PLATINUM METALS REVIEW

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IAN E. COTTINGTON

A TRIBUTE ON HIS RETIREMENT AS EDITOR

As many of you may already know, on 30th June 1994, Ian E. Cottington retired as Editor of “Platinum Metals Review”, a position he had held since the death of Dr. L. B. Hunt on 9th April 1987. In 1956 when the Board of Johnson Matthey, with the encouragement of the Directors of Rustenburg Platinum Mines, took the decision to launch a quarterly technical journal, “Platinum Metals Review”, the task was entrusted to Leslie Hunt. Thus in 1975 when Ian accepted an invitation to transfer from the Johnson Matthey Physical Metallurgy Laboratory and join the staff of “Platinum Metals Review” as Editorial Executive, the journal was in its nineteenth year of publication. By this time a reputation had been established for the accurate and timely reporting of advances in scientific knowledge and technical know-how concerning the platinum metals, and an international readership had been built-up, although largely in the Western World.

The attributes required of an Editor, including attention to detail, accuracy of reporting, the use of unambiguous language, importance of presentation of results, having work completed on time and within budget, and especially perhaps the ability to lead a small group of individuals having a variety of skills to work as an effective team, were, Ian claimed, much the same as those he had needed to run a successful metallographic department. Over the years Ian became involved in all aspects of the production and distribution of the journal, and even found time to research and write on some early applications of the platinum metals, and on platinotype photography, which is his special interest.

Ian has worked diligently to expand the distribution of the journal in the developing world, especially to the universities and colleges where future generations of platinum users will be educated. In fact the journal is now sent to over 100 countries. Ian has also increased the number of contributions published in “Platinum Metals Review” from authors in the C.I.S. and from Asia, and it is of satisfaction to him that while he was Editor the precious metals company Tanaka K.K. began the demanding task of publishing a Japanese language version of the journal.

In wishing Ian a long and happy retirement the editorial team renew their commitment to provide the platinum-using industries of the world with information which will enable platinum technology to be further applied for the benefit of mankind. We are happy that Ian’s expertise, geniality and courtesy will remain available to Johnson Matthey in his new role as consultant, and Ian can still be reached via the Editorial Office in Hatton Garden.
Highly Efficient Nanocrystalline Photovoltaic Devices

CHARGE TRANSFER SENSITISERS BASED ON RUTHENIUM AND OSMIUM ACHIEVE OUTSTANDING PERFORMANCE

By Michael Grätzel

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A new molecular photovoltaic system for solar light harvesting and conversion to electricity has been developed. It is based on the spectral sensitisation of a nanocrystalline semiconductor film by transition metal complexes. The film consists of nanometre-sized colloidal titanium dioxide particles sintered together to allow for charge carrier transport. Ruthenium and osmium based sensitisers have so far achieved the best performance both from the efficiency as well as the stability point of view. Carboxylated polypyridyl complexes of these two metals give extraordinary efficiencies for the conversion of incident photons into electric current, exceeding 90 per cent within the wavelength range of their absorption band. The outstanding performance of cis-di(thio-cyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylate)ruthenium(II) is unmatched by any other known sensitisers. The present paper discusses the underlying physical principles of these astonishing findings. Exploiting this discovery, we have developed a low-cost photovoltaic cell whose overall light to electric energy conversion yield is 10 per cent under direct (AM1.5) solar irradiation. For the first time a device based on a simple molecular light absorber is attaining a conversion efficiency commensurate with that of silicon based photovoltaic cells, but at a much lower cost.

In a conventional p-n junction photovoltaic cell made, for example, from silicon, the semiconductor assumes two roles at the same time: it harvests the incident sunlight and conducts the charge carriers produced under light excitation. In order to function with a good efficiency the photons have to be absorbed close to the p-n interface. Electron-hole pairs produced away from the junction must diffuse to the p-n contact where the local electrostatic field separates the charges. In order to avoid charge carrier recombination during the diffusion the concentration of defects in the solid must be small. This imposes severe requirements on the purity of the semiconductor material, rendering solid state devices of the conventional type very expensive. Molecular photovoltaic systems separate the functions of light absorption and carrier transport. Light harvesting is carried out by a sensitisers which initiates electron transfer events leading to charge separate. This renders unnecessary the use of expensive solid state components in the system. While being simple from the conceptual point of view, the practical implementation of such devices must overcome formidable obstacles if the goals are to develop molecular systems which convert sunlight to electricity at an efficiency comparable to that of silicon cells, and meet the stability criteria for practical applications.

