reaction.
Rhodium Complex Catalyzed Hydroformylation Reactions of Linear and Cyclic Mon- and Diolefins

The hydroformylation of cyclopentene, cyclohexene, 4-vinylcyclohexene, cycloheptene and cyclooctene was performed by Rh(acac)(P(O)Ph),/P(O)Ph). (I) catalyst at 80°C and 10 atm (CO + H2). Only cyclopentene and 4-vinylcyclohexene were hydroformylated at 1 atm and 40°C. The hydroformylation of some cyclic dienes at 10 atm and 80°C was studied by system (I) and by Rh(acac)(CO)(PPh3)/PPh3. The main reaction products of cyclohexadienes and pentadiene were unsaturated monocarboxylic acids.

Regioselective Hydroformylation of Alkenes Catalyzed by Di(n-carboxylato)rhodium(I) Complexes
M. F. DOYLE, M. S. SHANKLIN and M. V. ZLOKAZOV, Synlett, 1994, (8), 615–616

Hydroformylation of substituted styrenes, 3,3-dimethyl-1-butene and vinyl acetate, catalysed by [Rh(cod)(OOCR)], (cod = 1,5-cyclooctadiene) in the absence of phosphine or phosphite ligands, occurred at 25°C giving high yield and regioselectivities of > 95:5 for branched:linear aldehydes from styrenes and vinyl acetate. An important feature of this Rh pre-catalyst is its exceptional selectivity for monosubstituted alkenes relative to disubstituted alkenes, such as dihydropyran, indene, etc., which are completely unreactive under the hydroformylation conditions. Only the linear aldehyde was obtained with 3,3-dimethyl-1-butene.

Catalysis of Phosphine-Coordinated Rhodium(I) Complexes for 2-Propanol Dehydrogenation

The Wilkinson complex RhCl(PPh3), which is usually inactive for 2-propanol dehydrogenation (1), showed catalytic activity on addition of Et3N or by using a hydride complex, instead of chloride. This also worked for ketone hydrogenation (2). RhH(PPh3), complex exhibited catalytic activity for both (1) and (2). Dissociative and rate-determining dihydrogen evolution steps are proposed.

Isomerization Mechanism of Dinuclear Chloro-Bridged Rhodium(I) Complexes
G. GIORDANO and E. ROTONDO, Polyhedron, 1994, 13, (17), 2507–2511

Room temperature studies of the cis- and trans-halide-bridged dimers {[Rh(CO)(PPh3)(μ-Cl)]2} showed a rather fast equilibrium of interconversion. NMR shows no Rh-P or Rh-C bond cleavage. This suggests that the equilibrium occurs through dissociation of the dinuclear Rh’ species into the trico-ordinated 14-electron T-shaped [Rh(CO)(PPh3)Cl] (1). The rate of the isomerisation is accelerated by the presence of small amounts of cis-[Rh(CO)(PPh3)(μ-Cl)], which is a precursor of the trico-ordinated fragment (1).
CHEMICAL TECHNOLOGY

Methane Steam Reforming in Asymmetric Pd- and Pd-Ag/Porous SS Membrane Reactors


Electrolessly deposited Pd- and Pd-Ag/porous stainless steel (SS) composite membranes were used to steam reform CH4, using a Ni/Al2O3 catalyst. The CH4 conversion was greatly enhanced by partial removal of H2 from the reaction location by diffusion through the Pd-based membranes. At a pressure of 136 kPa, 500°C and a molar steam:CH4 ratio of 3 with continuous pumping on the permeating side, a CH4 conversion twice as high as the conversion in a non-membrane system was reached by the Pd/SS membrane.

ELECTRICAL AND ELECTRONIC ENGINEERING

Electronic Conduction Processes in Pt-Doped Tin Oxide Thin Films Prepared by RF Magnetron Sputtering


DC and AC conduction measurements were performed at atmospheric pressure and under vacuum on Pt-doped SnO2 thin films prepared by RF magnetron sputtering. DC conduction at < 1 V was due to Poole-Frenkel excitation of electrons from donor-like impurities. At higher voltages space-charge-limited conductivity was observed. AC conduction showed an increase with angular frequency, ω, of the form ωα, where α ≤ 1, and was identified with hopping between localised states in the amorphous films.

Ohmic Contact Formation in Palladium-Based Metallizations to n-Type InP


Two Pd-based metallisations Au/Ge/Pd (1) and Pd/Ge (2) contacts to n-type InP have been studied. Ohmic contacts were obtained with minimum specific resistances of 2.5 × 10-4 Ωcm2 and 4.2 × 10-4 Ωcm2 for (1) and (2), respectively. The annealing regime for ohmic contact formation is 300–375°C for the Au/Ge/Pd/InP and 350–450°C for the Pd/Ge/InP system. Pd reacts with InP giving good metalisation adhesion and contact morphology.

Pd/Zn/Pd/Au Ohmic Contacts to p-Type InxGa1-xAs/InP


Optimum conditions for the fabrication of Pd/Zn/Pd/Au contacts to p-type InxGa1-xAs/InP were established. The value of the specific contact resistance for the as-deposited contacts was reduced to pS = 1.2 × 10-4 Ωcm2 with increasing thickness of the interface Zn and Pd layers to 300 Å. Annealing of all of the contact configurations except the Zn = 0 and 20 Å structures produced a reduction in pS to a minimum value of 7.5 × 10-4 Ωcm2 at 500°C.

Reactive Ion Etching of PbZr1-x, TiO2, and RuO2 Films by Environmentally Safe Gases


Reactive ion etching (RIE) of both PbZr1-x, TiO2, (PZT) thin films and RuO2 electrodes was performed, using etching gases with low ozone depletion potential and global warming potential. The etching characteristics for both PZT and RuO2 films are reported as a function of etching time, discharge power density, chamber pressure and additive gas. Etch rates were 250–650 Å/min and 100–400 Å/min for PZT and RuO2, respectively. An optimised etching condition was obtained for the RIE of ferroelectric capacitors. Etched surfaces showed smooth morphologies.

