Contents

Development of the Noble Metal/Oxide Coated Titanium Electrode
By P. C. S. Hayfield
46

Electroless Platinum Deposition for Medical Implants
55

Emission Control Technology at Detroit
By M. V. Twigg
56

Autocatalysts for South America
By Pablo Gómez
59

Polymers of Platinum Metals Complexes Immobilised on Electrodes
By Alain Deronzier and Jean-Claude Moutet
60

Structural Nickel-Doped Iridium-Aluminium Materials
By R. B. McGrath
68

The Technology of Catalyst Supports
By James T. Richardson
69

Homogeneous Catalyst for Alkane Dehydrogenation
By David T. Thompson
71

Catalysis Technical Guide
72

Some New Aspect of the Photoreactions of Platinum Metals Complexes
By Liu Weiping, Yang Yikun, Xiong Huizhou and Fu Wenfu
73

Abstracts
78

New Patents
84

Communications should be addressed to
The Editor, Susan V. Ashton, Platinum Metals Review
Johnson Matthey Public Limited Company, Hatton Garden, London ECIN 8EE
Development of the Noble Metal/Oxide Coated Titanium Electrode

PART II: THE MOVE FROM PLATINUM/IRIDIUM TO RUTHENIUM OXIDE ELECTROCATALYSTS

By P. C. S. Hayfield
Bickenhill, West Midlands, England

In the first part of this paper, published in the January issue, development work resulting in the first noble metal oxide coated titanium electrode was described and some of the teething problems encountered were discussed. Here, the story is continued with the further development of paint compositions: platinum-only and platinum/iridium, for coating the electrodes, and their utilisation in chlorate, mercury- and diaphragm-type chlor-alkali cells. Later, these coatings were replaced by ones containing ruthenium dioxide. This part begins with the early platinum paint compositions.

One commonly-used, early, resinate-based, platinum-only paint, Engelhard '05X', had an aromatic smell that operators at that time are unlikely to forget. Because of its original function for metallising ceramic capacitors used in the electrical industry, the paint contained small amounts of rhodium and traces of tin and bismuth, to help with wetting and coating adhesion. Even as late as 1965, '05X'-coated titanium electrodes were being evaluated in the U.K. in both mercury- and diaphragm-type chlorine cells. Performance in the former was disappointing, mainly because of the inevitable anode/amalgam shorts and the formation of 'mercury butter' (a localised thickening of the electrolyte), but the performance of the '05X' platinum coatings in diaphragm-type chlorine cells was more encouraging.

Resinate Based Paint: 70/30 Pt/Ir Coatings, ‘Ir1’

By 1965, there was an increasing switch from pure platinum to a nominal 70/30 platinum/iridium, Pt/Ir, coating; the origin of the 70/30 ratio can be traced back to ad hoc trials at International Nickel. Once it was ascertained that this composition was superior to platinum, the 70/30 formulation became rather ‘written in stone’. The fact that platinum will dissolve in aqua regia, and also alloys with up to 30 per cent iridium is fortuitous, and apparently had no bearing on the original selection. The Hanovia Division of Engelhard made up a resinate-based paint to the nominal 70/30 Pt/Ir ratio, their so-called ‘Ir1’, but without any additives – as no-one asked for them.

The ‘Ir1’ paint was destined to have a long history, and still has residual commercial use today. After repeated paint/thermal decomposition cycles, see Figure 3, to build up a significant deposit, it was thought appropriate – for no good technical reason at the time – to apply a Beer-type post heat treatment. Industry would not tolerate the uncertainties of the ammonia/butane component of Beer’s post heat treatment, but there were on hand various non-oxidising atmospheres, such as cracked ammonia and hydrogen-containing burnt town gas. So, completely by arbitrary selection, after the paint/thermal decomposition of the ‘Ir1’ paint, air was flushed out of the furnace using argon, followed by cracked ammonia for 15 minutes, then argon again and finally flowing air for 60 hours. Those chlorine and chlorate producers who tested the nominal 70/30 Pt/Ir coated electrodes in long-term trials (~2 years) with and without the ‘full...
Fig. 3 Laboratory track and tunnel furnace used in the preparation of small electrodes by the paint/thermal decomposition process. The small electrodes are suspended between large heat-conserving baffle plates.

post heat treatment’, invariably selected electrodes that had received the full heat treatment. All this may seem to be laboured unimportant commercial practice, but later examination of coatings done by techniques not available in the mid 1960s revealed some interesting findings: while the as-deposited ‘Ir1’ coating was basically a solid solution alloy of platinum and iridium, it did contain a small quantity of iridium oxide. However, after the full post heat treatment, the composition changed almost entirely to Pt + IrO₂. Thus, the preferred composition for electrocatalysts, found by testing in chlorate and diaphragm-type chlorine cells, comprised platinum metal and iridium oxide, and not as once thought a solid solution of iridium in platinum.

It was later discovered that coatings of platinum and iridium oxide can be formed, without the need for the complex post heat treatments, if a paint is made up from chlor-platinic and chlor-iridic acids dissolved in an alcohol, and then thermally decomposed at a higher temperature than is used for the resinate-based ‘Ir1’ paint. This is now the favoured method of depositing the so-called 70/30 Pt/Ir coatings.

First Large Commercial Chlor-Alkali Application

In 1968, and still unaware that the true composition of the nominal 70/30 Pt/Ir was a metal/oxide mixture, ‘Ir1’ resinate-based paint was used to coat titanium-based electrodes in two custom-built European sodium chlorate plants, belonging to Solvay et Cie. This was to be the first sizeable commercial application of titanium-based electrodes for chlor-alkali use. The loading of the applied electrocatalyst was low, under 5.0 g m⁻², because the plant was planned to operate at low current density, compared with more recently constructed chlorate plants. Details of the electrode performance remain commercially confidential, but it is understood that the original coatings were still
being used after more than 10 years. The electrodes were later recoated, not because the original coating had worn, but because it had become passivated, resulting in increased operating cell voltage and hence more costly chlorate production.

In the latter part of the 1960s, and early 1970s, the nominal 70/30 Pt/Ir coating was applied to electrodes in several chlorate plants worldwide, at the end of which time it was estimated that over half of world chlorate was being produced using this electrocatalyst. The applied loading for later plants was raised to ~10 g m\(^{-2}\) to ward off 'passivation', often using staggered higher loadings to assist in smooth recoating programmes, which have, so far, been unnecessary.

Passivation of Platinum Electrodes

Passivation requires some explanation. Platinum exhibits an anodic passivation characteristic not unlike that of titanium, namely, an active corrosion zone, and at higher anode potentials a region of passivation – the currents involved in both active corrosion and passivation are small for all practical purposes.

Iridium oxide produced by the optimised paint/thermal decomposition method is believed to be non-stoichiometric in composition but capable of passivation to a stoichiometric, less-electrocatalytically active form.

It was initially difficult to accept that the platinum and iridium oxide components had to be in an active corrosion form for the nominal 70/30 Pt/Ir to have a low chlorine overpotential, though the rate of platinum anodic dissolution is very small even in the active corrosion region.

During operation of the electrodes the platinum selectively dissolves with respect to the iridium oxide; the latter is presumed to be the principal electrocatalyst. If 70/30 Pt/Ir is applied initially at too low a loading, or operated at too high a current density, then the platinum passivates and allows the iridium oxide to follow. The coating rarely wears away completely, but in this passivated condition the electrical energy cost for chlorate formation increases.

Irrespective of knowing the true composition, the nominal 70/30 Pt/Ir coating has been the subject of scares. For example, if there are even a few parts per billion of soluble iridium in the brine then serious decomposition of chlorate will result. Fortunately iridium solubilisation has always been so low that it has never become a commercial problem.

Another example cropped up just when it seemed that the technology of the 70/30 Pt/Ir coating was on a sound course. Electrodes were supplied to one chlorate plant where ‘graphitic’ brine was used as the electrolyte feed, the latter being regenerated brine from the output of mercury-type chlorine cells fitted with graphite electrodes. The 70/30 Pt/Ir coating, assessed by non-destructive monitoring, dissolved unexpectedly fast. When, by chance, the feed was changed to fresh brine, the high wear rate of the Pt/Ir coating reverted to the expected very slow rate. Evidently an example of coating corrosion rate being affected by impurity in the electrolyte.

Just as the corrosion rate of platinum increases as dilution of brine increases, so a similar effect occurs in chlorate technology. The feed to a chlorate plant may begin as saturated brine, but as chlorate forms the residual brine level decreases. If the brine content falls below 100 g l\(^{-1}\), and certainly below 80 g l\(^{-1}\), there is an increase in the corrosion rate. With only a few g l\(^{-1}\) of residual brine, coatings which might otherwise last for 5 or 10 years, dissolve in a matter of hours. It is presumed that this is another example of the effects of cojoint chlorine and oxygen generation.

The nominal 70/30 Pt/Ir coating has now largely been replaced by ruthenium-based coatings, probably because of the lower initial cost rather than for technical reasons.

Beer's Ruthenium Oxide-Based Coatings

By 1965, even with the improved performance from the nominal 70/30 Pt/Ir coatings compared with pure platinum, there was general frustration that more successful coated titanium electrodes for mercury-type chlorine cells, see Figures 4 and 5, had not been found.

In Europe at that time mercury-type chlorine technology predominated, whereas in North
A prototype titanium anode for a mercury-type chlorine cell, consisting of a central column or post in-filled with copper for the electrical connection; a cross-piece spine connects to a grid coated on the lower part with noble metal oxide. Such anodes come in a range of designs and sizes, larger ones having two or four posts. Much development has gone into ensuring the lowest electrical resistance in the structure to the blades, for minimum usage of titanium.

America diaphragm-type cells were mainly used. Beer (still linked with Magneto Chemie in the Netherlands) then proposed another change of coating – to ruthenium oxide. Now, every change of coating type required considerable retesting in the well-established, but costly-to-run, test rigs. Was ruthenium oxide to be another ‘wild goose chase’? Ruthenium oxide electrocatalyst did seem, on initial consideration, to work, but there existed in industry an inertia to the change from the noble metal to the oxide. It was accepted, with resentment, that if a noble metal oxide did confer attractive chlorine evolution characteristics (many minerals exist in a stable state).
oxide form) then oxides might just be suitable.

However, the grudging acceptance of Beer’s work, and his desire to speed up exploitation, led him to sell his technical concepts and join forces with de Nora, an electrochemical company in Italy, and to relinquish all ties with ICI.

At about the time of the changeover, Beer filed his now celebrated first oxide patent, ‘Beer 65’, sometimes affectionately known as Beer 1 (17). He claimed the deposition of ruthenium oxide, and admixing a soluble titanium compound to the paint, to approximately 50 per cent. There are several key aspects to Beer 1:
- codeposition
- depositing a coating of improved adhesion, and
- producing a coating of improved durability in mercury-type chlorine cells.

In 1967, Beer filed his ‘Beer 2’ patent (18). It would seem routine now to accept a coating composed principally of titanium oxide, but in 1967 it seemed quite ludicrous. All the subtleties of the mixed metal oxide coating could hardly have been appreciated then, when improvements to durability under mercury-type chlorine cell conditions were important.

However, the fact that Beer recognised the advantage of lowering ruthenium oxide content below 50 per cent must be to his lasting credit. Thus, the big breakthrough in chlorine technology was achieved in the manufacture of commercially viable anodes for mercury-type chlorine cells. To give the user confidence, (a master stroke in commerce) the electrode producer leased anodes and guaranteed performance!

During the 1970s, a method, believed to have originated from the Electrode Corporation (a joint activity between de Nora and Diamond Shamrock) of classifying the performance of coated titanium electrodes for diaphragm-type chlorine cells, was to use a single electrode potential difference as follows:

Chlorine single electrode potential w.r.t. nHE:
310 g l⁻¹ sodium chloride
current density 1 A inch⁻²
temperature 70°C

Oxygen single electrode potential w.r.t. nHE:
1 M sulfuric acid
current density 1 A inch⁻²
temperature 25–30°C

The required difference in potential between the above two values for efficient use in diaphragm-type chlorine cells was held to be 325 ± 40 mV.

It is of interest to compare the variation in the above electrode potential difference with those of RuO₂/TiO₂ compositions, see Figure 6. In order to achieve the required high values, it is
clear that a Beer 2 rather than a Beer 1 formulation must be chosen. The more expensive 70/30 Pt/Ir coating is characterised by potential differences of over 400 mV. The potential difference is effectively a method of stating that an electrocatalyst must have low chlorine overpotential and high oxygen overpotential for chlorine to be selectively released from brine solution (especially from dilute brines).

The potential difference of an electrode is affected by its composition. It is evident that ruthenium oxide is a more powerful chlorine electrocatalyst than oxygen electrocatalyst. By decreasing the effective area of exposed ruthenium by adding titanium oxide, the chlorine overpotential remains low while the net oxygen overpotential rises. Chlorine overpotential remains sensibly low with changing composition, while oxygen overpotential rises with decreasing ruthenium oxide content.

**Beer 2 Coatings**

Much emphasis has been given in the literature to the fact that codeposited RuO$_2$/TiO$_2$ coatings are true mixed crystals, and that this is the secret of their durability. Both RuO$_2$ and TiO$_2$ (rutile) possess the same crystal symmetry, and their lattice constants are similar. For patent reasons (rather than coating performance) there have been many high precision X-ray diffraction studies of such coatings. In general the X-ray lines of the two components are so close that they merge to give apparent single broad peaks displaced in the direction of mixed crystal formation. A complicating factor in lattice parameter considerations has been the relatively large contribution from chloride ions in the lattice (19, 20). If the deposit is heated to ~ 100°C or higher, above the normal paint decomposition temperature, the X-ray lines separate into ruthenium oxide and titanium oxide compounds (possibly recrystallisation or perhaps coalescence of like species).

In practice, it does not really matter whether such codeposits are true mixed crystals or exceedingly fine-scale intermixes. But, to reiterate, the importance of the Beer 2 patent is the codeposition of ruthenium and titanium oxides to give a deposit with the required electrode potential difference.

Since the 1970s, titanium-based electrodes coated with Beer 2 type RuO$_2$/TiO$_2$ have totally transformed the chlorine, chlorate and hypochlorite industries and their economics. This success has resulted from an interplay between anode producer and users, which has been far too complex to describe here.

**Sodium Amalgam Shorting**

In mercury-type chlorine technology there have been various methods, over and above Beer 2 type coatings, of improving resistance to sodium amalgam shorting. In one anode construction a thick, electrically-conducting inter-layer was deposited between the titanium and the electrocatalyst. In another, there was deliberate admixture of ceramic particles within the codeposit paint. Previously, graphite electrodes were massive and heavy, and the anode/cathode gap was adjusted by a manually operated screw mechanism. The much lighter titanium-based
electrode structure can be electrically raised and lowered, and sensors have been used to raise anodes automatically during expected amalgam shorts. Sodium amalgam shorts in mercury cells cannot be totally eliminated, but their frequency can be minimised.

Diaphragm-Type Chlorine Cells

There have also been comprehensive changes in diaphragm-type chlorine cells, see Figures 7 and 8. To decrease the anode/cathode gap, there was a change in anode design from the 'thin' box to the 'thick' box construction, and then to expandable anodes, where the ends of the diaphragm were left open for springiness. The natural asbestos-based diaphragms have been replaced by synthetic ones, and the cathodes have also been changed; a succession of modifications now leaving little room for improvements to either current or power efficiency.

During the change-over from graphite to titanium-based electrodes in diaphragm-type chlorine technology, K. O'Leary of Eltech Corporation filed an interesting patent claim (21). He proposed that coatings would be cheaper and electrode life extended if part of the ruthenium oxide was replaced by tin oxide. For example, where a 20 g m⁻³ Beer 2 coating might have a life of 8 years, the O'Leary composition (with half the RuO₂ content) raised life expectancy to around 12 years.

It is interesting to conjecture why the O'Leary modification is successful. Decreasing the ruthenium oxide content to below about 30 per cent raises the potential difference of the electrode in sulfuric acid and chloride solutions, see Figure 6. A restriction on decreasing the RuO₂ content too far is that the associated electrical resistance of the RuO₂/TiO₂ mixture progressively increases, and the voltage drop across the coating contributes significantly to the net overpotential. It would seem that the more electrically conducting SnO₂ compared to TiO₂, allows the RuO₂ level to be decreased without unduly raising the overall electrical resistance of the coating.

A similar explanation could explain the successful coatings patented by Solvay (22) which allow the RuO₂ content to be lowered, compared to TiO₂, by adding RhSbO₄. The Canadian company Chemetics would seem to have ‘fine tuned’ this variety of coating (23).

During the years where the Beer 2 patent owners and licensees held a monopoly, many attempts were made to compete. There were also professional patent breakers, whose aim was to damage the validity of the Beer patents, but none met with much success.