Our success in bringing this project close to commercial maturity owes much to the recent progress in molecular engineering of stable and efficient charge transfer sensitisers based on the
on the molecular engineering of suitable ruthenium and osmium compounds which exhibit the most promising properties so far. Thus we have developed bis(bipyridyl)Ru(II) complexes which have the general formula $\text{cis-X}_2\text{bis}(2,2\prime\text{-bipyridyl}-4,4\prime\text{-dicarboxylate})\text{ruthenium(II)}$, where $X = \text{Cl}, \text{Br}, \text{I}, \text{CN}$, and SCN. We have performed a systematic study of their luminescence, visible light absorption, electrochemical and photoredox behaviour (2). Among these compounds, $\text{cis-di(thiocyanato)bis}(2,2\prime\text{-bipyridyl}-4,4\prime\text{-dicarboxylate})\text{ruthenium(II)}$, (I), displays outstanding performance as a solar light absorber and charge-transfer sensitisier, unmatched by any other dyestuff known so far. Its broad range of visible light absorption and relatively long-lived excited state render it an attractive sensitisier for homogeneous and heterogeneous redox reactions. The structural features of this complex are shown in Figure 1, and salient photophysical features of the $\text{cis-X}_2\text{bis}(2,2\prime\text{-bipyridyl}-4,4\prime\text{-dicarboxylate})\text{ruthenium(II)}$-type charge transfer sensitisers have also been documented (2).

For light harvesting by sensitisers attached as a monolayer on a flat surface, there is the notorious problem of insufficient light absorption. On a smooth surface the monolayer absorbs less than 1 per cent of the incident light in the wavelength range of maximum absorption. One could naturally think, then, of depositing several molecular layers of sensitisier on the semiconductor in order to increase the light absorption. This would however be a mistaken tactic, since the outer dye layers would act only as a light filter, with no contribution to electrical current generation. The application of only a monomolecular film of sensitisier is therefore unavoidable.

We found a solution to the problem of light absorption through such extremely thin molecular layers by the use of nanocrystalline systems. It is possible, using the sol-gel method, to produce transparent films consisting of colloidal titanium dioxide particles with diameters of 10 to 30 nm. Electronic contact between the particles is produced by a brief sintering at about 500°C. A nanoporous structure with a very high

**Light Harvesting by Platinum Metal Complexes**

The fundamental processes involved in photovoltaic conversion are:
- the absorption of sunlight
- the generation of electrical charges by light and
- the collection of charge carriers to produce electricity.

In any case, the components of the synthetic system must be selected to satisfy the high stability requirements needed for practical applications. A photovoltaic system must remain serviceable for 20 years without significant loss of performance. One of the most remarkable achievements of research in inorganic chemistry during the last two decades has been the development of a great variety of platinum metal complexes (1) mainly of the elements rhodium, osmium and ruthenium, and also rhenium, many of which are very stable and display good absorption in visible light. Our work has focused
internal surface area is thereby formed. For example, the effective surface of a 8 μm thick layer of such a colloidal structure is about 720 times greater than that of a smooth film. On the geometric projection of such a surface a sensitisier concentration of $\Gamma = 1.2 \times 10^{-7}$ moles/cm$^2$ is reached when nanocrystalline films are used. The optical density:

$$\text{OD}(\lambda) = \Gamma \times \epsilon(\lambda)$$  \[i\]

calculated for this coating level is 1.68 using $\epsilon = 1.4 \times 10^7$ cm$^2$/mole for the extinction coefficient, which is the value obtained for complex (I) at 536 nm. The light harvesting efficiency of the device, LHE($\lambda$), is then given by:

$$\text{LHE}(\lambda) = 1 - 10^{-\text{OD}}$$  \[ii\]

With an optical density of 1.68, 98 per cent of the light is absorbed by the film at the wavelength of the absorption maximum of the sensitisier. When derivatised with cis-di(thiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylate) ruthenium(I1) the light harvesting capacity of such films becomes superior to that of amorphous silicon. Nature, in fact, uses a similar means of absorption enhancement by stacking the chlorophyll containing thylakoid membranes of the chloroplasts to form the grana structures.

**Light Induced Charge Separation**

The role of the ruthenium complex is the same as that of chlorophyll in the green leaf: it must absorb the incident sunlight and exploit the light energy to induce a vectorial electron transfer reaction. In place of the biological lipid membrane a titanium dioxide film is employed. Apart from acting as a support for the sensitisier, it also functions as the electron acceptor and electronic conductor. The electrons injected by the sensitisier travel across the nanocrystalline film to the conducting glass support serving as current collector. The driving force necessary for the rapid vectorial charge displacement is small, corresponding to about 0.1 eV, which is required to drive the electron injection process.

The efficiency of light induced charge separation at the oxide semiconductor surface is expressed by the quantum yield of charge injection ($\phi_{\text{inj}}$). This represents the fraction of the absorbed photons converted into conduction band electrons. Charge injection from the electronically excited sensitisier into the semiconductor is in competition with other radiative or radiationless deactivation channels. Taking the sum of the rate constants of these non-productive channels together as $k_{\text{eff}}$ results in:

$$\phi_{\text{inj}} = \frac{k_{\text{inj}}}{k_{\text{inj}} + k_{\text{eff}}}$$  \[iii\]

One should remain aware that the deactivation of the electronically excited state of the sensitisier is generally very rapid. Typical $k_{\text{eff}}$ values lie in the range from $10^6$ to $10^9$/s. To achieve a good quantum yield the rate constant for charge injection, $k_{\text{inj}}$, should be at least 100 times higher than $k_{\text{eff}}$. This means that injection rates which exceed $10^{11}$/s must be attained. In actual fact, in recent years sensitisers have been developed that satisfy these requirements. These dyes should incorporate functional groups ("interlocking groups") as, for example, carboxylates or other chelating groups, which besides bonding to the surface of the titanium dioxide, also effect, as is illustrated in Figure 2, an enhanced electronic coupling of the sensitisier with the...
conduction band of the titanium dioxide semiconductor.