TEMPERATURE MEASUREMENT

Design of Platinum Resistance Thermometer with Small Magnetic Field Correction


A new design for the Pt resistance thermometer has been developed to reduce its magnetic field induced errors. A reduction in the magnetoresistance is obtained by combining four sensor elements together to allow their magnetoresistances to cancel each other. The performance of prototype sensors was studied at 16–140 K under magnetic fields of ≤ 8 T. The optimum result showed a reduction in the magnetic field induced error by a factor of 20 at 19 K. The thermometer can be used in varying magnetic fields, etc.

Immersion Characteristics and Reproducibility of the Gold/Palladium Thermocouple


A new Au/Pd thermocouple, studied at the Al and Ag freezing point cells, showed generation of a high thermal emf, reproducibility of ± 0.2 μV at 961.78°C, excellent immersion characteristics and high sensitivity. The Au/Pd thermocouple has very stable and reproducible thermoelectric properties and could thus be used as a precise secondary reference thermometer in industrial applications at the maximum 50 mK level of uncertainty for the range 0–1000°C.

MEDICAL USES

Aquatlon of the Anticancer Complex trans-[RuCl4(Him)2] (Him = imidazole)


Aquatlon of the anticancer complex trans-[H2im][RuCl4(Him)2] was studied in D.O at pH 2.4–10 by the observation of paramagnetically shifted 1H NMR resonances. The complex readily undergoes aquatlon in aqueous solution with a half-life of 3.4 h at 310 K, a time-scale similar to that for aquatlon of the Pt drug cisplatin. The three detected products were assigned as mono- and di-aqua species. The rate was similar at low pH, but differed at high pH.
NEW PATENTS

ELECTROCHEMISTRY

Electrode for Electrolysis of Metallic Electrolyte
TDK CORP. Japanese Appl. 6/122,988
An electrolytic electrode comprises a layer of Ir oxide and Ta oxide containing 75–95 at. % Ir and 5–25 at. % Ta on a conductive substrate and a glue or thiourea component. The process is applied to electrodes used in the electrolysis of a metallic electrolyte containing organic hydrophilic compound for producing O₂ at an anode. The electrode has excellent durability and low O₂ overvoltage.

Electrode for Electrolysis of Drinking Water
TDK CORP. Japanese Appl. 6/158,378
The electrode comprises a conductive base coated with Pt metal and oxidised Ta containing 30–99 mol% Pt and 1–70 mol% Ta. The coating preferably also contains 40 mol% Ir metal. The electrode is used as the anode of an ion water generator, and provides high voltage polarity inverse electrolysis for long periods.

Electrode for Cold Fusion Reaction
OSAKA GAS CO. LTD. Japanese Appl. 6/160,559
The Pd electrode is partially covered with material of lower H gas generation activity than Pd, such as Zn, Cd, Ni, or Hg, by electrolycrystallisation or vapour deposition. The electrolysis of heavy H₂O under constant current density, with the Pd electrode results in the efficient diffusion of heavy H into the electrode which increases heat generation based on nuclear fusion.

Production of Alkylurea Compounds
MITSUBISHI GAS CHEM. CO. INC. Japanese Appl. 6/173,056
An alkylurea compound is produced electrolytically from CO and an alkylamine using a cathode containing a Pt group element. The alkylamine is preferably a primary or a secondary aliphatic amine with 1–8C atoms, and the solvent has an oxidation potential lower than that of the starting alkylamine. The supporting electrolyte is I₂ ions and is added 0.1–20 wt. % with respect to the starting amine. The process is carried out under mild manufacturing conditions without using an oxidising agent and without producing any by-products, such as H₂O.

Simultaneous Electrolytic Production of Carbonate Ester and Formate Ester
MITSUBISHI GAS CHEM. CO. INC. Japanese Appl. 6/173,057
A carbonate ester and a formate ester are manufactured simultaneously from CO and alcohol using a cathode containing a Pt group metal, with alkali metal halide as the supporting electrolyte. The electrolysis is performed at 0–100°C at a current density of 1–20 A/dm². The electrolytic cell is partition-free and uses a capillary gap cell. The carbonate ester is a starting material for polycarbonate resin and alkylating agents.

Power-Saving Gas Electrode Structure for Electrolysis
DENBO KOGYO K.K. Japanese Appl. 6/192,871
The electrode comprises an ion-exchange resin base with a thin layer of a conductive C having a Pt group metal or oxide as electrode catalyst, and a porous collector in close contact with the side opposite to that having the ion exchange membrane and metal. This power-saving electrode structure is used in the cathodic chamber of an electrolytic cell, with the porous side alone being in contact with the electrolytic solution for electrolysis.

Noble Metal Coated Metallic Electrode
PERMELEC ELECTRODE LTD. Japanese Appl. 6/192,872
An electrode is prepared by firing the precipitate co-deposited by alkali from an aqueous solution containing Pt group metal and at least one Group IV or Group V element, mixing the fired particles with a binder and applying the mixture onto an ion exchange membrane. In an example, co-deposited precipitates of IrCl₃ and TaCl₅ were prepared. The electrode has a low electrolysis voltage with long life.

Production of Electrode for Electrolysis of Aqueous Solutions
NITTETSU HARD K.K. Japanese Appl. 6/200,391
The electrode is formed from a primary layer on a valve metal base, with the valve metal being different to that used for electrical discharge machining, followed by forming a surface layer by plating a Pt group metal or alloy on the primary layer. Aqueous solutions are electrolysed using the electrode. The electrode is suitable as the one at which O₂ is generated.