One route taken to circumvent the codeposition aspects of the Beer coatings was a two stage process. In the first part, a bed of porous titanium oxide was formed electrochemically on etched titanium from a Ti⁺ solution (24). This
was then infilled with RuO₂ by a paint/thermal decomposition route. The resultant coating was a fine scale mixture (not mixed oxide) of RuO₂ and TiO₂ at an approximately stable ratio of ~50/50 weight per cent. When electrodes coated in this way were first introduced into diaphragm-type chlorine cells, the chlorine efficiency was claimed to be marginally lower than in cells fitted with Beer 2 codeposited coatings. The two stage method did produce slightly more oxygen in the chlorine, slightly increasing the risk of explosion during liquefaction of the gas, but it also gave rise to less chlorate in the anolyte than occurred with Beer 2 coatings. In at least one chlorine plant it was thought better to accept slightly more oxygen in the chlorine so that less chlorate in the anolyte would pass through the diaphragm, thus minimising plant corrosion in the evaporator stage.

Now that the Beer patents have expired, any adjustment to the RuO₂/TiO₂ ratio can easily be achieved by adjusting the starting composition of the paint. This two stage coating process, which in the fullness of time gave electrodes with lives comparable to those of Beer 2 coated electrodes, would seem to disprove the need to use true mixed oxides for maximum electrocatalytic activity.

The efficiency of diaphragm-type chlorine cells is acutely dependent upon the properties of the diaphragm, and one method of in situ control was to add common sugar. Some plants, it is understood, used to thrive on this. Ruthenium-based coatings corrode more quickly in the presence of sugar, as does platinum electroplate. Fortunately the warning of the possible increased corrosive effects due to sugar meant that it was not added in plants equipped with ruthenium oxide-based coatings.

Using titanium-based electrodes in chlor-alkali cells caused a number of unfortunate incidents. For instance, diesel fuel spilled from dumper trucks used to take salt from a salt dome caused 'blinding' (deposition of film on the surface) of anodes in a mercury-type plant, thereby raising net chlorine overpotential to economically unacceptable levels. When the chlorine compressor in a diaphragm-type chlorine facility failed, the emergency procedure was to divert chlorine in the plant into sodium hydroxide solution where it was safely converted to sodium hypochlorite. Somehow the hypochlorite in one plant was inadvertently fed back into the chlor-alkali cells. Such an accident indelibly reminds one that alkaline brine strongly attacks ruthenium-based electrodes! Despite losing ~25 per cent of the anodic coating in just a few hours, the plant went on to function normally for the next 5 years without the need for anode replacement.

**Membrane-Type Chlorine Cells**

The introduction of membrane-type chlorine technology, see Figures 9 and 10, has also seen wide use of Beer 2 RuO₂/TiO₂ coatings. Because the ion exchange membrane is usually highly alkaline, conditions of use can exist where the anolyte may also go alkaline, for example, during a shut-down. Upon re-energising the plant,
alkalinity in the anolyte encourages oxygen, rather than chlorine, formation; and at above a pH of about 12, see Figure 11, the anodic reaction produces only oxygen, even in saturated brine. Hence, upon start-up of a membrane-type plant with alkaline anolyte there can be either only oxygen produced, or cojoint oxygen and chlorine. Even if the alkaline conditions are only transient, there can be significant dissolution of the anode coating. To improve overall durability, at a small loss in anode efficiency, some RuO$_2$ in Beer 2 RuO$_2$/TiO$_2$ codeposits may be replaced by IrO$_2$. The colour change from light grey to near black is usually an indication that the coatings contain some IrO$_2$. It is likely that a range of proprietary modifications to coatings are now used.
in the many membrane-type chlorine cells.
There is no longer justification for continued heavy expenditure on chlorine cell anode coatings. This does not mean that further worthwhile improvements cannot be made (25). Apart from the continuing desire for cost effective use of noble metals, the industry has to live with fluctuations in the noble metal base prices in deciding which coating to use for specific applications.

References

17 H. B. Beer, British Patent 1,147,442; 1965
18 H. B. Beer, British Patent 1,195,871; 1967
21 K. O'Leary, U.S. Patent 3,776,834; 1973
22 Solvay & Cie, British Patent 1,358,926; 1971

Electroless Platinum Deposition for Medical Implants

The metallisation of polymers enables such materials to be used in a wide range of industries, such as automotive, and in electronic applications. Most recently, the electroless deposition of metal onto polymers is finding use in medical applications for fabricating electrodes used in implantable medical devices. Platinum, being biologically inert, is one of the metals used to coat implantable electrodes. However, as metallic deposition only takes place on conducting surfaces, it is necessary to metallise, or seed, the non-conducting polymer prior to electroless deposition. A suitable catalyst is thus required to provide the insulating surface with conducting properties.

In commercial electroless platinum deposition a tin sensitiser and a palladium chloride, PdCl₂, activator are used to provide the catalytic centres, but tin is toxic and therefore unsuitable for use in medical implants.

Now, researchers based at the Royal North Shore Hospital in Sydney, Australia, describe a method for the electroless deposition of platinum onto films and fibres of polyethylene terephthalate (PET) using a new tin-free catalyst to activate the PET surface (Z. Rao, E. K. Chong, N. L. Anderson, M. G. Stevens, R. Driver and K. V. Paulose, J. Mater. Sci., Lett., 1998, 17, (4), 303–305). The catalyst was made by dissolving PdCl₂ into dimethylsulfoxide (DMSO).

The electroless deposition of platinum onto PET involved a number of steps with thorough rinsing in de-ionised water between each step. The PET films or fibres were first carefully washed to remove wax or oil residues, followed by etching in a hot alkaline bath consisting of sodium hydroxide and a surfactant. The etching roughened the PET surface and rinsing in de-ionised water between each step. The PET films or fibres were then washed to remove wax or oil residues, followed by etching in a hot alkaline bath consisting of sodium hydroxide and a surfactant. The etching roughened the PET surface. The PET samples were then dipped into the DMSO-Pd catalyst, followed by dipping into a reducer of an aqueous solution of hydrazine at room temperature. Lastly, catalysed samples were immersed in an electroless platinum deposition bath preheated to 60°C.

The resulting electrolessly plated platinum coatings were characterised by various techniques and compared with commercially available samples. Peel tests to evaluate the adhesion showed it to be good for platinum coatings of up to 200 nm thickness, but thicker coatings were less adhesive.

Palladium was present on the PET surface in metallic form but with an irregular distribution. These very fine palladium particles or clusters may act as catalytic sites for the subsequent electroless platinum deposition. However, as platinum deposition appeared to start simultaneously over all the catalysed PET surface, the role of the palladium is unclear, and further studies are required. This tin-free catalyst may thus find use in producing adhesive platinum coatings for implantable medical applications.
Emission Control Technology at Detroit
A SELECTIVE REPORT FROM THE 1998 SAE ANNUAL CONGRESS

The 1998 Detroit “Congress and Exposition” of the Society of Automotive Engineers (SAE) took place in the Cobo Center during the last week in February, with the theme “Engineering the Product Development Revolution”. There were 46,100 registered attendees, with representatives from all countries concerned with the manufacture of motor vehicles and their components. In total, 1146 papers were presented, covering all the technologies associated with the industry. This review focuses on the roles that platinum group metals (PGM) play in exhaust aftertreatment, the demands of diesel engine technology and the new lean-burn gasoline engine technologies. The numbers of the relevant SAE papers are given in parentheses.

Legislative Trends
R. Becker and R. Watson (Environex) reviewed (980413) trends in emissions control, emphasising that 1997 U.S. LEV (Low Emissions Vehicles) standards already typically require more than 98 per cent reduction in hydrocarbons (HC), and 95 per cent reduction of carbon monoxide (CO) and nitrogen oxides (NOx). Future standards require even higher conversions, and the use of on-board diagnostics demands the optimisation of sophisticated engine emissions feedback control, in combination with high performance catalysts incorporating activity monitoring.

Fuel-efficient diesel engines may help towards lowering carbon dioxide (CO₂) emissions. Diesel engines operate under very lean conditions, and their low CO and HC emissions are further reduced by platinum oxidation catalysts. However, removal of particulate matter (PM) and NOx emissions is not straightforward, and Michael Walsh, consultant, reviewed (980186) how regulatory authorities are focusing on these pollutants. Current PM regulations target the mass of the particulates, but the size and numbers of PM may also be important, and future regulations could be concerned with both.

Decreasing the emissions from automobiles continues, irrespective of the type of internal combustion engine, and some of the strategies for accomplishing this are described below.

Three-Way Catalysts
Renault and Johnson Matthey discussed (980936) gas flow variations across catalyst faces. Cone dimensions and inlet pipe sizes were modelled, and their effects on catalyst ageing, lightoff and performance on bench engines and cars were measured. Exhaust gas maldistribution significantly affected catalyst performance. In a related paper, Eberspächer and Fachhochschule Darmstadt, considered (980424) cone geometry and the distance between two monoliths in a converter. The space between the monoliths influences flow distribution in the first and second catalysts, and a distance of about 10 mm may be optimal. W. Maus and R. Brück (Emitec) gave a paper (980414) on the catalyst in converter cones. These “conical catalysts” provide additional catalyst, and possibly allow a reduction in volume of the main catalyst. Other benefits resulting from conical catalysts should be a shortened cone length and more efficient catalyst usage by forcing gas impinging on the main catalyst into desirable flow patterns. M. Laurell, I. Gottberg and T. Idoffsson (Volvo) reported (980416) converter optimisation with three catalysts; this included modifying the gas flow distribution, the cell density and the PGM loadings.

Mounting the catalyst close to the engine reduces the warm-up time, but this location is “materials demanding” in terms of thermal durability. Corning described (980042) how the high-temperature matt deterioration experienced with oval-shaped ceramic catalysts was overcome by new designs. Emitec indicated (980420) that low thermal mass catalysts can facilitate fast warm-up, while G. Faltermeier and B. Pfalzgraf (Audi), R. Brück (Emitec) and A. Donnerstag (Volkswagen) reported (980417) some conflicts.
in close-coupled designs. These include mechanical deterioration due to vibration and turbulence, and good gas flow distribution to obtain maximum catalyst efficiency while maintaining engine torque and optimised warm-up times. E. Otto, F. Albrecht and J. Liebl (BMW) discussed a six cylinder engine programme which came to broadly similar conclusions.

Johnson Matthey reported progress in developing a new ultra-low emissions concept involving close-coupled three-way catalysts for NOx control, and underfloor trap technology with a novel palladium ambient-temperature CO oxidation catalyst operating under lean conditions. With this catalyst, CO oxidation has positive order kinetics in CO concentration, and a large exotherm occurs during rich start-up. Data were given for a standard 1995 model year vehicle, modified for rich start-up. This achieved emissions 50 per cent lower than the ULEV (Ultra Low Emissions Vehicles) requirement.

Honda described how ULEV emissions can be achieved with underfloor catalyst, by the optimisation of a variable valve timing and lift mechanism, a new catalyst, precise air/fuel control with a lean air/fuel ratio after starting, and exhaust components having low heat capacity. A high loading palladium catalyst facilitated light-off, and effective oxygen storage enhanced hot HC oxidation. A substrate of high cell density (600 cpsi) and low thermal mass was additionally employed.

Lean-Burn Gasoline Engines

In paper Johnson Matthey described a high temperature stable aftertreatment system for lean-burn engines. A new close-coupled fast light-off catalyst was formulated not to degrade reduction under rich conditions of stored NOx, in a new high-capacity underfloor trap.

Sulfur compounds in fuel are detrimental because they are oxidised to sulfur dioxide (SO2) in the engine and then block NOx storage sites on the catalyst. Sakai Chemical Industry Company and Tottori University reported results for a variety of sulfur oxides (SOx) traps. These absorb SOx under lean conditions and desorb it at high temperature under rich conditions. A contribution from Next Generation Catalyst Research Institute in Japan, discussed a two-catalyst, SOx resistant system. The first catalyst is copper/zeolite which stores SOx as sulfate, so protecting the rear, platinum/gold catalyst supported on titania.

Reliable ageing cycles are important for the development of lean-NOx catalyst systems. J. M. Kisenyi (Ford) presented work by Ford and Tickford Ltd where the relationships between vehicle emissions and catalyst, aged in a high temperature dynamometer cycle, were established. The cycle had significant lean phases obtained by periodic injection of air into the exhaust of an engine running rich. Good correlation was achieved, with 75 hours of dynamometer ageing being equivalent to a distance of 80,500 km.

Diesel Aftertreatment

Oxidation and NOx Removal Catalysts

Diesel engines are very fuel-efficient under part-load/idle conditions, and the University of Central England confirmed that exhaust gas temperature might then be too low for underfloor oxidation catalysts to perform well. At higher load, temperatures are higher, resulting in good oxidation conversions. One improvement that could be made to meet more stringent emissions is to mount catalysts in a hotter location close to the engine, and in the usual underfloor position. N. E. Chemcat Corporation discussed two-catalyst systems, and the role of zeolites in platinum catalysts to enhance NOx conversions. They highlighted a need to control HC/NOx ratios for optimum performance. A. Peters (Daimler-Benz) presented a paper with Degussa on the optimisation of a two-catalyst system on an engine with common rail fuelling. Here it is possible to control the exhaust HC/NOx ratio for optimum NOx reduction, and with two catalysts it is possible, during low speeds, to have the front one operating in the NOx reduction temperature window characteristic of platinum catalysts, and to have the underfloor one operating in this temperature range at high speeds.
Optimal NOx removal can then be obtained under most operating conditions. Toyota illustrated (980195) that zeolites can absorb HC when the catalyst is cool, and enhance NOx reduction. Zeolite can convert high molecular weight soluble organic fraction (SOF) to smaller molecular fragments, so aiding their oxidative destruction; and sulfate production can be minimised by using washcoat materials having low affinity for SO2.

**Particulate Control**

Sulfur is a catalyst poison, and can affect the amount of particulate present in diesel exhaust after oxidation catalyst treatment. Degussa, ICT and The Technical University Darmstadt confirmed (980196) that the SOF of diesel particulate can be reduced by a platinum oxidation catalyst at the temperatures present in automobiles, whereas at higher temperatures, around 350°C, oxidation of SO2 to sulfur trioxide (SO3) and hence sulfuric acid takes place. This is adsorbed on PM. As a result, at low temperatures, SOF is oxidised and PM mass is reduced, but at higher temperatures the formation of sulfate increases the observed amount of PM. They also described how PM analysis itself can influence the measured values, due to droplet formation. A related paper (980525) from the University of Minnesota and Perkins Technology Ltd came to broadly similar conclusions.

The European VERT project described (980539) a new hypothesis for diesel engine soot formation involving fuel dissociation to produce fast diffusing hydrogen which is then burned, leaving carbon in oxygen-depleted zones. A range of aftertreatment diesel particulate filters (DPFs) were tested, and their characteristics reported in combination with different hydrocarbon soluble fuel additives. These are converted to metal oxides in the engine, and appear to reduce raw emissions and to catalyse the combustion of trapped soot at moderate temperatures. Concerns include the build-up of soot during extended low speed driving and nanosized metal oxide particles possibly passing into the environment, which would not be "toxicology permissible" for many additives.

L. Montanaro and A. Negro found (980540) sodium compounds, derived from fuel additives, were the most reactive species, in potentially detrimental reactions with filter materials; and a contribution from Aristotle University, Rhône-Poulenc and Renault reported (980543) results for different filter positions on a light truck.

A well-attended paper (980189) from Johnson Matthey, HJS Fahrzeugtechnik, Corning, Fraunhofer-Institute of Toxicology and Aerosol Research, and FEV Motorentechnik described further studies on Continuously Regenerating Traps (CRTs) which can overcome some diesel particulate filter deficiencies when low sulfur fuel is used. In this system a high proportion of CO and HC (including non-regulated emissions like aldehydes) are oxidised over a platinum-based catalyst. Most HC species downstream of the CRT were too low to be measured accurately. Most of the nitric oxide in the exhaust gas is oxidised to nitrogen dioxide (NO2) over the catalyst, and particulate emissions retained in a filter are burnt via reaction with NO2. Because this is a relatively low temperature reaction, particulate removal from the filter takes place at all but very low temperatures. It is well established that this system dramatically reduces particulate mass emissions, so the work described focused on particle number emissions. These were recorded down to a primary diameter of 15 nm, and had been reduced by one to two orders of magnitude, and even the nanosized particles were effectively reduced.

**Conclusions**

Most of these papers are collected in SAE "Single Publications"; the most pertinent being: "Diesel Exhaust Aftertreatment 1998" (SP1313), "General Emissions (SP1335), "Advanced Converter Concepts for Emission Control" (SP1352) and "Catalysts Emission Control and Lean-NOx Technologies" (SP1353). Once again, the Detroit SAE Congress provided a focus for developments in emissions control technology, and it is clear that PGM-containing catalysts have a major role in achieving the emissions standards soon to be introduced.

M. V. TWIGG
The countries of the South American continent presently constitute one of the fastest growing economies in the world and Mercosur, the common market area made up of Argentina, Brazil, Paraguay and Uruguay, is committed to expanding its manufacturing capability to respond to the needs of the region.

Since April 1997 Johnson Matthey has been supplying its Mercosur customers with autocatalysts manufactured in Belgium, South Africa and the United States of America, but in deference to the wishes of these customers the decision was taken to set up a manufacturing facility in the region.