Very promising results have so far been obtained with ruthenium complexes where at least one of the ligands was 4,4'-dicarboxy-2,2'-bipyridyl. Examples are shown in Figure 3. The carboxylates serve to attach the ruthenium complex to the surface of the oxide and to establish good electronic coupling between the π' orbital of the electronically excited complex and the 3d wavefunction manifold of the titanium dioxide film, see Figure 4. The substitution of the bipyridyl with the carboxylate groups also lowers the energy of the π' orbital of the ligand. Since the electronic transition is of MLCT (metal to ligand charge transfer) character, this serves to channel the excitation energy into the correct ligand, that is the one from which electron injection into the semiconductor takes place. With molecules like these, the charge injection is in the picosecond or even femtosecond time domain (4).

As the last step in the conversion of light into electrical current, a complete charge separation must be achieved. On thermodynamic grounds, the preferred process for the electron injected into the conduction band of the oxide film is recapture by the sensitiser cation. This reaction is obviously undesirable, since instead of generating electrical current it merely generates heat. An important kinetic parameter for the characterisation of the recombination rate is the rate constant, $k_e$. It is of great interest to develop sensitiser systems for which the value of $k_{\text{rec}}$ is high and that of $k_e$ low. Fortunately, for the transition metal complexes we use, the ratio of the injection rate to the recapture rate $k_{\text{inj}}/k_e$ is greater than $10^5$, and in some cases it exceeds even one million. The reason for this behaviour is that the molecular orbitals involved in the back reaction overlap less favourably with the wavefunction of the conduction band electron than those involved in the forward process. For example, for $\text{cis}$-dithiocyanato$\text{bis(2,2'-bipyridyl-4,4'-dicarboxylate)}\text{ruthenium(II)}$ bound to the nanocrystalline oxide film, the injecting orbital is the π' wavefunction of the carboxylated bipyridyl ligand, since the excited state of this sensitiser has a metal to ligand charge transfer character. The carboxylate groups interact directly with the surface titanium(IV) ions resulting in good electronic coupling between the π' wavefunction and the 3d orbital manifold of the conduction band of the titanium dioxide. As a result, electron injection from the excited sensitiser into the semiconductor membrane is an extremely rapid process occurring in less than a picosecond, see Figure 4.

By contrast, the back reaction of the electrons with the oxidised ruthenium complex involves a d-orbital, localised on the ruthenium metal, having only a small electronic overlap with the titanium dioxide conduction band. The spatial contraction of the wavefunction upon oxidation of the ruthenium(II) to the ruthenium(III) state further reduces this electronic coupling. This, together with the fact that the driving force for the back electron transfer is
large enough to place it in the inverted Marcus domain explains the relatively slow backward electron transfer which, typically, is in the microsecond time domain.

Thus, in analogy to natural photosynthesis, light-induced charge separation is achieved on kinetic grounds, the forward electron transfer being orders of magnitude faster than the back reaction. As a consequence, the presence of a local electrostatic field is not required to achieve good efficiencies for the process. This distinguishes the nanocrystalline devices from conventional photovoltaic cells (5-9), in that the successful operation of the latter is contingent upon the presence of a potential gradient within the p/n junction.

**Photovoltaic Performance of Ruthenium Based Sensitisers**

In our nanocrystalline cell, the electrons injected into the semiconductor from the excited transition metal complex are collected as an electrical current and result in photovoltaic conversion of light energy. The incident monochromatic photon to current conversion efficiency is given by the equation:

\[
\eta_i(\lambda) = \text{LHE}(\lambda) \times \Phi_{\text{ir}} \times \eta_e
\]  

where \(\eta_i(\lambda)\) expresses the ratio of the measured electrical current to the incident photon flux for a given wavelength, while \(\eta_e\) is the charge collection efficiency. Using ruthenium or osmium complexes of the type shown in Figure 3, in conjunction with nanocrystalline titanium dioxide films, solar cells are now available for which all three factors in Equation [iv] are close to unity (2, 10–14). Thereupon, within the wavelength range of the absorption band of the sensitiser a quantitative conversion of incident photons to electrons is obtained.

A graph which presents the monochromatic current output as a function of the wavelength of the incident light is known as a "photocurrent action spectrum", and Figure 5 shows such action spectra for three ruthenium complexes, illustrating the very high efficiency of current generation, exceeding 75 per cent obtained with these complexes. When corrected for the inevitable reflection and absorption losses in the conducting glass serving to support the nanocrystalline film, yields of practically 100 per cent are obtained. Historically, RuL, (L = 2,2'-bipyridyl-4,4'-dicarboxylate) was the first efficient and stable charge transfer sensitizer to be used in conjunction with high surface area titanium dioxide films (10). In a long term experiment carried out during 1988 it sustained 9 months of intense illumination without loss of performance. However, the visible light absorption of this sensitizer is insufficient for solar light conversion. A large improvement...
in the harvesting of light is achieved with the trinuclear complex of ruthenium (11, 16, 17) whose two peripheral ruthenium moieties were designed to serve as antennas (16). However, the most successful charge transfer sensitisier investigated so far is without doubt cis-dithiocyanatobis(2,2'-bipyridyl-4,4'-dicarboxylate)-ruthenium(II). This achieves close to quantitative photon to electron conversion over the whole visible range (2). Even at 700 nm the current generation is still 40 to 50 per cent efficient.