High Durability Anodes
FURUKAWA ELECTRIC CO. LTD. Japanese Appls. 6/248,484–85
High durability anodes for electrolytic operations and O₂ generation comprise metal (alloy) base, a diffusion N-containing layer and a Pt group metal oxide layer, or a metals(alloy) base, a nitride layer, a layer of oxide of an element other than Pt group metal, such as Ti, and a catalyst layer containing Pt group metal. The N-containing layer is treated to remove its top surface, followed by dipping in catalyst solution containing IrCl₃ for a catalyst coating. The electrode can operate in H₂SO₄ at a current density of 100 A/dm² and a terminal voltage >10 V can be sustained for > 910 h.

ELECTRODEPOSITION AND SURFACE COATINGS

Rosy Pink Coloured Coating
ETA FAB. EBAUCHES S.A.  European Appl. 603,673A
A rosy pink coating is made up of a nitride coating of Ti, Zr, Hf or a mixture, and Al, C or Group Vb and Vlb element, with a second coating of Pd and In. The process is used for coating jewellery, glasses and clocks, giving better clarity of coloration.

Palladium and Platinum Colloidal Dispersion
MINNESOTA MINING & MFG. CO.
U.S. Patent 5,332,646
The process comprises reducing organo-metallic Pd and/or Pt salts in a dispersing medium at 0.001–2/(0.005–1) wt.%. The Pd and/or Pt colloidal dispersion produced is useful as a metallic toner fluid, for electrophoretic deposition to form a non-conductive metal coating and for electroless plating. Process requires only mild conditions, allowing easy control of the concentration of particles formed.

An Anode for Electroplating Sheet Steel
DAISO CO. LTD.  Japanese Appl. 6/146,047
The anode is produced by sputtering, ion plating and/or vacuum deposition of a layer of SiO, and Ta on a metallic base and forming an active layer by pyrolysis of a salt of Ir and Ta. The process results in an insoluble anode used for electrolytic processes with accompanying O2 generation, and is used particularly in electroplating sheet steel with Sn, Zn and Cr.

Ruthenium Plating Solution
JAPAN ENERGY K.K.  Japanese Appls. 6/146,054–56
A Ru plating solution comprises an inorganic acid salt of Ru, sulphamic acid and/or sulphuric acid as stabiliser and a halogen element, added in the form of NHx halide or an alkali metal halide. The Ru plating solution has high stability and a high rate of electrodeposition. High quality plating of ≥ 5 µm in thickness is obtained.

Platinum Plating Solutions
SEIKO INSTR. INC.  Japanese Appl. 6/146,057
A Pt plating solution giving a mirror-finished surface, contains 1–30 g/l Pt, 10–200 g/l of a sulphate, 0.5–10 g/l of a sulphite, and Na or K as an alkali metal, with the pH being controlled to ≤ 2. The Pt plating, on top of a Au strike layer, finally coated with Au, provides a white coloured article, has low stress and high adhesion strength to the base.

Stable Palladium Alloy Plating Baths
BISO JAPAN K.K.  Japanese Appls. 6/146,058–59
A Pd-In alloy plating bath comprises 10–200 g/l of a carboxylic acid, 1–200 g/l of a sulphate or sulphite, 1–50 g/l Pd in the form of a Pd salt, 0.1–30 g/l In, at pH 6–11 and gives black-coloured plating. A Pd-Co-In alloy plating bath provides a white to pale grey plating. The Pd salt is selected from dichlorotetraamine Pd, Pd(I) chloride, etc. The bath is stable and colour tone is controlled by changing the Pd:In content.

High Speed Rhodium Plating Process
JAPAN ENERGY K.K.  Japanese Appl. 6/173,071
The plating process produces a crack-free bright thick Rh film by using a low stress Rh electroplating solution comprising a Rh salt, free acid, and S or a S-containing substance, by spraying the solution against the article to be plated. Preferably, the plating bath contains 8–12 g/l Rh, 70–90 g/l H2SO4 at 50–70°C, 20–40 A/dm2 and has a spray rate of 0.3–1.0 m/s. Process provides a low stress Rh plating at high speed.

Anti-Oxidising Metallic Component
ASAHI GLASS CO. LTD.  Japanese Appl. 6/184,789
An anti-oxidising metallic component comprises an oxidising metal coated with a composition containing 0–35% Pt, 0–60% Pd, 30–99.5% Ag, 0.5–70% Au and 0.0001–0.01 wt.% of Group IIIB element, but not B or Al. The coating component is suitable for use in lead pins of semiconductor packages and can be treated by heating in air.

Electroless Colouring of Aluminium Alloy
PENTEL K.K.  Japanese Appl. 6/184,792
Electroless colouring of Al or Al alloy comprises anodising Al alloy, treating with silane coupler, dipping in Pd complex salt, followed by electroless plating to deposit metal on the anodised film for colouring. Uniform colouring is obtained while maintaining film adhesiveness, weatherability and corrosion resistance.

Manufacture of Electroless Plated Material
NIPPON VILENE K.K.  Japanese Appl. 6/212,439
Electroless plated material is made in a catalyst holding process by electroless plating by carrying a complex of PVA resin and 0.004–0.05 mol%/monomer unit of the resin of a Pd salt on a matrix, followed by heat treatment at 110–160°C. The process continuously plates electrolessly, without eluting the Pd metal ions, when the matrix is dipped into the plating bath.

Palladium Surface Coatings
ATOTECH DEUT. G.m.b.H.  German Appl. 4,316,679
Cu, Ni and their alloys are surface coated with Pd by deposition from an acidic, case-hardening bath containing a Pd salt and an oxidising agent; Pd is deposited from a HCHO-free bath containing a Pd salt, and a nitrogenous complex-forming substance and methanoic acid. The process is used for printed circuit boards and corrosion-resistant coatings, giving adhesive, bright, thin, low-porosity Pd coatings.