In 1998 it is expected that Argentina will manufacture more than 436,000 cars, while Brazil will produce 1.6 million to satisfy the local markets. Johnson Matthey's new facility is well placed to provide our customers with their needs into the next century and has been designed with expansion in mind.

Officially opened on 26th March, 1998, the facility is a joint venture between Magneti Marelli and Johnson Matthey. It is Johnson Matthey's first manufacturing plant in Argentina and its eighth autocatalyst manufacturing plant worldwide. Situated some 65 km north of Buenos Aires, the plant was constructed during the period April to December 1997. With the capacity to produce one and a half million autocatalysts per year, the facility includes its own noble metals salts preparation unit. The first validation batches of catalysts were produced in November 1997 and commercial production has just begun, during the first quarter of 1998.

An interesting feature of the facility results from the fact that in Brazil cars use a fuel containing up to twenty per cent alcohol, a by-product of the local government supported sugar industry. It is therefore a requirement that all autocatalysts manufactured for use in Brazil have to be formulated to perform well under these local conditions. Indeed, to ensure customer satisfaction Johnson Matthey has set up a sales and technical support group in São Paulo.

PABLO GÓMEZ
Interest is growing in using polymeric electrode materials containing platinum group metal complexes in molecular electrochemistry. Here, the synthesis of functionalised polypyrrole film electrodes, formed by the oxidative electropolymerisation of pyrrole-substituted rhodium, iridium and palladium complexes is reviewed, and recent results are presented concerning the electrocatalytic reduction of protons and the hydrogenation of unsaturated organic substrates in aqueous electrolyte. Metal hydride intermediates and their involvement in reactions at the electrodes are considered, as are preliminary results of asymmetric electrosynthesis on a molecular electrode material.

The deliberate modification of electrode surfaces by polymer films containing transition metal complexes is a new field of study. It combines coordination-, polymer- and electrochemistry, and aims at developing new materials for electrocatalysis, electroanalysis and photoelectrochemistry (1, 2). As the electrode is the key component in all electrochemical systems, the development of new electrode materials possessing the high activity and selectivity of transition metal catalysts is important for many uses.

Recently, rhodium, iridium and palladium complexes have been electrochemically transformed to their hydride derivatives and used for proton electroreduction and electrocatalytic hydrogenation of organics. Immobilising these homogeneous platinum metal catalysts on electrodes improves product and catalyst recovery, and operational stability. Reactions using very small amounts of reagents can then be performed.

Electroreductive Generation of Hydrido Complexes

The relevance of transition metal hydride complexes in coordination chemistry is now well recognised, particularly in chemical catalysis (3). Additionally, it has been postulated that transition metal hydride complexes are the key intermediates in a number of electrocatalytic and photocatalytic systems, for instance, in the photoreduction and electroreduction of protons to dihydrogen (4), and in the electrochemical regeneration of the coenzyme NADH (nicotinamide adenine dinucleotide) from NAD⁺ (5).

Electrochemical investigations of metal hydrides may be able to explain their activation by electron transfer and may lead to the development of new synthetic routes for the formation of transition metal hydrides. In fact, the successful electroreductive generation of transition metal hydride complexes in homogeneous media has recently been demonstrated for a number of metal complexes, including those of ruthenium (6), osmium (7), tungsten (8), iridium (7, 9), and rhodium (10, 11).

As an example, Figure 1 shows that the reduction of the cationic iridium(III) complex, [(η⁵-C₅Me₅)Ir(bpy)Cl]⁺, in an organic electrolyte before (Curve (a)) and after (Curve (b)) the addition of formic acid which is the proton source, leads to the formation of its stable
hydrido derivative $\left[\left(\eta^5-C_5Me_5\right)Ir^{III}(bpy)(H)\right]^+$
(9). The latter exhibits a characteristic one-electron, reversible bpy ligand-based reduction (Figure 1, Curve (b)). Its quantitative production (Figure 1, Curve (c)) by the oxidative addition of a proton to the reduced $\left[\left(\eta^5-C_5Me_5\right)Ir^{IV}(bpy)\right]^+$ complex, Equation (i), has been further corroborated from $^1$H NMR
(nuclear magnetic resonance) analysis of the resulting solution:

$$\left[\left(\eta^5-C_5Me_5\right)Ir^{IV}(bpy)\right]^+ + H^+ \rightarrow \left[\left(\eta^5-C_5Me_5\right)Ir^{III}(bpy)(H)\right]^+$$ (i)

In addition, electrochemical and $^31P$ NMR data have demonstrated the electroreductive generation of the rhodium dihydro complex $\left[Rh(bpy)(PPh_3Et)_2(H)\right]^+$, in acidic acetonitrile electrolyte, from its dichloro parent complex $\left[Rh(bpy)(PPh_3Et)_2(Cl)\right]^+$ (10). Formation of the dihydro complex takes place via its corresponding monohydridoro complex, $\left[Rh(bpy)(PPh_3Et)(Cl)(H)\right]^+$. As in homogeneous solution, the electroreductive build-up of hydrido complexes in polymer films containing rhodium and iridium chloro parent complexes has been well established.
These studies have been carried out using electrodes modified by polymer film, synthesised by the oxidative electropolymerisation of complexes, such as $[\text{(q}^5\text{-C}5\text{Me}5)\text{M(L)Cl}]^+$ ($\text{M} = \text{Ir} \ (12) \text{ and Rh} \ (11, 13)$) and $[\text{Rh}(\text{L})(\text{PPh}2\text{Et})2(\text{Cl})]2^-$ (10), where $\text{L}$ is a pyrrole-substituted polypyrpyridyl ligand, see Figure 2.

A striking example of hydrido complex formation is shown in Figure 3, for a film of a cationic Rh(III) complex containing both phosphine and nitrogen ligands (10). In acetonitrile electrolyte, the reduced Rh(I) complex, Equation (ii), is characterised by a reversible, one-electron bpy-centred redox wave (Equation (iii); Figure 3, Curve (a)) which remains stable during repeated scans.

By contrast, a fast and efficient transformation of this complex to its dihydro derivative, Equation (v), is obtained by scanning down to the second bpy-localised reduction (Equation (iv); Figure 3, Curve (b)), which forms a more strongly reducing intermediate, able to react with traces of water contained in the electrolyte. The dihydro complex is easily characterised from its reversible one-electron reduction wave (Equation (vi); Figure 3, Curve (c)).

$$[\text{Rh}^\text{III}(\text{bpy})(\text{PPh}2\text{Et}),\text{Cl}],^+ + 2 \text{e} \rightarrow [\text{Rh}(\text{bpy})(\text{PPh}2\text{Et}),],^+ + 2 \text{Cl}^- \quad \text{(ii)}$$

$$[\text{Rh}(\text{bpy})(\text{PPh}2\text{Et}),],^+ + \text{e} \rightarrow [\text{Rh}(\text{bpy}^+)(\text{PPh}2\text{Et}),],^+ \quad \text{(iii)}$$

$$[\text{Rh}(\text{bpy}^+)(\text{PPh}2\text{Et}),],^+ + \text{e} \rightarrow [\text{Rh}(\text{bpy}^+)(\text{PPh}2\text{Et}),],^+ \quad \text{(iv)}$$

$$[\text{Rh}^\text{III}(\text{bpy})(\text{PPh}2\text{Et}),\text{(H)}],^+ + 2\text{H}^+ + 2\text{e} \rightarrow [\text{Rh}^\text{III}(\text{bpy})(\text{PPh}2\text{Et}),\text{(H)}],^2+ \quad \text{(v)}$$

$$[\text{Rh}^\text{III}(\text{bpy})(\text{PPh}2\text{Et}),\text{(H)}],^2+ + \text{e} \rightarrow [\text{Rh}^\text{III}(\text{bpy}^+)(\text{PPh}2\text{Et}),\text{(H)}],^3+ \quad \text{(vi)}$$

**Electrocatalytic Activity of Films for Proton Reduction**

Hydrido complexes of the type $[\text{(q}^5\text{-C}5\text{Me}5)\text{Ir(L)H}]^+$ ($\text{L} = \text{bpy or phen}$) when studied by cyclic voltammetry, in neutral acetonitrile, are characterised by a reversible one-electron, L-centred reduction (see Figure 1, Curve (c), for example). This occurs in homogeneous solution (9) and in films (12).

However, reduction of the parent rhodium (III) complex $[\text{(q}^5\text{-C}5\text{Me}5)\text{Rh}^\text{III}(\text{L})\text{H}],^-$, Equation (vii), is only partially reversible (11, 13), due to the higher instability of its reduced form. The complex $[\text{(q}^5\text{-C}5\text{Me}5)\text{Rh}^\text{III}(\text{L'})\text{H}],^-$ decomposes to give dihydrogen and the rhodium complex $[\text{(q}^5\text{-C}5\text{Me}5)\text{Rh}(\text{L})],^+$, see Equation (viii). This is shown in Figure 4 for a film of poly[$[\text{(q}^5\text{-C}5\text{Me}5)\text{Rh}(\text{L})],^+$, where the gradual growth of the reversible two-electron wave corresponding to the $[\text{(q}^5\text{-C}5\text{Me}5)\text{Rh}(\text{L})],^2+$ redox
couple (Equation (ix), Figure 4, Curves (b)) is seen upon repeated scanning, at the expense of the hydride reduction wave.

\[
[(\eta^1-C_5Me_5)Rh^{III}(L')Cl]^+ + 2e^- \rightarrow [(\eta^1-C_5Me_5)Rh^{II}(L)Cl]^2+ \quad (vii)
\]

\[
[(\eta^1-C_5Me_5)Rh^{III}(L')Cl]^+ + e^- \rightarrow [(\eta^1-C_5Me_5)Rh^{II}(L)Cl]^+ \quad (viii)
\]

These films, therefore, exhibit a strong electrocatalytic activity towards proton reduction and hydrogen generation in protic media, that is, in acidic organic and aqueous electrolytes, see Figure 5A, for example. The experimental data agree with the catalytic cycle shown in Figure 5B, which involves the spontaneous decomposition of the reduced hydride complex, Path (a), and its reaction with protons, Path (b), both resulting in the release of dihydrogen. These studies clearly demonstrate that metal hydride species are the key species in the electroreduction of protons catalysed by such platinum metal complexes.

When preparative-scale electrolysis is carried out, in acidic organic and aqueous electrolytes, on vitreous carbon plate electrodes of area 5 cm² modified with poly[(η^1-C_5Me_5)Ir(L)Cl]⁺ films (L = Lₘ, Lₚ), dihydrogen is produced in quasi-quantitative yields, with turnovers as high as 1000 without appreciable loss of activity by the catalytic material (12). Similar behaviour occurs with cathodes modified by polymer films derived from a number of platinum metals complexes, including [(η^1-C_5Me_5)Rh(L)Cl]^+ (11, 13–15), [Rh(L₂Cl)]⁺ (16), [Rh(L)(PPh₃)₃Cl]⁺ (10) and [Rh(L)(COD)]⁺ (17), where L = bpy or phen derivatives.

**Electrocatalytic Hydrogenation of Organics**

These new materials have attractive potential applications for electrosynthetic processes, such as the electrocatalytic hydrogenation (ECH) of organic molecules (18). ECH is the reaction of an unsaturated substrate with the hydrogen produced at a cathode by discharging protons with electrons. ECH can thus be considered as the electrochemical analogue of conventional catalytic hydrogenation using a catalyst and molecular hydrogen; its main advantages are the in situ production of hydrogen at the surface of the catalyst (thus avoiding the use of hydrogen gas in cylinders) and much milder reaction conditions.

---

**Fig. 4** Reductive degradation by repeated scans in MeCN + 0.1 M n-Bu₄NClO₄ (scan rate 0.1 V s⁻¹) of a poly[(η^1-C_5Me_5)Rh(L)Cl]⁺ film prepared by the electroreduction in acidic MeCN of a film containing its parent chloro complex (Γₐ = 2 × 10⁻⁵ mol cm⁻²).
conditions, since the kinetic barrier for mass transport and splitting of the barely soluble hydrogen molecule is bypassed. However, the hydrogen consuming hydrogenation reaction is in competition with hydrogen evolution, and efficient ECH processes need to use cathodes that are more active than the conventional solid transition metal cathodes. Catalytic cathodes based on Raney nickel and noble metal particles deposited on carbon or dispersed in polymers have been developed for this purpose, and applied to a number of potentially useful electrosyntheses (18). However, the use of immobilised molecular hydrogenation catalysts, such as metal complexes, is a more appealing route, as their ability to co-ordinate substrates in a specific manner leads to high activity, regio- and stereospecificity in the ensuing catalytic reaction.

**Hydrogenation on Poly[Rh(L)₂Cl₃]⁺ Film Electrodes**

Platinum metals complexes have only recently been used as catalysts for the ECH of organic compounds. Undeniably, the best results have been obtained with polymer films grown on carbon electrodes by oxidative electropolymerisation of [Rh(L)₂Cl₃][BF₄] complexes (L = Lₙ, L₁, Lᵢ). These materials are very active for the hydrogenation of ketones and enones in aqueous electrolytes (16, 19, 20). Some striking
results are summarised in the Table; these show that hydrogenated products can be produced in high yields, and with good current efficiencies.

One important factor is the good operational stability of the cathodes, which could be re-used several times to hydrogenate millimolar amounts of different substrates, despite the low amounts (a few μmol) of immobilised catalyst, see the Table. Turnovers as high as 5000 have been reached with polymer films based on complexes containing ligands L₁ and L₂, see Figure 2, without significant loss of catalytic activity at the cathodes (20).

Comparative experiments, performed with similar complexes in homogeneous solution, have shown that the modified electrode is a more efficient system, as higher currents are obtained with lower amounts of catalyst. These observations can be explained by the high concentration of the active catalyst (up to 1 M) at the electron source, when the complex is polymerised onto the electrode surface.

Furthermore, differences between regio- and diastereoselectivity have been noted in homogeneous systems and polymer supported electrodes during ECH, especially with bulky substrates. For example, the major isomer formed upon catalytic hydrogenation of 4-tert-butylcyclohexanol on catalytic cathodes is always the trans-alcohol, while the major product in homogeneous catalysis is the cis-alcohol (19, 20). Changes in diastereoselectivity have also been observed during the hydrogenation of carvone to dihydrocarveol, because of polymer crosslinking, which has resulted in restricted permeability of the polymer matrix. This forced selectivity is attributed to the modification of the steric environment around the catalytic centre in the polymerised complexes; access and conformational mobility of the substrate being controlled by the polymeric matrix.

Enantioselective Electrocatalytic Hydrogenation

Of the methods reported for electrochemical asymmetric induction (21), the use of electrodes that are chemically modified by chiral complexes display the best results, as they can achieve asymmetric induction with extremely small amounts of the inducing reagent. It is expected that polymer films containing transition metal complexes with optically active ligands can be used in the preparation of catalytically active and chiral electrode/electrolyte interfaces, which can then be applied to asymmetric electrosynthesis.

The validity of this approach has recently been demonstrated using catalytic cathodes synthesised from [Rh(L₁)₂Cl₂][BF₄], where L₁ is a pyrrole-substituted chiral 2,2'-bipyridine (22), see Figure 2. Hydrogenations carried out with aryl ketones, such as acetophenone, 1-tetralone and 1-indanone, have shown that the corresponding alcohols are produced in moderate optical yields (5 to 12 per cent; the prevailing configuration

| Electrocatalytic Hydrogenation on C/poly[Rh(L)₂Cl]⁺ Modified Electrodes* |  |
|---|---|---|---|---|
| Ligand | Amount of complex, μmol | Substrate, amount, mmol | Product | Yield | Current efficiency, %⁺ |
| L₁ | 1.1 | | | 100 | 66 |
| L₂ | 1.4 | | | 100 | 87 |
| L₃ | 5.3 | | | 99 | 52 |
| L₄ | 6.6 | | | 98 | 63 |

* Carried out at -1.2 to -1.4 V vs SCE in water-ethanol mixtures, pH 8, containing 0.1 M LiClO₄ on modified carbon felt electrodes of dimensions 15 × 15 × 4 mm

⁺ The ratio mol of product to mol of electron passed  

R(++)-Carveol  

Mixture of diastereoisomers of dihydrocarveol
was always (S)). Results compare well with those obtained from hydrogen transfer promoted by homogeneous rhodium catalysts with various chiral bipyridines (23), which give a maximum enantiomeric excess of 15 per cent.

Comparative experiments performed in homogeneous solutions with \([\text{Rh}(L_2)\text{Cl}]^+\) as the electrocatalyst have shown that the enantioselectivity of the rhodium complex was fully retained in the films. Acetophenone was hydrogenated to (S)-phenylethanol with the same stereoselectivity (enantiomeric excess 12 per cent) on the \(L_r\)-based modified electrode and with the soluble catalyst containing \(L_s\). This preliminary study clearly shows that for asymmetric electrocatalytic hydrogenation, effective use can be made of the selectivity of a chiral platinum metal complex, in homogeneous solution, or better still, on a polymer film modified electrode.

