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Production of No-Carrier-Added $^{105}\text{Rh}$ from Neutron Irradiated Ruthenium Target

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*Nuclear medicine radiotherapy involves the administration of a radiolabelled drug whose purpose is tissue damage and/or destruction at the point of localisation. Radionuclides useful for this application are those which emit particles (that is alpha, beta or Auger electrons) because they deposit their decay energy over a relatively short range (for example, at the tumour site). Rhodium-105 is a radionuclide with desirable nuclear properties for therapeutic applications (its half-life is 35.4 hours, the maximum $\beta^-$ energy is 0.56 MeV and it produces a 319 keV $\gamma$-ray suitable for imaging). However, this radionuclide is not readily available to most of the interested investigators due to the difficulty in production scale-up. The work reported here was designed to develop a viable method to produce and purify multi-millicurie quantities of $^{105}\text{Rh}$ for radiotherapy research. Rhodium-105 was produced at the University of Missouri Research Reactor by the nuclear reaction, $^{106}\text{Ru} (n, \gamma) \rightarrow ^{106}\text{Ru} (\beta^-\text{decay}) \rightarrow ^{105}\text{Rh}$ and a new procedure was developed to chemically separate the no-carrier-added $^{105}\text{Rh}$ from the neutron irradiated ruthenium target. Rhodium-105 production yields, for 10 runs, averaged about 5 mCi per milligram of ruthenium from a 72-hour irradiation at a thermal neutron flux of $8 \times 10^{17}$ neutrons cm$^{-2}$ s$^{-1}$. Rhodium-105 was successfully isolated from the ruthenium radionuclides and the non-radioactive ruthenium. This new separation technique was fast (a total time of 3 hours) and highly efficient for removing the ruthenium. The decontamination factor of ruthenium averaged 16,600, indicating that only 0.006 per cent of the ruthenium remained after separation.

A therapeutic radiopharmaceutical typically consists of a biomolecule (such as an antibody, hormone or polypeptide) to which is bound a radionuclide of appropriate half-life, high specific activity and high radionuclidic purity. The biomolecule is generally labelled with the radionuclide by the incorporation of a bifunctional chelate which covalently bonds to both. There has been much recent interest in the use of monoclonal antibody (MAb) and peptide conjugates of $^{109}\text{Rh}$ for radioimmunotherapy (1–6). Bifunctional chelates of $^{109}\text{Rh}$ conjugated to MAbS and peptides have been designed to target cancer cells through interactions with specific receptors on the tumour surface. The specificity of MAbS and peptides for their particular receptor makes them excellent candidates for delivering radionuclides to cancer cells containing the receptor. The kinetic inertness of rhodium(III) complexes (low spin $d^4$ configuration) is expected to result in a much higher in vivo stability for $^{109}\text{Rh}$ labelled monoclonal antibodies and peptides compared to those labelled with other radionuclides, such as $^{64}\text{Cu}$, $^{90}\text{Y}$, $^{166}\text{Re}$ and $^{186}\text{Re}$. Various multitentate bifunctional ligands have been prepared and shown to form kinetically stable complexes in vivo with $^{109}\text{Rh}$. Examples of these ligands are 1,7-bis(2-hydroxybenzyl) 4-[(p-aminobenzyl)-diethylenetriamine (2), hematoporphyrin (1), 3-[N-(4-aminobenzyl)]amino-3-methyl-2-butanoneoxime (7), N,N'-bis(2-hydroxybenzyl)-1,3-diaminopropane (3), cysteine (4), p-aminobenzylopopyleneamine-oxime (6), and also 16-ane-S4-diol-macrocycle (8).

Rhodium-105 is a reactor-produced radio-
Fig. 1 Possible routes for the production of $^{105}\text{Rh}$ in a nuclear reactor.

1. This reaction does not yield $^{105}\text{Rh}$ of high specific activity.
2. Fission of $^{235}\text{U}$
3. Using stable $^{100}\text{Pd}$ gives a reaction of very low efficiency (it has a very low probability).
4. The most common method to produce $^{105}\text{Rh}$, used at University of Missouri Research Reactor with ruthenium as the target.

$^{105}\text{Rh} \rightarrow ^{105}\text{Pd} + \beta^- + \gamma$

In addition, the decay half-life (35.4 hours) of $^{105}\text{Rh}$ is well matched to the in vivo pharmacokinetics of many peptides and antibody fragments.

Production of Rhodium-105

Radiotherapeutic research which uses $^{105}\text{Rh}$ requires a route for the production of high specific activity $^{105}\text{Rh}$. Unfortunately, this radionuclide is not readily available to researchers (primarily due to the relatively stringent conditions and requirements in the isotope production and separation). Rhodium-105 can be produced in a reactor by several routes, see Figure 1; the simplest of which is via a $(2n, \gamma)$ reaction from a $^{105}\text{Rh}$ target. Unfortunately, this does not yield $^{105}\text{Rh}$ of high specific activity. $^{105}\text{Rh}$ is also a product (about 1 per cent) of the fission of $^{239}\text{U}$. However, the most commonly used method for the production of no-carrier-added $^{105}\text{Rh}$ is the indirect $(n, \gamma)$ reaction using ruthenium metal as the target to produce $^{105}\text{Ru}$, which then decays to $^{105}\text{Rh}$. Significant byproducts from the production are $^{99}\text{Ru} (T_{1/2} = 2.89 \text{ days})$, $^{105}\text{Ru} (T_{1/2} = 39.27 \text{ days})$, $^{100}\text{Pd}$ (stable) and $^{105}\text{Pd}$ (stable). The use of enriched ruthenium metal ($^{99}\text{Ru} > 99 \text{ per cent}$) as the target material minimises the radionuclidic impurities from ruthenium and increases the production yield of $^{105}\text{Rh}$ by five-fold.

A procedure proposed by Troutner and colleague has previously been used for the preparation of 5 to 150 millicuries of no-carrier-added $^{105}\text{Rh}$ at the University of Missouri Research Reactor (MURR) (9). The separation of $^{105}\text{Rh}$ from its $^{105}\text{Ru}$ parent was based on a combination of procedures previously described by Kobayashi and Morris (10, 11). An irradiated metal target of enriched $^{105}\text{Ru}$ is dissolved in alkaline solution in a reaction vial and oxidised to $\text{RuO}_3$ using chlorine gas. The $\text{RuO}_3$ is then removed from the solution by distillation (b.p. $108^\circ\text{C}$) into a series of hydrochloric acid (HCl) and sodium hydroxide (NaOH) traps. The $^{105}\text{Rh}$ remains in the reaction vial and is converted to a mixture of $\text{Cl}^-$ complexes by the addition of HCl solution and heating. However, the major disadvantage of this process is the use of chlorine gas, which is a corrosive material (in the presence of water) and a highly toxic gas which requires a very effective trapping system. These disadvantages have somewhat discouraged the scale-up of this procedure for the production of higher quantities of $^{105}\text{Rh}$. In addition, the subsequent distillation of the oxidised product $\text{RuO}_4$, which is a highly toxic volatile chemical, also requires extreme precautions and a cumbersome trapping system. Although the system can be designed to trap both distilled $\text{RuO}_4$ and excess chlorine gas by the use of a series of HCl and NaOH solutions, the amount of liquid used in the traps would increase the volume of the radioactive waste, which mainly contains $^{109}\text{Ru} (T_{1/2} = 39.27 \text{ days})$. This would be a major disadvantage when scaling-up production.
A new separation procedure is reported here using magnesium oxide, MgO, as the adsorbent to purify no-carrier-added $^{108}$Rh in quantities of 10 to 100 mCi. The method eliminates the use of chlorine gas and the distillation of ruthenium tetraoxide, and has thus significantly increased the feasibility for scale-up (12).

**Production of $^{105}$Ru and $^{105}$Rh**

Rhodium-105 was produced in quantities of 5 to 100 mCi at MURR using isotopically enriched $^{104}$Ru (99.08 per cent, natural abundance: 28.2 per cent). The thermal and epithermal capture cross-sections of $^{105}$Ru are 0.47 barns and 6 barns, respectively, while the burn-up thermal cross-section of $^{106}$Ru toward the formation of $^{106}$Ru is 0.3 barns. Rhodium-105 is produced from the radioactive decay of the $^{106}$Ru intermediate ($T_{1/2} = 4.44$ hours) both during and after the irradiation. The irradiation samples were prepared by accurately weighing the target material into clean quartz vials, which were then sealed under vacuum. The sealed quartz vials were encapsulated in high purity aluminum capsules and loaded into reflector positions within the MURR reactor for 72 hour irradiations at neutron fluxes of $8 \times 10^{15}$ n cm$^{-2}$ s$^{-1}$. The irradiated samples were allowed to decay for more than 12 hours and processed in a dedicated glove box. For shorter irradiations, natural ruthenium metal and potassium ruthenate were used as target materials for process development. Ruthenium metal samples were prepared in quantities of 1 to 10 mg and sealed in high purity polyethylene vials (of diameter 11 mm and length 23 mm). These vials were embedded in Styrofoam cylinders to cushion shock and placed in high density polyethylene containers known as “rabbits” for neutron irradiation for up to 1 hour in the pneumatic tube facility at MURR. The activities of the $^{105}$Rh produced from these irradiations were in $\mu$Ci quantities (less than 0.5 mCi).

**Separation and Purification of $^{105}$Rh**

The irradiated ruthenium metal was placed into the $^{105}$Rh glovebox and transferred into a reaction vial which was connected to a trapping system containing HCl and NaOH solution. Sodium hypochlorite (NaOCl) (4 ml, 5 per cent) was added into the reaction vial and the mixture was stirred at room temperature for 30 minutes. About 2 ml of 2 M NaOH solution was added into the vial after the ruthenium target was dissolved. While stirring, 100 $\mu$l of 0.1 M magnesium chloride solution was carefully added into the ruthenium solution. The magnesium hydroxide suspension was then filtered through a 0.45 $\mu$m Teflon filter. After washing twice with water, the magnesium hydroxide precipitate and adsorbed $^{105}$Rh were dissolved with 0.5 M HCl in a new reaction vial. About 1 ml of NaOCl solution was added to the new vial and the $^{105}$Rh solution was stirred for 5 minutes. The $^{105}$Rh was re-precipitated on hydrous MgO on the addition of 1 ml of 5 M NaOH. The re-precipitated $^{105}$Rh and MgO were filtered, washed with water, and dissolved with 2 ml of 0.5 M HCl solution. This $^{105}$Rh solution was mixed with 1 ml of 4 M NaCl solution in a clean reaction vial and boiled for approximately 30 minutes. After cooling, the $^{105}$Rh solution was passed through a cation exchange column to remove Mg$^{2+}$. The final pH of $^{105}$Rh solution, as measured with pH paper, was ca. 1.

**Radioactivity Measurements**

Aliquots of the sample were taken throughout the process and analysed to assess the recovery and radionuclidic purity of the $^{105}$Rh. Gamma spectra were obtained using an intrinsic hyperpure germanium (HPGe) spectrometer attached to a 4000 channel analyser. All fractions for spectral analysis were prepared as 10 ml solutions in glass scintillation vials.

Trace quantities of $^{103}$Ru in the $^{105}$Rh product processed from the enriched, irradiated ruthenium target were determined on the HPGe detector after the decay of $^{105}$Rh. Ruthenium decontamination factors were calculated by comparing the initial ratio of $^{103}$Ru:$^{105}$Rh prior to chemical separation to the ratio of $^{103}$Ru:$^{105}$Rh in the final $^{105}$Rh sample after the separation.

**Results**

The radionuclide production resulting from the irradiation of an enriched ruthenium target in a reflector position in the MURR is shown in Figure 2.
Ru-105
Rh-105
Rh-106

IRRADIATION TIME, hours

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Fig. 2 
Rh production at MURR's Reflector Row-1 position (~ 6.5 x 10^13 n cm^-2 s^-1) using 1 mg of enriched ruthenium metal (99.05 per cent) as target material.

The average perturbed neutron flux at this position is about 6.5 x 10^13 n cm^-2 s^-1. Ruthenium-105 reaches maximum activity after the first 20 hours of irradiation due to its short decay half-life (T_1/2 = 4.4 hours). Its decay product, ^106Rh, gradually builds up and approaches saturation activity after 140 hours.

One important factor, which needs to be considered in the production, is that the product, ^106Rh, has very high neutron cross-sections (thermal: σ_θ = 16,000 barns and epithermal: σ_e = 17,000 barns) and thus will tend to capture a neutron to form ^106Rh, a short-lived radionuclide with T_1/2 = 30 seconds. Thus, ^106Rh is produced in fairly high quantity and the actual production yield of ^106Rh becomes significantly lower than the theoretical calculation which does not take into account such an "isotope burn-up" process.

The short-lived ^105Ru and ^106Rh, produced during the production process of ^106Rh, are allowed to decay before the irradiated samples are radiochemically processed. The maximum activity of ^106Rh is obtained about 14 hours after the end of irradiation (EOI), see Figure 3. This is, indeed, ideal "timing", since the short-lived and high dose rate radionuclides, such as ^106Ru, ^106Rh and ^31Si (2.62 hours, from irradiation of the quartz vial) are decaying and approaching their minimum quantities. The radiochemical separation of the samples can then usually begin 12 to 20 hours after the EOI.

Hydrous MgO adsorbed or co-precipitated rhodium(III) with very high efficiency. Rhodium-105 was collected and concentrated with a small quantity (typically ~500 μg) of solid MgO/Mg(OH)_2, which was then readily separated from the alkaline solution containing radioactive ruthenate. Both natural and enriched ^106Ru metal targets were used to develop the MgO separation procedure, and the distillation procedure which uses chlorine gas was used as a control for comparison of method efficiency. A decontamination factor of 11,300 was obtained from this control procedure (distillation) using chlorine gas as the oxidant and a natural ruthenium target. The decontamination factor from the procedure employing hydrous MgO averaged 16,600 for both natural and enriched ruthenium targets, for over 3 trials each. Total ^105Rh recovery averaged above 85 per cent from either procedure.

Discussion

The solution chemistry of ruthenium is complicated since, in most cases, ruthenium is present as more than one chemical species (13). Therefore it

![Fig. 3 The decay of a ruthenium target after irradiation, showing that the maximum activity of ^105Rh is obtained ~ 14 hours after the end of the irradiation](image-url)
is necessary to use a multi-step separation procedure to remove these various ruthenium species. The use of MgO to separate the $^{105}$Rh from the Ru (ruthenate) solution followed by a re-precipitation and column separation step for purification of $^{105}$Rh seems to be a good choice. The decontamination factor obtained from this procedure was as good or better than that of the distillation procedure (control).

This new procedure is superior to the distillation procedure in terms of simplicity and the radionuclidic purity of the isolated $^{105}$Rh. In addition, this procedure can be readily scaled up to processing multi-curie quantities of $^{105}$Rh, because the use of hazardous materials, such as chlorine gas and volatile ruthenium tetraoxide, is avoided.

One important concept that this paper is intended to address is that there are always isotopic carriers and radiochemical contaminants present in a “pure” or “no-carrier-added” sample, which are produced during the currently available separation methodologies. Because of the trace quantity of the “no-carrier-added” radionuclide (the concentration for 10 mCi of $^{105}$Rh in 5 ml solution is about $2 \times 10^{-11}$ M), the major components or elements present in the product may not be the specific radionuclides of interest. The ratio of ruthenium:rhodium at the end of a 72-hour irradiation is calculated to be around 200,000, from a comparison of the number of atoms of $^{105}$Rh produced during the irradiation and the total number of ruthenium atoms available. The theoretical ratio of ruthenium:rhodium in the $^{105}$Rh sample separated from a ruthenium target using the MgO adsorption method is in the region of ~12, assuming a decontamination factor of 16,600 is achieved.

In other words, in the separated $^{105}$Rh sample, the major metal element is ruthenium, rather than rhodium, even though nearly 100 per cent of the ruthenium has been chemically removed.

Additionally, it is probably worth mentioning that the $^{105}$Rh is recovered as a mixture of chloroaquorhodium (III) complexes. In dilute HCl solution where chloride [Cl$^-$] is less than 1 M, there is a mixture of $\text{RhCl}_5(\text{H}_2\text{O})_3^-$, $\text{RhCl}_6(\text{H}_2\text{O})_2^2-$, and $\text{RhCl}_4^2-$. $\text{RhCl}_5(\text{H}_2\text{O})_3$ may also exist in the solution (14).

$\text{RhCl}_5(\text{H}_2\text{O})_3 \leftrightarrow \text{RhCl}_6(\text{H}_2\text{O})_2^2- \leftrightarrow \text{RhCl}_4^2-$

It has been reported that at high temperature (> 50°C) and at a high concentration of chloride ([Cl$^-$] = 1.5-3 M), the above reaction is effectively unidirectional toward the formation of $\text{RhCl}_5(\text{H}_2\text{O})_3^-$ and $\text{RhCl}_4^2-$ which may undergo aquation by the release of chloride to form neutral or cationic species when reaction conditions are changed (14). It is difficult, in most cases, to directly use the processed $^{105}$Rh for radiolabelling due to its unknown speciation. The problem of converting all rhodium chloroaquo complexes to one chemical form for the subsequent radiosynthesis with bifunctional ligands or proteins – in order to obtain a uniform product with high efficiency – remains.