APPARATUS AND TECHNIQUE

Electrochemical Gas Sensor
MATUSHTA ELECTRIC WORKS LTD.
Japanese Appl. 6/160,349
An electrochemical gas sensor comprises a counter and reference Pt electrodes on a substrate of Al2O3, Al nitride, Si, an epoxy or phenolic resin; with an ion conductive solid electrolyte film covering the electrodes and a gas diffusion working electrode. The sensor maintains its sensitivity and is used for detecting CO2, CO, H2, alcohol or NOx.
Apparatus for Liquid Phase Epitaxial Growth
MURATA MFG. CO. LTD.  *Japanese Appl.* 6/206,793
A magnetic-garnet monocrystalline thin film is grown over a substrate plate surface using apparatus in which the crucible and holder for the substrate plate are made of Pt mixed with ZrO₂ powder and Au. The specified material is resistant to corrosion by the PbO-base flux, and permits the manufacture of good quality monocrystalline garnet films.

Lithium Tantalate Single Crystal
SHINETSU CHEM. IND. CO. LTD.  *Japanese Appl.* 6/234,597
The Ir and Rh contents of Li tantalate single crystals are ≤ 1 ppm so that absorption at wavelengths 400–500 nm is eliminated. The Li tantalate is an excellent material for second harmonic generation. The crystal is prepared by the Czochralski method using an Ir crucible having an after-heater of Rh-free noble metal or Ir, for the parts where the temperature would allow Rh evaporation. When inert gas having an O₂ concentration of 0.2–1.5 vol. % is used, colouring by O₂ deficiency is eliminated.

JOINING
Alloy for Solder to Connect Electronic Component and Wiring Board
WORLD METAL CO. LTD.  *World Appl.* 94/18,350A
An alloy to be plated for solder connecting electronic components to wiring boards comprises Pd-Sn-Pb alloy. If the alloy further contains P or B, the drop in solderability of the alloy due to heat is reduced. When In is included, the melting point of the alloy can be lowered, and when it contains Ag, leaching can be reduced. This alloy to be plated is preferably formed by electrolytic or electroless plating.

High Strength Solder Joint Structure
A method to form a high strength solder joint comprises forming a Pt and Ag conductor, containing 0.8 wt.% Pt, on a substrate, and further applying a Sn and Ag solder layer onto the conductor. A preferred solder joint structure is obtained by screen printing a circuit pattern and is used in hybrid ICs. High joint strength is obtained and can be maintained during repeated heating cycles.

HETEROGENEOUS CATALYSIS
Reduction Catalyst for Nitrogen Oxides
AGENCY OF IND. SCI. & TECHNOLOGY  *European Appl.* 602,602A
A catalyst for reduction of NOx using a HC as a reducing agent, such as CH₄ or CH₃OH, is prepared by co-precipitation of Pd particles and metal oxide particles, such as Fe(III) oxide, Ce(IV) oxide, and Sn oxide. The catalyst is used in car exhaust systems to measure catalyst performance. The operating temperature of the reaction is reduced, and reactions can be performed at ambient temperature. The catalyst does not require further activation by calcination.

Catalytic Reforming of Naphtha
EXXON RES. & ENG. CO.  *European Appl.* 606,007A
A naphtha feedstream is catalytically reformed to give an improved 5C₇ liquid yield in a series of reactors or reaction zones, in which one lead reactor or zone contains 0.1–1 wt.% Pt and 0.01–0.1 wt.% Re/or inorganic oxide; and one tail reactor or zone contains 0.1–1 wt.% Pt, 0.1–1 wt.% Ir and 0.02–0.4 wt.% Sn, uniformly dispersed throughout a particulate solid support. The catalyst improves octane quality. It has high activity and selectivity in reforming feedstreams.

Aromatic Olefin Preparation
HOECHST A.G.  *European Appl.* 606,057A
Aromatic olefins are prepared from aryl diazonium salt and olefin in the presence of a heterogeneous Pd catalyst in an organic solvent at ~20 to 150°C. The method is generally applicable, and gives a high olefin yield without any impurities. The catalyst is stable and can be easily recovered.

Selective Hydrogenation of 4-Substituted Benzaldehydes
DEGUSSA A.G.  *European Appl.* 606,072A
The process for the selective catalytic hydrogenation of the carbonyl group in aromatic aldehydes to the corresponding alcohols and methyl compounds comprises hydrogenation in the presence of a catalyst containing 0.01–3 wt.% Pt, Pd or Rh on a TiO₂ support. The catalyst is in pellet form 1–10 mm in diameter and has a fracture resistance of ≥ 40 N. The process is useful for the production of benzyl ethers.

Aqueous Quaternary Ammonium Hydroxide
MITSUBISHI GAS CHEM. CO. INC.  *European Appl.* 608,545A
A high purity aqueous quaternary NH₄OH (I) is produced by reacting quaternary NH₃, organic acid salt with H₂O₂, or an O-containing gas in the presence of a Pt group metal catalyst, preferably Pd, Pt, Ru, Rh or Ir, supported on C, SiO₂ or Al₂O₃. (I) is used as a developing agent for resists for LSIs and LCDs.

Platinum Recovery Catchment Gauze
JOHNSON MATTHEY PLC  *European Appl.* 611,041A
A catchment gauze for Pt recovery from the NH₃ oxidation process, which uses a Pt-based catalyst, is formed from fibres of Pt-Co alloy containing ≥ 70 wt.% Pt. NOx emission is reduced. The knitted gauze may be one of a pack of other gauzes of Pt-Co alloys, pure Pt, Pt alloys with other metals, or of ceramics.
Hydrogenation Catalyst

KEMIRA OY. *European Appl. 611,126A*
A catalyst for H₂O₂ manufacture by hydrogenation of anthraquinone in an organic solvent comprises finely divided particles of a Pt group metal containing ≥ 50% Pt and a transition metal, and contains finely grained suspensible metal particles. The inclusion of the transition metal gives a durable catalyst which maintains high activity for longer periods, thus reducing regeneration requirements.