**Role of Hydride Complexes in the Mechanism of Electrocatalytic Hydrogenation**

The electrocatalytic hydrogenation of organics using 2,2'-bipyridine rhodium(III) complexes can be explained either by the catalytic reaction of an unsaturated compound with molecular hydrogen produced at the cathode, or by its reaction with a rhodium hydride intermediate. The former hypothesis can be ruled out by taking into account the poor solubility of hydrogen in aqueous media; also quantitative current yields (close to 100 per cent) have been reached for the hydrogenation of a number of substrates. This means that all the dihydrogen, or “hydrogen equivalents” produced have been consumed. However, hydrogenation via a reactive rhodium hydride intermediate is likely to take place, by analogy with the mechanism postulated for hydrogen transfer catalysed by \([\text{Rh}(bpy)]^+\) complexes in 2-propanol/KOH (23). A plausible electrocatalytic cycle is depicted in Figure 6. The hydride complex, formed by reaction of the electrochemically reduced \(\text{Rh}(I)\) complex with water, Step (a), reacts with a substrate \(S\), Step (b). In Step (c), the hydrogenated product \(SH_2\) and a \(\text{Rh}(III)\) complex are released following attack by water. In Step (d), the \(\text{Rh}(III)\) complex is then reduced at the applied potential, to regenerate \([\text{Rh}(L_2)]^+\), which can then enter a new cycle.

This rhodium hydride complex has been postulated as the key intermediate in other catalytic reactions, such as photochemical water reduction (24) and electrochemical regeneration of
NADH from NAD⁺ (5) with rhodium polypyridyl complexes. However, under these catalytic conditions it is too reactive to be detected, although its formation upon protonation of [Rh(bpy),]⁺ has been well established (25).

The participation of metal hydride complexes in the electrocatalytic hydrogenation process has been further corroborated by study of the electrocatalytic activity of different rhodium and iridium complexes. Indeed, it has been unambiguously demonstrated that complexes of [(η⁵-C₅Me₅)MⅢ(L)Cl]⁺ (M = Rh and Ir) and [Rh(L)(PPh₂Et₂)Cl₂]⁺ in polymer films are readily transformed to their hydride derivatives upon electroreduction in protic electrolytes, see above. Their ability to act as electrocatalysts for the hydrogenation of unsaturated organic substrates in aqueous electrolytes (10, 11) is in good agreement with a mechanism involving hydride species. These complexes appeared much less active than [Rh(L)₂Cl₂]⁺ complexes. Thus, the electrocatalytic activity of such transition metal complexes for the hydrogenation of organics is strongly dependent on the stability of their hydrido derivatives.

A similar trend has been observed for the electrocatalytic reduction of carbon dioxide into formate by [(η⁵-C₅Me₅)Rh(bpy)Cl]⁺ complexes (M = Rh and Ir), where it appears that the best catalyst is the rhodium complex which gives the less stable, thus more reactive, reduced hydrido species (13).

**Catalytically Active Films of Other Platinum Metal Complexes**

Polymer materials derived from other platinum metal complexes, such as [Rh(bpy)(COD)]⁺ (17) and [Pd⁶(bpy)₆]²⁺ (26), have also been applied to the ECH reaction. In particular, modified electrodes synthesised by oxidative electropolymerisation of [Pd(L)₃][2BF₄] are active for the selective hydrogenation of activated olefins in aqueous media (26). The latter reaction is likely to proceed via a metal hydride species, formed from the doubly reduced Pd(0) complex.

However, there is no experimental evidence for such an intermediate hydrido complex. It must be emphasised that the reduced form of the palladium complex is stable in its polymerised form, as well as in organic and aqueous electrolyte, while it decomposes to metallic palladium and free bpy in homogeneous electrolytes. This increased stability of the polymerised complex could result from a slower deco-ordination reaction associated with electron transfer in the polymeric matrix.

**Conclusions**

The development of catalytic cathodes by immobilising molecular hydrogenation catalysts on conducting surfaces may elicit new interest in the electrocatalytic hydrogenation process, alongside the already growing interest in electrosynthesis using metal complexes. These new electrode materials offer several advantages over the same complexes used in homogeneous solution: greater stability in the immobilised form, smaller amounts of catalyst and the possible avoidance of solubility problems in aqueous media. Furthermore, entrapping a metal complex in a polymer film coated onto an electrode surface improves its operational stability, and increases turnover. Stereoselective hydrogenations using electrode materials based on chiral metal complexes may also provide a way to asymmetric electrosyntheses, a goal that has been attempted, but not yet satisfactorily achieved.

Lastly, further development could make use of grouping, in the same polymer matrix, different selected catalytic partners, with a view to achieving electrocatalytic syntheses which involve multielectronic steps.

**References**


*Platinum Metals Rev.*, 1998, 42, (2)
Structural Nickel-Doped Iridium-Aluminium Materials

Materials used in high temperature structural applications are now required to withstand higher operating temperatures than ever before in the drive for more efficient function of equipment and plant. This is particularly true for materials used in high performance gas turbine engines where the nickel-based superalloys currently used reach their operational limit at $<1200^\circ$C. One focus of work in this area for the next generation of materials has been the ordered intermetallics, and NbAl has been intensively investigated, but it shows poor ductility and low oxidation resistance.

Now, scientists at Iwate University in Japan report on the high temperature strength and ductility of ordered intermetallics, based on iridium, specifically IrAl and Ir$_{x}$Ni$_{1-x}$Al (with $x=0-0.8$) at temperatures of 25 to 1400°C (A. Chiba, T. Ono, X. G. Li and S. Takahashi, Intermetallics, 1998, 6, (1), 35–42). The high melting point of iridium at 2243°C may impart excellent high temperature strength, while the formation of a surface film of Al$_2$O$_3$ is anticipated to give good oxidation resistance.

Compression testing confirmed the postulated high room-temperature strength of IrAl at $\sim$1900 MPa but revealed little ductility below 800°C. The ductile-brittle transition occurs between 800 and 1000°C, and above this there is pronounced compressive ductility resulting in steady state deformation after yield. The Ir$_{0.3}$Ni$_{0.7}$Al exhibits good ductility above 800°C but work hardens during deformation at 1000°C. Below 800°C its ductility is inferior to that of IrAl.

Adding nickel improves the ductility of IrAl, but the ductile-brittle transition temperature decreases with increasing nickel. At yielding IrAl is an order of magnitude stronger than NiAl, and Ir$_{0.3}$Ni$_{0.7}$Al shows improved strength by a factor of $\sim$5. Generally, the strength of Ir$_{x}$Ni$_{1-x}$Al decreases with increased nickel content.

The creep behaviour of the materials also differs markedly. Both IrAl and NiAl exhibit normal primary creep where the creep rate decreases with increasing strain, but Ir$_{0.3}$Ni$_{0.7}$Al exhibits inverse primary creep. The steady state secondary creep of Ir$_{0.3}$Ni$_{0.7}$Al was measured between 950 and 1100°C, giving an activation energy, $Q_a$, of 400 kJ mol$^{-1}$ and steady-state exponent $n = 3.2$, typical of class I behaviour. Microstructural analysis revealed that only Ir$_{0.3}$Ni$_{0.7}$Al and NiAl exhibited a single-phase type B2 structure; IrAl contained secondary phase precipitates, contradicting earlier reports of an ordered single-phase structure from 48 to 52 mol%. The authors postulate that this may be due to deficiencies in their homogenisation heat treatments, and thus could not accurately produce the activation energy and exponent for IrAl. However, an exponent of 4.2 and class II behaviour are suggested. Creep strengths of IrAl and Ir$_{0.3}$Ni$_{0.7}$Al were four orders of magnitude higher than for NiAl for a given applied stress.

Overall, results are promising for the IrAl/NiAl based systems, although the relatively low temperatures of the present study would suggest that further evaluative work would be of considerable benefit.
This book covers the science and technology of structured catalyst supports which exhibit significant improvements in performance compared to conventional fixed bed catalysts. Each chapter is dedicated to a specific topic and written by eminent authorities (thirty-six of them). It is well balanced, with a good combination of fundamental and practical information about areas already penetrated by this technology and also in general catalysis. Many of the applications discussed involve the noble metals.

Structured catalysts are ceramic and metallic configurations, usually prefabricated, which constitute both the catalyst support and the reactor. There are three basic types:

- monoliths, in the form of continuous unitary structures containing small passages with walls loaded with catalytically active agents;
- membrane catalysts – structures with permeable walls between passages, thus allowing selective transport of reactants or products; and
- arranged catalysts, which are either arrays of particles or sheets superimposed, to allow cross-flow. Each type has distinct advantages over beds of packed particles. For example, monoliths have large void fractions (0.7 to more than 0.9) resulting in a very low pressure drop in the structure. Membrane reactors allow selective products to diffuse from the reaction zone, thus driving reversible reactions beyond normal equilibrium conversions and arranged catalysts are characterised by intensive radial mixing. These advantages have led to significant commercial applications.

Chapter 1 begins with an overview of structured catalysts, classifying them in terms of their design, support material, mixing conditions and mode of operation, while emphasising their lack of randomness when functioning as a reactor bed. Much of this chapter is devoted to monoliths used as automotive exhaust converters and stationary devices.

Monoliths, with no convective mass transfer over the reactor cross-section (honeycombs), are treated in Part I, with four chapters dealing comprehensively with automotive exhaust catalysis. There is considerable overlap, but it is refreshing to find similar material treated with a different approach by authors from disparate backgrounds. For example, the emphasis in Chapter 2 is upon ceramic monoliths used in exhaust converters, their structure, properties and fabrication, and attention is paid to materials as viewed by ceramic science. Chapter 3 briefly reviews general industrial applications of metal catalysts and looks at the properties and performance of coated metallic monoliths. Autocatalysts are reviewed from the perspective of catalytic science in Chapter 4. These chapters emphasise the systems approach to optimising these devices. Finally, Chapter 8 looks at the salient features in modelling the performance of converters.

The next largest application for monolithic catalysts – the selective reduction of NOx with ammonia and catalytic combustion or oxidation of fuel – is covered in Chapters 5 and 6. Chapter 5 describes the monolith structures used in stationary devices and how they differ from automotive converters, and then discusses modelling the reactors and the process, with clear descriptions of steady- and unsteady-state operations and reverse flow systems. These devices treat the effluent from combustion processes. Chapter 6 introduces the benefits of using catalytic combustion to reduce emissions. Combustion chemistry is invoked to demonstrate the advantages of monolithic beds loaded with metal catalysts, most of them from the platinum group. In particular, the role of the washcoat and its relationship to performance is thoroughly covered.

Unconventional utilisations of monolithic catalysts are described in the remainder of Part I.
where the low pressure drop across the monolith allows very fast flow rates and short contact times, is reviewed; this facilitates oxygen insertion reactions without complete combustion. The coverage of monolithic honeycomb catalysts ends with their use for three-phase reactions, involving gas-liquid reactors in different modes. This includes chapters on technical descriptions of the reactors, modelling of gas-liquid flow in the monoliths and applications to gas-liquid counter flows, illustrating how monolith technologies may reach into innovative areas.

Part II considers structured catalysts with convective mass transfer over the cross-section of the reactor. Four chapters occupy just under a hundred pages, which may indicate that this is still an emerging field. Chapter 12 reviews parallel-passage reactors (PPR) and lateral-flow reactors (LFR), which are devices in which flow occurs along catalyst layers instead of through a bed of particles. The chapter ends with a description of a commercial flue gas desulphurisation process utilising these concepts. Chapter 13 introduces the “bead-string reactor”, consisting of conventional catalyst particles fixed on arrangements of parallel strings. The potential advantages of the bead-string reactor are explained, but it “is still in an early stage of development”. The flow patterns and mass and heat transport in the reactor and modelling techniques are described, but no practical applications.

Open cross-flow-channel catalysts, such as those encountered in catalytic distillation packing, are described in Chapter 14. Washcoated metal, the particle-filled sandwich, and ceramic extrudates are used as examples of these structures. Two-phase operations are discussed.

Part III concentrates on monolithic reactors with permeable walls (or membrane reactors). It includes metal membranes, inorganic membranes, diesel exhaust aftertreatment, zeolitic membranes, and cross-flow reactors with permeable walls. Although these topics are covered in more detail elsewhere, they are a useful extension to the general subject of structured catalysts. Chapter 16 is predominately concerned with palladium-containing membrane reactors, in which the selective diffusion of hydrogen alleviates thermodynamic equilibrium limitations found in hydrogenation and dehydrogenation processes. The principles are briefly explained, and examples of metallic wall and metal loaded porous ceramic wall reactors are given. Tables give referenced applications, but there are no large-scale operations. Economic processing of the ceramic components will no doubt evolve, leading to greater utilisation of this technology.

Inorganic membrane reactors offer a wide range of molecular and ionic permeability and Chapter 17 gives a very thorough overview. Tables list examples from the literature, but there are as yet no large scale applications.

Ceramic catalytic filters for diesel exhaust after-treatment are reviewed in Chapter 18. Except for the fact that the device contains micropores which trap and oxidise soot, the material seems strangely out of place in this section and would be better in Part I. However, innovative methods for solving an important problem are addressed.

Zeolitic membranes (Chapter 19) are well referenced, with the fundamentals clearly presented, giving an appreciation of the importance and challenges of this topic. Finally, Chapter 20 reviews cross-flow reactors with permeable walls, such as those in solid oxide fuel cells and electrochemical cell reactors. Design, modelling and scale-up are covered to a limited degree.

Part IV discusses catalyst preparation and characterisation. Chapter 21 gives details, recipes and references for preparing ceramic monoliths, washcoating and dispersing the active species. It is a valuable collection of data for researchers and designers. The last chapter is almost an afterthought, but very necessary to readers using porous structures. Descriptions of models for systems of pores help to clarify an otherwise complex subject.

“Structured Catalysts and Reactors” is a welcome addition to the catalysis bookshelf, adding to our understanding of the functions of these advanced structures, but it is disappointing that ceramic foams in catalysis or recent advances in micro-scale reactor devices were not included. Part I will be particularly useful to readers of this journal, while catalysis practitioners will find all of benefit. JAMES T. RICHARDSON
Homogeneous Catalyst for Alkane Dehydrogenation

AN IRIDIUM CATALYST NEEDING NO HYDROGEN RECEPTOR

By David T. Thompson
Consulting Chemist, Reading, England

The removal of hydrogen from alkanes to give alkenes is an important commercial objective, as alkenes are widely used as organic feedstocks in industrial processes involving chemical synthesis and polymerisation. This reaction is, however, significantly endothermic, needing up to 30 kcal per mole, and normally occurring at temperatures exceeding 400°C in the presence of heterogeneous supported metal catalyst systems in the gas phase. The conversion of alkanes to aromatic molecules (as part of ‘catalytic reforming’) is even more important and is also effected using supported metal catalysts, such as platinum on high surface area alumina. For these kinds of reactions to be achieved with a homogeneous catalyst in solution, under milder conditions, the use of hydrogen acceptors has been thought essential; that is, the conversions have been achieved via ‘transfer hydrogenation’. A possible alternative means for achieving the dehydrogenation reaction would be irradiation with UV light, but this is not usually industrially attractive.

In early work, R. H. Crabtree and co-workers (1) used IrH₂{(O₂CCF₃)(PPr')₂ to effect the dehydrogenation of alkanes to arenes via oxidative addition at 150°C in the presence of the hydrogen acceptor, tert-butylethylene. However, it was thought that this system was not catalytic because hydrogenolysis of the phosphine P-C bonds occurs at temperatures of 135°C or above: the temperatures needed to release arenes from the intermediate complexes.

The five-co-ordinate iridium P-C-P pincer complex (PCP)IrH₂{(O₂CCF₃)(PPr')₂, where PCP = n²-C₆H₆(CH₂P(tert-C₆H₅)₃)₃₋₁₆, was reported by Jensen, Kaska and their colleagues (2) to be a highly active homogeneous catalyst for the transfer dehydrogenation of cyclooctane, with unusually long-term stability for temperatures as high as 200°C. This catalyst was subsequently demonstrated to be useful for the catalytic transfer dehydrogenation of cycloalkanes to arenes (3). For example, cyclohexane was dehydrogenated to cyclohexene and benzene in the presence of (I) and tert-butylethylene, the latter being converted almost quantitatively into tert-butylethane. This special reactivity is ascribed to the presence of the P-C-P ligand, which renders the metal centre reactive with saturated hydrocarbons, but restricts its access to the ligand P-C bonds. It was claimed that the P-C-P pincer complex could promote accessibility to previously unattainable catalytic pathways.

In collaborative research between members of the Chemistry Departments of Rutgers, New Jersey, the University of Hawaii and the University of California, Santa Barbara, Goldman, Jensen, Kaska and co-workers (4) have now shown that cycloalkanes can be efficiently dehydrogenated using (I) as catalyst to give the corresponding cycloalkene and dihydrogen, without using a hydrogen acceptor; and several hundred mol product are produced per mol catalyst. However, after several hundred catalytic cycles, conversion decreases, and this is thought to be due to the alkene product increasingly inhibiting the catalyst by co-ordination to catalyst sites, as its concentration increases.

In principle, the temperatures used are sufficiently high to overcome the large positive enthalpy of dehydrogenation without the use of...
a hydrogen acceptor. The dehydrogenations reported are the first efficient homogeneous dehydrogenations of alkane not using light irradiation (5) or a sacrificial hydrogen acceptor.