Conclusion

Rhodium-105 can be produced in quantities and purities suitable for radiotherapy research using a novel separation method based on MgO adsorption. The contamination from residual ruthenium does not apparently cause a problem for the practical use of $^{105}$Rh. Ruthenium removal is less an issue than making sure all the rhodium is in the same chemical form.

This adsorption method eliminates the use of chlorine gas and the production of ruthenium tetraoxide, and thus is desirable for use in large-scale isotope production. This will lead to the potential availability of $^{105}$Rh in multicurie quantities. However, at present no clinical trials are underway or are planned.

References


Pressure Tuning of a Platinum Kondo Insulator

The application of high pressures to a material can alter its internal interaction parameters, such as the magnetic and electronic effects, structures and densities, so that new solid state materials with useful properties may result. The high pressures affect the properties of a material, often giving it a completely new set of characteristics and behaviours. Pressure can be varied rapidly and be applied in particular directions, and thus be used to 'tune' the interaction parameters, and hence the properties. Thermolectric materials are especially sensitive to pressure, so the use of pressure tuning techniques to study their thermolectric properties and to search for new, improved semiconductor materials, is of interest.

One class of compounds known as Kondo insulators, which are semiconducting insulators with a narrow band gap energy, exhibiting intermediate valence properties, have some of the highest thermolectric properties known. Scientists at Pennsylvania State University, Cornell University and the Carnegie Institution of Washington have now managed to pressure tune a neodymium-doped Kondo insulator, Nd$_x$Ce$_{3-x}$Pt$_6$Sb$_4$, where $x = 0.27$ or 0.45, so as to increase its thermolectric properties significantly (J. F. Meng, D. A. Polvani, C. D. W. Jones, F. J. DiSalvo, Y. Fei and J. V. Badding, *Chem. Mater.*, 2000, 12, (1), 197–201).

On placing Nd$_{50}$Ce$_{20}$Pt$_6$Sb$_4$ in an octahedral multi-anvil pressure cell, its thermopower was increased from 80 $\mu$V K$^{-1}$ near ambient pressure at 298 K to 100 $\mu$V K$^{-1}$ at 2 GPa. However, when it was compressed inside a nonhydrostatic diamond anvil cell, its electrical conductivity increased by a factor of 1.5–2 and its thermopower increased from 82 $\mu$V K$^{-1}$ at ambient pressure to a maximum of 263 $\mu$V K$^{-1}$ at 1.9 GPa. Upon further increase in pressure, the thermopower dropped and when the pressure was reduced hysteresis was seen, probably due to irreversible structural changes. No hysteresis occurs if pressure is only increased to produce the maximum thermolectric power.

Pressure tuning can therefore act as an indicator of which materials, in this case thermolectric materials, are worthy of chemical synthesis for further study at ambient pressures.

"High Purity Metals" Catalogue

Alfa Aesar has published a new "High Purity Metals" 284-page catalogue which covers almost the entire periodic table of metallic elements with over 3000 metal products available in a variety of forms, including powder, wire, foil, shot, thermocouple wire and target. High purity platinum group metals and their alloys are included. Data on the physical properties of the metals, a mesh size conversion table for powders and expansivity data for the platinum metals are also given.

The catalogue may be obtained by Fax: +978-521-6350; E-mail: info@alfa.com; and online via the Alfa Aesar website at http://www.alfa.com.
Platinum in South Africa, a Review

To commemorate the seventy-fifth anniversary of the discovery of the Merensky Reef in South Africa, the major part of a recent issue of the *South African Journal of Science* has been given over to ten articles reviewing various scientific aspects of the platinum group metals (*S. Afr. J. Sci.*, 1999, 95, (11/12)). The papers were commissioned by R. G. Cawthorn, the Platinum Industry's Professor of Igneous Petrology at the University of the Witwatersrand, Johannesburg, who contributed an introductory commentary and two significant papers.

The platiniferous resources of the Bushveld Complex and their processing were considered in papers by R. G. Cawthorn: 'The platinum and palladium resources of the Bushveld Complex' and 'Geological models for platinum-group metal mineralization in the Bushveld Complex'; R. T. Jones: 'Platinum smelting in South Africa'; I. W. S. Smith and M. Laing: 'Solving hydrometallurgical problems in a platinum group metal refinery with X-ray powder diffraction'; and by T. V. Ashworth, V. E. Francois and M. J. Laws: 'The platinum-group metals – an analytical challenge'. These five papers complement two published in this Journal recently (1, 2), and together they present most informative pictures of the three very different ore bodies that are currently the source of about three-quarters of the world's platinum demand, and of some of the efforts being made to improve the recovery of platinum metals from them.

Of particular importance to users and potential users of the platinum metals are the data from mining companies of ore less than 2 kilometres in depth, which indicate proven and probable reserves of platinum and palladium in the Bushveld Complex of about 204 and 116 million ounces, respectively, sufficient to satisfy platinum consumption at the current rate for forty years. Inferred resources amount to another 939 and 711 million ounces of platinum and palladium, respectively. However mining has already taken place at 1987 metres and plans to mine at 2365 metres are being implemented, so inferred resources – and ultimately mineable ore – could be very much greater that the figures given above. Furthermore, assuming a demand increasing at 6 per cent per year, it is suggested that total worldwide reserves and resources could satisfy needs for over fifty years. Beyond that, improvements in mining and metallurgical operations could extend resources significantly, with exploitation governed by price and demand for the metals.

The other five papers are concerned with applications for the platinum metals. V. I. Okafor and N. J. Coville describe some of the chemical and physical properties that enable platinum to be used widely as a catalyst ('Platinum in catalysis'). They then consider: platinum in the refining industry, platinum in the automobile catalyst, platinum clusters and colloids in catalysis, and enantioselective heterogeneous platinum catalysts. In each case further developments are expected from ongoing investigations.

After pointing out that South Africa has one of the highest cancer incidence rates in the world, E. W. Neuse focuses on platinum coordination compounds of interest as antiproliferative agents ('Platinum coordination compounds in cancer research and chemotherapy'). A major part of the discussion is devoted to the strategy of binding platinum complexes to macromolecular polymer carriers with the aim of altering the pharmacokinetic pathway of medicinal agents, in order to enhance overall bioavailability while minimising present obstacles. Tests have confirmed the soundness of the polymer conjugation approach in platinum drug research.

The aluminium-ruthenium, aluminium-iridium, aluminium-nickel-ruthenium, and aluminium-iridium-rutenium phase diagrams are reviewed by L. A. Cornish, M. J. Witcomb, P. J. Hill and I. J. Horner ('Aluminide compounds of selected ternary ruthenium and iridium systems'). Vicker's pyramidal hardness measurements can show the relationships between structure and properties; therefore hardness testing was undertaken across these systems in order to characterise their mechanical properties and indicate possible applications for some of the compositions. The
hardness of AlIr was about 1000 VPN, the presence of the eutectic on the aluminium-poor side had a toughening effect; nickel or iridium can be added to AlRu without compromising the mechanical properties.

With only limited applications, ruthenium is generally in a state of over-supply, a situation which has been exacerbated as the Upper Group 2 chromitite layer has been exploited, as it is richer in ruthenium than the Merensky Reef. However, ruthenium has a number of unique properties and in recent years Mintek, the South African research and development organisation for mining, mineral and metallurgical technology, has undertaken work, in collaboration with local platinum mining companies, to create additional markets for ruthenium. Some of the more interesting developments that have resulted over the last ten years are reviewed by I. M. Wolff (‘New applications for ruthenium’). In addition to phase relationship studies, ongoing studies include corrosion-resistant stainless steels and titanium alloys, cemented carbides for drilling applications, and intermetallic compounds for spark plug electrodes.

Over the past ten years Mintek has also undertaken a research programme intended to enable South Africa to play a more comprehensive role in the international platinum jewellery industry, which now accounts for about forty per cent of platinum consumption. Initial work, summarised by S. S. Taylor and T. Biggs (‘Innovations in platinum jewellery materials’), sought to introduce a colour variation to platinum but the new materials were too hard and brittle to be formed by traditional jewellery operations. However, they were eminently suitable as gemstones and a white, hall-markable, platinum alloy suitable for use as a gemstone has also been developed. Additionally, a hardenable platinum-titanium alloy with all the properties required for jewellery applications has been produced, and research on the forming of platinum-gold composites by powder metallurgy is in progress.

Interested individuals may obtain a copy of this issue of the South African Journal of Science from: Mr Graham Baker, Editor, P.O. Box 2600, Pretoria, 0001 South Africa; E-mail: sajs@nrf.ac.za; http://www.nrf.ac.za/sajs.

I. E. COTTINGTON

References

Ian E. Cottington retired as editor of *Platinum Metals Review* in 1994. He retains his interest in the history of platinum and its uses, and in new developments in platinum technology, especially for clean energy applications.

Detecting Gas Emissions with an Electronic Nose

Gas emissions inside cars, caused by the release of volatile organic compounds (VOCs) from the interior trim materials, such as leather or plastics, contribute greatly to their internal air pollution. When the VOCs condense on surfaces, they leave an oily film, visible as fogged windscreen. Leather produces gas emissions, which can be high enough to cause nuisance and discomfort. Existing methods of analysing such emissions are a DIN standard fogging test and tests for total VOCs using a gas chromatography-flame ionisation detector (GC-FID) or a GC-mass spectrometer (MS). However, these give inconsistent readings, are time consuming and in the DIN test only one material at a time can be measured.


Aimed at mimicking the human olfactory system, the electronic nose is an analyser which can recognise, classify and quantify gaseous emissions and odours. The sensor array consists of 10 metal-oxide semiconductor field-effect transistors (MOSFETs) with gates of thin platinum, iridium and palladium of different thicknesses and combinations operated at two different temperatures, and five sensors based on semiconducting metal oxides (MOS).

Sensor array data gave similar and additional information to GC-MS. The electronic nose could also detect deviating leather samples with unusual gaseous emissions. The method is rapid, simple and inexpensive and while having problems with drift, may find use as an on-line monitor of interior trim materials.

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Metathesis Catalysed by the Platinum Group Metals

A NEW STRATEGY FOR THE SYNTHESIS OF ORGANIC COMPOUNDS AND POLYMERS
PART I: TYPES OF CATALYSTS, METATHESIS ACTIVITY AND SELECTIVITY

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Metathesis (from the Greek meta tithemi = change place) describes in chemistry the interchange of atoms between two molecules. The metathesis of olefins is the formal scission of a pair of double bonds, followed by the interchange of their carbon atoms. Metathesis polymerisation of cycloolefins refers to the apparent ring cleavage at the double bond, accompanied by polymerisation to unsaturated polymers (1a, 1b). Nowadays metathesis is established as a powerful method of synthesis in organic and polymer chemistry (1), and platinum group metal catalysts have played a prominent role in this achievement. Metathesis has resulted in both unique syntheses and novel compounds. In this review metathesis reactions catalysed by platinum group metals are described, specifically the types of catalyst, their metathesis activity and various ring-opening and ring-closing reactions. Part II of this paper will be published in the July issue of this Journal.

With the discovery of highly active and selective non-classical metathesis catalysts which tolerate various functional groups, olefin metathesis has become a powerful synthetic tool in organic and polymer chemistry (1). These new catalytic systems contain mainly late transition metals and particularly several platinum group metals. As compared to the early transition metal counterparts derived from titanium (2), tungsten (3) and molybdenum (4), these catalysts add numerous advantages to the metathesis reactions, for example: they enable working in polar and protic solvents, including alcohols and even water, and in much more acidic environments, such as cases where phenols or strong acids (for example, trichloroacetic acid) are used as solvents. They tolerate well many functional groups which contain heteroatoms (for example, O, N, P, Cl, Br) and hence a wide variety of substrates. They allow working under normal temperature and pressure in common solvents without special purification. They can be conveniently stored for several weeks under an air atmosphere without substantial decomposition. Their catalytic activity is not changed significantly by various additives and co-solvents. Importantly, these catalysts are still active at the end of the reaction and can be used in a new reaction cycle.

There are several carbon-carbon bond formation processes occurring by metathesis and induced by these types of catalytic system, that have been reported in the literature; for instance, metathesis of functionalised olefins (5), ring-opening metathesis (6), ring-closing metathesis (7), ring-opening metathesis polymerisation (ROMP) of functionalised cycloolefins (8) and ROMP of heterocyclic olefins (9).

Types of Catalysts

The main types of metathesis catalysts containing platinum group metals belong to three classes: (a) metal salts, (b) metal coordination complexes and (c) well-defined metal carbenes. Each class displays a specific activity and selectivity in metathesis reactions depending on the nature of the transition
metal, the type of coordination, the nature of the ligands and substrate, and on the reaction conditions. Some of the catalysts are readily available as commercial products while more sophisticated compounds can be prepared by conventional methods or by other specific routes.

(a) Metal Salts

The following rhodium, iridium, osmium and ruthenium salts find most use as metathesis catalysts: RhCl₃, IrCl₃, OsCl₃(hydrate), RuCl₃, K₂RuCl₆, RuCl₃(hydrate) and Ru(H₂O)₆(tos), where tos = tosyl (10-15). Initially, the chlorides (RuCl₃, IrCl₃ and OsCl₃) were employed in the metathesis polymerisation of strained cycloolefins, such as norbornene and its derivatives, but shortly afterwards the process was extended by using their corresponding hydrates (RuCl₃.3H₂O, IrCl₃.3H₂O and OsCl₃.3H₂O) for the metathesis polymerisation of heterocyclic olefins. It should be pointed out that RuCl₃ in butanol/HCl has been efficiently employed in the industrial process for the manufacture of polynorbornene (1b). Other related salts, such as K₂RuCl₆ and Ru(H₂O)₆(tos), have served as catalysts for several specific substrates (16).

(b) Metal Coordination Complexes

Mononuclear rhodium complexes of the type Rh(PPh₃)₅LCl (where L is CO or PPh₃, Ph is phenyl) have been used in metathesis and co-metathesis of electron-rich olefins (17). In addition, monodentate and bidentate iridium and ruthenium complexes with olefins or dienes as coordinated ligands have been successfully used as catalysts in olefin metathesis and ring-opening polymerisation of cycloolefins (18-20). The main iridium catalysts used include [IrCl₃(cyclooctene)], [IrCl₃(1,5-cyclooctadiene)] and [IrCl₃(norbornadiene)]. Ruthenium complexes, such as [RuCl₃(norbornene)] and [RuCl₃(norbornadiene)], are reported to have promoted ring-opening polymerisation reactions of several substrates.

(c) Metal Carbenes

A series of well-defined ruthenium carbene complexes has been conveniently prepared and successfully applied in numerous ring-opening and ring-closing metathesis reactions (21, 22). A first group consists of alkylidene and vinylalkylidene complexes, such as RuCl₃(PPh₃)₂(=CHPh), 1, and RuCl₃(PR₃)₂(=CHCH=CHPh), (R = Ph, 2; cyclohexyl (Cy) or isopropyl), which promote the living polymerisation of strained monomers such as norbornene and cyclobutene derivatives (23) or the ring-closing metathesis to O- and N-containing heterocycles (24).

A second group comprises water-soluble ruthenium complexes 3 and 4, containing preformed alkylidene fragments which initiate rapid and quantitative ring-opening polymerisation of norbornene derivatives in neat aqueous solutions (25).

The third class consists of bimetallic alkylidene ruthenium catalysts, RuCl₃(PR₃)₂(=CHC₆H₅CH=)= RuCl₃(PR₃)₂ (R = Ph, Cy or cyclopentyl (Cy)), for example 5, in which R = Ph. These have been used as initiators in the synthesis of ABA triblock copolymers with low polydispersities, starting from heterocyclic olefins (26).
A new generation of ruthenium carbene complexes, 6 to 10, which have proved to be highly active and selective in metathesis reactions, contain a variety of ligands, some of them of half-sandwich metallocene type with an ansa-bridged structure, 10, (27, 28).

Synthesis of Well-Defined Ruthenium Alkylidene Complexes

The most spectacular developments in this area are the recent syntheses and applications of Grubbs's ruthenium alkylidene complexes in metathesis reactions. These ruthenium complexes are readily accessible by the reaction of a ruthenium(II) complex, RuCl₂(PPh₃)₃ with phenyldiazo-methane (22), bis(α-diazomethyl)benzene (26) or the highly strained 3,3-diphenylcyclopropene (23).