Catalysts for Purification of Automotive Exhaust Gases

CATERER IND. CO. LTD. *European Appl. 613,714A*
A catalyst for purification of exhaust gases at lean operation comprises a porous support which is loaded with Pd and/or Pt as first ingredient and with at least two other ingredients selected from rare earths, La, alkali metals, alkaline earths, Fe, Ni, Co, Mn and Ba. The catalyst is used for simultaneously purifying CO, HC and N oxides in O-rich exhaust gases.

Catalyst for NOx Denitrising

SAKAI CHEM. IND. CO. LTD. *European Appl. 614,692A*
A catalyst for selective denitrising NOx using HC as a reducing agent comprises a substituted zeolite containing 0.1–20 wt.% Ti, Zr, and/or Sr ion and alkali metal, alkaline earth metal or H, and Pd, Pt, Ru, Rh or Ag metal, or at least one oxide of V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Nb, etc. A method for catalytic denitrising NOx in the presence of a HC, even with O₂ present, using the above catalyst is also claimed.

A Catalyst for Dehydrogenation Reactions

EXxon Res. & Eng. CO. *European Appl. 614,698A*
A catalyst composition comprises an alloy of a Pt group metal and Zn or Ga on a support, such as Zn or Ga modified SiO₂-pillared clays, respectively, etc. The catalyst is used in dehydrogenation reactions and also in hydrogenation of olefins. The catalyst maintains high activity and selectivity for at least five days.

Dehydrogenating Light Hydrocarbon Feed

CHEVRON Res. & TECHNOLOGY CO. *World Appl. 94/13,605A*
Light paraffinic hydrocarbon feed is dehydrogenated in a reactor zone which may be subjected to periodic exposure to > 100 ppb S, by contact with a catalyst of Pt or Pd; an intermediate pore SiO₂·Al₂O₃ zeolite of mole ratio ≥ 30; and an alkali; the molar ratio alkali:Al in the zeolite is 1–5. The alkali content of the catalyst is very important for high activity and selectivity to olefins, and low deactivation or fouling rates. The catalyst is S resistant up to 2 ppm S.

Exhaust Gas Cleaning Catalyst

MITSUBISHI JKOGYO K.K. *World Appl. 94/19,103A*
An exhaust gas cleaning catalyst, with a special X-ray diffraction pattern, comprises at least one Pt group metal and also at least one of Ti, Zr, Cr, etc., supported on a layer-complex crystalline silicate. The catalyst is used in cars with lean-burn petroleum and diesel engines, has excellent durability and denitrification performance.

Catalyst for Hydrocarbon Hydrogenation

AMOCO CORP. *World Appl. 94/19,429A*
The catalyst (I) suitable for the hydrogenation of a HC feedstock comprises 0.1–2.0 wt.% each of Pd and Pt on a zeolite β support containing a specified Na content which improves the hydrogenation, aromatic saturation, desulphurisation, denitrogenation and cetane number. Feedstock volume can be expanded. A feedstock of HC boiling at 150–700°C and atmospheric pressure can be hydrogenated by contact with H and (I).

Preparation of Ethyl Acetate

STANDARD OIL CO. OHIO *U.S. Patent 5,334,751*
EtOAc is prepared by reaction of EtOH and O₂ in the presence of a solid Pd catalyst containing crystalline TiP₂O₅ of formula Pd₅MₓTiP₂O₅ where M = Cd, Au, Zn, Ti or alkali(ne earth) metal; a = 0.0005–0.2; b = 0.3; c = 0.5–2.5; x is to satisfy the valence. The crystalline TiP₂O₅ is an effective and mechanically tough support for the Pd component of the catalyst, and also contributes to the catalytic activity.

Preparation of Vinyl Acetate

QUANTUM CHEM. CORP. *U.S. Patent 5,336,802*
Vinyl acetate is prepared by passing C₂H₂, H₂OAc and O₂ over a Pd-Au catalyst which was pretreated by heating in the presence of an oxidising then a reducing agent. The catalyst shows improved initial selectivity to vinyl acetate, while maintaining high conversion. The frequency of regeneration or replacement of the catalyst is reduced.

Fluorocarbon Ion Exchange Membrane

UNITED TECHNOLOGIES CORP. *U.S. Patent 5,343,494*
A catalytic fluorocarbon ion exchange membrane is manufactured by repeatedly exchanging H ions in the membrane with replacement cations, exchanging these with Pt ions and reducing these ions to Pt metal. Any remaining replacement cations are exchanged with H. The membrane is equilibrated, Pt metal being present as discrete particles. The membrane is used to produce consistently high purity O₂ and H₂.

Alkenyl Alkanoate Production

UNION CARBIDE CHEM. & PLASTICS TECHNOL. *U.S. Patent 5,342,987*
Alkenyl alkanoates are prepared by reaction of an alkene, an alkanoic acid and O₂ containing gas in the presence of a Pd-Au catalyst, on a low-Na content support, and a K promoter. The conventionally prepared impregnated support particles are washed with a cation exchange solution to reduce the Na content which thus increases the activity of the catalyst.

Dehydrogenation Catalyst

PHILLIPS PETROLEUM CO. *U.S. Patent 5,344,805*
A dehydrogenation catalyst is prepared by impregnating a Zn aluminophosphate with Pt and Sn from an impregnation solution containing H₂O, a Pt compound and oxalic acid, and H₂O₃, a Sn compound and an inorganic acid solution. The catalyst has improved performance for alkane dehydrogenation with respect to activity, selectivity and deactivation.
Co-production of Di-Tertiary-Butyl Alcohol and Tertiary-Butyl Alcohol

TEXACO CHEM. CO. U.S. Patent 5,345,009

A tertiary-butyl hydroperoxide (TBHP) charge stock containing a solution of TBHP in tertiary-butyl alcohol (TBA) is contacted with 0.1–1 wt. % Pt catalyst supported on pelleted C to co-produce and recover TBA and di-tertiary-butyl peroxide (DTBP) from the hydroperoxide decomposition products. The reaction is carried out at 40–160°C and 0–10,000 psig pressure. DTBP is useful as a high temperature free radical initiator in chemical reactions. The method gives four times higher DTBP yields than are obtained for conventional Pd/Al₂O₃ catalysts.