The photovoltage of our cell represents the difference between the Fermi level of titanium dioxide under illumination and the redox potential of the electrolyte, see Figure 6. Using the triiodide/iodide redox couple in N-methylloxazolidinone solution, under full sunlight an open-circuit cell voltage of 0.7 to 0.9 V can be measured. Under a 1000-fold lower intensity the cell voltage is about 200 mV

Fig. 5 A photocurrent action spectrum obtained from three different ruthenium based sensitiser attached to the nanocrystalline titanium dioxide film. The blank spectrum obtained with the bare titanium dioxide surface is shown for comparison. The incident photon to current conversion efficiency is plotted as a function of the wavelength of the exciting light.

Fig. 6 Representation of the principle of the new photovoltaic cell showing the electron energy level in the different phases. The cell voltage observed under illumination corresponds to the difference in the quasi-Fermi level of the titanium dioxide under illumination and the electrochemical potential of the electrolyte. The latter is equal to the Nernst potential of the redox couple (R/R') used to mediate charge transfer between the electrodes.
smaller, a relative change of cell voltage of only 20 to 30 per cent. For the conventional silicon cell the cell voltage decreases by a factor of 3 for a comparable change of light intensity, showing that the photovoltage of our cells is significantly less sensitive to variations in light intensity than are conventional photovoltaic devices.

This is an important advantage for the application of the nanocrystalline cell in consumer electronic devices. At this stage industrial companies are already involved in production of such cells which will reach the market quite soon.

The overall efficiency, $\eta_{\text{global}}$, of the photovoltaic cell can easily be calculated from the integral photocurrent density ($i_{\text{ph}}$), the open-circuit photovoltage ($V_{\text{oc}}$), the fill factor of the cell (ff) and the intensity of the incident light ($I_0$).

$$\eta_{\text{global}} = i_{\text{ph}} \times V_{\text{oc}} \times f/f \times I_0$$

In Figure 7, the current-voltage characteristic of a nanocrystalline cell sensitised by (I) is shown. The photocurrent measured at 96.4 mW/cm² of simulated solar intensity was 18.3 mA/cm², the open circuit voltage was 0.72 V, and the fill factor was 0.73, yielding a value of 10 per cent for the overall efficiency of the cell.

**Practical Development of Nanocrystalline Solar Cells**

Meanwhile, the development and testing of the first cell module for practical applications has begun. The layout of the module is presented in Figure 8. The cell consists of two glass plates which are coated with a transparent conducting oxide (TCO) layer. The nanocrystalline...
titanium dioxide film deposited on one plate functions as a light trap. Visible light is absorbed by a monomolecular layer of the ruthenium complex which functions as the charge transfer sensitisier. On illumination, this injects an electron into the titanium dioxide conduction band. The electrons pass over the collector electrode into the external current where they perform work. They are then returned to the cell via the counter electrode. The sensitisier film is separated from the counter electrode by the electrolyte. In the electrolyte there is a redox couple, for example triiodide/iiodide, whose role is to transport electrons from the counter electrode to the sensitisier layer, which has been left positively charged as a result of the electron injection. The counter electrode is made of glass covered with a transparent conducting oxide (TCO) layer that serves as a current collector. A small amount of platinum (5–10 μg/cm²) is deposited onto the TCO to catalyse the cathodic reduction of triiodide to iiodide.

By developing a new mode of platinum deposition we have engineered an extremely active electrocatalyst, which attains exchange current densities of more than 0.1 A/cm² at a platinum loading below 0.1 g/m². Furthermore this electrocatalyst is very stable and does not show long term anodic corrosion, as was seen to be the case for platinum deposits produced by conventional sputtering or galvanic methods. These favourable characteristics have allowed overvoltage losses to be minimised, thus increasing the efficiency and stability of cell operation (18).

Upon long term illumination, complex (I) sustained more than 5 × 10⁷ redox cycles without noticeable loss of performance, which corresponds to about 10 years of continuous operation in natural sunlight. By contrast, practically all organic sensitisers tested so far have undergone photo-bleaching after less than 10⁴ redox cycles. This clearly outlines the exceptionally stable operation of the newly developed ruthenium charge transfer sensitisers, which is of great advantage for the practical application of these devices. It may be argued that the presence of ruthenium renders the price of the sensitisier too high for commercial exploitation, or that there is an insufficient supply of ruthenium. However, the required amount of ruthenium is only 10⁻⁴ moles/m² of cell module surface, and corresponds to an investment of around U.S.$ 0.07/m² for the noble metal. One ton of ruthenium alone incorporated into the charge transfer sensitisier (I) could provide 1 gigawatt of electrical power under full sunlight. This is more than twice the total photovoltaic capacity presently installed worldwide.