Relevant examples are given below for the ruthenium complexes RuCl₂(PPh₃)₂(=CHPh), 1, RuCl₂(PR₃)₂(=CHCH=CHPh), 2, and RuCl₂(PR₃)₂(=CHC₆H₅.CH=)RuCl₂(PR₃), 5, see Equations (i) to (iii). The activity of these ruthenium alkylidene complexes can be tuned by changing the structure of the phosphine ligand.

Several new ruthenium alkylidene complexes, 11, can be prepared, starting from the above ruthenium catalysts, by a metathesis reaction with appropriate olefins (29), see Equation (iv). Their activity and stability are strongly influenced by the nature of the R substituent.

Bidentate phosphine ligands with large natural bite angles (for example xanthene or C₆H₅P(CH₃)₂PC₆H₅, n ≥ 5) were attached to the ruthenium alkylidene complexes, 1, to obtain the novel
ruthenium alkylidene catalysts, 12, which have *trans* coordination of the phosphine ligands (30), see Equation (v). These bidentate phosphines are also potentially useful for immobilising the ruthenium complexes on solid supports such as functionalised polystyrene or dendrimers.

Metathesis Activity and Selectivity

The metathesis activity of platinum group metal catalysts is strongly dependent on the nature of the metal, ligand, substrate and particularly the alkylidene moiety. In the metal salt series of catalysts, rhodium salts are the least active and ruthenium salts are the most active. The activity follows in the order: \( \text{Rh} < \text{Ir} < \text{Os} < \text{Ru} \).

In the series of ruthenium alkylidene catalysts, the activity can be gradually tuned by choosing an appropriate ligand and alkylidene pair. The functional groups of the substrate affect the catalyst activity in different ways, depending upon their nature. They also interfere with the tolerance of the catalyst towards functionalities.

Rhodium complexes of the type \( \text{LRhCl} \left( \text{PPh}_3 \right)_2 \), where \( L \) is \( \text{PPh}_3 \) or CO, proved to be active in the metathesis of electron-rich olefins of types A and B, see Equation (vi), below. However, the activity is retained only when ligand \( L \) is \( \text{PPh}_3 \) or CO. It is noteworthy that almost 30 years ago, based on these results, Cardin, Doyle and Lappert (17a) proposed a metal-carbene mechanism similar to the metal-carbene/metalacyclobutane mechanism proposed by Herisson and Chauvin (17b) for olefin metathesis with WCl₆-based catalysts, see the Scheme, below.

\[
\text{[Mt]} \quad \text{[cat]}
\]
Table I

<table>
<thead>
<tr>
<th>Catalyst system</th>
<th>Temperature, °C</th>
<th>[Monomer], mol dm⁻³</th>
<th>cis-Content, σ_c</th>
</tr>
</thead>
<tbody>
<tr>
<td>RuCl₃·3H₂O</td>
<td>60</td>
<td>0.9</td>
<td>0.00</td>
</tr>
<tr>
<td>IrCl₃·3H₂O</td>
<td>90</td>
<td>1.1</td>
<td>0.24</td>
</tr>
<tr>
<td>OsCl₆</td>
<td>60</td>
<td>0.9</td>
<td>0.13</td>
</tr>
<tr>
<td>Ru-TFA</td>
<td>70</td>
<td>0.9</td>
<td>0.56</td>
</tr>
</tbody>
</table>

*Data from reference (31)*

Iridium complexes display a wide range of activity and selectivity in metathesis reactions, as functions of the complexing ligand and cocatalyst. The classical iridium catalyst system, reported by Porri and coworkers (18, 19), comprising [Ir(cyclooctene)Cl]₂/AgO₂CCF₃/HO₂CCF₃ (1:2:14 equivalents), was found to catalyse the ROMP of unstrained or strained cycloolefins, for example, cyclopentene, cyclooctene or norbornene to polyalkenamers and the metathesis and isomerisation of acyclic olefins, such as 1-pentene, to yield C₄, C₅, C₆ and higher olefins. The activity and selectivity of the Porri catalyst system was directly conditioned by the presence of the acid and its silver salt, though their role was unclear at the time.

More recently, Grubbs and coworkers (20) found that a highly active catalyst for acyclic olefin metathesis/isomerisation can be prepared *in situ* from the two component system, [Ir(cyclooctene)Cl]₂/AgO₂CCF₃, the addition of acid being unnecessary. Interestingly, the molar ratio AgO₂CCF₃/[Ir(cyclooctene)Cl]₂ must be greater than 4:1 for metathesis. With a lower value of the ratio (for example 2:1) extensive olefin isomerisation occurred, and metathesis activity was not observed. From data obtained, the authors inferred that the silver salt served to precipitate silver chloride and oxidise the resulting Ir(I) trifluoroacetate complex.

An active and selective iridium catalyst for metathesis has also been obtained by addition of AgO₂CCF₃ (2 equivalents) to [Ir(cyclooctene)₂(O₂CCF₃)₂] (1 equivalent) in the presence of an acyclic olefin. In the absence of excess AgO₂CCF₃, only the isomerisation reaction has been detected. The system [Ir(cyclooctene)Cl]₂/AgO₂CCF₃ has also been selectively applied to the metathesis of functionalised acyclic olefins, such as methyl oleate.

There are several peculiarities concerning the metathesis activity and selectivity of classical Ru-, Ir- and Os-based catalysts used in ring-opening polymerisation of norbornene and norbornadiene derivatives. Firstly, although both RuCl₃ and OsCl₆ generally display a higher activity and selectivity compared to IrCl₆, in some cases their behaviour is greatly affected by the nature of the monomer. Thus, while RuCl₃ is very active and highly trans stereoselective (content of cis double bonds, σ_c = 0.00) for the polymerisation of norbornene-type monomers, see Table I, (31), it is totally inactive with norbornadiene derivatives.

Secondly, OsCl₆, which forms polynorbornene and substituted polynorbornenes with a relatively low cis content (σ_c = 0.1–0.4), also forms highly cis polymers from norbornadiene and their derivatives (σ_c > 0.9) (32). Moreover, it was also found that the σ_c for norbornene homodyad units (that is successive pairs of norbornene units with the same stereochemistry) in copolymers of norbornene with norbornadiene, has the same high value. These findings provide evidence that the cyclic diene may act as a di-endo-chelating spectator ligand at the metal, crowding the reactive centre and forcing the metallacyclobutane transition state to adopt the less bulky cis configuration. For OsCl₆, this phenomenon leads to a high cis stereospecificity with diene monomers, while in the case of RuCl₃ (which is a highly trans catalyst with monoene substrates) it renders the RuCl₃ inactive.

The particular activity of a new series of ruthenium alkylidene complexes, RuCl₅(=CHR)(PPh₃)₂,
(R = Me, Et) and RuCl₂(=CH-₃-C₅Hₓ)(PPh₃)₂ (X = H, NMe₂, OMe, Me, F, Cl, NO₂), has been described by Grubbs and coworkers in the ROMP of cycloolefins (29). These catalysts are easily prepared by the reaction of RuCl₂(PPh₃)₃ with the corresponding diazoalkanes, see Equation (vii).

Kinetic studies on the living ROMP of norbornene, using substituted benzylidene complexes as catalysts, have shown that the initiation (with reaction rate $k_{i}$) is in all cases faster than the propagation (with reaction rate $k_{p}$), see Table II, and that the electronic effect of $X$ on the metathesis activity is relatively small.

When the phosphine in the benzylidene complexes was exchanged with tricyclohexylphosphine (PCy₃), RuCl₂(=CH-₃-C₅Hₓ)(PCy₃)₂ was formed; this is an efficient catalyst for the ROMP of cyclooctene and 1,5-cyclooctadiene. Several of these substituted benzylidene complexes have also displayed good activity in the metathesis of acyclic olefins, see Table III.

The metathesis of conjugated and cumulated olefins with the benzylidene complex RuCl₂(=CHPh)(PCy₃)₂ resulted in the formation of

![Equation (vii)](image)

### Table II

<table>
<thead>
<tr>
<th>$X$</th>
<th>$10^3 k_i$</th>
<th>$10^3 k_p$</th>
<th>$k_i/k_p$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>11.5</td>
<td>1.28</td>
<td>9.0</td>
</tr>
<tr>
<td>NMe₂</td>
<td>3.32</td>
<td>1.28</td>
<td>2.6</td>
</tr>
<tr>
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<td>3.34</td>
<td>1.28</td>
<td>2.6</td>
</tr>
<tr>
<td>Me</td>
<td>3.69</td>
<td>1.28</td>
<td>2.9</td>
</tr>
<tr>
<td>F</td>
<td>6.19</td>
<td>1.28</td>
<td>4.8</td>
</tr>
<tr>
<td>Cl</td>
<td>1.56</td>
<td>1.28</td>
<td>1.2</td>
</tr>
<tr>
<td>NO₂</td>
<td>2.91</td>
<td>1.28</td>
<td>2.3</td>
</tr>
</tbody>
</table>

### Table III

<table>
<thead>
<tr>
<th>$X$</th>
<th>$10^3 k_i$</th>
<th>$X$</th>
<th>$10^3 k_i$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>2.87</td>
<td>F</td>
<td>1.21</td>
</tr>
<tr>
<td>NMe₂</td>
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</tr>
<tr>
<td>OMe</td>
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<td>NO₂</td>
<td>1.77</td>
</tr>
<tr>
<td>Me</td>
<td>2.15</td>
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<td></td>
</tr>
</tbody>
</table>

*The data are taken from reference (29)*
vinylalkyldiene and vinylidene complexes, as shown for the synthesis of RuCl₂(=CHCH=CH₂)(PCy₃)₂ and RuCl₂(=C=CH₂)(PCy₃)₂ from 1,3-butadiene or 1,2-propadiene, respectively, see Equation (viii).

Although less active than their early transition metal counterparts, ruthenium alkylidene complexes have a broader synthetic utility due to their tolerance of functional groups and protic media. For example, it has been found that the ruthenium vinylalkyldiene complexes, RuCl₂(=CHCH=CPPh₂)(PR₃)₂ (R = Ph or Cy) react readily with electron-rich olefins such as vinyl ethers, H₂C=CHOR' (R' = alkyl), to yield the metathesis inactive complex, RuCl₂(=CHOR')(PR₃)₂. However, electron-deficient olefins are not metathesised by the triphenylphosphine complex RuCl₂(=CHCH=CPPh₂)(PPh₂)₂, and the tricyclohexylphosphine complex RuCl₂(=CHCH=CPH₂)₂(PCy₃)₂ displays only limited activity toward these substrates.

The enhanced activity of the benzylidene complex RuCl₂(=CHPh)(PCy₃)₂ allowed a metathesis reaction with alkenes, such as allyl chloride, or with unprotected unsaturated alcohols, such as 4-penten-1-ol, which generated the corresponding functionalised alkylidene, see Equation (ix).

Functionalised alkylidene complexes are active in ROMP of low-strain cycloolefins, which makes them attractive catalysts for the synthesis of telechelic polymers and other functionalised polymers. (Telechelic polymers have remote functional groups which are frequently end groups).

To increase the activity and selectivity of the ruthenium family, new derivatives of complex 1a have been prepared. The derivatives of 1a include bidentate salicylidene ruthenium complexes (33), binuclear ruthenium complexes (34) and ruthenium complexes with a family of imidazolylidene ligands (35). These structures are based on mechanistic studies which have demonstrated that the activity of the system is related to the large cone angle and basicity of the cyclohexylphosphine ligand (36). Continued improvements have led to a new family of functional group containing ruthenium catalysts; the activity and efficiency of this family approaches those of molybdenum alkylidene complexes (37).

The water-soluble ruthenium complexes 3 and 4 display a high metathesis activity, showing rapid and quantitative initiation of the ring-opening polymerisation of norbornene derivatives. Further investigations indicated that the propagating species in these reactions decomposed before polymerisation was complete. This behaviour was attributed to the presence of hydroxide ions which
could have resulted from the autoprotolysis of water. Grubbs and coworkers (25) found that norbornene derivatives were completely polymerised when up to 1.0 equivalent of DCl was added to the reaction mixture, and that the polymerisation rate was enhanced up to 10 times, compared to reactions where no acid was added. The enhanced activity of these catalysts was assigned to the generation of a monophosphine derivative of the ruthenium alkylidene complex, due to the protonation of a phosphine ligand by the acid, and followed by its elimination as a phosphonium salt, see Equation (x).

These systems represent significant improvements over "classical" aqueous ROMP catalysts. The stability of the living propagating species has been demonstrated by \(^1\)H NMR spectroscopy. Sequential monomer addition allowed the synthesis of water-soluble block copolymers. However, the polymerisation of norbornene derivatives in water is not a living polymerisation in the absence of a Brønsted acid.

Conclusion

In this first part of the review the major types of metathesis catalysts containing platinum group metals have been described and their specific activity and selectivity discussed, highlighting the newest representatives which are the well-defined ruthenium alkylidene complexes. The latter catalysts, discovered in the last decade, have changed the impact of olefin metathesis in many synthetic applications. The importance of a RuCl\(_3\)-based catalyst for the industrial manufacture of polynorbornene is also evidenced.

The next part of this review will examine metathesis reactions as a special and new area for utilisation of platinum group metal catalysts. An array of versatile applications, such as ring-closing metathesis (RCM), acyclic diene metathesis (ADMET) and ROMP will be covered.

References


Platinum(II) Used in Red Organic Light Emitting Devices

Red organic light emitting diodes (OLEDs) are usually produced by doping red dyes into a suitable host, such as aluminium(III) tris(8-hydroxyquinolate) (AlQ3). Obtaining saturated red emission with high quantum and luminous efficiencies is challenging, and the most effective complex to date to show a red colour, platinum(II) octaethylporphyrin, has been described by a group of researchers in the U.S.A. (1).

Now, this group have prepared two new Pt(II) porphyrins, PtOX and PtDPP, as phosphorescent dyes in OLEDs, by refluxing etioporphyrin III and 5,15-diphenylporphyrin, respectively, with PtCl2 (R. C. Kwong, S. Sibley, T. Dubovoy, M. Baldo, S. R. Forrest and M. E. Thompson, Chem. Mater., 1999, 11, (12), 3709–3713).

The PtOX and PtDPP were codeposited with AlQ3, at optimum doping level of 6 mol%, in the emitting layer, and the highest saturated red emission and quantum efficiencies were observed at low to moderate current densities. Energy transfer occurred between the AlQ3 and the Pt porphyrin. PtOX-doped devices reached a quantum efficiency of 1.1 per cent at 100 cd m⁻² with a luminous efficiency of 0.17 lm W⁻¹.

Reference

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Reference
Advanced Exhaust Emissions Control
A SELECTIVE REVIEW OF THE DETROIT 2000 SAE WORLD CONGRESS

This selective review covers papers, involving platinum group metal (PGM) catalysts, presented at the Society of Automotive Engineers (SAE) annual Detroit World Congress, held from 6th to 9th March, 2000. The Congress attracts large numbers of attendees (49,249 this year from more than 80 countries), and there were some 1,300 exhibiting companies with a similar number of papers presented at the well-attended technical sessions. Almost all of the published papers referred to here are conveniently collected together in SAE “Single Publications” (1), and reference is given in parenthesis to each cited paper to enable those interested to easily access them.

Towards and Beyond SULEV
The effectiveness of PGMs in three-way catalysts (TWCs) has increased over recent years as more advanced washcoat formulations have been introduced. The distribution of PGMs in the catalyst is important, and ASEC (2000-01-0860) found that by having a palladium-only front catalyst followed by one containing platinum and rhodium was an effective solution in some LEV/ULEV applications because the palladium catalyst ensured optimal hydrocarbon light-off. The design of such low emissions systems has become relatively commonplace. The next major emissions target is the American SULEV (half ULEV levels) which seriously challenges all of the available technologies. Here advanced catalysts are incorporated into systems that push technology to the limits to give the lowest possible emissions for conventional gasoline engines.

High Cell Density Catalysts
Thin wall high cell density substrates provide high geometric surface area, that can be accompanied by low heat capacity which can shorten the time it takes for catalysts to light-off during the cold start of conventional gasoline engines – the key parameter in achieving very low emissions. This was an important theme at the last congress (2), and the trend continued this year. Denso (2000-01-0496) discussed ultra thin wall 3 or 2 mil (75, 50 μm) corderite substrate, and highlighted material requirements of the front face, particularly when located close to the exhaust manifold. To increase strength, the walls of the outermost cells were made thicker than the inner ones. This could exacerbate radial maldistribution of gas across the catalyst, and the practical consequences of this have yet to be explored. NGK and Environex (2000-01-0494) developed computer models to predict performance of catalysts based on ultra thin wall high cell density substrates. Their results showed that reducing wall thickness to reduce thermal mass offers the greatest benefit in reducing light-off time. Higher cell density per se is however accompanied by extra thermal mass, and a cell density of around 1200 cps reported optimum light-off. Johnson Matthey (2000-01-0502) also reported computer simulation of these effects, and gave extensive results for catalysts with cell densities up to 900 cps (2 mil walls) on laboratory engines and cars. Significant benefits were observed with palladium/rhodium and palladium-only formulations on high cell density substrates, but appropriate engine calibration is vital. There may be little benefit obtained from using high cell density catalysts if the engine calibration is poor: for example, a European Stage 2 car with a rich start-up strategy showed a nitrogen oxides (NOx) advantage with high cell density catalyst, but hydrocarbon (HC) and carbon monoxide (CO) advantages were swamped.