Catalyst for Purifying Nitrogen Oxides

SUMITOMO METAL MINING CO. Japanese Appl. 6/126,172

A catalyst of Pt and Ir on a high specific surface area support has 0.01–5 wt. % Pt and 0.01–5 wt. % Ir, with an Ir:Pt atomic ratio of 0.1–1. The catalyst can purify NOx over a wide temperature range even for atmospheric exhaust gas containing excess O₂ and at a lean air:fuel ratio. Changing the Ir:Pt ratio sets the Pt-Ir catalyst active temperature region to a desired range in the NOx-hydrocarbon selective reduction reaction.

Catalysts for Purifying Exhaust Gas

ZH. NIPPON JIDOSHÅ DENKYUSHO Japanese Appl. 6/126,173

The catalyst consists of multistage catalyst layers of (a) Pd, Pt or Rh (0.3–10 g/l) on γ-Al₂O₃ substrate on an acid-resistant three-dimensional ceramic honeycomb and (b) a lanthanide-based catalyst such as La, Nd or Pr, and (c) Mg oxide catalyst. The catalyst can be used for purifying exhaust gas released from a natural gas engine. It reduces formaldehyde production.

High Frequency Exothermic Material

MATSUSHITA DENKI SANGYO K.K. Japanese Appl. 6/126,190

An exothermic material having catalytic ability, for rapid auto catalyst warm-up, consists of a ceramic support, coated with a high frequency absorber, such as a semiconductor, microparticles and a catalyst containing at least one of Pt, Rh and Pd, or at least one metal oxide of Cu, Mn, Co and Fe. The exothermic material generates heat by absorption of high frequency and decomposes HC and CO in the exhaust gas of automobiles.

Decomposition Catalyst for Nitrogen Oxides

SAKAI KAGAKU KOGYO K.K. Japanese Appl. 6/142,509–510

A decomposition catalyst for N suboxide is composed of Ru, Rh, Re, Os or Ir supported on α-Al₂O₃. (1), or is composed of Ru/Ir (mole ratio = 0.3–5.0) on a hydrophobic support (2). Catalyst (1) shows high activity at low temperature and under a moist atmosphere. In an example, activated Al₂O₃ was immersed in ethanol solution containing Ru and H₂ for 2 h, burned at 400°C for 5 h, and reduced with H₂ at 400°C for 2 h to form catalyst (2) supporting 1.5% Ru/Ir. Catalyst (2) is highly active and stable.

Nitrogen Oxide Decomposing Catalyst

SUMITOMO METAL MINING CO. Japanese Appl. 6/154,602

A NOx decomposing catalyst consists of an inorganic oxide support loaded with Pt in which acidic anions, preferably SO₄²⁻ or Cl⁻ remain after firing. The catalyst is used to remove NOx from combustion exhaust discharged under fuel-lean conditions and which contains excess O₂. NOx is reduced selectively to N₂, and so the amount of by-product N₂O is minimised.

Nitrous Oxide Decomposition Catalyst

SAKAI KAGAKU KOGYO K.K. Japanese Appls. 6/154,603–604

A N₂O decomposition catalyst consists of a hydrophobic support loaded with Ir and at least one component selected from Nb₂O₅, TiO₂ or ZrO₂, or La₂O₃, CeO₂, Pr₂O₃, etc. The catalyst decomposes N₂O contained in the waste gas discharged from factories, car engines, garbage or sewage incinerators, etc. It provides a higher decomposition efficiency and a longer operating life.

Dualistic Alumina Carrying Platinum Catalyst

CHISSO CORP. Japanese Appl. 6/165,936

Dualistic Pt/Al₂O₃ catalyst for dehydrogenation and alkylation includes no surface hydroxyl group by burning the Al₂O₃ at ≥ 923 K in Cl gas. The Al₂O₃ is carried with Pt chloride by CVD at 623–873 K to produce Pt/Al₂O₃. The catalyst has a dual function as a solid Lewis ultra strong acid and as a Pt metal. It has high catalytic activity for alkylation of aromatic compounds by paraflin and for dehydrogenation of cyclohexane.

Removal of Nitrogen Oxide from I.C.E.

NIPPON SHOKUBAI CO. LTD. Japanese Appl. 6/165,937

A catalyst for NOx removal contains Ir, fire resistant inorganic oxide, such as Al₂O₃, and a metal, which is at least one of Ta, Nb, Y or rare earth. The catalytic active matter is coated onto the structure body, and exhaust gas for NOx removal is passed, in an oxidising atmosphere, through the catalyst in the presence of hydrocarbon. NOx from the exhaust gas of gasoline or diesel engines, or boiler industry plant is removed. The added metal improves the high temperature thermal resistance of the catalyst.

Noble Metal Loaded Anion Exchange Fibre

NICHIBI K.K. Japanese Appl. 6/170,236

A new anion exchange fibre, made of polyvinylalcohol fibre containing primary, secondary, tertiary or quaternary ammonium groups, is loaded with 0.1–20 wt. % of Pt, Pd or Rh or Ir. The fibre is used as a catalyst to replace conventional Al₂O₃, SiO₂, TiO₂ or zeolite catalyst, and has a higher catalytic activity. It is easier to handle than organic polymer granule catalysts.