Apart from its efficiency and stability any future photovoltaic technology will be valued according to its environmental and human compatibility. There is great concern about the adverse environmental effects and acute toxicity of CdTe or CuInSe, which are being considered for practical development as thin solar cells. Such concerns are unjustified for our nanocrystalline device. Titanium dioxide is a harmless environmentally friendly material, remarkable for its very high stability; it occurs in nature as ilmenite, and is used in quantity as a white pigment and as an additive in toothpaste. Similarly ruthenium has been used without adverse health effects as an additive for bone implants.

Commercial applications will begin in the near future. Contracts for the industrialisation of these cells have been signed with the Wissenschaftspark Gelsenkirchen for modules of 100 peak watts output and higher, which it is hoped will lead to applications in the utility market. Meanwhile for consumer applications co-operation has been established with Leclanché and Glass Trösch, and the first product – a self powered bathroom scale will be marketed during the present year. In full production, a cost estimate commissioned from the Research Triangle Institute (North Carolina, U.S.A.) predicts a module cost of U.S. $0.60, per peak watt rating.

Quite aside from its intrinsic merits as a photovoltaic device, the sensitised nanocrystalline photovoltaic device will undoubtedly promote the acceptance of alternative energy technologies, not least by setting new standards of convenience and economy for the photovoltaic industry as a whole.

*Platinum Metals Rev.*, 1994, 38, (4) 158
by building metal microframeworks on support
pose into fragments, or aggregate together into
larger clusters, and while the states of such cat-
tionally supported catalysts. In conventional
alysts are known before and after the reaction,
whose activity originates from promoters inside
framework, was examined during ethene hydro-
a metal framework, or their effects.
rhodium clusters ("CO-Breathing Ruthenium
chemicallings in metal microframeworks during catalytic reac-
cluster, (NMe,CH,Ph)+(RqC[CO] ,&le)-, which
utable to binding between the framework and
port interactions. It was observed,
when supported on basic oxides, that the metal
core framework of the surface-attached ruthe-
nium species shrank on loss of CO ligands; while
expansions in the framework were induced by
Also on supports, a switchover in the reaction
path was observed during carbon monoxide hy-
hydrogenation as carbido carbon was inserted
into the Ru₆ cluster framework, from disso-
itive to oxidative carbon monoxide hy-
genation, the latter having higher turnover fre-
cuencies and selectivities. Products changed from
hydrocarbons and methane to methanol,
dimethyl ether and formaldehyde, respectively.
Electronic effects of the carbido carbon and clus-
ter metal framework were also found, and inverse
isotope effects for hydrogen, dependent on sup-
port, were observed for the supported clus-
ers.
Two other supported rhodium and ruthenium
clusters show structural chemical control by µ₆-
ligands; and elements, such as carbon and nitro-
gen inside metal cluster frameworks behave as
a new type of catalytic promoter, not interact-
with reactant molecules, but affecting the
catalytic properties without blocking the catal-
ysis. These promoters also act like a central
spring making the cluster flexible at the surface.
This feature could be used with a wide range of
main and transition metal elements.

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Ruthenium Clusters Breathing Carbon Monoxide

It has been noticed that catalysts constructed
by building metal microframeworks on support
surfaces have a different chemistry to conven-
tionally supported catalysts. In conventional
cluster catalysis the supported clusters decom-
pose into fragments, or aggregate together into
larger clusters, and while the states of such cat-
alysts are known before and after the reaction,
not much is known about them during cataly-
sis. Additionally little is known about catalysts
whose activity originates from promoters inside
a metal framework, or their effects.

Therefore work has been undertaken by
researchers in Japan to discover what happens
in metal microframeworks during catalytic reac-
tions involving supported ruthenium and rhodium clusters ("CO-Breathing Ruthenium
and Rhodium Clusters", Y. Izumi and Y. Iwasawa,
Chemtech, 1994, 24, (7), 20–27). The ruthenium
cluster, \((\text{NMe},\text{CH},\text{Ph})\text{Ru}_6\text{C}[\text{CO}]_\text{µ}_6\text{Me}\) , which has a µ₆-carbido ligand inside the octahedra Ru₆
framework, was examined during ethene hy-
donate rearrangement. The stability of this cluster is attrib-
utable to binding between the framework and
the carbido carbon, and perhaps to metal-sup-
port interactions.

The reactions were followed by extended X-
ray absorption fine structure. It was observed,
when supported on basic oxides, that the metal
core framework of the surface-attached ruthe-
nium species shrank on loss of CO ligands; while
expansions in the framework were induced by
CO uptake. When CO was released again, either
by evacuation or decreasing the CO pressure,
the expanded cluster shrank. This process can
be called "CO breathing". The µ₆-carbido car-
bond inside the cluster acted, in effect, like a cen-
tral spring making the cluster freely expand
and shrink.