Another requirement for advanced substrates is that the catalyst formulation must have very good thermal durability, because high cell density catalyst will experience high temperatures caused by more intensive chemical exotherms.

Metallic Substrates
These can be made from very thin metal foil to achieve high cell densities; but disadvantages can include the higher thermal capacity of metals.
compared to porous ceramic materials. For several years Bosal (2000-01-0497) have been working with pre-coated metal foil, and they described how they produce a modular block design catalyst using 50 μm metal foil. These are assembled into V-shapes across the exhaust gas flow. This design offers the advantage of being able to use high cell density units without overly increasing pressure drop as the facial area can be increased in proportion to the cell density, provided the necessary space is available.

In a joint paper AVL and Emitec (2000-01-0500) used computer simulation to probe the behaviour of normal high cell density catalyst designs in a cascade modular arrangement with an electrically heated catalyst. Tests were carried out on an ULEV production vehicle, and with the electrically heated catalyst operating for 25 seconds at 2.5 kW the light-off time shortened from 30 to 22 seconds, but SULEV HC levels were not achieved.

Hydrocarbon Traps

Trapping HCs formed during the cold start in a material such as a zeolite until the TWC has reached light-off temperature is a potential route to very low emissions. The University of Thessaly (2000-01-0655) developed a computer model for a system with a HC-trap in front of a main catalyst. With this configuration, desorption from the HC-trap, before the catalyst reaches operating temperature, is a major problem that is difficult to circumvent. Ford (2000-01-0654) modelled a catalysed HC-trap, that combines catalyst and HC-trap on a single substrate. Here the thermal problems associated with separate units were overcome, and the model predicted good performance on a vehicle. The computer model should permit design of optimised systems in the future. Nissan (2000-01-0892) presented results for systems comprising a closed-coupled TWC followed by underfloor two-layer catalysed hydrocarbon traps. These had a lower layer HC absorber, and a top TWC layer, and the overall system demonstrated potential for SULEV applications.

Vehicle Demonstrations

Volvo (2000-01-0894) discussed three SULEV approaches: hydrogen (H₂) injection onto the catalyst when starting, a rich start-up with rapid temperature rise and air injection, and storing start-up HCs in a canister until the catalyst is operating.

Each has the potential of providing SULEV requirements, but the most attractive is the second, requiring least modification to current designs. By bringing together several different technologies on vehicles, emissions below the SULEV levels can be achieved. Nissan (2000-01-0890) described the combination of ultra thin wall (2 mil) substrate coated with low light-off catalyst, and a two-stage catalysed HC-trap, on an engine with tight air:fuel ratio control. The cold start HCs from the engine were minimised by incorporating an electronically actuated swirl control valve, and a high-speed starter. The resulting vehicle emissions were exceptionally low, as they also were from a car
described by Honda (2000-01-0887). Honda used 1200 cpsi (2 mil walls) substrates made possible by a new canning method, which overcomes strength problems. However, to meet SULEV standards it was necessary to adjust the spark timing to decrease the time to reach catalyst light-off temperature, and to control intake air (early lean operation), and use an advanced secondary oxygen sensor feedback system. This identifies different catalyst models in real time and predicts the post-catalyst sensor output, so eliminating emissions that would be released while the control system adjusted to the actual secondary sensor signal.

NOx-Traps for Lean-Burn Gasoline Engines

The new generation of direct injection, lean-burn gasoline engines offers potential improved fuel economy, but requires NOx emissions to be trapped when running lean, and periodic regeneration under rich conditions to release the stored NOx as nitrogen (N$_2$). This developing NOx-trap technology, which uses platinum and rhodium, suffers from sulfur poisoning, and NOx-traps need to be purged of sulfur periodically. Both regeneration conditions require careful engine management to achieve the desired effects without affecting driveability, but desulfation is the more difficult because of the higher temperatures involved.

Ford (2000-01-1200) described a novel way of sustaining high catalyst temperature by rapid air/fuel ratio fluctuations. The oxygen storage components in the NOx-trap respond to this and generate isotherms of around 300°C, without being overall rich. Toyota (2000-01-1196) investigated ways of restricting the amount of accumulated sulfur, and found that incorporating titania and zirconia into the formulation was beneficial. Honda (2000-01-1197) also reported formulation work, and found addition of "mixed metal oxides" of different types improved performance.

Diesel Aftertreatment

Control of Diesel Particulate Emissions

Diesel soot, formed by incomplete combustion of fuel, is a potential health hazard and it is desirable to minimise soot emissions into the environment (3). It comprises a high surface area carbon core with adsorbed HC, partially oxidised species like aldehydes, carboxylic acids, etc., with water, sulfur compounds (including sulfuric acid), and some nitric acid derived from nitrogen oxides. Over recent years improved fuelling, better combustion system characteristics, and enhanced engine management have contributed to a reduction of soot. However, the introduction of finer fuel spray from new injector nozzles, made possible by higher-pressure fuel systems, was probably the single most important advance (4). The development of the high performance modern high-speed diesel engine also provided means of reducing exhaust pollutants, and additional benefits are now coming from use of increasingly-available ultra low sulfur fuel with low polyaromatic content which produces less soot than conventional diesel fuel (5).

Johnson Matthey (2000-01-0479) described a procedure to lower particulate emissions from older American diesel buses (built before 1994) by 25%, or to below 0.1 g bhp$^{-1}$ h$^{-1}$, by replacing some engine components, and fitting a platinum oxidation catalyst to provide additional particulate
reduction. Platinum oxidation catalysts can remove some organic components from soot, but usually significant amounts of carbon are not oxidised.

Diesel Particulate Filters

Future legislation demands much lower particulate emissions than are made possible by engine modifications and oxidation catalysts, and a particulate filter, of which there are several kinds, will have to be used. Corning (2000-01-0184) derived and experimentally verified a pressure-drop model for clean cordierite wall-flow filters. Agreement between predicted and measured pressure drop was excellent. The approach is being extended to filters loaded with soot, and preliminary data for lightly loaded filters were presented: lower cell densities are appropriate for longer filters, and higher cell densities for short ones. Extension of this work should permit prediction of optimised filter length, volume, and cell density for particular applications. Ibiden and Peugeot (2000-01-0185) studied the characteristics of silicon carbide wall-flow filters along similar lines, and concentrated on the thermal durability and high temperature resistance. Their model for a loaded filter assumed a uniform soot layer, with ash collecting at the end of the channels forming an inert zone.

The Continuously Regenerating Trap

For continued operation it is necessary to remove trapped soot from a diesel particulate filter, and several ways of doing this have been investigated. Johnson Matthey (2000-01-0480) reviewed heavy-duty diesel experiences with a successful approach which uses nitrogen dioxide (NO₂) to combust trapped soot at temperatures much lower than it burns in air. The required NO₂ is obtained by oxidation of nitric oxide (NO) over a platinum catalyst before the filter, this also oxidises HCs and CO. Under most operating conditions soot is continuously removed, so the system is referred to as a continuously regenerating trap (CRT™). Over six years more than 6000 of these have been utilised in European countries where the necessary low sulfur fuel was promoted – Sweden, Germany, the U.K., and to a lesser extent in several other countries. A selection of CRTs which had been used for up to 600,000 km was tested under laboratory conditions. There was virtually no deterioration of performance, confirming the robustness of this system in actual use. A lighter duty application of the CRT™ was described by AVL (2000-01-0181) who have developed a diesel engine for Sports Utility Vehicles (SUVs) which meets the American Tier 2 emissions levels.

Peugeot (2000-01-0473) used a CRT configuration of a platinum oxidation catalyst in front of a silicon carbide wall-flow filter on a European diesel car which should soon be in production. Strategies are incorporated to increase exhaust gas temperature through post combustion fuel injection, and the fuel is dosed with a cerium additive to facilitate soot combustion. Faurecia (2000-01-0475) discussed cordierite and silicon carbide wall-flow filters, and proposed an oxidation catalyst in front of the filter in a CRT configuration that included an electrical heater close to the filter to increase gas temperature when appropriate.

Control of Diesel NOx Emissions

Lean-NOx Catalysts

Diesel exhaust contains low levels of reductant (CO, HC) in the presence of a vast excess of oxygen, and most of the reductant is oxidised by the oxygen over platinum oxidation catalysts. Little reductant remains to reduce NOx (and only over a small temperature range), so normally only a relatively small amount of NOx is removed by what are called lean NOx catalysts under normal conditions, and this can be somewhat increased if additional reductant is added to the exhaust.

Selective Catalytic Reduction

To achieve significant direct NOx reduction additional reductant that selectively reduces NO in the presence of oxygen must be introduced – a process called selective catalytic reduction (SCR). Ammonia is an excellent reductant in SCR systems, and although at present it appears inappropriate to use PGM-based SCR catalysts, platinum catalysts are used in two different roles in these systems. Urea is potentially a convenient source of ammonia, and Degussa (2000-01-0189) described a urea-based SCR system for heavy-duty
Health Effects of Vehicle Emissions

A Review from the Second International Conference

The Second International Conference on Health Effects of Vehicle Emissions was held in London from 23rd to 24th February, 2000. Some 165 delegates from 16 nations, and a variety of industrial, environmental, government and academic backgrounds, met to discuss issues concerned with reducing the environmental impact and health risks associated with vehicle emissions.

J. Wallace (Ford, U.S.A.) summarised some U.S. steps with respect to vehicle emissions. Since 1966 vehicle emissions have been reduced by a factor of 25. Hydrocarbon emissions have decreased by many challenges have to be overcome, SCR systems have demonstrated high efficiencies for NOx reduction, and in combination with particulate control capability, the way towards ultra clean diesel engines is being defined.

Conclusions

Emissions of exhaust pollutants from internal combustion engines in automotive applications have been dramatically reduced over recent years. This trend continues, and new technologies are being successfully developed to meet increasingly demanding requirements. The Detroit 2000 SAE Congress provided a focus for discussion about these developments, and confirmed the critical role PGM-containing catalysts have in this important area.

M. V. TWIGG

References

1 "Diesel Exhaust Aftertreatment 2000", SP-1497; "General Emissions Research", SP-1506; "LEV-II Emissions Solutions", SP-1510; "Advanced Catalysts Substrates and Advanced Converter Packaging", SP-1532; "Exhaust Aftertreatment Modeling and Gasoline Direct Injection Aftertreatment", SP-1533. These and individual technical papers are available from SAE, 40 Commonwealth Drive, Warrendale, PA 15096, U.S.A. See also: http://www.sae.org


4 See papers in: "In-Cylinder Diesel Particulate and NO Control 2000", SAE SP-1508 (2000)

5 In the U.K. diesel fuel typically now contains less than 50 ppm sulfur

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diesel applications. This had a platinum pre-oxidation catalyst, a hydrolysis catalyst and a vanadium-based SCR catalyst, followed by a platinum guard catalyst to prevent traces of ammonia from escaping into the environment by oxidising it to NO which is environmentally less sensitive. Using a simple urea dosing strategy a NOx reduction of 77% was recorded in the ESC test procedure (European Stationary Cycle, a heavy-duty diesel test cycle).

Mack Truck and Siemens (2000-01-0190) reported results for an American 12 litre heavy-duty diesel engine, and a Class 8 truck equipped with a vanadium SCR system. This returned NOx reductions averaging 65% in road tests, with a urea solution consumption of a little less than 100 mpg, and with another catalyst 140 mpg based on OICA test cycle data (Organisation Internationale des Constructeurs d'Automobiles, a heavy-duty diesel test cycle).

Johnson Matthey (2000-01-0188) described a urea-based SCR unit integrated with a CRT™. Combined particulate and NOx control was evaluated on several engines over a number of different test cycles. Simultaneous NOx conversions of 75-90% and particulate control up to 90% on current engines in both American and European test procedures were measured. A platinum oxidation catalyst was used before the particulate filter, SCR catalysts after ammonia injection for NOx reduction, and a platinum oxidation catalyst to control ammonia slip. The platinum pre-catalyst significantly enhances low temperature SCR performance by converting some NO to NO2 which reacts faster, perhaps via reactive surface species of a N2Ox type. Although

HEALTH EFFECTS OF VEHICLE EMISSIONS

A REVIEW FROM THE SECOND INTERNATIONAL CONFERENCE

96% and NOx (nitrogen oxides) by 75%, although the number of cars being sold every day is increasing. Overall in the U.S., vehicle miles travelled have increased by 127%, but net emissions have decreased – by 31%. Ford are working on Alternative Fuel Vehicles (AFVs) and the Ford “TH!NK” group investigates ideas to lower vehicle emissions. Ford has a commitment to fuel cell technology, as shown by projects such as the P2000 hydrogen fuel cell vehicle and the Focus FC5 methanol reformate vehicle.

M. T. Oge (EPA, U.S.A.) discussed improved U.S. air quality. Mobile sources contribute one third of the volatile organic compounds (VOCs), one quarter of the particulate matter (PM) and 40 to 50% of NOx to air pollution in urban areas. As data become available, standards will have to be updated. The emission of air toxics (such as benzene and formaldehyde) should be addressed by standards aimed at lowering them, as follows: (i) reduce air toxics from the new fleet (ii) introduce a voluntary retrofit programme for heavy-duty diesel vehicles, and (iii) improve characterisation of mobile source toxic exposure: data for modelling purposes.

International Air Pollution Issues

M. P. Walsh (International Consultant, U.S.A.) discussed concerns and regulation trends associated with vehicle emissions (1). Progress has been made with air pollution in the U.S.A., Europe and Japan, by use of unleaded gasoline and catalyst technology, but PM emissions are an issue, with a diesel vehicle emitting more PM_{10} (PM of < 10 \mu m in diameter) than a gasoline vehicle. However, the larger number of gasoline vehicles together emit roughly three times more mass of PM_{10} than diesel.

In the U.S.A. by 2004, federal “Tier 2” standards and low sulfur gasoline will be phased in with a programme aimed at heavy-duty diesel vehicles. This will be introduced with tighter heavy-duty PM and NOx standards. Legislation to reduce the sulfur content in diesel is likely. It is hoped that sulfur levels will be reduced to 10 ppm. Particle filters for ultra fine particles will be used in future.

H. Tsuda and F. Okada described the Japan Clean Air Programme which aims to reduce emissions and improve air quality by 2010, and investigate and develop future vehicle and fuel technologies. It is hoped that tailpipe emissions from gasoline vehicles can be reduced by 70% from 2000–2002 (Step 1) with further reductions by 50% between 2005–2007 (Step 2), while for diesel it is hoped that tailpipe emissions can be reduced by 50% between 2007–2009.

The Canadian aim of reducing the ambient levels of PM_{2.5}, over a 24 hour average, to 30 \mu g m^{-3} by 2010, and ozone levels to 65 ppbv by 2015, measured over an 8 hour average was described by B. McEwan and M. Tushingham (Environment Canada). Canada requires sulfur levels in gasoline fuel to be no higher than 170 ppm by 2004 with a further reduction to 40 ppm from 1st January 2005.

Air pollution and control in north east U.S.A. were discussed by M. Treadwell (NESCAUM, Northeast States for Coordinated Air Use Management). There is little information about health effects from emissions, such as benzene, formaldehyde, 1,3-butadiene and acetaldehyde. Ambient concentrations of these air toxics currently exceed most cancer risk thresholds in the majority of north east areas. Mobile sources could account for 80 to 90% of primary emissions.

Sources of Pollution

Professor R. Harrison (University of Birmingham, U.K.) discussed U.K. pollutants. Based on data from 1996: 47% of the NOx, 71% of the CO and 30% of VOCs in ambient air are from road transport. For PMs, 25% of PM_{10} in the atmosphere was due to road traffic exhaust, increasing to 77% in the London area; 31% of PM_{2.5} and 60% of PM_{10} come from road transport.

R. Edwards and K. Koistinen (National Institute of Public Health, Finland) pointed out that in-vehicle concentrations of VOCs are 3 to 8 times higher than ambient levels, and a significant contribution to VOC compounds indoors is associated with traffic emissions.

The problems in measuring particle emissions were discussed by J. Andersson (Ricardo Consulting Engineers, U.K.). Present testing methods for light-duty particulate sampling are not ideal.
and a system representing real world conditions is needed. It was suggested that gasoline vehicles do not emit carbonaceous particles.

**Health Effects**

A. Peters (GSF, Institute of Epidemiology, Germany) presented evidence which related disease type, such as respiratory and cardiovascular, and trends in increases in mortality and hospital admissions, to air-borne particulate matter. Current data do not reflect the impact of urban air pollution.