When refluxing a cyclooctane solution of (I), with a stream of argon passing over the condenser, the initial rate of cyclooctene formation is 11 turnovers h⁻¹. After 44 hours, 104 turnovers are obtained and after 120 hours, 190 turnovers. These results should be compared with those from IrH₂(O₂CR)(PCy₃)₂, the most active soluble 'acceptorless' dehydrogenation catalyst previously investigated. This was reported to give 1.41 turnovers h⁻¹ cyclooctene, with a maximum of 28.5 turnovers obtained after 48 hours (6, 7).

The potential for industrial applications of the present iridium catalyst system requires further development, and the chemistry reported to-date needs extending and evaluating (8). It will be necessary to increase the rates achieved so far by two to three orders of magnitude and improve efficiency. As indicated above, conversion drops after several hundred turnovers, probably because the olefinic product bonds to the vacant co-ordination sites on the catalyst. Since the reaction slows down when the product alkene concentration reaches 5 to 10 per cent, continuous removal of product by distillation or by some other means may be possible, so that catalyst activity is maintained. The catalyst also needs evaluating with linear alkanes, since the biggest commercial rewards lie here. For instance, cyclooctane has a dehydrogenation enthalpy of only 23.3 kcal mole⁻¹ but alkanes typically require about 28 to 30 kcal mole⁻¹ for the elimination of hydrogen from two secondary C-H bonds (4). The ability to promote the conversion of alkenes or cycloalkanes to aromatics by direct dehydrogenation in the absence of a sacrificial hydrogen acceptor, would also constitute a significant advance.

As the iridium system (I) catalyses the hydrogenation of arenes to cycloalkanes, as well as the reverse reaction, the potential of these systems for hydrogen storage could be explored. By coupling the dehydrogenation and hydrogenation reactions, hydrogen could be cyclically stored and released, for applications such as the supply of hydrogen to the fuel cells used in electric cars. When all the cycloalkanes have been dehydrogenated, the arene products could be 'refuelled' by re-hydrogenation from an external hydrogen source. The idea of using alkanes as a hydrogen storage source is not new, but until now there has been no means of dehydrogenating them at moderate temperatures.

References

Catalysis Technical Guide
Johnson Matthey Chemicals North America has just published a “Catalysis Technical Guide”, containing information on heterogeneous and homogeneous catalysis using the platinum metals.

The “Heterogeneous Catalysis” section begins with a concise description of the critical factors to be considered in the design and selection of the most appropriate catalyst for each application. Commercially significant hydrogenations using powdered and particulate catalysts are described individually and specific catalysts are recommended. Hydrogenation of aromatic rings, aldehydes, ketones, nitro compounds and benzyl protecting groups are only a few examples of the reactions described.

The “Homogeneous Catalysis” section begins with a brief introduction to the concepts and terminology, key to understanding these processes. Among the synthetic reactions individually described are hydrogenation, isomerisation, carbonylation, Heck coupling and allylic alkylation. A section is devoted to the increasingly critical area of chiral homogeneous catalysis.

Each section has guidelines for the safe handling of catalysts. For more information contact: Johnson Matthey, telephone: (+1)(609) 384-7000 or (+1)(800) 444-1411; fax: (+1)(609) 384-7282.
Some New Aspects of the Photoreactions of Platinum Metals Complexes

By Liu Weiping, Yang Yikun and Xiong Huizhou
Institute of Precious Metals, Kunming, P. R. China

and Fu Wenfu
Department of Chemistry, Yunnan Teacher’s University, Kunming, P. R. China

Photochemical reactions of platinum metals complexes are of great importance in contributing to the understanding of the chemical reactivity and catalytic properties of platinum metals catalysts. This paper reviews some new aspects of this photochemistry and discusses potential applications in synthesising novel complexes and in exploiting platinum metals-containing catalysts. Among aspects examined are recent trends in the photochemistry of co-ordination compounds, particularly photointramolecular rearrangements, photoredox elimination and addition reactions, and the photoredox reactions of polynuclear complexes.

The photochemistry of co-ordination compounds, particularly of the platinum metals complexes, is regarded as an important area of chemical research (1). The photochemistry of platinum metals complexes has been studied since 1962 when the photochemical behaviour of PtCl$_2^-$ was first reported (2). Previously, researchers in this area concentrated mainly on classical platinum metals complexes, and identified three typical types of photoreactions: photosubstitution, photoisomerisation and photoredox reactions (3). Recently, however, some new types of photoreactions, such as photointramolecular rearrangements, photoredox elimination and addition reactions, and photoredox reactions of polynuclear complexes, have been identified and investigated. These interesting reactions may contribute to the understanding of the reactivity of chemical compounds, and to the exploitation of novel catalytic processes. This increased interest in these new photoreactions of the platinum metals complexes is reviewed here briefly.

Photointramolecular Rearrangements

Photointramolecular rearrangements consist mainly of redox and non-redox isomerisations. Photoredox intramolecular isomerisations of platinum metals complexes are reactions in which the molecular formula of the complex is preserved, but the composition of the individual ligands, the oxidation number of the central atom and also, in some instances, the coordination number of the central atom are changed.

A photoredox rearrangement reaction is frequently one of the steps that occurs in the mechanism of catalytic processes and syntheses of organometallic compounds (4). For example, the photochemical transformation of the π-complex, [Pt$^0$(PPh$_3$)$_2$(NCC$_2$CN)], gives rise to a reactive Pt(II) intermediate which can be isolated. The intermediate, which is prepared by continuous photolysis of the π-complex, is also the first example of a complex that contains a -CC=CN group as a ligand (4).

Upon irradiation of the related tetracyanoethylene platinum(0) π-complex, the reaction

\[ (\text{PPh}_3)_2\text{Pt}^0 \xrightarrow{\text{hv, MLCT}} (\text{PPh}_3)_2\text{Pt}^+ \]
These reactive Pt(II) intermediates may release radicals -CN, -C≡CN or -C(CN)=C(CN), which can be further reacted with other compounds to form desired products, such as R-CN, R-C≡C-CN or R-C(CN)=C(CN),.

Continuous photolysis of [Pt(PPh₃)₂(C,H₄)] at 254 nm also results in a photoredox intramolecular rearrangement, forming a tetra co-ordinated π-complex (6). This is an interesting and potentially useful photochemical transformation of an olefin complex into an ethyl complex. This phototransformation may hold promise for the hydrogenation of olefinic compounds.

Photoisomerisation reactions of geometrical isomers are non-redox intramolecular rearrangements. So far, studies have been directed particularly towards photochemical cis ↔ trans and mer ↔ fac conversions of platinum metal complexes. This type of photoconversion has been used as a method to synthesise isomers which are difficult to obtain via thermal reactions, as shown in the following Equations (3, 7, 8):

\[
\text{trans-}[\text{PdCl}_2(\text{P} \text{Et}_3)_2] \xrightarrow{313 \text{ nm}} \text{cis-}[\text{PdCl}_2(\text{P} \text{Et}_3)_2] \quad \text{Yield} = 70 \%
\]

\[
\text{cis-}[\text{PtCl}_2 \text{Py}_2] \xrightarrow{362 \text{ nm}} \text{trans-}[\text{PtCl}_2 \text{Py}_2] \quad \text{Yield} = 60 \sim 80 \%
\]

\[
\text{fac-}[\text{Rh(acac)}_2] \xrightarrow{\text{hv}} \text{mer-}[\text{Rh(acac)}_2] \quad \text{MLCT}
\]

Another type of non-redox intramolecular rearrangement is the photoisomerisation of co-ordinated ligands, such as the thermally stable trans-4-styrylpyridine to the cis-form (9):

In some cases, intramolecular rearrangement involves proton transfer between two co-ordinated ligands, as is observed during the irradiation of [Ir(bpy)₂(H₂O)]⁺ in which one of the 2,2'-bipyridine ligands is bonded monofunctionally (10).

For reactions of this type, a knowledge of the photochemical generation of reactive intermediates may possibly be applied to the catalytic processes in organic syntheses, where the complex can activate the shift of hydrogen from the water molecules to other compounds under irradiation.

**Photoredox Elimination and Addition Reactions**

Photoredox elimination and addition reactions are characterised by changes both in the oxidation number of the central atom and in the co-ordination number of the platinum metal complex. Photoredox reactions depend on the nature of the excited states. In the case of metal-to-ligand charge-transfer (MLCT) excitation, the nature of the excited state will determine the process of the reaction (11). An increase in the oxidation number is usually accompanied...
by an increase in the co-ordination number and vice versa. The former reactions are called oxidative addition and the latter reductive elimination.

The localisation of the excited electron in the ligand π* orbital causes a decrease in the electron density on the metal centre and an increase in electrophilicity, which will promote nucleophilic attack on the metal centre, that is, oxidative addition. The reactive part of the ligand, particularly organic compounds, bonds to the vacant, unoccupied site on the central atom with simultaneous oxidation of the central atom, for example (12, 13):

\[
\text{[Pt}^\text{II}(\text{Me})_2(\text{phen})] \rightarrow \text{[Pt}^\text{III}(\text{Me})_2(\text{phen})]^* \\
\text{MLCT excited state} \\
\text{hv} \rightarrow \text{[Pt}^\text{II}(\text{Me})_2(\text{phen})] \\
\text{hv} \rightarrow \text{[Pt}^{IV}(\text{Me})_2(\text{phen})]
\]

The release of nitrogen from trans-\[Pt^{IV}(CN)_4(N_2)_2\] during irradiation at 254 nm is another example of reductive elimination (17):

\[\text{trans-}[\text{Pt}^{IV}(\text{CN})_4(\text{N}_2)_2]^{2-} \rightarrow [\text{Pt}^{VI}(\text{CN})_4]^{2-} + 3\text{N}_2, \text{LMCT}\]

The tetrameric complex \[\text{[Pt}(\text{CH}_3)_2\text{I}]\], consists of monomeric components which undergo a photochemical reductive elimination releasing methyl radicals (18):

\[\text{[Pt}^{IV}(\text{CH}_3)_2\text{I}] \rightarrow \text{[Pt}^{II}(\text{CH}_3)_2\text{I}], + 2\cdot\text{CH}_3, \text{LMCT}\]

Ligand-to-metal charge-transfer (LMCT) states involve electronic transitions from a ligand orbital to a metal orbital. The elimination reactions of LMCT states are different from those of MLCT states since a decrease in the oxidation number of the central atom is usually accompanied by the release of the co-ordinated ligands.

The electronic transitions of the LMCT excited state are usually observed at a high energy band in organometallic complexes. The metal centre is in a high oxidation state and delocalisation of the electron density from the occupied ligand orbital to an empty metal orbital may occur in such an excitation. For example, irradiation of trans-[PtHX(PPh,P)]₂, where X = CH₂CN or CF₃, produces free HX (16):

\[
\text{hv} \rightarrow \text{[Pt}^\text{II}(\text{PPh}_2)_2] + \text{HX}
\]

The photoredox addition reaction has been successfully used to synthesise platinum blue (14-15):

\[
\text{cis-}[\text{Pt}(\text{NH}_3)_2(\text{H}_2\text{O})_2]\text{SO}_4 \rightarrow \text{cis-}[\text{Pt}(\text{NH}_3)_2(\text{H}_2\text{O})_2]\text{SO}_4
\]

This is, in fact, a photoinduced activation of C-H bonds. C-H bond activation is very important for a number of industrial processes which cleave C-H bonds (20). For example, \[\text{L}_2\text{PtH}_2\], where L is (t-Bu)_2P(CH₂)₂P(t-Bu)_₂ or (Men)_2P(CH₂)₂P(Men)_₂ (Men = menthane) is thermally stable and shows no tendency to lose hydrogen.

However, it is quite photoactive, and irradiation in benzene leads to reductive elimination of hydrogen to generate \[\text{L}_2\text{Pt}\] fragments which produce \[\text{L}_2\text{Pt(Ph)H}\] as the exclusive oxidative
product (21). As a result, benzylic C-H bonds have been activated.

\[ \text{L}_2\text{PtH}_2 \xrightarrow{hv} \text{MLCT} \quad \text{L}_2\text{PtC}_6\text{H}_6 \xrightarrow{\text{L}_2\text{Pt}} \text{L}_2\text{Pt} \]

Irradiation of mixed ligand azido complexes of Pd(II) and Pt(II) in MLCT processes produces \( \text{L}_n\text{M}^n \) where \( n = 1, 2 \) with the release of \( \text{N}_2 \), followed by \( \text{L}_2\text{M} \) activation of C-C bonds, which catalyses the oligomerisation and cyclisation of acetylene and derivatives (22, 23).

\[ \text{ML}_n\text{N}_3 \xrightarrow{hv} \text{N}_2 + \text{L}_n\text{M} \]

In particular, the very convenient photochemical generation of the catalytically active species \( \text{L}_2\text{M} \) should be stressed. Compared with thermal reaction pathways, catalysts are formed photochemically in one reaction step and hence with high selectivity (24). As selectivity is the essence of catalysis, its achievement is central to chemical research. Furthermore, the population of different electronically excited states, depending upon the wavelength of the radiation, provides a method of tuning between different reaction pathways (25).

Solvent effects play an important role in a number of photoinduced electron-transfer reactions. In some aerated solvent systems, such as CHCl₃, which contain [Ru(bpy)₂Cl₂] or [Ru(bpy)₂Cl₂]⁺, irradiation causes transformation to the other complex, induced by a solvent-initiated radical chain reaction (26, 27). The photolysis of aqueous Carboplatin, see below, demonstrates that under a nitrogen atmosphere at 254 nm irradiation, a photoredox reaction occurs to produce platinum (28, 29).

Thus, studies of photoredox elimination and addition reactions are very promising, as the formation of the intermediates as well as the final stable products may find practical application.

**Photoredox Reactions of Polynuclear Complexes**

Polynuclear complexes of the platinum metals undergo redox reactions different from those of mononuclear complexes where charge transfer usually occurs between the central atom and the ligands. Irradiation of a polynuclear complex involves an intramolecular electron-transfer reaction between the central atoms, which are connected by a bridging ligand (30, 31).

Photoredox reactions of ligand-bridged metal complexes induced by metal-to-metal charge transfer (MMCT) excitation have been investigated extensively (31):

\[
\frac{[\text{NH}_3\text{Ru}^n\text{(PZ)}\text{Ru}^m\text{(EDTA)}]^+}{\text{PZ} = \text{pyrazine}} \xrightarrow{hv} \text{MMCT} \quad [\text{NH}_3\text{Ru}^n\text{(PZ)}\text{Ru}^m\text{(EDTA)}]^+ \\
\]

If a binuclear complex has at least one central atom which forms kinetically labile complexes during irradiation, decomposition of the complex from the MMCT excited state can happen (32).

\[
[\text{NH}_3\text{Co}^m\text{-NC-Ru}^n\text{(CN)}] \xrightarrow{375 \text{ nm}} \text{MMCT} \quad [\text{NH}_3\text{Co}^m\text{-NC-Ru}^n\text{(CN)}]^{-} \xrightarrow{} \text{Co}^{m+} + 5\text{NH}_3 + [\text{Ru(CN)}]^+ \\
\]

The dinuclear rhodium complex, \( (\mu\text{-tetraphenylporphinato})\text{bis(dicarbonyl)rhodium(I)} \) \( ([\text{TPP}]\text{Rh}^1\text{(CO)}_2] \) also undergoes a photodecomposition reaction (33):

\[
[\text{TPP}]\text{Rh}^1\text{(CO)}_2] \xrightarrow{hv} \text{MMCT} \quad [\text{TPP}]\text{Rh}^1\text{(CO)}_2] + \text{Rh}^0 + 2\text{CO} \quad \text{b} \text{enzene} \quad [\text{TPP}]\text{Rh}^0 + \text{CO} \\
\]

Irradiation of the complex \( [\text{Cp}^*\text{Rh}^1\text{(CO)}_2]_2 \) in the presence of \( L \) (\( L = \text{tetracyanoethylene} \))
causes a dissociative reaction, to give a mononuclear product (34).

\[ \text{[Cp}^*\text{Rh(CO)}_3] \text{L} \xrightarrow{\text{hv}} \text{Cp}^*\text{Rh(CO)}_2\text{L} \]

Oxidative addition of ArX (Ar = aryl, X = Br, I) to the excited state of \([\text{Pt}_3\text{(μ-P}_2\text{O}_2\text{H}_2)]^4^-\) can be observed, giving the axially distributed complex (35, 36).

\[ \text{[Pt}^\text{n}(\text{μ-P}_2\text{O}_2\text{H}_2)^{\text{μ-Br}}]^4 + \text{ArX} \xrightarrow{\text{hv}} \text{[ArPt}^\text{μ}(\text{μ-P}_2\text{O}_2\text{H}_2)^{\text{μ-Br}}]^4^- \]

Photoexcitation of mononuclear complexes may result in the production of polynuclear complexes. The composition of the product and its structure depend on the properties of the central atom. With \([\text{IrH(PF)}_3]\), a complex with a metal-metal single bond is formed:

\[ 2[\text{IrH(PF)}_3]\xrightarrow{\text{hv}} \text{H} + [(\text{PF})_2]\text{Ir}^\text{μ}-\text{Ir}^\text{μ}(\text{PF})_3]\]

While a double-bridged compound is produced from a mixture of \([\text{IrH(PF)}_3]\) and \([\text{CoH(PF)}_3]\) (37):

These different photoreactions of various platinum group metals complexes could open up pathways to the formation of further interesting complexes, and the increasing knowledge of the photochemical behaviour of polynuclear complexes may indeed lead to the development of new types of platinum metals catalysts.