Preparation of Hexafluoropropanol

CENTRAL GLASS CO. LTD. Japanese Appl. 6/184,025

1,1,1,3,3,3-Hexafluoropropan-2-ol (HFIP) is prepared in high purity by hydrogenolysis of hexafluoroacetone hydrate with H₂ in the presence of Pd and Ru mixed catalysts, preferably Pd/Al₂O₃. Ru/Al₂O₃ at 40–150°C and a H₂ pressure of 1–30 kg/cm².
Palladium Catalyst Production
NIKKO SC. K.K.  
Japanese Appl. 6/190,277
The catalyst is produced by addition of aqueous solution of Na silicate to PdCl₂ to deposit Pd hydroxide on the surface of a support, such as C or Al₂O₃; the Pd hydroxide is then reduced. The Pd catalyst has a higher activity, is hardly sintered and is used for hydrogenation reduction of nitrobenzene to aniline.

Efficient Catalyst for Burning Hydrocarbons
TOKYO GAS CO. LTD.  
Japanese Appl. 6/190,283
The catalyst comprises a mordenite zeolite carrier, an auxiliary Ce catalyst and an active component of 0.5–1.5 wt.% Pd supported by ion exchange. Pd can be supported by dipping a carrier supporting Ce into an aqueous solution of Pd nitrate, drying and calcining. The catalyst is used to burn hydrocarbon, particularly small amounts of methane of < 5000 ppm, which also contains steam and O₂, from, for example, combustion fuel exhaust. The catalyst has a high activity and heat efficiency at low temperature.

Trifunctional Catalyst
TOSOH CORP.  
Japanese Appl. 6/198,190
A catalyst able to remove NOx from exhaust gas containing excess O₂, NOₓ, CO and HC is made of ZSM-type zeolite of molar ratio SiO₂:Al₂O₃ > 15 which carries Zn and Pt, where the zeolite is impregnated by ion exchange. The catalyst changes NOx to N₂.

Heat Utilisation System for Car Engine
TECHNOVA K.K.  
Japanese Appl. 6/207,993
A cathode working both as a heavy H₂O-containing electrolyte decomposer and an excess heat generator comprises micropores of ≤ 0.1 mm diameter formed in a cathodic base of Pd or Pd alloy with porosity of 5–25%. Excess heat vapour effectively generated from the electrolyte decomposer cathode is directed to the engine cylinder chamber by a radiating fin, thus driving the piston rotatively, to power steer the engine.

Photocatalytic Purification of Gases and Brines
R. AALBERS  
German Appl. 4,240,558
Photocatalytic purification of contaminated gases, vapours and brines involves photocatalysis on a catalyst in a closed chamber. The catalyst has high surface area, stability and chemical inertness. It contains at least one semiconductor oxide or Group IIA or IIB oxide, and a Pt group metal, such as Pd or Pt, at least one actinnide, lanthanide or Group IIIIB element, supported on TiO₂. Also required is a light source of wavelength 250–400 nm. The catalyst can be regenerated by washing or by the short-wave light source.

Silencer for Large Engine
F. HOERSTING  
German Appl. 4,303,548
A silencer has an array of metal-walled diverging ducts coated with Pd which catalyses automobile exhaust gases. The ducts expand the gas which generates additional thrust, while simultaneously dampening the sound waves. The ducts can have different cross-sectional shapes. The silencer is used in large or aero engines.

Catalyst for Hydrogen Preparation from Carbon Monoxide and Steam
SUED-CHEMIE A.G.  
German Appl. 4,303,715
Cr-free catalyst for reacting CO with steam to form H₂ and CO₂; contains Fe oxide, CuO, rare earth oxide and/or ZrO₂ 0.1–30% base metal oxides of ionic radius 50–72 pm (except Cr), 0–0.1% Pt group metals and 0–3% BaO. The process produces H₂ or H₂-rich synthesis gas. The catalyst has higher catalytic activity and thermal stability than a Cr-containing catalyst, which could cause health and environmental hazards.

Catalyst for Oxidative Purification of Carbon Dioxide
LEUNA-WERKE G.m.b.H.  
German Appl. 4,305,386
The catalyst which removes organic impurities, especially saturated HC, from CO₂; used in the food industry, contains Pt and/or Pd on a support of α-Al₂O₃ with specific surface area of ≤ 50 m²/g. The catalyst preferably contains 0.05–0.1% Pt, 0.03–0.05% Pd and 0.03–0.05% Cu, Fe or Ni. The heavy metal compounds are enriched on the outside by precipitation from a metal solution at pH 6–8. The catalyst is highly active, heat stable and converts 90–99% of saturated HC and also converts S to SO₂.

Production of Mono-Oxidised Products
VER ZUCKERINDUSTRIE  
German Appl. 4,307,388
Mono-oxidised products from carbohydrates, carbohydrate derivatives and primary alcohols are prepared by feeding the raw material to a continuous oxidation process which has supported Pt group metal catalysts, such as Pt/C, and continuously separating the mono-carboxylic acid products at an electrodialysis stage. Selectivity to mono-oxidised products is improved and the space/time yield is high.

Active Carbon-Supported Platinum Group Metal Hydrogenation Catalyst
DEGUSSA A.G.  
German Appl. 4,308,101
A process is claimed for the production of hydrogenation catalysts containing at least one Pt group metal and optional promoters and/or modifiers on a HNO₃-washed active C support, which is pretreated with H₂O₂ or Na hypochlorite before adding the catalyst metal. The catalysts are stable and have increased activity.

Zeolite Containing Palladium Catalyst
NIPPON SHOKUBAI CO. LTD.  
German Appl. 4,340,650
An absorbent for hydrocarbons in waste gas contains 0.001–10 wt. % Pd/zeolite catalyst, preferably H-type zeolite. It can absorb C-H and hydrocarbons from exhaust gases from engines, especially petrol and diesel engines, steam boilers and industrial plant.