Professor K. Donaldson (Napier University, U.K.) described the penetration depths of particles in the lungs. Particles, 0.01–0.1 μm in diameter, are thought to cause real problems. The lungs can deal more efficiently with larger particulate, such as PM₁₀, which is more detrimental to the upper airways. Particle surface area and size distributions should be considered in setting legislation.

**Solutions**

A. Friedrich (UBA, Federal Environmental Agency, Germany) stressed that for improved standards an increased public awareness, financial incentives to aid the introduction of cleaner vehicles and retrofitting programmes were needed. He emphasised NOx and PM diesel emissions and described the vanadium-based selective catalytic reduction (SCR) and NOx adsorbers. Detrimental effects to diesel particulate filter systems are caused by the sulfur in fuel, which requires reduction to at least 50 ppm and preferably to 10 ppm.

Changes in engine and chassis design to reduce vehicle emissions were described by K.-P. Schindler (Volkswagen, Germany). Customers are important, but car manufacturers have to obey legislation. Reducing drag, friction and vehicle mass can be critical in achieving reduced emissions, besides improving powertrain efficiency, by using Turbo Diesel Injection (TDI) with a high pressure injector, Gasoline Direct Injection, alternative fuels and fuel cell technologies. The VW vehicles Lupo 3L TDI and 1.4L FSI (Fuel Stratified Injection) are being developed. Aftertreatment technologies, particularly NOx storage catalysts and diesel particulate filters, such as the Johnson Matthey continuously regenerating trap (CRT™) were discussed.

Developments in conventional fuels were examined by J. Unsworth and A. Clarke-Sturman (Shell, U.K.). Lead in gasoline has been dramatically reduced, while MTBE use (to improve octane) increased when restrictions on the aromatic content of gasoline were introduced in January 2000. Shell propose that the European oil industry should address this. Problems with electrical conductivity and lubricity have occurred due to the lower sulfur content in fuel.

Catalyst aftertreatment systems and their operation, for instance continuously regenerating particulate traps and SCR technology and the need for retrofitting were discussed by R. A. Searles (Association for Emissions Control by Catalysts, Belgium).

"Conventional" and "advanced" diesel technologies were compared by J. Toulmin (BMW, U.K.) with respect to particulate emission. Both technologies emitted PM in the same size range but the "advanced" diesel emitted fewer particles on average. More research is needed on the relationship between particle number and mass emissions.

**Conclusion**

It is clear that more data are needed for better analysis of results and modelling purposes. The level of sulfur in fuels and its effect on catalyst systems, and particulate emissions from gasoline vehicles were contentious issues, with some supporting the need for technology to deal with the latter issue, while others suggest it is insignificant. With the predicted growth in population and continued increase in miles travelled, oil companies, and vehicle and aftertreatment-technology manufacturers will have to cooperate to improve upon achievements already made. Governments must provide legislation, information and incentives to encourage the application of future vehicle emission technologies.

J. M. McNAMARA

**Reference**


John McNamara is a research scientist at the Johnson Matthey Technology Centre. He is working on the development of a method of aftertreatment of particulate emissions from gasoline-powered automotive vehicles.
Investigations on Platinum Gauze Surfaces Used in the Manufacture of Nitric Acid

THE DEPENDENCE OF THE ACTIVITY OF A PLATINUM CATALYST ON THE COMPOSITION OF SUB-SURFACE LAYERS

By P. A. Kozub, G. I. Gryn and I. I. Goncharov

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The oxidation of ammonia for the production of nitric acid is a well known process which has been in constant use since the 1890s for the manufacture of fertiliser. Ammonia is oxidised on the surface of a woven or knitted catalyst gauze made of noble metals. Fertiliser production throughout the world partly depends on this technology and research is continuously being undertaken aimed at optimising output and reducing the noble metal loss from the catalysts. Here, some investigations carried out in Ukraine on the surface composition of binary (platinum-palladium) and ternary (platinum-palladium-rhodium) alloys used for the ammonia oxidation process are described. Samples of catalyst received different pretreatments, and their activity was then measured in a laboratory reactor, paying particular attention to the composition of the first few nanometres below the surface. Analysis of the experimental data showed that the role of carbon is different to that of other elements and that the activity of the catalyst is a maximum for carbon concentrations in the range 6 to 10 atomic per cent. It seems most probable than the carbon is present as microcrystals embedded in the alloy and concentrated on the faces of the metal crystals.

Although many investigations into the industrial oxidation of ammonia have been carried out using base metal catalysts and base metal oxide catalysts, platinum, alloyed with additions of rhodium and palladium, is still the main catalyst material (1–3). However, the cost of the process has encouraged research into the amounts and causes of metal loss and how this may be prevented or reduced (4). Volatilisation and erosion of platinum are regarded as the most probable causes of platinum loss, and most published work describes the surface structure of the catalyst and its relationship to the operating conditions (1, 5). Such studies have shown that changes in the metal structure are the principal cause of platinum loss.

During the ammonia oxidation reaction:

\[4\text{NH}_3 + 5\text{O}_2 \rightarrow 4\text{NO} + 6\text{H}_2\text{O}\]

the catalyst surface is transformed into “cauliflower-like” structures which have low mechanical strength and can be easily broken off and swept away in the gas stream (6). Palladium-gold or palladium-nickel alloy catchment gauges, or oxide-catching mixtures of calcium and aluminum oxides, are generally used to trap the platinum oxide and platinum metal particles, and this, together with techniques to activate and regenerate the catalyst gauze, are generally considered to be the most promising ways of increasing the efficiency of using the platinum metals (7–10).

Surface morphology and composition have an effect on the activity of the catalyst (1). By changing the surface morphology (activation) before placing the catalyst in the reactor, it is possible to increase its activity, reduce the time of firing (time for the catalyst to achieve operating performance) and decrease the platinum lost by hardening the surface layer of the metal. However, there is no generally accepted explanation for the mechanisms of surface changes occurring during activation. In an attempt to clarify all aspects of the activation process, we carried out a series of experiments on the effects of different surface treatments under various operating conditions on the surface morphology of fresh
Table I
Treatment of the Alloy Gauzes and Surface Concentrations of Carbon and Oxygen

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Treatment</th>
<th>Alloy</th>
<th>Carbon, at.%</th>
<th>Oxygen, at.%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Initial/non-treated</td>
<td>Pt-Pd-Rh</td>
<td>45.8</td>
<td>17.2</td>
</tr>
<tr>
<td>2</td>
<td>Heating/burning in H₂ (10 s)</td>
<td>Pt-Pd-Rh</td>
<td>4.9</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>Heating/burning in H₂ (20 min)</td>
<td>Pt-Pd-Rh</td>
<td>10.2</td>
<td>-</td>
</tr>
<tr>
<td>4</td>
<td>HCOOH solution (15%, 60°C, 4 h)</td>
<td>Pt-Rh</td>
<td>35.0</td>
<td>-</td>
</tr>
<tr>
<td>5</td>
<td>Electrolysis in 10% CH₃COOH solution (20°C, 4 h)</td>
<td>Pt-Rh</td>
<td>90.1</td>
<td>8.7</td>
</tr>
<tr>
<td>6</td>
<td>CO treatment (240°C, 1 h)</td>
<td>Pt-Rh</td>
<td>18.7</td>
<td>8.2</td>
</tr>
<tr>
<td>7</td>
<td>CO₂ treatment (240°C, 1 h)</td>
<td>Pt-Rh</td>
<td>65.9</td>
<td>4.2</td>
</tr>
<tr>
<td>8</td>
<td>O₂ treatment (240°C 1 h)</td>
<td>Pt-Rh</td>
<td>8.4</td>
<td>8.4</td>
</tr>
<tr>
<td>9</td>
<td>CH₃COOH vapour (over 40% solution, 100°C, 4 h)</td>
<td>Pt-Rh</td>
<td>16.2</td>
<td>5.9</td>
</tr>
<tr>
<td>10</td>
<td>H₂O₂ solution (33%, 20°C, 4 h)</td>
<td>Pt-Pd-Rh</td>
<td>34.6</td>
<td>12.8</td>
</tr>
<tr>
<td>11</td>
<td>H₂O₂ solution (24%, 20°C, 4 h) + burning in H₂ (10 s)</td>
<td>Pt-Pd-Rh</td>
<td>13.3</td>
<td>-</td>
</tr>
<tr>
<td>12</td>
<td>H₂O₂ solution (33%, 20°C, 4 h) + burning in H₂ (10 s)</td>
<td>Pt-Pd-Rh</td>
<td>48.2</td>
<td>9.2</td>
</tr>
<tr>
<td>13</td>
<td>H₂O₂ solution (16%, 20°C, 4 h) + burning in H₂ (10 s)</td>
<td>Pt-Pd-Rh</td>
<td>6.3</td>
<td>6.8</td>
</tr>
<tr>
<td>14</td>
<td>H₂O₂ solution (4%, 20°C, 4 h) + burning in H₂ (10 s)</td>
<td>Pt-Pd-Rh</td>
<td>5.2</td>
<td>-</td>
</tr>
<tr>
<td>15</td>
<td>H₂O₂ solution (33%, 20°C, 0.5 h) + burning in H₂ (10 s)</td>
<td>Pt-Pd-Rh</td>
<td>6.3</td>
<td>5.8</td>
</tr>
<tr>
<td>16</td>
<td>Sample 1 after 100 h on-stream</td>
<td>Pt-Rh</td>
<td>58.2</td>
<td>5.7</td>
</tr>
<tr>
<td>17</td>
<td>Sample 2 after 100 h on-stream</td>
<td>Pt-Rh</td>
<td>16.5</td>
<td>5.6</td>
</tr>
<tr>
<td>18</td>
<td>Sample 10 after 100 h on-stream</td>
<td>Pt-Rh</td>
<td>9.3</td>
<td>8.8</td>
</tr>
<tr>
<td>19</td>
<td>Sample 12 after 100 h on-stream</td>
<td>Pt-Rh</td>
<td>27.9</td>
<td>7.9</td>
</tr>
<tr>
<td>20</td>
<td>Sample 9 + burning in H₂ (10 s) after 100 h on-stream</td>
<td>Pt-Rh</td>
<td>28.9</td>
<td>5.9</td>
</tr>
</tbody>
</table>

Alloy compositions are, at.% (wt. %): Pt86.9(92.5)-Pd6.9(4.0)-Rh6.2(3.5) and Pt87.5(93.0)-Rh12.5(7.0); solution concentrations in wt. %. For Sample 5 the current density was 40 mA g⁻¹ of gauze (~ 2 mA cm⁻² for gauze with smooth surface).

The high surface concentration of carbon is assumed to come from the diamond wire dies used for wire drawing, the lubricating oil in the weave unit and oiled paper in which woven gauze is transported. Some oil remains on the surface after cleaning.

The oxygen most probably comes from Na₂O, reasons unknown, but other studies also indicate this. Na₂O was also observed on the foil surface, so may come from the melting process or metal pretreatment.

Experimental Technique
To optimise practical benefits from this work, samples of the two most used industrial catalyst gauzes, developed by GIAP (scientific research and project institute for the (Russian) nitrogen industry) (1, 2) were employed. The woven platinum-rhodium (Pt-Rh) and platinum-palladium-rhodium (Pt-Pd-Rh) gauzes had wire diameter 0.09 mm and 1024 mesh cm⁻², see Table I. The samples underwent various initial surface treatments, for example, etching in liquid, heating in gas, annealing using a hydrogen torch (to remove impurities), to enable all surface effects to be identified before the samples were used for ammonia oxidation for 8 and 100 hour periods, see Table I.

Profiles of the compositions of the surface and sub-surface layers were analysed by AES with a surface microanalyser and a profiler LAS-3000 at a pressure of 10⁻⁷ to 10⁻⁴ Pa. Concentration profiles of the surface were obtained by an Ar⁺ ion gun, the angle between the surface and the argon ion beam being 30° with a 4 mm² area of cut. Auger depth profiling gave information about the variation in composition with depth below the surface. With this technique, material from the surface region is gradually removed by sputtering on exposure of the surface to the ion flux. Auger signals corresponding to the elements present in...
each layer were measured as the ion beam etched away the surface material. By collecting Auger spectra during etching, information is obtained on the changes in composition below the surface.

AES spectra were measured for the surface and for three sub-layers. However, the high intensity ion beam can lead to upper layer atoms being pushed inwards (ion hammering). This can modify the composition of the next layer. Another negative effect of the high intensity ion beam is that it may cause mixing of surface atoms and sub-surface layers. To minimise these negative effects, the rate of sputtering was kept at ~ 0.20 to 0.25 nm μA⁻¹ min⁻¹, and the ion etching was performed in 3 cycles of 5 minutes each. The average thickness of each removed layer was 4 nm and the thickness of all the layers was 12 nm.

In order to determine the relative atomic composition of each etched surface, the range of the kinetic energy in the scanned spectra was 120 to 540 eV, which allowed the Pt, Pd, Rh, C and O Auger lines to be identified with a relative error of 5 to 7 per cent. However, for Samples 1, 2, 12 and 19 of the Pt-Pd-Rh alloy, the spectra were examined in the kinetic energy range 550 to 1900 eV, to look for other elements in the metal body which could be present from the reagents.

As Table II shows, the total amount of trace elements, chlorine (Cl), sodium (Na), magnesium (Mg), aluminium (Al) and sulphur (S), is less than 8 per cent and they are concentrated on the metal surface, most probably in an adsorbed form. The presence of Na in the sub-layers can be explained by the method of alloy manufacture (similar results were obtained by studying platinum foil). However, Na is absent in all treated samples because of its high reactivity. The source of adsorbed Cl, S and Al is the reagent mixture. Other elements, such as Ba, K, Ca and P, were not detected. Elements Pt, Pd, Rh, C and O were used for further data processing.

### Data Processing

Each sample was described by compositions measured at the surface and at sub-surface layers at depths of 4, 8 and 12 nm. The main aim was to establish if there were correlations between the concentrations of elements and the layers, and between the composition of the surface and the surface treatment. Correlations were verified for both alloys and relationships between the concentrations of elements in each layer were also verified.

Non-linear regression analysis was used to process the data and the coefficient of multiple correlation (coefficient of determination, R²), widely used for estimating the closeness of calculated and experimental data, was used for the goodness-of-fit. A value for this parameter of more than 0.5 indicates a statistically significant correlation between estimated parameters. The
Composition of the Catalyst Surface

The elements investigated can be grouped according to their concentration profile, surface pretreatment and the effects on catalyst activity:

- carbon and oxygen: the amounts depend on the depth of the layer and on the surface treatment
- palladium and rhodium: the concentrations depend on the times of catalyst operation
- platinum: which determines the catalyst activity.

Examples of typical depth profiles are shown in Figure 1. The most significant changes in composition are observed for the layer between the surface and 4 nm. Changes in composition are smoother for layers deeper than 4 nm. The best correlation with depth is found for carbon, but samples containing small amounts of carbon show little variation in their depth profile, see Figure 1(c).

Carbon Effects

On average, the amount of carbon moving into the metal bulk decreases according to:

\[ [C] = 29 - 7.3 \text{(Depth)}^{0.19} \]

where \([C]\) is the atomic concentration of carbon, measured in at.%; (Depth) is the depth of ion beam etching, in nm.

This dependence is very stable and departures from the relationship only occur for samples with large amounts of carbon in the top 4 nm surface layer. Due to different sputtering coefficients for the metals and carbon, in a given time, different amounts will be removed from the surface. The high carbon concentration at the surface also changes the surface relief and leads to error in the measurement of carbon (11).

No obvious and reliable correlations were established between the carbon concentration and the surface treatment. For example, treating Sample 10 with H₂O₂ solution gives the same surface concentration of carbon as treating Sample 4 with formic acid solution (34.6 and 35 at.%, respectively). However, treatment with H₂O₂ at different concentrations (Samples 12 and 14) leads to a different surface carbon content (48.2 and 5.2 at.%, respectively), see Table 1.

The carbon concentration is also dependent on the total amount of palladium and rhodium. This relationship is observed for each layer, independent of its depth. As Figure 2 shows, an increase in the concentration of rhodium and palladium leads to a considerable reduction in the amount of carbon. This dependence holds true for all layers and all surface treatments. From this relationship...
we conclude that rhodium and palladium prevent the sedimentation of carbon and its compounds in the alloy. When chemical compounds are formed between carbon and the metals, the dependence between their concentrations has to be linear. In fact, the shape of the dependence (close to hyperbolic) indicates the physical nature of the interaction between carbon and rhodium and between carbon and palladium.

**Oxygen Effects**

The variation in the oxygen concentration profile is much smaller than for carbon. The maximum oxygen concentration was observed for Sample 1 of Pt-Pd-Rh (17.2 at.% on the surface and 6.4 at.% at 8 nm depth). Almost the same amount of oxygen was observed for Sample 5 which was treated electrolytically in acetic acid solution. Samples treated with the hydrogen torch do not have oxygen in their sub-surface layers, probably due to the high reactivity of hydrogen and its relatively high diffusion rate in the sub-surface layers.