References

3. Liu Weiping and Yang Yukin, Precious Metals (China), 1997, 18, (2), 53
ABSTRACTS
of current literature on the platinum metals and their alloys

PROPERTIES
High Temperature Phase Transitions in Al\textsubscript{1-x}Pt\textsubscript{x}
Pt-rich Al-Pt alloys were produced from the reaction of Al oxide and Pt in H\textsubscript{2} at 1200°C. Upon heating, alloys with a slight tetragonal distortion underwent a second order phase transition into a cubic phase, while alloys with a stronger tetragonal distortion underwent a corresponding first order phase transition. In the former case this distortion was progressively relieved with increasing temperature, but discontinuously in the latter case.

Structure and Chemical Composition of Surfactant-Stabilized PtRu Alloy Colloids
In situ XRD was used to study unsupported and SiO\textsubscript{2}-supported clusters of PtRu[N(Oct)\textsubscript{2}Cl], (Pt:Ru ~ 1:1).

Permeability of Hydrogen in Amorphous Pd\textsubscript{1-x}Si\textsubscript{x} Alloys at Elevated Temperatures
H\textsubscript{2} permeabilities of amorphous Pd\textsubscript{1-x}Si\textsubscript{x} (x = 0.15, 0.175, 0.2) alloys, formed as ribbons by a single roller spinning technique, were measured at ≤ 390°C. The H\textsubscript{2} permeability decreased with increasing Si content and the amorphous alloys had 3–5 times higher permeability than corresponding crystallized alloys.

A New Molecular Superconductor β'-Et\textsubscript{2}Me\textsubscript{5}P[Pd(dmit)\textsubscript{2}]
The anion radical salt β'-Et\textsubscript{2}Me\textsubscript{5}P[Pd(dmit)\textsubscript{2}] is non-metallic at ambient pressure but metallic under pressure with a superconducting transition in the range 6.9–10.4 kbar with T\textsubscript{c} = 4.0–1.8 K (onset). At higher pressures it is non-metallic at low temperature. The isostructural salt β'-Et\textsubscript{2}Me\textsubscript{5}Sb[Pd(dmit)\textsubscript{2}] also shows pressure induced metallic behaviour, but no superconducting transition above 1.6 K, and remains metallic at pressures up to 16.4 kbar.

Phase Formation Process of Ir\textsubscript{x}Si\textsubscript{1-x} Thin Films. Structure and Electrical Properties
Phase formation processes in amorphous Ir\textsubscript{x}Si\textsubscript{1-x}, thin films with 0.30 ≤ x ≤ 0.41 were studied in relation to electric transport properties. Distinct phases were observed depending on the initial composition: Ir\textsubscript{x}Si\textsubscript{1-x}, Ir\textsubscript{x}Si and Ir\textsubscript{3}Si. However, for a Si concentration of 61–64 at.%, an unknown metastable phase was found in films after annealing above the crystallisation temperature of 970 K. This was found to be monophasic, b.f.c. with lattice constants a = 1.027 nm, b = 0.796 nm, c = 0.609 nm and γ = 113.7°.

The Optical Properties of RuSi: Kondo Insulator or Conventional Semiconductor?
Single-phase RuSi acts as a simple metal in its high temperature phase (CsCl type). In its low temperature phase (FeSi type) it is a semiconductor with a narrow band gap of ~0.4 eV at room temperature and an even smaller gap of ~20 meV in the optical spectra below 100 K. Its physical properties are strongly influenced by impurities and stoichiometric deviations and resemble those of a heavily doped semiconductor.

CHEMICAL COMPOUNDS
The Preparation and Crystal and Molecular Structure of the Complex cis-PtCl\textsubscript{2}(razoxane)
Treatment of the anti-cancer drug razoxane (3,5-dioxo-piperazin-1-yl-propane) (1) with K\textsubscript{2}[PtCl\textsubscript{4}] in aqueous HCl gave cis-PtCl\textsubscript{2}(razoxane), which is the first metal complex of (1) reported. (1) is co-ordinated as a bidentate ligand and was not hydrolysed during the reaction. The complex is unusual as the Pt is bonded to the ligand via tertiary N atoms only.

Synthesis and Structural Characterization of an Authentic Platinum(IV) Carbonyl Compound
Oxidative addition of Br\textsubscript{2} to [NBu\textsubscript{4}][Pt(C\textsubscript{6}F\textsubscript{5})\textsubscript{2}] followed by halide extraction with AgClO\textsubscript{4}, in the presence of CO gave [NBu\textsubscript{4}[trans-Pt(C\textsubscript{6}F\textsubscript{5})\textsubscript{2}Br(CO)]. This is the first structurally characterised Pt(IV) carbonyl derivative with a mainly α-donor CO ligand.
Synthesis and Characterization of Palladium and Nickel Complexes with Positively Charged Triphosphine Ligands and Their Use as Electrochemical CO₂-Reduction Catalysts


The synthesis of [Pd(Bu₃P⁺etpE)Br](BF₄) (Bu₃P⁺etpE = [Bu₃PCH₂CH₂P(CH₂CH₂PEt₂)₂⁺]) was described. Treatment of (1) with AgBF₄ in CH₃CN gave [Pd(Bu₃P⁺etpE)-(CH₂CN)](BF₄), which, along with [Pd(Me₃P⁺etpE)-(CH₂CN)](BF₄), is a catalyst for the electrochemical reduction of CO₂ to CO.

ELECTROCHEMISTRY

Cleavage of the C-C Bond during the Electrooxidation of 1-Propanol and 2-Propanol: Effect of the Pt Morphology and Pt/Ag Electrode Composition


The electrooxidation of 1-propanol (1) and 2-propanol (2) was studied on smooth Pt and electrodeposited Pt and Pt₆₃Ru₁₁. On smooth Pt, partially oxidised products were detected, propionic acid from (1) and acetone from (2), as well as CO₂. For (1), CO₂ production increased as the roughness of the electrode increased (electrodeposited Pt) and propionic acid production was totally eliminated on the Pt₆₃Ru₁₁ alloy. For (2), acetone formation was inhibited on the electrodeposited Pt but no additional effects were noted on the Pt₆₃Ru₁₁.

A Novel Polymer Electrolyte Based on Oligo(Ethylene Glycol) 600, K₂PdCl₄ and K₁Fe(CN)₆


Polymer electrolytic systems were prepared by reacting K₁Fe(CN)₆ and K₂PdCl₄ in a mixture of H₂O and poly(ethylene glycol) 600 (PEG). This reaction occurs in two steps: formation of a gel, then shrinkage to release the solvent. The product is very stable and has a conductivity of ~1.4 x 10⁻² S cm⁻¹ at 25°C. This is ~2 orders of magnitude higher than those of Li polymer electrolytes used in rechargeable batteries.

Catalytic Behaviour of Osmium(II), Rhodium(III) and Ruthenium(II) Phthalocyanines Towards the Electrooxidation of Cysteine on Glassy Carbon Electrodes

M. SEKOTA and T. NYOKONG, Electroanalysis, 1997, 9, (16), 1257–1261

Glassy carbon electrodes modified with phthalocyanine complexes: (DMSO)₄Rh₄Pc, [(CN)₄]Rh₄Pc, (DMSO)₄Os₄Pc and [(DMSO)₄Ru₄Pc]₂DMSO were autocatalytic for the oxidation of cysteine. This is attributed to the formation of dimeric π cation radical species at the electrode surface.

Electrochemical Behaviour of [Ru(4,4'-Me₂bpy)₂(PPh₃)₃(H₂O)](ClO₄)₃ in Homogeneous Solution and Incorporated into a Carbon Paste Electrode. Application to Oxidations of Benzylc Compounds


The catalytic activity of [Ru(4,4'-Me₂bpy)₂(PPh₃)₃(H₂O)](ClO₄)₃ (1) was studied during the homogeneous electrooxidation of benzylc compounds. Reactivity decreased in the order 1-phenylethanol > phthalic alcohol > benzyl alcohol > 4-methylbenzyl alcohol > ethylbenzene > toluene. C paste electrodes containing (1) also showed catalytic activity.

PHOTOCONVERSION

Interaction of Iridium Trihydridophosphine Complex with Fullerene C₆₀ under Thermal and Photochemical Stimulation


The interaction of H₂Ir(PPh₃)₃ (1) with C₆₀ under thermal and photochemical stimulation was studied under anaerobic conditions. Heating of a (1)-C₆₀ mixture (~1:1) or excitation by visible light resulted in new absorption bands characteristic of an n¹-co-ordinated C₆₀ in a fullerene-containing metal complex.

Interactions between Positively Charged Starburst Dendrimers and Ru(4,7-(SO₂C₆H₄)-phen)₄⁺


The emission intensity and emissive lifetimes of Ru(4,7-(SO₂C₆H₄)-phen)₄⁺ (1) were studied in solutions containing various cationic starburst dendrimers (SBD) with and without potential quenchers. Binding constants of (1) to SBD were determined by changes in the probe’s excited state lifetime. An increase in the probe lifetime was observed in the presence of SBD. The quenching constants between (1) and methylviologen (MV⁺), K₁Fe(CN)₆ and K₁PdCl₄, were determined by laser flash-photolysis.

Photoaddition of Ru(tap)₄(bpy)²⁺ to DNA: A New Mode of Covalent Attachment of Metal Complexes to Duplex DNA


Covalent adducts with guanine were formed by near-UV or visible light irradiation of Ru(tap)₄(bpy)²⁺ (1) (tap = 1,4,5-tetraazaphenanthrene; bpy = 2,2'-bipyridyl) with duplex DNA. The adduct was isolated as both its nucleotide and nucleobase derivatives. Two isomeric covalent adducts were formed in which the exocyclic amino group of a guanine nucleobase was linked to the C2 or C7 position of one of the tap ligands. This is a new type of site specific modification of DNA by a photoexcited Ru complex.
Defect-Free Palladium Membranes on Porous Stainless Steel Support


Defect-free Pd membranes were prepared by an electroless plating technique on porous stainless steel tubes. The effective surface of Pd membranes was ≤ 75 cm² and H₂ permeances of ≤ 8 m³ m⁻² h⁻¹ atm⁻¹ were achieved at 350°C. No He flux was detected at room temperature and a pressure difference of 3 atm. At a pressure difference of 1 atm and at 350°C, selectivity coefficients (H₂/N₂) of 5000 and H₂ fluxes ≤ 4 m³ m⁻² h⁻¹ were observed. The membranes were stable at 350°C for 1100 h, with no significant changes in the steady-state H₂ flux, leading to a recrystallisation texture and aggregation of Pd grains.

Cathodic Electrosynthesis of Titanium and Ruthenium Oxides


The electrosynthesis of RuO₂, TiO₂ and composite RuO₂-TiO₂ films on Pt substrates was performed cathodically via hydrolysis of TiCl₄ and RuCl₃nH₂O salts dissolved in H₂O or mixed MeOH-H₂O. The films can be obtained as monolayers or multilayers, as the amount of deposited material and its composition can be controlled. The crystallisation behaviour of the deposits and a possible mechanism of electrosynthesis are discussed.

APPARATUS AND TECHNIQUE

SnO₂ and SnO₂:Pt Thin Films Used as Gas Sensors


Thin films of SnO₂ (< 20 nm) and SnO₂:Pt, prepared by chemical spray deposition on glass substrates at various temperatures, have been assessed as CO gas sensors. Ultrathin SnO₂:Pt films with an amorphous structure were found to be highly sensitive, with an optimum Pt concentration of ~ 3 at.% in the starting solution. Sensitivities of 5 for SnO₂ and ~ 4 x 10² for SnO₂:Pt were obtained in the presence of 3.8 torr of CO partial pressure.

Study on Fence-Free Platinum Etching Using Chlorine-Based Gases in Inductively Coupled Plasma


A Cl₂/Ar gas combination, in an inductively coupled plasma, was successfully used to etch Pt thin films without redeposition of etch products. Most of the redeposited material formed on the pattern sidewall was determined to be PtCl₄ by X-ray photoelectron spectroscopy and secondary ion mass spectroscopy. The addition of SiCl₄ to the gas enhanced the formation of volatile compounds and significantly reduced redeposition to give a clean etch profile for the Pt films.
Effect of Fluorination of Alumina Support on Activity of Platinum Catalysts for Complete Oxidation of Benzene


A hydrophobic Pt-F/Al2O3 catalyst (1) was more active for the total oxidation of benzene than a hydrophilic Pt/Al2O3 catalyst (2) with the same Pt loading. (1) contained well-dispersed small Pt particles, in contrast to the larger particles on (2), with the high dispersion being due to a strong interaction of the metal particles with strong electron-acceptor sites formed by the fluorination of Al2O3.


Studies of Pd-y-Al2O3 catalysts used for the low temperature deep oxidation of MeOH showed them to be highly active with good selectivity. A 0.1% Pd-y-Al2O3 catalyst, prepared by impregnating (NHL)2PdCl precursor solution into the y-Al2O3 powder, followed by calcination in a reducing gas, had the highest activity in the absence of CO. The yields of partial oxidation products were low, and components of the feed gas, such as O2 and CO, strongly affected the activity and selectivity of the reaction.

Pd/Al2O3 Catalysts for Isoprene Selective Hydrogenation: Regeneration of Water-Poisoned Catalysts


Isoprene containing H2O was partially hydrogenated over Pd/Al2O3 eggshell catalysts with a weight-hourly space velocity of 18 h-1 at 40°C and 30 atm total pressure. The isoprene conversion decreased with time on stream. Catalyst activity loss was not restored by the introduction of H2O-free isoprene. However, H2 pretreatment reactivated the H2O-poisoned catalyst, by increasing the number of Pd sites available for CO chemisorption. At nearly steady state, the isoprene conversion by catalysts reactivated at 200°C was ~93% of that by catalysts without H2O-poisoning.

Investigation of the State of Palladium in the Pd/SO4/ZrO2 System by Diffuse-Reflectance IR Spectroscopy


Pd/ZrO2 and Pd/SO4/ZrO2 systems were studied by diffuse-reflectance IR-spectroscopy using CO as a probe molecule. The Pd/ZrO2 system showed a weak metal-support interaction which was increased by modification of the ZrO2 support with SO42- anions, as was the stability of the metal towards reduction. Surfaces modified by SO42- anions contained the positively charged metal particles Pd+ and Pd++. Acidic protons and surface sulfur compounds influenced the metal state, with smaller metal clusters having a higher charge on the sulfur atom.

Structure of Rh-Mo-K/Al2O3 Catalysts and Their Activity for Alcohol Synthesis


A series of Rh-Mo-K/Al2O3 catalysts was prepared with Rh loadings of 0-1.0% and a constant Mo and K content. The addition of 0.2% Rh into the oxidised Mo-K/Al2O3 system resulted in the aggregation of surface K-Mo species, while higher amounts of Rh gave an increased dispersion of the K-Mo species. The addition of Rh into the sulfided Mo-K/Al2O3 system improved both the selectivity for mixed alcohols and the activity of the catalyst, and shifted the distribution of oxygenates towards higher alcohols.

Impact of Molecular Order in Langmuir-Blodgett Films on Catalysis

K. TOLLNER, R. POPOVITZ-BIRO, M. LAHAV and D. MILSTEIN, Sciences, 1997, 278, (5346), 2100-2102

Catalytically active LB films of a Rh complex, prepared from the reaction of 4,4'-dibenzylidene-2,2'-(N,N-bis(mtolylpheny1amino)biphenyl)pyridine with [Rh(hexadiene)Cl]2, were prepared to determine the effect of the molecular order of metal complexes on catalytic activity. The LB films were highly active for the hydrogenation of carbon-oxygen double bonds, whereas in a homogeneous solution the Rh complex exhibited low activity. The catalyst also showed remarkably high substrate selectivity and was highly dependent on the order and orientation of the films. Above 30°C, however, catalytic activity decreased but was reversible on cooling.

HOMOGENEOUS CATALYSIS

Synthesis of Unsymmetrical Triarylamines for Photonic Applications via One-Pot Palladium-Catalysed Aminations


Unsymmetrically substituted triarylamines were prepared in multigram quantities by a high-yielding one-pot procedure, by azide coupling of two aryl bromides to an arylamine in the presence of Pd(dba)3, (dba = dibenzylideneacetone). This method can be used to synthesise a number of analogues of 4,4'-bis(m-tolylphenylamino)biphenyl which may find use as the hole transport component of vapour-deposited organic light-emitting diodes.

A New Route to Concentrated Microlatex of Homogeneous Particle Sizes: Oligomerization of Norbornene in Aqueous Emulsion Catalyzed by PdCl2


Norbornene was polymerised in aqueous micellar solutions of Na dodecyl sulfate (SDS) using PdCl2 as the catalyst. This gave small latex particles ~10 nm in size consisting of oligomers of norbornene, whereas the reaction in pure H2O precipitated high molecular weight polymers. This emulsion system was adapted to give a continuous process with a turnover of 70 moles of norbornene h-1 mole-1 of catalyst.