Also on supports, a switchover in the reaction
path was observed during carbon monoxide hy-
drogenation as carbido carbon was inserted
into the Ru₆ cluster framework, from disso-
itive to oxidative carbon monoxide hydrogena-
tion, the latter having higher turnover fre-
cuencies and selectivities. Products changed from
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Electronic effects of the carbido carbon and clus-
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Two other supported rhodium and ruthenium
clusters show structural chemical control by µ₆-
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gen inside metal cluster frameworks behave as
a new type of catalytic promoter, not interact-
with reactant molecules, but affecting the
catalytic properties without blocking the catal-
ysis. These promoters also act like a central
spring making the cluster flexible at the surface.
This feature could be used with a wide range of
main and transition metal elements.
The growing concern over environmental issues has resulted in the successful implementation, in several countries, of legislation on automobile exhaust pollution. However, there are still many types of pollution emitters which cause concern. One of these being the emission into the air of noxious gases, potentially damaging and injurious to the atmosphere, from various industrial and manufacturing processes, and resulting generally in poorer air quality, and contributing to the damage to the protective ozone layer, or to the greenhouse effect.

It has thus become apparent, that more stringent control of the waste products of industrial processes would be required. In the U.K. this has resulted in the Environmental Protection Act of 1990.

Within Part I of the Act operators of industrial processes that result in the production of waste gases into the atmosphere must reduce the concentrations of these products to below specified limits. Volatile organic compounds, VOCs, arising from industrial solvent use in paint, ink and adhesive manufacture, and also from the petrochemical and chemical industries, have been implicated in a wide range of environmentally damaging processes, due to, in some cases, their own toxicity and in others resulting from chemical reactions within the atmosphere.

A large number of industrial processes generate VOC emissions significantly greater than the permitted limits, and therefore operators of these plants will have to assess the feasibility of greatly reducing these emissions before the stated date of compliance for their particular industry.

Many companies have completed a collection of data on their emissions to the atmosphere, which they have undertaken to enable them to determine the scale of the problem, and they are now considering selection of the most suitable method of emission reduction. Some may be able to reduce their VOC emissions satisfactorily by modifications to their processes or by changing the raw materials which they use; but the majority will need to install some form of pollution control system in order to achieve the required emission levels.

The range and types of pollution control systems are so many and varied that the selection of technology most suitable for a given process is a complex procedure. The financial investment required for such a system can be significant in both capital expenditure and running costs. Thus, the services of an experienced environmental consultant are recommended in order to identify the appropriate air pollution control system for an individual company.

Thermal Incineration: Benefits and Limitations

The most effective way of ensuring essentially complete destruction of VOCs present in gaseous effluent is by incineration. Thermal incineration of VOCs is a widely used technology, and can be performed by direct-flame heating in a combustion chamber, at temperatures of 760°C or more, depending upon the nature of the VOCs.

The three principles of thermal incineration are: time, temperature and turbulence. In order to achieve a high destruction of VOCs the following criteria must be satisfied: sufficient time – of 0.5 to 2 seconds, temperature – of 760°C or greater, and turbulence – to achieve good mixing of the VOCs with air. If any one of these criteria is not achieved, then the VOC
oxidation reactions will not be completed and excess emission levels will be generated.

Thermal incinerators can also suffer extreme thermal stresses, due to their high working temperatures, especially during cycles of heating to the operating temperature, and cooling during shutdown. This can result in the distortion of ductwork and heat exchange surfaces, creating the potential for cracks and leaks. Thus dirty process gases with high VOC content can contaminate the cleaned incinerator exhaust gas. Operating companies may then be faced with the prospect of a major capital outlay either to modify or replace equipment within their incinerator.

**Return to Compliance with a Retrofitted Catalyst System**

One technology which can help in this situation is catalytic oxidation. The technology for the successful catalytic oxidation of VOCs as an alternative to direct thermal incineration has been proven over many years through installation of catalytic oxidation systems to treat VOC emissions from a wide range of industrial processes. More recently catalysts have been brought to public awareness by fitting of catalytic converters to new cars.

The main advantage of catalytic oxidation is the ability of the catalyst to operate at significantly lower temperatures than direct thermal incineration. In many applications this can give lower capital costs and/or lower operating costs.

When the performance of a thermal incinerator is falling short of legislated requirements, either due to a design limitation or to thermal stress-induced leakage, then the addition of an oxidation catalyst into the exhaust of the thermal incinerator can bring the incineration system back into compliance. The basic layout of a thermal incineration system fitted with a catalytic reactor is shown in Figure 1. The system comprises an incineration unit operating at a minimum temperature of 760°C together with a primary heat exchanger which preheats the inlet gases from the process. A secondary heat exchanger is normally installed to recover energy for other purposes. The temperature of the exhaust gas, after passing through a secondary heat exchanger, is typically around 400°C.

The temperature needed for the catalytic oxidation reaction for the majority of VOCs is between 280 and 400°C, and for carbon monoxide which can arise from partially combusted VOCs between 200 and 250°C. Therefore, the addition of a catalytic reactor into the exhaust duct of the incinerator presents the catalyst with the optimum temperature it needs to facilitate the complete oxidation of VOC and carbon monoxide emissions. Moreover, the catalyst is capable of operating at up to a temperature of 750°C, and it is therefore unlikely to be damaged, even under emergency venting of the thermal incinerator.