The concentrations of carbon and oxygen appear to be independent of the surface treatment, but dependent on other parameters, such as the amount and type of the reagent (its carbon content), its reactivity (oxidising or reducing power), the phase state of the reagents (gas or liquid), and how long the surface treatment lasts. These factors all affect the determination of the \( \text{O}:\text{(C + O)} \) ratio, which can be interpreted either as the concentration of oxygen in the non-metal elements or as the relative concentration of oxygen.

The minimum relative concentrations of oxygen are shown in Figure 3 for samples treated by carbon-containing substances or by reducing agents. Treating samples with the hydrogen torch reduces the amount of oxygen to zero, while using hydrogen peroxide increases the \( \text{O}:(\text{C + O}) \) ratio to 60 per cent.

The effects on surface composition could be observed by comparing the surface composition at the start (after surface treatment but before the reaction mixture was admitted) and after 100 h exposure in the reactor, see Table III. Irrespective of the type of reagent, surface treatment or initial oxygen content in the layers, processing the catalyst for 100 h always resulted in an equilibrium oxygen concentration of \( \sim 3 \) to \( \sim 6 \) at.% for 4–12 nm layers, and an increase in the carbon concentration in all the layers. However, Samples 10 and 18 are exceptions; these were treated in \( \text{H}_2\text{O}_2 \) solution without annealing in the hydrogen torch, and are explained by special surface modification.

The increase of carbon concentration, regardless of initial treatment, during the ammonia-
Palladium concentrations were found to be determined solely by the time on-stream. The relative concentration of palladium in the metal phase after 100 h of reaction dropped from 12–17 to 4–5 at.% The decrease does not depend on the surface treatment of the initial samples, but leads to an increase in carbon concentrations in all layers.

The rhodium concentration, in contrast to palladium, does not depend on the processing time, but is closely related to the concentrations of palladium and oxygen. The effects of oxygen on the composition of the metal phase (Pt, Rh, Pd) is different for Pt-Pd-Rh and Pt-Rh alloys, see Figure 4.
In Pt-Pd-Rh alloy, the rhodium concentration is proportional to the total concentration of palladium and oxygen (proportionality factor is 0.3 to 0.5). As this alloy loses palladium from the metal phase during processing (in the ammonia-air mixture), it should also lose rhodium after samples are exposed to the reaction mixture.

The replacement of palladium by rhodium (to give Pt-Rh alloy) may promote the formation of platinum-oxygen composites (perhaps oxides) which displace platinum-rhodium compounds. As a result, when the oxygen concentration is 12 at.%, there is no rhodium present in the alloy (proportionality factor \( \sim 1 \)). It should be noted that an increase in the oxygen concentration reduces the rhodium concentration, but the reverse is not true. This is because the oxygen concentration is determined by the surface treatment. Furthermore, most pretreatments were not at high temperature (except those where the hydrogen torch was used) or samples were prepared quite quickly in solution. This prevented the formation of volatile rhodium species and their rapid diffusion from the sub-surface layers.

Although there are no data on changes in the metal phase of Pt-Rh alloy after exposure to the ammonia-air mixture, our observations of the surface indicate that, as for the Pt-Pd-Rh alloy, the \( \text{Rh}:(\text{Rh} + \text{Pt}) \) ratio will fall.

These relationships allow predictions to be made about the compositions of the surface and sub-surface layers, depending on the surface preparation, the type of reagent used, the time of reaction with the ammonia-air mixture and the composition of the metal phase. We are then closer to finding the optimum surface treatment needed to produce a required catalyst surface. However, the relationship between the surface composition and catalyst activity still needs to be explained.

### Relationship between Surface Composition and Catalytic Activity

The relationship between the catalytic activity of the samples and the composition of the layers was studied after the ammonia oxidation reaction was performed for 8 and 100 hours in the laboratory reactor.

The reactor was a glass tube of diameter 1 cm with external electric heating. Reaction mixtures were fed at
Fig. 5 The calculated effects of the concentrations of carbon and oxygen, at a depth of 4 nm, on the catalytic activity:
1 effect of carbon for stable concentrations of Pd, Rh and O
2 effect of oxygen for stable concentrations of Pd, Rh and C
The optimum concentration for carbon is more than for oxygen. Only concentrations of more than 30 per cent significantly affect the yields of NO.

Atmospheric pressure onto the catalytic gauze. The temperature was held at \( \sim 780^\circ C \) and the flow rate was kept constant giving a contact time of \( \sim 2 \times 10^{-4} \) seconds. The ammonia concentration was 11 per cent, to be similar to that in an industrial reactor. To estimate the activity, a rate constant, \( k \), was used, assuming that the kinetics of the chemical process can be described by a first order equation (1).

One of the most important conclusions from these experiments is that the correlation of catalytic activity with the surface composition is smaller than the correlation with the composition of the sub-surface layers. The most reliable relationship is obtained between catalytic activity and the compositions of the 4 and 8 nm layers (coefficient of determination \( R^2 = 0.93 \) and 0.89, respectively). The corresponding relationship between catalytic activity and the surface is less reliable (\( R^2 = 0.63 \)).

The empirical equation linking rate constant, \( k \), for the 4 and 8 nm layers (experimental conditions 780°C, ammonia concentration, \( C_{NH_3} = 11 \) per cent by volume, pressure = 0.1 MPa) can be written:

\[
k = -0.22 - \frac{1.0}{[C]} + 2.6 \times 10^{-4} \times [Pt]^2 \times (1+2[C])
\]

where \([C]\), \([O]\) and \([Pt]\) are concentrations, in at.%\(^{\circ}\), of the respective elements, and \(k\) is the rate constant, measured in s\(^{-1}\) \(\times 10^4\).

For carbon concentrations > 5 at.\%, the effects of oxygen, rhodium and palladium on the alloy are all similar: they reduce the platinum concentration, thus decreasing catalytic activity.

The effects of carbon are more complicated. The shape of the rate constant/concentration curve, for constant concentrations of palladium, rhodium and oxygen (5 at.% of each), shows that there is an optimum carbon concentration (maximum NO yield and rate constant, \( k \)) in the range 6 to 10 at.%; see Figure 5. However, in contrast to earlier mentioned effects due to oxygen, rhodium and palladium, only increases in carbon concentrations > 30 to 35 at.% in the sub-surface layers affect catalytic activity.

Effects due to carbon can be explained by its modification of the platinum surface and an increase in platinum activity in spite of the reduction in total surface area. An increase in the carbon:platinum ratio of 1 per cent increases the alloy activity by 2 per cent. This compensates for the reduction (by up to 30 per cent) of the accessible surface area caused by the carbon. The probable mechanism for the effects due to carbon is the increase in the number of embedded microcrystalline carbon particles which contribute to the formation of catalytically active platinum centres. This was confirmed by the effects of small concentrations of carbon and oxygen. Removing
non-metallic elements from the surface reduces the number of defects in the crystal structure, which decreases catalytic activity. This is noticeable for total carbon and oxygen concentrations < 5 at.%, both elements having a similar effect on activity.

The above mentioned results for \( k \) were obtained at depths of 4 and 8 nm. Calculating the activity using only the surface layer composition underestimates the values of the rate constant, \( k \). The more carbon on the surface, the larger the error in the calculated values. This is because there is an error in measuring the actual composition of the metal surface accessible for the reaction.

**Surface Structure**

Reviewing the depth profiling technique confirms that there is a measurement error and provides a way of obtaining new data about surface structure and its effects on catalytic activity and on the overestimated amount of carbon on the surface layer. The main cause of this error may be the presence of microcrystals of carbon on the alloy surface. When the surface is examined with the depth profiling technique, it produces a systematic error in measuring the composition, and the greater the concentration of microcrystals on the surface, the larger is the distortion, see Figure 6.

The sputtering coefficients, which indicate the number of etched ions caused by one atom of ion beam, are approximately equal for Pt, Pd and Rh, but about three times larger than that for carbon (11). After allowing for this, it was calculated that for crystallites of height \( \sim 20 \) nm and base width \( \sim 10 \) nm, the spectra of the surface would indicate that platinum was not present, although about 60 per cent of the surface would be accessible to the ammonia-air mixture.

After sputtering for 5 minutes, the surface profile becomes smoother. Most of the carbon crystallites are now smaller: 5 nm high and 7 nm base width. The reduced profile now only slightly distorts the measured concentration of elements on the active surface and the composition obtained most evidently determines catalyst activity. The next sputtering cycle removes both impurities from the surface and the top 4 nm of the catalytic layer. Thus, after sputtering for 10 min (8 nm) the measured concentrations correspond to a sub-layer approximately 6 to 8 nm from the surface but not to the active surface. The relationship between composition and activity becomes less evident.

After the final cycle of etching (15 min, 12 nm), the sub-layer lies further from the active surface.
and the measured concentrations even less determine the activity of the catalyst.

The large quantities of carbon and oxygen present in the sub-surface layers – compared to other impurity elements found only on the surface – indicate either that they are forming chemical compounds with the metals or that they are embedded in the crystalline alloy lattice as microcrystals. Oxygen most probably forms chemical compounds or solutions in the metal. Increased oxygen reduces the rhodium concentration in the binary Pt-Rh alloy but increases the rhodium concentration in the ternary Pt-Pd-Rh alloy. After 100 h on-stream, all the catalyst samples have the same oxygen concentration (≈ 3 to 6 at.%) independent of the depth and amount of carbon at that depth.

Carbon is most probably present as microcrystals embedded in the alloy and concentrated on the crystal faces. Adding carbon can increase the specific surface area of the catalytically active sites and the total activity of the samples, so surface carbon is not the reason for the low catalytic activity. Only a large amount of carbon in the 4 to 8 nm sub-surface layer can radically decrease the active platinum surface and decrease the total activity of the catalyst.

Discussion

If the concentration of oxygen in the alloys is greater than 5 at.%, it behaves as an inert component, like palladium and rhodium, and only reduces platinum within the alloy; that is, enriching the surface with oxygen (during chemical treatment) reduces the catalyst activity.

Carbon additions (in amounts of 9 to 12 at.%) increase the number of metal lattice defects. An absence of carbon therefore has a detrimental effect on the catalytic activity. This contrasts with work where carbon is considered to have a negative effect on the reaction. However, carbon concentrations of > 30 at.% do adversely affect the catalytic activity of platinum alloys.

There are two ways in which the composition of the metal phase (surface and top few nm layers) could be changed. First, by the diffusion of palladium and rhodium deep into the metal bulk, by co-diffusion of the reagent flow. Second, by the diffusion of metals on the surface, their reaction with either solution or gas (during surface treatment or during the ammonia-oxygen reaction) and transfer into the bulk of the reagent. Our data do not indicate which process occurs, but as changes in the metal phase were observed both for different reagents and aggregative states, and as the low temperature surface treatment (the high temperature hydrogen torch was applied for only a short time) excludes the formation of volatile compounds (the usual explanation for metal phase changes), then the most probable means by which changes occur on the metal surface is by co-diffusion of palladium and rhodium deep into the metal bulk.

Conclusions

For the ammonia oxidation reaction, on Pt-Rh and Pt-Pd-Rh alloys, we have shown that:

- The amount of non-metallic elements in the alloy can be described by two parameters: first, the total concentration of carbon and oxygen depends on their depth in the alloy, and second, the choice of surface treatment determines the O: (C + O) ratio.
- Using oxidants increases the proportion of oxygen in the non-metallic elements, while using reducing agents (especially those containing carbon) increases the carbon concentration.
- The most important factor affecting the metal phase is the on-stream time in the ammonia-air mixture. The amount of palladium in the alloy after 100 h of exposure in the reactor drops to a third.
- The ammonia oxidation reaction occurs on the faces of the crystal lattice and carbon is one of the most important contributors to the lattice. The optimum concentration of carbon, in the 4 to 8 nm layer, is ~ 9 to 12 at.% (but high activity is observed from 5 to 20 at.%).
- Changes in surface structure on activation, before exposure in the reactor, can lead to unexpected changes in catalyst activity during ammonia oxidation (for example due to the decrease of carbon content in Sample 18 treated in hydrogen peroxide).
- The effect of solutions (organic acids and...
hydrogen peroxide) on surface composition indicates that there could be a distortion in measurement during chemical analysis, and even when preparing samples for analysis.

- The most exact measurements of reaction surfaces can be obtained, after surface preparation, by using an ion beam at a small angle of incidence and following AES measurements.
- Comparing the surface composition before and after ion etching provides information about structural particles of different elements.
- The composition of the preliminary etched surface best represents the composition of the active surface and gives the most accurate measure of catalyst activity for nitric oxide formation.

References

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Palladium-Based Catalysts for Nitrate Reduction

Nitrogen is essential for plant growth and, in the form of nitrates, is their primary source of nitrogen. Nitrates occur naturally in soil and water, but extensive farming can deplete the soil of its natural nitrogen, so nitrogen-containing fertilisers are often added. However, when more nitrogen is added to the soil than plants can use, excess nitrate can leach into groundwater supplies and could become a potential health risk.

Technologies for the removal of nitrate from drinking water and waste water are therefore of great importance. Palladium-based catalysts for the hydrogenation of nitrates to nitrogen represent one of the most promising approaches.


Catalysts were prepared either as microspheres or in the form of membranes deposited on alumina tubes. The use of catalysts under diffusion control conditions reduced the amount of the byproduct ammonia formed while retaining a high catalytic activity.

Researchers in Germany, however, used palladium-tin and palladium-indium catalysts for the nitrate reduction (U. Prüsse, M. Hähnlein, J. Daum and K.-D. Vorlop, Catal. Today, 2000, 55, (1–2), 79–90). In situ buffering with formic acid as a reductant instead of hydrogen and polyvinyl alcohol-encapsulated catalysts with superior diffusion properties have both been demonstrated. The above Pd-Sn and Pd-In catalysts are reported to be more efficient than prior palladium-copper regarding the nitrogen formation activity, the selectivity and the long-term stability.

As the removal of nitrates from drinking water and waste water is becoming more necessary, these concepts may lead to the establishment of a technical-scale nitrate reduction process.
ABSTRACTS
of current literature on the platinum metals and their alloys

PROPERTIES
Collision Dynamics and Decomposition of NaCl Nanometer Particles on Hot Platinum Surfaces

The collision dynamics of NaCl particles (15-80 nm) on a hot Pt surface (1200-1500 K) were studied by molecular beam techniques. The particles were directed toward a polycrystalline Pt surface with a velocity of 260 m s⁻¹. The particle-surface interactions were found to be highly inelastic, and the angular distributions indicated that the scattered particles lose > 90% of their kinetic energy in the surface normal direction. On (1) NaCl melts and decomposes.

Template-Assisted Growth of Hexagonal Poly- or Single-Crystalline Quasi-2D Palladium Nanoparticles

Quasi 2D Pd nanoparticles were obtained using a graphite lattice as a template. The precursor PdCl₂-graphite intercalation compounds were synthesised by mixing highly oriented pyrolytic graphite with anhydrous PdCl₂ in ampoules under anhydrous conditions. (1) NaCl melts and decomposes.

The Effect of Carbon Monoxide and Steam on the Hydrogen Permeability of a Pd/Stainless Steel Membrane

Measurements of the H₂ permeation rate through a Pd/stainless steel membrane were carried in the presence of CO and steam and with CO/steam mixtures. Significant reductions in H₂ permeability were observed because the adsorption of CO or steam on the Pd surface decreases the actual permeation area of the Pd membrane, which changes the rate-controlling step of H₂ permeation. Low concentrations of CO additions had little effect on H₂ permeability, whereas addition of steam had much more effect.

Magnetic Properties of RRh₃Ge₂, Single Crystals (R = Gd, Tb, Dy)

RRRh₃Ge₂ (1) show a magnetic behaviour characteristic of various isomorphous ternary compounds, namely sharp and smooth metamagnetic transitions, flat and non-flat intermediate plateaux in the magnetisation curves. (1) exhibit a complex low-temperature behaviour due to the interplay of exchange and crystal field interactions. Successive phase transitions occur below the Néel temperature.

Constitution of the Al–Ir–Ru System

The phase diagram of Al–Ir–Ru was investigated using optical microscopy, SEM, EDAX and XRD. The B2 phase was found to extend across the ternary with a minimum width around the centre of ~ 2 at.% Al within the ternary. Solid solubilities for the extensions of various binary extensions were observed. A previously unreported ternary phase ~ Al₁Ir₀Ru₀ was identified and shown to form peritectically from B2. Al₁Ir₀Ru₀ was found to be soluble up to ~ 10 at.% in (Ru) and nearly 20 at.% in (Ir). The hardness measurements of the B2 phase increased with Ir substitution.