Platinum Metals Rev., 1998, 42, (2) 81
Catalysis of Giant Palladium Cluster Complexes. Highly Selective Oxidations of Primary Allylic Alcohols to α,β-Unsaturated Aldehydes in the Presence of Molecular Oxygen


The giant Pd cluster Pd6(phen6)(OAc)2 (phen = 1,10-phenanthroline) (1) is highly catalytic for the selective oxidations of primary allylic alcohols to the corresponding α,β-unsaturated aldehydes in the presence of O2 under mild reaction conditions. (1) can also be anchored to TiO2 to give an effective heterogeneous cluster catalyst for the above reactions which can be easily separated from the reaction mixtures and reused with minimal loss of activity and selectivity.

Homogeneous Catalysis in Liquefied Gas. Complex-Catalyzed Selective and Direct Conversion of Propane to Butanal at Room Temperature


Conversion of Propane to Butanal at Room Temperature


Upon illumination with a high pressure mercury lamp, RhCl(CO)(PMe3)3, catalyses the carbonylation of liquefied propane at room temperature to yield butanal with high regioselectivity, giving an n:iso ratio of 98:2 after 48 h at 15°C. Turnover rates can be improved by increasing the relative irradiation intensity.

Influence of the Reaction Temperature on the Regioselectivity in the Rhodium-Catalyzed Hydroformylation of Vinylpyrroles


The influence of temperature on the regioselectivity in the hydroformylation of vinylpyrrole isomers and the corresponding N-tosylated substrates is reported at 50–100°C in the presence of Rh(CO)3(benzobarrelene). The proportion of branched aldehyde was always higher (α-regioselectivity) but the amount of linear aldehyde increased as the temperature rose. 'H NMR studies showed that this behaviour is connected to α-hydride elimination process occurring at high temperature for the branched alkyl-rhodium intermediate only.

Synthesis of Columnar Polyaacetylenes by Rh Complex Catalyst


A highly stereoregular polymerisation of phenylacetylene and its homologues was performed using a Rh catalyst, such as [Rh(cyclopentadiene)Cl]2, in the presence of Et3N or alcohol, giving polyaacetylenes with a high cis content. The solvents dissociated the dimer complex catalyst to generate monomeric species as a possible propagation species for the polymerisation. A pressure induced cis-trans isomerisation generated fairly long trans conjugate sequences when pressure was exerted on the aromatic polyaacetylene polymer at room temperature under vacuum.

Reduction of Amides to Amines via Catalytic Hydroboration by a Rhodium Complex


The reduction of a wide range of tertiary amides with 2 molar equivalents of Ph3SiH in the presence of 0.1 mol% RhH(CO)(PPh3), (1) at room temperature gave the corresponding tertiary amines in high yields. Amides with bromo, ester or epoxy functional groups were reduced chemoselectively, in contrast to conventional reductions with LiAlH4 and/or BH3, although amides with C-C double and triple bonds and α-active methylene gave complicated mixtures. Primary and secondary amides did not react with hydrosilane in the presence of (1).

Stereoselective Metal Catalysed Hydroboration of 4-Substituted 1-Methylidenecyclohexanes


The hydroboration of 4-substituted 1-methylidenecyclohexanes in the presence of a Rh catalyst gives cis-4-substituted cyclohexane-1-methanols in high yield and stereoselectivity. This system gave a cis-trans ratio of 13.3:1 under catalytic conditions, compared to a ratio of ~1:2:1 obtained from conventional hydroboration. The best results were obtained with Rh catalysts prepared in situ by reacting [Rh(COD)Cl]3 with 4 equiv. of PPh3.


IrCl(TFB)(PPr3)2 (TFB = tetrafluorobenzobarrelene) reacts with AgBF4 in the presence of triisopropylamine to give [Ir(TFB)(PPr3)2]BF4, (1) in 93% yield. This complex reacts with H2 to give cis-trans-[IrH2(TFB)(PPr3)2]BF4, in 87% yield, which is also an active catalyst for the hydrogenation of a variety of olefins, including styrene. Although (1) reacts with phenylacetylene to give Ir(CPh)(TFB)(PPr3)2, it catalyses the hydrogenation of alkenes to alkenes in dichloromethane, giving selectivities close to 80% at 25°C and atmospheric pressure.

A New Ruthenium-Catalyzed Reaction with Propargyl Alcohol: Cyclopropagation of Norbornene


The reaction of propargyl alcohol and norbornene was catalysed by cationic (η4-cyclopentadienyl)-tris(acetonitrile)Ru complexes to give a cyclopropagation product, acetyltricyclooctane, in excellent yield. The Ru-catalysed reaction of 2-propyn-1-ol with norbornene proceeded smoothly at room temperature in alcoholic solvents, with methanol being the best choice, although almost no reaction occurred in benzene, THF or dichloromethane.
Asymmetric Hydrosilylation of Ketones Catalyzed by Ruthenium Complexes with Chiral Tridentate Ligands
A new chiral ligand containing two phosphines and one pyridine is highly effective for the Ru-catalysed hydrosilylation of simple ketones. Using 1 mol% of a Ru catalyst, such as [RuCl₂(C₅H₅)₂], and 2.2 mol% of the chiral tridentate ligand, enantioselectivities of 47–66% were obtained in yields of 85–98%.

FUEL CELLS
Reduction of Nitric Monoxide to Nitrogen at Gas Diffusion Electodes with Pd Catalysts
The electrochemical reduction of NO to N₂ was studied at a gas diffusion electrode with Pd catalysts for varying NO flow rates. At a flow rate of 5 ml min⁻¹ the reaction occurs selectively at potentials < 0.1 V, giving a current efficiency of ~ 95%. A H₂–NO fuel cell reactor allows simultaneous electricity generation and NO decomposition, with a N₂ formation current efficiency of ~ 80% at a cell voltage of 0.23 V.

ELECTRICAL AND ELECTRONIC ENGINEERING
Variation of Electrical Conduction Phenomena of Pt/(Ba, Sr)TiO₃/Pt Capacitors by Different Top Electrode Formation Processes
Electrical properties of Pt/(Ba, Sr)TiO₃/Pt thin film capacitors with top Pt electrodes deposited at various deposition powers were studied before and after post-annealing in N₂. The capacitor with a top Pt electrode deposited at 0.2 kW had Schottky emission behaviour under positive and negative biases, with interface potential barrier heights of 1.88–2.08 eV and 1.24–1.48 eV, respectively. However, for deposition at 0.5 kW, Schottky emission was observed only under positive bias at the bottom electrode at a barrier height of 1.61–1.89 eV.

Thermal Stability of the Non-Alloyed Pd/Sn and Pd/Ge Ohmic Contacts to n-GaAs
The thermal stability of a non-alloyed Pd/Sn ohmic contact to n-GaAs was compared to a non-alloyed Pd/Ge metallisation. The Pd(50 nm)/Sn(125 nm) contacts (1) showed a lowest ρₓ of 2.22 × 10⁻⁴ Ω cm² which was higher than for similar Pd/Ge samples. The Pd/Sn ohmic contacts however showed superior thermal stability at 410°C; after annealing at 410°C for 4 h, the ρₓ of (1) remained in the low 10⁻⁴ Ω cm² range whereas that of the Pd/Ge contacts increased by two orders of magnitude.

Improvement of Shape Memory Characteristics by Precipitation-Hardening of Ti–Pd–Ni Alloys
Non-equiatomic Ti–Pd–Ni high temperature shape memory alloys (Ti:(Ni, Pd) ≠ 50:50) were precipitation-hardened to improve their shape memory characteristics. For Ti₆₀PdₓNi₄₀ alloys, homogeneously distributed fine particles could be produced by ageing at 773 K. These precipitates increased the critical stress for slip and greatly improved the shape memory characteristics at high temperature.

Deposition of Ruthenium Nanoparticles on Carbon Aerogels for High Energy Density Supercapacitor Electrodes
A new type of composite electrode using C aerogels as high surface area substrates for pseudocapacitive RuO₂ nanoparticles was prepared by the chemical vapour impregnation of Ru into C to produce a uniform distribution of adherent ~ 20 Å nanoparticles on the aerogel surface. The Ru particles dramatically improved the energy storage characteristics of the aerogel so that specific capacitances of > 200 F g⁻¹ were obtained in comparison to 95 F g⁻¹ for the untreated aerogel.

Electrical Properties of All-Perovskite Oxide (SrRuO₃/Ba₅Sr₂Ti₃O₁₀/SrRuO₃) Capacitors
Perovskite oxide thin film capacitors (SrRuO₃/Ba₅Sr₂Ti₃O₁₀/20 nm/SrRuO₃) were fabricated on Si and SrTiO₃ substrates and their electrical properties studied. The relative dielectric constants for polycrystalline and single crystal epitaxial capacitors were 274 and 681, respectively. The lowest SiOₓ equivalent thickness for a single crystal epitaxial capacitor was 0.11 nm. The leakage current density was < 1 × 10⁻¹⁰ A cm⁻² for a ±1.2 V bias. Comparison of samples with SrRuO₃ and Pt top electrodes showed a large difference in the dielectric constants, which was attributed to differences in the interface between the dielectric and the top electrodes, and the existence of a low-e layer.

MEDICAL USES
Synthesis, Structure, and Antimetastastic Activity of trans-[Pt(NC₅H₄C(O)NHC₅H₄ONO₂)₃Cl] Complex
Complex trans-[Pt(NC₅H₄C(O)NHC₅H₄ONO₂)₃Cl] was prepared in H₂O by interacting K₂PtCl₄ with nicorandyl (N-nitroxy nicotinamide), a complex used in cardiology. This complex displayed high antitumour activity, unlike a Br-containing Cu²⁻ analogue.
NEW PATENTS

METALS AND ALLOYS

Amorphous Magnetic Alloy
READ RITE CORP. European Appl. 803,882A
An amorphous magnetic metal alloy comprising T,T,T,T, where T, includes 75–98 at.% of Fe and/or Co; T, includes 2–20 at.% of Rh; and T, includes 2–15 at.% of Zr, has a saturation magnetic induction B, of ≥ 1200 Gauss and a saturation magnetostriction constant λ, < 10 x 10⁻⁶. Also claimed is a similar alloy which contains 2–15 at.% Rh and additionally 3–20 at.% of Pt and/or Pd. The alloys have a high corrosion resistance and are used in magnetic transducers or heads for use in magnetic recording devices.

ELECTROCHEMISTRY

Anode with Enhanced Durability
ELECTRICITE DE FRANCE World Appl. 97/43,465A
An anode with enhanced durability and long cycle life consists of a metallic substrate, preferably Ta, coated with a layer of electrocatalytic Ir oxide. The cycle life measured is preferably > 25 h m⁻² g⁻¹. The Ir oxide layer is deposited on a prepared substrate by applying a solution of IrCl₃ in an organic solvent, followed by repeated thermal decomposition of IrCl₃.

Water Electrolysis Cell
JAPAN ENERGY CORP. Japanese Appl. 9/241,880
A high efficiency H₂O electrolysis cell comprises a solid polymer electrolyte of a fluoro-resin ion exchange membrane, a catalytic anode and cathode, and feeders consisting of Pt plated sintered metal powder or sintered Pt plated metal powder. This cell can decrease the amount of catalyst on the electrodes, and can depress cell voltage to a low level.

Photocatalyst for Hydrogen Production
MITSUBISHI JUKOGYO K.K. Japanese Appl. 9/262,473
A photocatalyst (1) used for H₂ production is composed of super micro particles, 10–100 Å in diameter of Pt and Fe₂O₃, and an insulating matrix comprising at least one of SiO₂, Al₂O₃, Ta₂O₅, TiO₂, etc., binding them together. H₂ is produced by immersing (1) into a basic aqueous solution with pH > 10 containing organic material and irradiating it. The energy transformation ratio of this method is 3 times that of conventional methods.

Amorphous Alloy Electrolysis Anode
HIRANUMA SANGYO K.K. Japanese Appl. 9/279,318
An amorphous alloy for use in NaCl electrolysis contains in at.%: 65–85 Pd+Pt (with 15–40 Pt), 4–15 Cu and 10–20 Si. It has a supercooled liquid range dT, of > 50 K, where dT, = T₂-T₁ (T₁ is the crystallisation temperature and T₂ is the glass transition temperature). The amorphous alloy electrode has high electrolyslic efficiency, good corrosion resistance, requires no activating and can be formed into shapes.

Electrodes for Electrolysis
TDK CORP. Japanese Appl. 9/279,381
An anode electrode for electrolytic O₂ generation has a coating layer containing at least one Pt group metal or its oxide and has orthogonal grooves, which form quadrangular pyramid and/or quadrangular frustum pyramid convex parts. The electrode is stable for long periods, has a long life and good durability, even when used in electroplating baths containing additives to promote consumption of the electrode.

ELECTRODEPOSITION AND SURFACE COATINGS

Platinum-Iridium Alloy Plating
NIPPON ELECTROPLATING ENGINEERS K.K. Japanese Appl. 9/256,189
A Pt-Ir alloy plating bath contains 1–30 g l⁻¹ of an Ir(III) complex containing halogen and either an acid or a salt, and 0.1–15 g l⁻¹ of a Pt(II) complex containing nitrous ion. The Pt-Ir alloy plating bath gives good deposition.

High-Purity Platinum Thin Film
MITSUBISHI MATERIALS CORP. Japanese Appl. 9/287,075
A thin Pt film, used in dielectric memory and in semiconductor devices, is formed on a substrate by organometallic chemical vapour deposition of an organic Pt compound by irradiation with light of wavelength ≥ 240 nm. This method forms a thin film of high-purity Pt at low reaction temperatures without deterioration of purity from decomposed ligands. Decreases in the film density by Pt coagulating into island shapes on the surface are also prevented.

Platinum Electroless Plating Liquid
JAPAN ENERGY CORP. Japanese Appl. 9/287,078
A Pt electroless plating liquid for plating the skin layer of electronic components contains a Pt nitro complex, a complexing complex such as ethylene diamine, a Pt nitroamine complex, a Pt chloroamine complex, a stabiliser such as ethylene amine, etc., a reducer such as B, and an additive, which tautomerises into a thiol compound. Plating is performed at pH 11–13.5 and 20–50°C. The liquid gives excellent bath stability and stable plating at low temperature.

APPARATUS AND TECHNIQUE

Oxygen Sensor
TOYOTA JIDOSHA K.K. Japanese Appl. 9/229,900
An oxygen sensor comprises a tube with inner and outer electrodes. A Pt coating layer is formed on the front face of a Si nitride heater, to deter Si sublimation from the heater at high temperature. The output characteristics of the sensor are maintained over a long time and the effective area of the electrode is maintained by the prevention of Si adhesion.
Sampling Uranium Oxide Fuel
MITSUBISHI JUKOGYO K.K. Japanese Appl. 9/276,658
NOx gas treatment equipment for sampling U oxide fuel has a catalyst containing Pt and Rh, arranged in a catalytic reaction treater, which accepts exhaust gas from the upper gas space of a coolant chamber of a cooling treater. The equipment is compact in structure and easy to install in an airtight analysis box. It eliminates gas such as NO.

HETEROGENEOUS CATALYSIS

Purification of Diesel Engine Exhaust Gases
DEGUSSA A.G. European Appl. 800,856A
A catalyst for purifying diesel engine exhaust gases contains zeolites and a Pt group metal deposited on metal oxide(s) selected from Al silicate, Al₂O₃, and TiO₂. The Al silicate has a weight ratio of SiO₂:Al₂O₃ of 0.005–1. The catalyst can oxidise long chain heavy paraffins in the exhaust gas and simultaneously reduce the NOx despite the high O₂ content of the diesel exhaust gas.

Polyhydroxycarboxylic Acids
AKZO NOBEL N.V. World Appl. 97/34,861A
Polyhydroxycarboxylic acids are prepared by oxidation of di-, tri-, oligo- and polysaccharides in an alkaline medium with an oxygenous gas using Pd/Al₂O₃ as a catalyst and Bi as a promoter. The Pd concentration is ≥ 40 mg ¹ and the molar ratio Pd:Bi is 1:5–1:40. Towards the end of the reaction, when the O₂ concentration in the liquid phase greatly increases, the O₂ supply is reduced to ≤ 20 ppm. This process gives higher conversions and minimises catalyst deactivation and product contamination by Pd.

Vinyl Ester Production
HOECHST CELANESE CORP. World Appl. 97/36,679A
A catalyst for producing vinyl esters, especially vinyl acetate, comprises a honeycomb carrier with SiO₂ coated cells extending the entire length of the carrier, and Pd and Au metals distributed throughout the SiO₂ coat. The catalyst has high activity and selectivity, long life and lower pressure drop across the catalyst. Heat distribution is improved. The SiO₂ coated honeycomb carriers eliminate problems with cracking and brittleness which could occur with honeycombs containing only SiO₂ or Al₂O₃.