**Catalyst Use in a Coil Coating Process**

One such retrofit of a catalytic reactor into a thermal incinerator was completed by Johnson Matthey at Alcoa Manufacturing (GB), Swansea. Alcoa is the world's oldest and largest manufacturer of aluminium sheet for the beer, beverage and general purpose can manufacturing industry. Problems had been experienced with the thermal incinerator which treats fumes from the coil coating line, causing general concern
VOCs when passed through a high temperature treatment oven to make the finished product. The high concentration VOCs are destroyed by the thermal incinerator before exhausting to the atmosphere. However, after operating for 6 years the incinerator was found to be suffering from a leakage of VOCs across the primary heat exchanger into the cleaned exhaust gas. There was also some concern that the VOCs were not being effectively destroyed at the design incineration temperature of 720 to 760°C.

An on-site demonstration was undertaken by Johnson Matthey using a pilot-scale platinum-based oxidation catalyst connected so as to take a sidestream from the incinerator exhaust gas flow, at 380 to 425°C. During the extended trial the catalyst proved its capability not only in removing the odour from the incinerator exhaust gas, but also in achieving emissions containing very low levels of VOCs and carbon monoxide. As a result a full-scale catalytic reactor was designed for the maximum process flowrate of 70,000 Nm³/h, taking into account the pressure drop limitations of the existing process exhaust fan and the available space in and around the incinerator exhaust duct.

The platinum-based catalyst was supplied in the form of metal honeycomb monoliths which were welded together to form two large panels and then lowered into a purpose-designed reactor housing, see Figure 2. The catalytic reactor was fully insulated to ensure maximum temperature of the gases reaching the catalyst, in order to attain the highest oxidation performance about the odour and the level of VOC and carbon monoxide emissions into the atmosphere.

In the coil coating plant continuous aluminium sheet is coated with lacquers, which produce

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**Fig. 2** The platinum-based catalyst, supplied in the form of metal honeycomb monoliths welded together to make two large panels, is being lowered into a purpose-designed reactor housing. The catalytic reactor is fully insulated to ensure maximum temperature of the gases reaching the catalyst, in order to attain the highest oxidation performance about the odour and the level of VOC and carbon monoxide emissions into the atmosphere.

As presented in a consultant's initial evaluation the catalytic reactor has shown significant savings both in capital cost and in process downtime when compared with the alternative methods for returning the thermal incinerator to compliance.
mance. Installation of the catalytic reactor was completed within 48 hours, requiring the minimum shutdown on the coil coating plant, see Figure 3.

As presented in the initial evaluation from the consultant of the options for Alcoa, the overall investment in the catalytic reactor installation has shown a significant saving both in capital cost and in process downtime when compared with the alternatives available.

Continuous monitoring of the stack emissions shows the catalyst to be achieving VOC and carbon monoxide emissions well within the limits set by the Environmental Protection Act.

**Continuing Benefits from a Catalyst Retrofit**

Once an oxidation catalyst has been retrofit- ted into a thermal incinerator exhaust duct there is the potential for significant savings in operating costs through a reduction of the combustion temperature in the incinerator. In Germany, following the retrofit of a platinum-based catalytic system by Johnson Matthey, the operator of a phenolic resin coating plant has been able to reduce his incineration temperature to less than 600°C. This has resulted in a reduced efficiency within the thermal incinerator which presents the downstream catalyst with greatly increased concentrations of VOCs and carbon monoxide.

However, the catalyst effectively oxidises these harmful gases and has brought the incinerator into compliance with the strict German air pollution control regulations (T. A. LUFT) while providing considerable savings in incinerator fuel for the operator. Moreover, operation at lower temperature has the added benefit of reducing thermal stresses in the incinerator, which would be expected to extend its operating life.

Platinum-based catalysts used for VOC control in industrial applications have been proven to have a typical lifetime of between five and seven years. Therefore, retrofitting a thermal incinerator with an oxidation catalyst represents a long-term solution to the problem of non-compliance with existing legislation, and can even be an answer to meeting future, more stringent, environmental legislation.

**Tunable Iridium Based Infrared Detector**

The detection of infrared radiation at wavelengths 0.75 to 20 micrometres is important for industrial process control, scientific imaging, thermography and radiometry, and surveillance; infrared cameras can be built from arrays of Schottky barrier detectors. The response of infrared detectors, based on Schottky diodes or heterostructures, to incident radiation is limited by the height of the internal potential barrier, and the cut-off wavelength depends on their construction. The longest cut-off wavelength, of 12 micrometres, has recently been achieved by iridium and platinum based Schottky barrier detectors. The response of infrared detectors, based on Schottky diodes or heterostructures, to incident radiation is limited by the height of the internal potential barrier, and the cut-off wavelength depends on their construction. The longest cut-off wavelength, of 12 micrometres, has recently been achieved by iridium and platinum based Schottky barrier detectors and by a SiGe/Si heterostructure. The cut-off wavelength can be changed only by lowering the Schottky barrier height, and the detectors can be tuned to only a few tens of meV.