Microstructure, Crystallography, and Shape Memory Effect in Equiatomic Nb₃Ru

The microstructure and crystallography of Nb₃Ru (1) were examined by TEM and electron diffraction. Strong similarities between (1) and Ta₆Ru (2) were demonstrated. Both alloys exhibit a highly twinned microstructure with a shape accommodating appearance. Electron diffraction indicated that, like (2), the room-temperature crystal structure of (1) is monoclinic. (1) exhibits shape memory effect.

CHEMICAL COMPOUNDS
Ferrocene End-Capped Palladium(II) and Platinum(II) Complexes with Thiophene Spacers

Heterobimetallics (1) containing ferrocene and Pt(II) or Pd(II) separated by a varying conjugation length constructed from vinylthiophene subunits were synthesised by oxidative addition of ferrocene-substituted halothiophenes with zerovalent Pt or Pd phosphine precursors. The reversible redox chemistry of (1) was dependent on the conjugation length.

Molecular Mechanics (MM3) Force Field Parameters for Calculations on Palladium Olefin Complexes with Phosphorus Ligands
H. HAGELIN, M. SVENSSON, B. ÅKERMARK and P.-O. NORMBY, Organometallics, 1999, 18, (22), 4574–4583

Molecular mechanics force field parameters were developed for the title complexes, based on crystal structure and quantum chemical data. The bonding to Pd is described by a valence bond approach, with interactions between the olefin and other ligands modelled by a combination of van der Waals forces and torsional interactions. The force field can yield useful predictions in the Pd-assisted allylic alkylation.
The Ternary Silicide ZrPd$_3$Si, a Stacking Variant of the α-FeSi$_2$ and Re$_3$B Structure Types
ZrPd$_3$Si (1) was synthesised by arc-melting powders of Zr, Pd and Si. (1) has a new structure type and crystallises in the orthorhombic space group Cmmm with $a = 3.9127(4)$ Å, $b = 15.551(1)$ Å, $c = 7.0390(5)$ Å and $Z = 4$. Structure calculations confirm the weak metallic behaviour of (1); support the simultaneous existence of metal-metal, metal-nonmetal and nonmetal-nonmetal bonding; and suggest a reduced state by the reaction of Nd, Rh and an excess of H$_2$O. A room temperature resistivity of 1.7 × 10$^{-2}$ Ω cm.

The new compound NdRhAl$_3$ (1) was prepared by the reaction of Nd, Rh and an excess of Al at high temperature and cooling at a slow rate. (1) has the tetragonal space group $P4_2/mnc$, $a = 912.4(1)$ pm, $c = 1561.6(3)$ pm, $Z = 4$. The atoms occupy twelve atomic sites, all with high coordination numbers. Four of the nine Al positions are very close to each other, forming a nearly straight row with partial occupancy. Similar to other structures of intermetallics with a high Al content, (1) is partitioned into layers of two types. One is h.c.p. and puckered and consists of Rh atoms. The other type of layer is less densely packed and contains Al, Rh and all of the Nd atoms.

ELECTROCHEMISTRY
Anion and Water Involvement in Hydrous Ir Oxide Redox Reactions in Acidic Solutions
Ir oxide films (1) grown in 0.6 M HClO$_4$, 0.4 M H$_2$SO$_4$, and 0.4 M HNO$_3$ solutions gave a super-Nernstian E/pH response of ~68 mV, using constant ionic strength H$_2$SO$_4$, Na$_2$SO$_4$, test solutions. This indicated the injection/expulsion of protons and some solution anions during the reduction/oxidation of Ir(III)/Ir(IV). An unaccounted mass change was interpreted as due to H$_2$O flux in/out of (1).

Preparations and Electrochemical Properties of Pyrazine-Bridged Ruthenium-Binuclear Complexes Exhibiting Molecular Hysteresis
$tis$-$tis$-[(NH$_3$)$_3$(L)Ru-pz-Ru(NH$_3$)$_3$(dms)]PF$_6$, (L = NH$_3$ (1), pyridine (2), benzonitrile (3)) exhibited molecular hysteresis. Simulations of both cyclic voltammograms and thin-layer cyclic voltammograms gave redox potentials, isomerisation rates and interconversion rates of (1), (2) and (3). The rates of conversions between two isomeric intermediate states were $5 \times 10^4$ s$^{-1}$ for (1), $4 \times 10^4$ s$^{-1}$ and $4 \times 10^3$ s$^{-1}$ for (2), and $2 \times 10^4$ s$^{-1}$ and $5 \times 10^3$ s$^{-1}$ for (3).

ELECTRODEPOSITION AND SURFACE COATINGS
Platinum Microelectrodes with Unique High Surface Areas
Nanostructured Pt films (1) were electrodeposited onto microelectrodes from an hexagonal isotropic liquid crystalline plating mixture of octaethylene glycol monohexadecyl ether, H$_2$O, and H$_3$PtCl$_6$·6H$_2$O. Cyclic voltammetry in dilute H$_2$SO$_4$ and Cu underpotential demonstrated that (1) have high surface areas (with roughness factors of ~210).

On the Voltammetric Behavior of a Platinized Titanium Surface with Respect to the Specific Hydrogen and Anion Adsorption and Charge Transfer Processes
The surface preparation of the Ti substrate by sand-blasting and the washing procedure to minimise or to avoid Cl$^-$ contamination are crucial steps for obtaining Pt/Ti electrodes (1) with H$_2$ adsorption-desorption behaviour similar to that of polycrystalline Pt electrodes. The Pt plating was carried out at a constant current density of 5 mA cm$^{-2}$ for 100 min at 90–95°C. Pt deposits with a thickness of 5–10 μm are obtained (with roughness factor of ~125).

Kinetics of Interfacial Reaction Between Eutectic Sn–Pb Solder and Cu/Ni/Pd Metallizations
The interfacial microstructure and the kinetics of interfacial reaction were studied using diffusion couples of eutectic Sn–Pb solder and electroplated Ni/Pd on Cu substrate. In the thin film limit of the Pd layer, the presence/absence of Pd-bearing intermetallic was determined by the initial thickness of the Pd layer and the processing temperature, and not by the processing time. Depending on the thickness of the Pd layer, both PdSn$_3$ and Pd$_5$Sn$_3$ phases were observed near the solder-substrate interface.

PdCl$_2$ Anchorage onto the Surface of Polystyrene Films via Oxygen and Ammonia Plasma Treatment
Plasma treatments of polystyrene in the presence of O$_3$ or NH$_3$ caused an increase in the surface free energy of the polymer. After treatment with PdCl$_2$, to prepare polymer-bound complex catalysts, the amount of Pd anchored to the NH$_3$ plasma-treated polymer surface is greater than in O$_3$ plasma treatments. This was explained on the basis of the higher nucleophilic character of the amine groups. No Pd was detected in the untreated polystyrene surface.
Preparation of Epitaxial Ultrathin RuO₂-TiO₂(110) Films by Decomposition of Ru₂(CO)₆
Ru₂(CO)₆ (1) has been used as a source for depositing Ru particles and RuO₂ films on a TiO₂(110) surface. At 300°C in ultrahigh vacuum (1) was completely decomposed, and the deposited Ru particles showed some residual C contamination. RuO₂ ultrathin epitaxial films were obtained by heating the Ru deposit at 300°C or by directly decomposing (1) in O₂. The new RuO₂-TiO₂ interface is reactive.

APPARATUS AND TECHNIQUE
An Amperometric Detector with a Platinum Tubular Electrode for High Performance Liquid Chromatography
An amperometric detector based on a Pt tubular electrode was constructed from a long narrow-bored Pt tube which was directly connected to the column outlet. The Pt tube was immersed in a vessel containing an electrolyte solution in which a common reference and counter electrodes were also immersed. As only the internal Pt wall was exposed to the electrolyte solution in which a common reference and counter electrodes were also immersed.

A Novel Gas Sensor Based on SnO₂/Os Thin Film for the Detection of Methane at Low Temperature
Os-doped SnO₂ thin films for CH₄ detection were prepared by the sol-gel method. Os doping was found to improve the gas sensitive properties of the SnO₂ films, enhancing the sensitivity to CH₄ and simultaneously lowering the best operating temperature. The Os probably catalyses the oxidation of CH₄.

HETEROGENEOUS CATALYSIS
HCN Synthesis from Methane and Ammonia: Mechanisms of Pt-Mediated C-N Coupling
The Pt-mediated coupling of CH₄ and NH₃ was studied. Mass spectrometry showed that C-N bond formation is catalysed efficiently by Pt. The B3LYP hybrid DFT/HF functional was used to investigate computationally the experimentally observed reaction channels. A comparison of Pt with Fe, Co, Rh, W, Os, Ir and Au shows that Pt is unique in its ability to activate 1 equivalent of CH₄ and to mediate C-N bond coupling.

Use of Periodic Variations of Reactant Concentrations in Time Resolved DRIFT Studies of Heterogeneously Catalysed Reactions
Amorphous PdₓZrₓ alloy catalyst (1) for CO oxidation was prepared by the melt spinning technique. Sine wave modulation of feed gas concentrations was used to induce dynamic variations in the concentrations of products, intermediates and reactants in the oxidation of CO over (1). These were monitored in situ in a DRIFT cell and consecutively analysed with a micro-kinetic model to obtain information on the reaction pathway and rate constants.

VOC Removal: Investigation of Ethylacetate Oxidation over Supported Pt Catalysts
Steady-state kinetic experiments on the oxidation of trace amounts of ethyl acetate over various supported Pt catalysts showed that Pt/W₆⁺ doped TiO₂ (1) is the most active. Acetic acid and acetaldehyde are the main byproducts at low and intermediate conversions. The high activity of (1) is attributed to the presence of a large number of acidic sites with appropriate strength on the W₆⁺-doped TiO₂ surface, which lead to the formation of a large pool of reactive intermediates with high mobility.

Reductive homocoupling of substituted chlorobenzenes to the respective biphenyls was achieved in H₂O using H₂ and NaOH in the presence of catalytic amounts of PEG-400 and Pd/C (1) at 90–120°C. The molecular H₂ acts as the in situ catalyst regenerator. The solid (1) can be efficiently recycled simply by filtration and washing with H₂O and MeOH. After 7 runs, (1) retained > 99% of its activity.

Catalytic Behavior of a Wool-Pd Complex in Asymmetric Hydrogenation of Diacetone Alcohol and 3-Methyl-2-butane
A chiral natural biopolymer wool-Pd complex (1) was prepared by the addition of a definite amount of wool-washed pieces with PdCl₂·2H₂O in EtOH. (1) catalysed the asymmetric hydrogenation of diacetone alcohol to (R)-2-methyl-2,4-pentanediol (2) and 3-methyl-2-butanone to (R)-3-methyl-2-butanol (3) at 30°C and under 1 atm H₂. At optimal Pd content, (2) and (3) could be obtained with 73% and 100% optical yields, respectively. (1) could be reused without appreciable change in optical catalytic activity.

Platinum Metals Rev., 2000, 44, (2)
Synthesis of Allylbenzenes by Cross-Coupling of Allyl Bro-rides with Arylboronic Acids Using a Palladium Chloride and Tetraphenylphosphonium Bromide Inter-caled Clay Catalyst
Suzuki coupling of allyl halides and arylboronic acids has been achieved using a reusable catalyst system of PdCl2 and tetraphenylphosphonium bromide intercalated clay (1). The rate of reaction with (1) is much faster when compared to homogeneous conditions. (1) was retrieved from the aqueous layer for further reuse without any loss in catalytic activity.

Liquid Phase Methanol Carbonylation Catalysed over Rhodium Supported on Hydrotalcite
Mg-Al hydrotalcites containing nanometre-size Rh particles (1) were synthesised and shown to be active for MeOH carbonylation at 473 K in the presence of MeI. The main products were methyl acetate (MeOAc) and dimethyl ether. An increase in Rh to 2.1 wt.% enhanced formation of MeOAc but a further increase of Rh to 3.0 wt.% resulted in a lower yield of MeOAc. The activity of (1) towards MeOAc mainly depended on the estimated surface area of Rh.

First Heterogenisation of Rh-MeDuPHOS by Occlusion in PDMS (Polydimethylsiloxane) Membranes
Immobilisation of Rh-MeDuPHOS was achieved by occluding the catalyst in a PDMS membrane. The occluded catalyst (1) was tested in methylacetoacetate hydrogenation. In ethylene glycol, the activity of (1) (membrane thickness 452 μm) was lower than in the homogeneous reaction but remained constant in a second run, in which the same enantioselectivity was maintained. In MeOH, the activity of (1) (thickness 578 μm) could be increased fourfold, while leaving enantioselectivity almost unaffected.

A Mesoporous Ruthenium Silica Hybrid Aerogel with Outstanding Catalytic Properties in the Synthesis of N,N-Diethylformamide from CO2, H2 and Diethylamine
Mesoporous Ru silica hybrid aerogel (1) containing well-dispersed bidentate RuCl3(PPh3(CH2)3PPh3) complexes was synthesised using a sol-gel method. (1) gave turnover frequencies up to 18,400 h-1 and 100% selectivity from CO2, H2 and diethylamine for the formation of N,N-diethylformamide. The most influential parameters were: amount of (1), reaction temperature and total pressure.

HOMOGENEOUS CATALYSIS
An Active Site Model and the Catalytic Activity Mechanism of the New Fullerene-Based Catalyst – (η5-C5H5)Pd(PPh3)3
A theoretical description of the adsorption of C2H2 on Pd-phosphine fullerene complexes has been developed based on quantum chemical calculations. This process can be considered as a model of the preliminary stage of triple C bond scission in acetylenes. Based on the calculations and experimental data, it was concluded that the preliminary interactions of the complex substrate-catalyst with the substrate facilitate the interaction of the complex substrate-catalyst with H2 by decreasing the energy barrier.

The Birth and Development of π-Allylpalladium Chemistry
A review of π-allylpalladium chemistry is presented. The Pd-catalysed decarboxylation of allyl carbonates, allyl β-keto carboxylates and allyl formates has now been achieved. A new generation of β-keto esters and malonates was obtained by the introduction of the Pd-catalysed reaction of their allylic esters. Hydrogenolysis of allylic compounds can be used for deprotection of the allyl protecting group. (57 Refs.)

Synthesis and Characterization of Monomeric and Dimeric Palladium(II)-Ammonium Complexes: Their Use for the Catalytic Oxidation of Alcohols
The addition of RNX to PdCl2 gave (R,N)PdX (1). A dinuclear complex (n-Bu,N)2PdCl4 was obtained from the crystallisation of the corresponding monomeric species under controlled conditions. For the Pd-catalysed oxidation of alcohols with 1,2-dichloroethane as stoichiometric oxidant, similar results were obtained using either (1) or PdCl2/Adogen 464 as catalyst. In the absence of R,NX, PdCl2 is rather ineffective.

Synthesis of Novel (Bis)(diaryl amino)thiophenes via Palladium-Catalysed Reaction of (Di)bromothiophenes with Diarylamines
Pd(OAc)2/PBu3 (1) was shown to catalyse the coupling of (di)bromothiophenes and diarylamines to afford (bis)(diaryl amino)thiophenes. Although 2,5-(di)bromothiophenes usually do not undergo the amination reaction due to strong coordination to the Pd catalyst, (1) allows the amination to occur in the presence of a small amount of Pd. The use of the bulky and electron rich PBU3 ligand realised the Pd-catalysed formation of (bis)(diaryl amino)thiophenes.
Preparation of Poly(aryleneethynylene) Type \( \pi \)-Conjugated Polymers Constituted of 2-Alkylbenzimidazole-4,7-diyl Units by Using Palladium Catalyzed Cross Coupling Reaction


Pd(PPh)₃-catalysed polycondensations between 4,7-dibromo-2-alkylbenzimidazoles (alkyl = n-C₆H₁₃, n-C₅H₁₁, n-C₆H₁₄) and 1,4-diethynyl-2,5-disubstituted benzenes (substituents: O-n-C₆H₁₃, O-n-C₅H₁₁, n-C₆H₁₄, O-n-C₅H₁₁) gave poly(aryleneethynylene) polymers including the benzimidazole unit in the \( \pi \)-conjugated main chain. Yields were 70–90%.

Methane Formation during the Iridium/Iodide Catalysed Carbonylation of Methanol


\[ \text{[Ir(CO)₃Me]} \] reacts with carboxylic acids or \( \text{H}_₂ \) at elevated temperatures to cleave the \( \text{Ir(III)} \)-methyl bond liberating \( \text{CH}_₄ \). The carboxylic acids remove alkyl groups by a concerted process via a cyclic transition state. \( \text{CH}_₄ \) can arise from (1) during MeOH carbonylation, either by reaction with \( \text{CH}_₃\text{CO}_2\text{H} \) or by hydrogenolysis.