Three-Way Catalyst for Engine Exhaust Gas Purification
MAZDA MOTOR CORP.  
German Appl. 4,402,436
An exhaust gas purification catalyst, effective at low temperature, has a support with a first and a second catalyst coat containing Pd/Al₂O₃ and Pd/CoO₂ respectively. The catalyst has better properties than usual for removal of HC in the low temperature region.

Platinum Metals Rev., 1995, 39, (1)  51
FUEL CELLS

Fuel Cell Manufacture
TOKYO GAS CO. LTD. Japanese Appl. 6/203,848-49
The production involves mixing catalyst containing Pt and C with solvent to dilute the ion exchange resin. A slurry is then made. The ion exchange resin film acts as a solid giant molecular electrolyte film on the Pt/C electrode base film, giving a H.O repellent electrode sheet. Two of the sheets are joined into one unit by hot pressing. Simplified production allows the generation of large electric current at low temperatures.

Preparation of Alloy Catalyst for Fuel Cell
TANAKA KIKINZOKU KOGYO K.K. Japanese Appl. 6/246,160
The method comprises adding a second and a third metal salt to a Pt catalyst; reducing, heating to obtain a Pt alloy catalyst, and acid treating the catalyst. Preferably, the second metal comprises Ni in atomic ratio 50% per Pt and the third metal comprises Co in atomic ratio 50% per Pt. The catalyst is used in fuel cells and retains a stable electric potential.

ELECTRICAL AND ELECTRONIC ENGINEERING

Electric Discharge Electrode
TANAKA DENSHI KOGYO K.K. Japanese Appl. 6/112,263
An electrode for automatic wire bonding is made of 99.9% pure Pt alloy and contains other alloying elements such as: 1-35 wt.% Ir, 1-30 wt.% Pd, 1-20 wt.% Au, 1-25 wt.% Ni, 1-15 wt.% Ru and 65 wt.% Pt. An electric discharge passing through the electrode fuses the electrode tip to a ball shape which stably bonds the tip electrode of a semiconductor device.

Anti-Oxidation Palladium Powder
SHOEI KAGAKU KOGYO K.K. Japanese Appl. 6/172,802
Anti-oxidation Pd powder contains ≥ 0.005 wt.% alkali earth metal, such as Mg, Ca, Sr or Ba. The Pd powder is used as the conductive material in thick conductive paste. The paste is used to pattern electrodes in sheets for layering in laminated ceramic capacitors.

High Density Recording Using Photomagnetic Medium
HITACHI LTD. Japanese Appl. 6/176,415
A recording film comprises reciprocal laminations of Pt and/or Pd and Co. An undercoat film 10-100 Å in thickness is selected from Pt, Pd, Au, Ag or Cu. The medium is suitable for high density recording, and has improved photomagnetic characteristics.

Conductive Paste Compositions
MURATA MFG. CO. LTD. Japanese Appl. 6/209,152
The conductive paste composition comprises 50-70 wt.% of Pd, Ag-Pd, Ni and Cu, 1.0-1.8 wt.% of resin such as (m)ethyl cellulose, etc., and a solvent. The paste is used for example in the preparation of the inner electrode of multilayered capacitors by screen printing.

Conductive Paste for Thick-Film Resistors
SUMITOMO METAL MINING CO. Japanese Appls. 6/223,616-18
Conductive paste comprises 15-35 wt.% PbO, 20-40 wt.% SiO2, 5-25 wt.% CaO, 5-20 wt.% Al2O3, 3-6 wt.% glass powder, 2-8 wt.% Bi oxide powder and Pt group metal powder. Bi oxide powders mixed with B oxide in Ag-Pd paste containing glass powders as binder can also form the conductive paste. Good solderability for resistors can be obtained.

Conductive Paste
ASAHI GLASS CO. LTD. Japanese Appl. 6/223,622
Conductive paste for the section between a package frame and the carrier for a circuit device comprises 60-95 wt.% Ag, 1-20 wt.% Pd, 1-5 wt.% glass frit and 3-20 wt.% Bi oxide. It allows reliable conductors to be buried in glass.

High Permeability Alloy for Magnetic Recording Heads
DAIDO TOSOKUHKO K.K. Japanese Appl. 6/228,718
The high permeability alloy comprises, by wt.%, 6.0-12.0% Si, 4.0-8.0% Al, one or more of Ti, V, Zr, Nb, Mo, Hf, Ta and W, and one or more of Ru, Rh, Pd, Os, Ir, Pt, Au and Ag, and balance Fe. The alloy is used for heads for magnetic recording/regeneration. Excellent magnetic characteristics and high wear resistance are obtained.

Thin Films for Hard Magnetic Disks
NEC CORP. Japanese Appl. 6/259,767
High density thin film medium is manufactured by forming Cr base film on a substrate, and then forming a magnetic film of Co-Cr-Ta alloy containing Pt on the base film, followed by heating. High coercive field strength is maintained, rectangularity ratio is improved and remanent magnetisation is heightened.

MEDICAL USES

Metallic Material for Dental Prostheses
P. SUNDER-PLASSMANN German Appl. 4,306,542
A mouldable dental crown is prepared from a uniform mixture of high melting point particles of average diameter 4-80 μm consisting of an alloy containing ≥ 12% each of Pd and Pt, and ≥ 20% Au; low melting point Au or Au alloy, and a volatile wax binder, the binder forming 30-80% by volume of the mixture. The material has uniform and repeatable porosity with minimised shrinkage. Properties are easily controlled by adjusting the metal ratio and porosity.

Dental Restoration Alloys
U.S. Patent 5,336,091
A mouldable dental crown is prepared from a uniform mixture of high melting point particles of average diameter 4-80 μm consisting of an alloy containing ≥ 12% each of Pd and Pt, and ≥ 20% Au; low melting point Au or Au alloy, and a volatile wax binder, the binder forming 30-80% by volume of the mixture. The material has uniform and repeatable porosity with minimised shrinkage. Properties are easily controlled by adjusting the metal ratio and porosity.

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