Three-Way Catalyst
ARD CO. PTE. LTD. World Appl. 97/40,923A
An exhaust gas purification catalyst comprises a carrier; a first catalyst layer made from magnetite, Ce oxide and Re which provides an O₂ reservoir during catalysis; and a second layer comprising fine Ni needles distributed over the catalyst surface and a Pt group metal, preferably Pt. The three-way conversion catalyst is manufactured by applying a first catalyst layer to the carrier; immersing in a Ni⁺ solution to form a Ni washcoat; autoclaving to form Ni needles then adding a coating of a Pt group metal. The catalyst has good stability at high temperature.

Palladium-Gold Catalyst
HOECHST CELANESE CORP. World Appl. 97/44,130A
A bimetallic Pd-Au catalyst for the production of vinyl acetate from ethylene, acetic acid and O₂ is prepared by the dispersion coating of colloidal Au on a shell dispersion coating of colloidal Pd on a porous support. The catalyst has high Au retention and is durable with long term selectivity and activity. The Pd and Au can both be deposited from organic solvent.

Benzene Saturation
UOP U.S. Patent 5,663,466
A process for the saturation of benzene involves passing a feedstream of 5C and/or 6C paraffinic hydrocarbons and benzene through a guard bed to remove S, admixing with a H₂-containing stream, contacting the feed with 0.1–1 wt.% Pt/Al₂O₃ catalyst and heating to 480–600°F. Controlled H₂ addition improves the efficiency and cost-effectiveness. It is used in the production of high octane gasolines.

Naphtha Reforming
UOP U.S. Patent 5,665,223
A catalytic composite comprises a combination of a refractory inorganic oxide support with 0.01–5 wt.% of a Group IVA metal, 0.01–2 wt.% Pt group metal and 0.05–5 wt.% Eu, with > 50% of the Eu being the oxide and the atomic ratio of Eu/Pt being > 1:3. The catalyst has improved selectivity for hydrocarbon conversion, especially for gasoline or aromatics.

Alkane Isomerisation Catalyst
PHILLIPS PETROLEUM CO. U.S. Patent 5,668,074
A catalyst used in alkane and/or cycloalkane isomerisation is prepared by reducing compounds of Pt and/or Pd on an Al₂O₃ support at 300–600°C, incorporating Nb and/or Ta, heating in non-reducing gas at 300–500°C and treating with halocarbon compounds selected from fluorokanes and chlorofluoroalkanes at 200–500°C. The catalyst has high activity and selectivity for (cyclo)alkane isomerisation.

Three-Way Catalyst for I.C.E.
ASEC MFG. U.S. Patent 5,672,557
A catalyst for reducing the amount of CO, hydrocarbons and NOx in exhaust gases of I.C.E. comprises Al₂O₃, CeO₂ and/or lanthana, and optionally 5–20 wt.% of a promoter, with 0.05–5 wt.% Pd. The amount of Ce and La metals in the support is 80–300 g·l⁻¹ at a ratio of Ce/La of 0.3:1–10:1 and the wt. ratio of Ce + La/Al₂O₃ in the support is > 3. This Pd-only catalyst has reduced levels of Al₂O₃ (< 50%) in the support and improved durability and activity.

One-Stage Alkane Conversion
AMOCO CORP. U.S. Patent 5,672,796
A one-stage process for the conversion of 3–6C alkanes to a low CH₄-containing hydrocarbon product rich in aromatics involves contacting a feed comprising the alkanes with a catalyst of a H-form, partially sulfided Pt/Re-loaded aluminosilicate molecular sieve. The catalyst is used for hydrocarbon aromatisation and gives high conversions and selectivity.
Unsaturated Ester Production  
HOECHST CELANESE CORP. U.S. Patent 5,691,267  
A catalyst for the synthesis of unsaturated esters is prepared by impregnating a carrier with H₂O-soluble Au and Pd compounds, fixing them to the carrier as H₂O-insoluble Au and Pd compounds, and reducing them to Au and Pd metal. The catalyst gives improved space time yield and, in the production of vinyl acetate, reduced selectivity to CO₂, ethyl acetate and heavy end products.

Fuel Additive  
PLATINUM PLUS INC. U.S. Patent 5,693,106  
A fuel additive composition for an I.C.E. comprises a Pt group metal compound sufficient to give 0.05–2 mg Pt 1⁻ fuel and a H₂O-functional lipophilic emulsifier and/or lipophilic organic compound in which H₂O is miscible. Degradation of catalyst activity is minimised by preventing the separation of H₂O from the fuel and maintaining the catalyst in the fuel.

Removing Non-Methane Hydrocarbons  
FARMTEC K.K. Japanese Appl. 9/113,486  
Non-CH₄ hydrocarbons are removed from exhaust gas by flowing the sample gas containing hydrocarbons and O₂ through a discharge tube with an applied A.C. voltage of 10–20 kV, 50–100 Hz, and feeding to a tube containing a Pt oxidation catalyst at 100–150°C to burn the hydrocarbons, except CH₄. Non-CH₄ hydrocarbon is almost completely oxidised and removed by suppressing the oxidation rate of CH₄.

Waste Gas Purifier  
HINO MOTORS LTD. Japanese Appl. 9/271,639  
A waste gas purifier for diesel engines comprises a first Pt/Al₂O₃ catalyst, a second Rh/CoO₂ catalyst and a third catalyst comprising Al₂O₃ carrier carrying Pt, Pd or a mixture of these, arranged by the exhaust-tube path, one-by-one from the upstream side of the waste gas circulation direction. Hydrocarbon gas flow is controlled by a rate-of-flow controller. NOx is converted into N₂ and nitrous oxide in atmospheric air is significantly reduced without releasing hydrocarbon gas to the atmosphere.

Purification Catalyst for Exhaust Gas  
TOYOTA JIDOSHA K.K. Japanese Appl. 9/271,665  
A catalyst for the purification of exhaust gas is composed of a spinel type composite oxide AB₂O₃ (A = Pt, Fe, Co, Ni, Cu, Zn, Cd or Hg; B = Ce). This catalyst allows the soot in diesel engine exhaust gases to be combusted efficiently at low temperature.

Silica Gel Catalyst with Platinum  
TANAKA KIKINZOKU KOGYO K.K. Japanese Appl. 9/276,698  
A manufacturing method involves adding to a SiO₂ gel a complex Pt cation produced by the pyrogenetic reaction of Pt chloride ammonium acid with surplus aqueous NH₄, which is removed by volatilisation to give a tetravalent Pt amine complex ion. This Pt/SiO₂ hydrocarbon hydrogenation catalyst uses less Pt but retains the same catalytic properties.

Exhaust Gas Purifier  
NISSAN MOTOR CO. LTD. Japanese Appl. 9/287,438  
A purifier for an I.C.E. consists of a three-way component catalyst carrying Pd and an absorption catalyst carrying a zeolite, both on a heat resistant inorganic carrier, arranged upstream and downstream, respectively, of the exhaust gas flow to form a catalytic converter. This tandem arrangement gives the catalyst superior purification activity. It absorbs and separates hydrocarbons by self purification even when the exhaust gas temperature is low at engine start-up.

Purification of Exhaust Gases  
NE CHEMOCAT K.K. Japanese Appl. 9/290,156  
A catalyst for purifying the exhaust gas from an I.C.E., gas turbine or boiler consists of Pd, Ag and Zn on an Al₂O₃ carrier. The catalyst purifies NOₓ in an O₂ rich environment and completely oxidises the reducing hydrocarbons. It is extremely efficient at purification, as it maintains high denitrification even when the exhaust gas flows at a high velocity.

Hydrogenation of Butyenediol  
LINDE A.G. German Appl. 1/96/25,189  
A two-stage process is claimed for the catalytic hydrogenation of butyenediol (1) to butanediol (2). Stage I is carried out in a stirred reactor with a suspended, Pd-Ag/Al₂O₃ catalyst giving complete conversion of (1) into butanediol (3) and 50–85% hydrogenation of (3) to (2). Stage II takes place in a solid-bed reactor. The process gives (2) in high yield with high purity.

Palladium Exhaust Gas Purification Catalyst  
MAZDA MOTOR CORP. German Appl. 1/97/13,103  
A Pd-carrying exhaust gas purification catalyst comprises CeO₂ and a mixed oxide of Ce and Pr. The catalyst is produced by mixing a porous base material with CeO₂ to form a carrier for the Pd; the Pd and carrier is then made into a slurry with a mixed oxide of Ce and Pr as solid components, followed by calcining. The catalyst has high heat resistance.

HOMOGENEOUS CATALYSIS  
Preparation of Aldehydes and Ketones  
BAYER A.G. European Appl. 794,168A  
A diaryl carbonate is produced by reacting the corresponding aromatic hydroxyl compound with CO and O₂ in the presence of a tetravalent alkylammonium Ru species under anhydrous conditions. (1) are useful as intermediates and products in the chemical industry.

Diaryl Carbonate Production  
BAYER A.G. European Appl. 794,168A  
A diaryl carbonate is produced by reacting the corresponding aromatic hydroxyl compound with CO and O₂ in the presence of a Pt metal catalyst, a cocatalyst, a quaternary salt and a base. Also claimed is the production of polycarbonates. The energy-coupled process with a closed material cycle avoids the use of phosgene and solvent, is easy to operate and gives pure products with a selectivity of > 99%.
Hydrogen Peroxide Production

ENICHEM S.P.A. European Appl. 808,796A

H₂O₂ is obtained by reacting CO, O₂ and H₂O vapour in a H₂O immiscible organic solvent in the presence of a soluble catalyst formed from a Pd salt, a non-co-ordinating organic or inorganic acid, and a ligand comprising a mono or polydentate nitrogenated compound which binds to Pd. High H₂O₂ yields are obtained with lower amounts of ligand and acid. It is used as a bleaching agent in the textile and paper manufacturing industries; in oxidation processes in the chemical industry or as a biocide.

Ethylidene Diacetate Production

AIR PROD. & CHEM. INC. European Appl. 808,820A

Ethylidene diacetate (EDA) is produced by reacting acetic anhydride, H₂, CO and acetic acid in the presence of an alkyl iodide and a catalyst which is stable to hydrogenation. The catalyst is bifunctional and comprises an insoluble polymer with pendant quaternised heteroatoms, some of which are ionically bonded to anionic Group VIII metal complexes and the remainder to iodide. Accelerators, such as 3-picoline, are not required and leaching of metal from the catalyst is minimised by bonding to the Group VIII metal. The catalyst can be recycled and the process is fast and highly selective towards EDA.

Preparation of Pesticidal Fluoro-Olefins

AMERICAN CYANAMID CO. European Appl. 811,596A

Pesticidal fluoro-olefins (1) are prepared by reacting a 4-aryl-2-fluoro-2-butene-1-ol with a brominating agent to form a 4-aryl-1-bromo-2-fluoro-2-butene and reacting with a Pd catalyst, a base and a boronic acid, boronic anhydride or borate ester. This is an efficient and effective method for the preparation of pesticidal agents (1).

Carboxylic Acid Production

RHONE-POULENC CHIM. World Appl. 97/35,826A

Carboxylic acids and/or their corresponding esters are prepared by the isomerisation of formic acid ester and an alcohol in the presence of H₂O₂, a solvent and an Ir-based catalyst with a halogen promoter, under partial CO pressure. With alcohols containing more than one OH, adipic acid (or esters) or terephthalic acid (or esters) can be produced. This process gives improved productivity without the addition of supplementary compounds such as strong acids.

Pentenoic Acid and Pentenoate Ester

F. P. W. AGTERBERG U.S. Patent 5,672,732

A pentenoic acid (1) or a pentenoate ester (2) is prepared with good selectivity and conversion by the carboxylation of butadiene or its derivatives in the presence of CO₃, an alcohol or H₂O and a catalyst system comprising Pd, a carboxylic acid and a monodentate phosphine ligand. (1) and (2) can be used as intermediates in the preparation of e-capro lactam and adipic acid, in nylon-6 and nylon-6,6 production, respectively. Good selectivity and conversions are achieved. The catalyst system is stable and may be reused several times without loss of activity.

Alkoxy-Silane Compounds

BASF A.G. German Appl. 1/96/49,998

The preparation of alkoxy-silane compounds containing vinyl ether groups comprises reacting divinyl ethers (1) with silanes (2) at 70-150°C in the presence of a homogeneous hydrosilation catalyst. The catalyst is a Pt or Rh compound and the amount of Rh or Pt is 0.05-10 ppm with respect to (1) and (2).

FUEL CELLS

Fuel Cell Electrode

S. SARANGAPANI U.S. Patent 5,683,829

A fuel cell electrode comprises an anode with a Pt electrocatalyst including a redox promoter composed of a Ru or Sn complex. The anode is resistant to poisoning, and low loadings of Pt are needed to give higher current densities. The electrode is used in the oxidation of MeOH or MeOH reformate in a fuel cell, and the fully assembled fuel cells may be of stack design.

Pt-Fe Alloy Fuel Cell Electrode

EQUOS RES. K.K. Japanese Appl. 9/161,811

An anode for high molecular electrolyte-type fuel cells comprises 84-99 at. % Pt and 1-16 at. % Fe held on a catalyst support. The anode catalyst has a long life, superior poisoning resistance and is free from elution.

Electrode Structure

MATSUDA K.K. Japanese Appl. 9/265,992

The electrode structure of a solid state polymer fuel battery used for electric vehicles includes a set of catalytic electrodes with two catalyst layers between which a solid state polymer electrolyte film is sandwiched. The first catalyst layer consists of a polytetraflouroethylene (1) dispersion solution mixed with C black containing 40% Pt, and the second layer consists of (1) mixed with C and 20% Pt. The electrode improves the electricity generation efficiency and reduces manufacturing costs.

Electrode Catalyst for Fuel Cells

TOSHIBA K.K. Japanese Appl. 9/293,517

An electrode catalyst layer for phosphoric acid fuel cells is manufactured by heat treating a mixture of C and fluoro resin, which has been uniformly applied to a support substrate. C is eliminated, giving a fluoro resin sheet onto which a catalyst layer is formed by impregnation with Pt and C. Reduction in surface area is prevented, and battery characteristics and the water proof nature of the catalyst layer are improved.
Zeolite Based Platinum Catalyst

DAIMLER-BENZ A.G. French Appl. 2,744,999

A zeolite based Pt catalyst is used in the catalytic reduction of CO from a starting mixture rich in H₂ and in the selective oxidation of CO from a MeOH reforming reactor. The catalyst is produced by dissolving Pt(NH₃)₂Cl₂·xH₂O in distilled H₂O and adding a zeolite, stirring the suspension, filtering, washing, drying, heating, reducing the heated material by adding a forming gas, and finally cooling under N₂. The catalyst is used in H₂ processing for use in fuel cells for electrical vehicles.

ELECTRICAL AND ELECTRONIC ENGINEERING

Wireless Bonding of IC Chips

TANAKA DENSHI KOGYO K.K. European Appl. 810,293A

A Au alloy wire containing 0.2-5 wt.% Pd and 1-100 ppm (by wt.) Bi is manufactured from Au of purity ≥ 99.99 wt.% A Au alloy bump is formed by forming a ball at the end of a Au alloy wire passing through in a capillary, bonding the ball to an electrode of an IC chip, and breaking the wire from the ball. The process is used for wireless bonding of IC chips. High bond strength is maintained at high temperatures.

Semiconductor Chip Package

MICRON TECHNOLOGY INC. U.S. Patent 5,677,566

A semiconductor chip package for connection to a lead frame has conductive leads connected to the chip and passing over the top, connected to bond pad areas on the chip via bond wires. The leads are coated with Pd/Ni, Au or Ag, and the chip and leads are encapsulated by a thermosetting epoxy resin. This package can be used with standard formats developed for larger chips without reconfiguration.

Fluoro-Polymer Metallised Substrate

GEO-CENTERS INC. U.S. Patent 5,696,207

A fluoropolymer substrate with a metallised surface is prepared by contacting a fluoropolymer substrate with an electroless metallisation catalyst, selected from Pd, Rh, Ir, Ni, Cu, Ag and Au, and then with an electroless metallisation solution. The metallised surface comprises a conductive layer of Ni, Cu, Au, Pt, Pd, Co, or an alloy, an intermediate layer of Ni and an outer layer of Pt, Au, Cu or alloys of Ni or Pt. The metallised surface exhibits good adhesion to the fluoropolymer substrate and may be patterned.

Ferroelectric Element

MATSUBISHI DENKI SANGYO K.K. Japanese Appl. 9/280,947

A ferroelectric element, for pyroelectric type infrared sensors, etc., has a contact layer made of a Ti film, which is arranged between a MgO single crystal substrate and a lower electrode made of Pt film. The element eliminates rupture and improves the yield in the manufacture of ferroelectric elements.

Semiconductor Chip Joining

WORLD METAL K.K. Japanese Appl. 9/283,557

A semiconductor chip joining method uses flip chip bonding, sequentially depositing a thin base layer of Pd-X alloy (X = Zn, Pb, etc.), a Ni layer and a metal layer, by non-electrolytic plating, on the surface of an input/output terminal. The chip improves the corrosion resistance of the input/output terminal and the junction reliability and allows high density mounting.

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