**FUEL CELLS**

Anodic Catalysts for Polymer Electrolyte Fuel Cells: the Catalytic Activity of Pt/C, Ru/C and Pt-Ru/C in Oxidation of CO by \( \text{O}_2 \)


Studies of the catalytic activity for oxidation of CO on Pt/C, Pt-Ru/C (Pt:Ru atomic ratio = 20, 3, 1, 1/3) and Ru/C (all containing 20 wt.% metal) catalysts claim that fuel cells with Pt-Ru/C anodes perform better than those with Pt/C anodes due to Ru active sites facilitating oxidation of CO present as an impurity in the \( \text{H}_₂ \)-reformed fuel. At 300–400 K, the TOF per active metal atom was 50–300 times higher on Pt-Ru/C than on Pt/C. Addition of H₂O markedly decreased the activation energy for the Pt-Ru(1:1)/C alloy.

Performance of Proton Exchange Membrane Fuel Cell Electrodes Prepared by Direct Deposition of Ultrathin Platinum on the Membrane Surface


PEMFC electrodes were fabricated using plasma-sputtering that deposited Pt directly onto the surface of the Nafton electrolyte. Multiple sputterings with application of the C/Nafton ink on the surface after each sputtering were found to enhance the utilisation of the catalyst. The reported Pt utilisation efficiency, equivalent to 0.043 mg Pt cm⁻³ loading of Pt, is ~ 10 times higher than that of electrodes produced by conventional methods.

Chemical Synthesis and Characterization of Mo₄Ru₃Se₇(CO)₉ Electrocataysts


Mo₄Ru₃Se₇(CO)₉ electrocatalyst (1) was prepared by the pyrolysis of Ru₄(CO)₁₆ + Mo(CO)₆ + Se at 140°C and sintering in a Se atmosphere at 250°C. (1) is almost amorphous in nature and possesses catalytic activity for \( \text{O}_2 \) reduction in a PEFC. The electrocatalytic activity diminished with Se incorporation in the lattice of the formed Mo-Ru-CO clusters.

**ELECTRICAL AND ELECTRONIC ENGINEERING**

Effect of Orientation of \( \varepsilon \)-Axis on Ba,CuPt,O₅ Compounds of Fluorine-Doped YBa₂Cu₃O₇ Superconductors


Ba₃Cu₃O₅ compounds (1) were synthesised by a solid state reaction at > 800°C. The influence of (1) on the critical current density of the title YBCO superconductors was investigated using two types of (1). One sample was not heat treated, i.e., source materials, and the other was heat treated at 950°C. The former affected the orientation of the \( \varepsilon \)-axis, but the latter did not have an influence on the orientation of the \( \varepsilon \)-axis, and damaged the superconductivity of the samples quenched above 850°C.

Integration of GaN Thin Films with Dissimilar Substrate Materials by Pd-In Metal Bonding and Laser Lift-off


GaN thin films grown on sapphire substrates have been bonded and transferred onto GaAs, Si and polymer “receptor” substrates using a low temperature Pd-In bond followed by a pulsed UV-laser lift-off process to remove from the sapphire. The GaN/sapphire structures were joined to the receptor substrate by pressure bonding a Pd-In bilayer coated GaN surface onto a Pd-coated receptor surface at 200°C.

Studies of Ir-Ta-O as High Temperature Stable Electrode Material and Its Application for Ferroelectric SrBi₂Ta₂O₉ Thin Film Deposition


An Ir-Ta-O/Si structure was fabricated with Ir-Ta-O as electrode and Ta as diffusion barrier layer on a Si substrate. The Ir-Ta-O film (1) was deposited by reactive sputtering. (1) exhibited extraordinary high-temperature stability with good conductivity and integrity. By using (1) as the bottom electrode for depositing SrBi₂Ta₂O₉ thin film at 800°C, good ferroelectric properties were achieved.
NEW PATENTS

ELECTROCHEMISTRY

Oxygen Reduction Electrode
UNIV. CASE WESTERN RESERVE. World Appl. 99/46,429
An O2 reduction electrode (1) has a Pt substrate and its surface is modified by S, Se or Te or their compounds, which renders it highly selective for the conversion of O2 to H2O2 (~100%). An electrochemical device is also claimed with the electrode as cathode, preferably with an acidic electrolyte, for concentrating O2 in a feed gas. (1) can function in acidic electrolytes and may be used in electrochemistry.

Electrode for Nitrate Reduction
UPSCALE WATER TECHNOLOGIES INC. U.S. Patent 5,935,392
An electrode (1) for the removal of nitrates from H2O or seawater, comprises a polycrylonitrile-based C fibre electrode (2) coated with Ir oxide. The electrode is made by dipping (2) in an Ir chloride solution, and heating at 225–350°C for 1.5–1.75 h. An apparatus for reducing nitrates in an aqueous solution which includes a cathode, a reference electrode and (1) as an anode, is also claimed. The cell operates at higher anodic voltages without Cl2 or O evolution.

Electrode for Hypochlorite Production Cell
ELTECH SYSTEMS CORP. U.S. Patent 5,989,396
An electrode for electrolytic cells used for hypochlorite production in desalinators, comprises a sheet metal plate with an anodic coating of oxides of Ir, Sn, Sb and Ti, and a cathode coating containing the oxides of one or more of Ru, Ir and/or Ti. The coatings are dried at 90–120°C and cured at 450–650°C. Improved disinfection efficiency is obtained at lower cost, without any safety risks.

Electrode for Electrolysis of Dilute Salts
TANAKA KIKINZOKU KOGYO K.K. Japanese Appl. 11/269,687–88
An electrode (1), used as an anode for electrolysis of dilute salt solutions for production of acidic H2O with a high sterilisation effect and for treating waste H2O containing organic matter, has Pt, Ir and Ir oxide layers sequentially coated on its base material containing Ti, Nb and/or Ta. (1) with Pt and Ir layers has a long life and can be maintained easily. Exhaustion of (1) under high current density conditions is restrained.

Catalyst Electrode Used in Electrolysis
SHINKO PANCED CO. LTD. Japanese Appl. 11/279,784
A catalyst electrode (1), used in electrolysis cells, is formed by adhering a Pt group metal from a cathode on a solid polymer electrolyte film in the presence of a magnetic field in an inert gas atmosphere. A predetermined voltage is impressed to the magnetic field which is formed parallel to the cathode surface, along the orthogonal direction, so the coated film becomes the anode. (1) has favourable adhesion and can be prepared easily and quickly at low energy.

ELECTRODEPOSITION AND SURFACE COATINGS

Electroless Plating of Specific Parts
K. TAKAGI European Appl. 967,299
An efficient process (1) for partial electroless plating deposits film only to specific parts of a substrate, without requiring the conventional etching step. Plating comprises forming and activating the resin film, imparting and activating a catalyst onto the film with an acidic solution containing Pd ions, and then reducing the Pd ions to metallic Pd. (1) is used for metal plating of plastic substrates, such as epoxy and polyimide, especially for printed circuit boards.

Electroless Palladium Plating
ISHIHARA YAKUHIN K.K. Japanese Appl. 11/269,658
An electroless Pd plating composition includes aqueous solution containing an organic compound with bivalent S, a Pd compound, amino-carboxylic acid and formic acid. Pd film of suitable thickness, high purity and catalytic activity is obtained. The plated layer has excellent soldering property and corrosion resistance and long life span. Generation of cracks is prevented, and as there is no P present, waste H2O treatment is easy.

APPARATUS AND TECHNIQUE

Hydrogen Permeable Film
TOKYO GAS CO. LTD. Japanese Appl. 11/286,785
Hydrogen permeable film (1) for oxy-hydrogen burners and fuel batteries contains multilayers of Pd and Pd alloy which are alternately plated by electroless or ionic plating on the surface of the porous support body, followed by heating to form H2 permeable film. (1) can be efficiently obtained without pinholes and can be easily reproduced.

Hydrogen Gas Permeable Membrane
OPTONICS SEMITSU K.K. Japanese Appl. 11/314,902
H2 gas permeable film used for H2 refiners contains heat treated Pd alloy laminated with Ag film. A laminated structure of repeated Pd and Ag layers is formed by electroplating on a conductive board and a lattice-like photoresist pattern is formed by photolithography. The in-plane thickness can be controlled and H2 permeability efficiency is greatly increased.

Photocatalyst Module for Purifiers
TOSHIBA K.K. Japanese Appl. 11/335,187
A photocatalyst module (1) for air or H2O purifiers has a base material made of a ceramic porous substance with a specific blow hole rate, containing Pt or Au alloy or transition elements, dispersed on its surface. (1) has a large catalyst area, thus giving high catalytic activity, optical attainment property, photocatalyst efficiency, corrosion resistance and reduced power consumption. (1) can also be used for exhaust purifiers, antifouling sterilisation, deodorising, etc.
HETEROGEOUS CATALYSIS

Fluid Bed Palladium-Promoted Catalyst

A fluid bed catalyst (1) for vinyl acetate manufacture is produced by impregnating an inert micro-spherical support (≥ 50% of particles < 100 μm) with a solution comprising a halide-free salt of Pd and M (M = Ba, Au, La, Nb, Ce, Zn, Pb, Ca, Sr, Sb or their mixtures) and reducing the metal salts to form a deposit of Pd and M on the support. (1) gives a high performance and attrition resistance in vinyl acetate production, giving ethylene conversion rates of ≤ 18.2% and selectivity of ≤ 87.8%.

Gas Particle Filter for Diesel Engines

A filter, for inserting into diesel engine exhaust pipes to trap particulates, is in the shape of a tube with its wall made from fritted metal grains, covered with metallic fibres of stainless steel. The tube is filled with grains of Al coated with a combustion catalyst, such as Pt. The filter traps the finest particles and has a long operating life.

Production of Acetaldehyde

Acetaldehyde (1) is produced by hydrogenation of acetic acid in the presence of a Fe oxide catalyst with a specific surface area containing 2.5–90 wt.% Pd at ~ 250–400°C. H₂ and acetic acid are fed to a reactor in a ratio of 2:1–25:1. High acetaldehyde selectivity of 84% is achieved by recovering volatile (1). (1) is used as a starting material in the manufacture of acetic anhydride, acetate esters, vinyl acetate resins, etc.

Catalytic Hydrogenation of Aromatic Amines

Hydrogenation of aromatic amines to cycloaliphatic amines is performed at low pressure (0.5–40 bar) on supported Rh metal catalysts (1), which may also contain Ir, Ru, Os, Pd or Pt, or their mixtures, with a support base coated with salts of Cr, Mo, W, Mn and/or Re. The conversion of aniline increases with increasing Rh content but the selectivity to cyclohexylamine decreases to 20% at 40% conversion. (1) have high selectivity > 97% for cyclohexylamine from aniline.

Exhaust Gas Purification Catalyst

A Pd-Au catalyst (1) is prepared by separately impregnating and fixing the Pd and Au water-soluble compounds, followed by reduction of the fixed solids to free metals on a suitable support. (1) has smaller variation in the Au/Pd ratio than products made by the double fix method, and exhibits high activity, good selectivity and long life. (1) are used for the production of unsaturated esters from olefins, O₂ and organic acids, particularly in the manufacture of vinyl acetate from ethylene, O₂ and acetic acid.

HOMOGENEOUS CATALYSIS

Production of Arylalkenes and Conjugated Dienes

Production of arylalkene or conjugated diene compounds (1) by Heck reaction comprises reacting an aryl or vinyl halide or sulfonate with an olefin in the presence of a catalyst comprising a Pd(0) complex or a Pd(II) salt and a phosphite ligand which has better oxidative stability than conventional phosphine ligands. (1) are useful as ultraviolet absorbers, intermediates for pharmaceuticals and agrochemicals, etc.

Production of Stanol Compounds

Stanols are produced by hydrogenating sterols (1) in the presence of a Pd catalyst in an organic solution using much reduced amounts of solvent. Alcohol, paraffin carbohydrates and mixtures of alcohol and carbohydrates can be used as solvents. The method is used for large-scale production due to its reduced consumption of solvent and good stanol yield.
FUEL CELLS

Fuel Cell Catalyst

DEGUSSA-HUELS A.G., European Appl. 951,084

A fuel cell anode for the electrocatalytic MeOH oxidation contains a Pt metal or a Pt metal alloy as a primary catalytic component (1) and a transition metal complex cocatalyst of an optionally substituted phthalocyanine to reinforce the catalytic effect of (1). This anode is claimed to have a comparable or better performance than one containing a Pt catalyst with a Ru cocatalyst. (1) is not poisoned by the phthalocyanine complex.

Platinum-Ruthenium Electrocatalyst

NE CHEMCA, European Appl. 952,241

An electrocatalyst (1) comprises a cubic Pt-Ru solid solution alloy and a hexagonal Ru alloy, each having a crystalline diameter of 10–100 Å, supported on a conductive C carrier. The total amount of the combined alloys is 10–80 wt.%, based on the electrocatalyst. (1) has excellent poisoning resistance to CO, thus allowing the use of a small, simplified fuel reformer. (1) is used in SPEFCs as a propulsion power source for transportation means.

CO-Tolerant Fuel Cell Oxidation Catalysts


A selective oxidation catalyst for fuel cells or oxidation of H₂ in the presence of CO comprises a C black-supported catalyst having an atomic composition PtₓMoᵧ, where x = 0.5–0.9 and y = 0.5–0.1. This catalyst has a gas diffusion electrode having a web and the above catalyst layer and an ion exchange membrane coated on one side with the catalyst. Activity of the catalyst is high and controllable, and H₂ can be oxidised in the presence of CO without adversely affecting the Pt.

Fuel Cell Electrodes

UNITED TECHNOLOGIES CORP., U.S. Patent 4,613,582

A ternary metal alloy catalyst (1) is made by intimately contacting a finely divided noble metal, preferably Pt, supported on an electrically conductive C black with a solution of a compound of a Group IV, V, VI or VII transition metal, preferably Cr, and a Co compound, then heating and reducing in N₂. Its catalytic activity for the electrochemical reduction of O₂ is 2.5 times that of the supported unalloyed noble metal alone. (1) is used for the electrochemical reduction of O₂ as a cathode in acid fuel cells.

Direct Liquid-Feed Organic Fuel Cell

CALIFORNIA INST. OF TECHNOL., U.S. Patent 5,945,231

A fuel cell for generating electrical power by electrochemical reactions of a liquid organic fuel comprises a solid electrolyte membrane, directly supporting anode and cathode catalyst (1) layers, each containing 7–10% Pt and Ru catalyst, 60–70% of perfluorovinyl ether sulfonic acid and 15–20% of PTFE. Efficiency is increased, permeation of (1) into backing layers is minimised and fuel crossover is reduced.

ELECTRICAL AND ELECTRONIC ENGINEERING

Magnetic Head Elements

TDK CORP., Japanese Appl. 11/273,036

A spin type magneto resistance effective element for a magnetic head (1) has an antiferromagnetic layer made of PtₓRₓMnᵧ, specific PtₓRhₓMnᵧ, where R = Rh, Ir or Ru with x = 5–30% and y = 40–60%. (1) has increased magnetic exchange energy.

Magnetic Alloy Film

SHOWA DENKO KK, Japanese Appl. 11/273,947

A non-magnetic substrate carries a non-magnetic foundation film, a magnetic film and a protective film. The magnetic film contains in at. %: 1–7 Pt, 10–26 Cr, 0.5–4 Cu, Re or V, ~ 1–16 Ta, and remainder Co. The composition is used in floppy disks for a magnetic disk drive and has excellent coercive force and noise characteristics.

Semiconductor for Light Emitting Diode

TOSHIBA K.K., Japanese Appl. 11/274,562

A nitride compound semiconductor composition comprises a metal layer (1) formed from one of Pd, Rh, Ir, Sc, V, Zr, Hf, Ta, Co and Cu; and a second metal layer of Ti, Ni, Mo or W, deposited on (1). The Pd, etc., has favourable ohmic characteristics so sheet and contact-resistance are greatly reduced, and thus wire bonding is easily performed. Light emitting devices of high brightness can be obtained at low cost.

Ceramic Circuit Board

MIYOSHI-DENSHI K.K., Japanese Appl. 11/274,696

The heat release structure of a ceramic circuit board used in portable electronic devices has a heat release hole filled with 0.5–20 wt.% of Ag, Pd, Ru and/or Rh. Excellent heat release properties and size reduction of the ceramic substrate are obtained as the heat release hole is present at the bottom of the device.

Processing PCB Substrate

HITACHI CHEM. CO. LTD., Japanese Appl. 11/279,766

Processing a substrate of a printed circuit board involves sensitising and heat treatment by a Pd complex on the board surface prior to electroless plating. The electroless plating is used to make multilayered printed circuit board with fewer plating blisters.

Metallisation of Polymeric Substrates

BLASBERG ETTHONE-OMI, German Appl. 1/98,220,075

Metallisation of polymeric substrates for the production of printed circuit boards, preferably with micro-holes and fine structure, comprises doping an electrically conductive polymer layer with a Sn containing colloidal Pd solution, prior to contact with a Cu salt solution. This process allows more rapid metallisation and a faster lateral growth rate.

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