However, if a detector had an asymmetrical metal-semiconductor-metal heterostructure, there should be modulation of several hundred meV, and an improved photoresponse. Now, researchers from France Telecom-CNET, have fabricated such a detector, which utilises an iridium electrode, and is tunable. The cut-off wavelength has moved from 2 to over 6 micrometres (I. Sagnes, Y. Campidelli and P. A. Badoz, J. Electron. Mater., 1994, 23, (6), 497–501).

The tunable infrared photoemission sensor, TIPS, of iridium/silicon/erbium silicide/silicon, is effectively two back-to-back Schottky diodes separated by silicon, creating an asymmetric potential barrier between the iridium and erbium silicide films. An iridium diode was made from evaporated iridium film; iridium and erbium silicide contacts were attached to the diode and an iridium dot, respectively.

With an external bias applied between the iridium and erbium silicide electrodes, the variation in the effective barrier height is over ten times larger than that of a standard Schottky barrier, and the cut-off wavelength can be modulated over a large range. On infrared illumination photocurrents are created, two, specific to TIPS, have tunable thresholds, of size depending on the incident photon energy, and on the applied bias. High detection levels are expected at 2 micrometres wavelength and at 125 K, and if it is combined with large focal plane arrays and with developing microelectronics technology novel detectors can be produced.

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Platinum and Palladium in Magnetic Storage Applications

The 6th joint MMM/Intermag conference (Magnetism and Magnetic Materials/Intermag), was held in Albuquerque, New Mexico, from the 20th to the 23rd June 1994. Thus this major combined magnetics conference covered most areas of magnetic research currently taking place worldwide. In this review some of the 17 papers presented on the topic of platinum and palladium in magneto-optical and perpendicular magnetic memory storage are discussed.

Magneto-Optical Memory Storage

In recent years platinum/cobalt multilayers have attracted a lot of interest, and much of the basic research into the properties of these multilayers has already been completed (1, 2). The work reported on platinum/cobalt multilayers at this conference was therefore concerned with improvements in the material properties required to enhance their potential as a second generation magneto-optical memory storage material.

It was reported by T. Suzuki, S. Iwata, H. Brandle and D. Weller from the IBM Almaden Research Centre, San Jose, California, that the wavelength at which the polar Kerr rotation peaked in platinum/cobalt multilayers could be altered by the addition of bismuth to the platinum layers. This property could then be used to match the peak in the polar Kerr rotation with the wavelength of the laser used to read the information from the multilayer. Unfortunately the shift in the peak was also accompanied by a reduction in the peak polar Kerr rotation obtained, thus reducing the benefit obtained from shifting the peak.

The subject of increased platinum/cobalt multilayer coercivity was reported by J. Miller, P. G. Pitcher and D. P. A. Pearson from the Johnson Matthey Technology Centre, Reading. The coercivity of their sputtered multilayers could be increased from 3.3 to 10.5 kOe by annealing the multilayers in air; this coercivity increase could be reversed by annealing the multilayers in a reducing atmosphere of 10 per cent hydrogen in nitrogen. The mechanism for the increase in coercivity was suggested to be the formation of cobalt oxide at the grain boundaries, which then acts as a magnetic domain pinning site. Similar results have been previously reported in both platinum/cobalt and palladium/cobalt (3) multilayers, but the coercivities obtained were smaller: 0.2 to 2 kOe for the platinum/cobalt multilayers and 0.5 to 3 kOe for the palladium/cobalt multilayers.

In first generation magneto-optical applications, improvements in the data writing speed can be obtained by reducing the external magnetic field which is required for data to be written, using a magnetic field modulated system. A reduction in the external magnetic field was achieved in work reported by S. Ohnuki and N. Ohta from Hitachi Maxwell, Japan, by the application of a platinum-cobalt alloy overcoat onto a TbFeCo magneto-optical storage layer. The 1 nm thick overcoat of platinum-cobalt alloy significantly reduced the magnetic field required to write information to the TbFeCo storage layer. Previously the same effect could only be achieved by using a platinum-cobalt alloy overcoat of 20 to 30 nm thickness, thus this 1 nm thick platinum-cobalt overcoat offers a more economically viable prospect.

Platinum-manganese-antimony alloys exhibit the largest known room temperature polar Kerr rotation and as a result have been studied as a potential magneto-optical memory storage material. However this polar Kerr rotation peaks at too large a wavelength for a second generation magneto-optical material, and the required magnetic properties have not yet been induced in this material. Improvements to the wavelength dependence of the polar Kerr rotation were reported by M. Takahashi, H. Shoji, Y. Hozumi and T. Wakiyama from Tohoku University, Japan, and Y. Takeda and Y. Itakura from Teijin Limited, Tokyo. They reported that they had
reduced the wavelength at which the polar Kerr rotation peaked by reducing the platinum concentration in the alloy. A reduction in platinum concentration from 21 to 6 per cent resulted in the peak polar Kerr rotation moving from 633 to 528 nm without any alteration in the peak polar Kerr rotation of 1.0°. Unfortunately this alloy did not possess magnetic properties suitable for magneto-optical storage applications. However it was suggested that perpendicular magnetisation could be induced in these alloys by manufacturing samples having their c-axis perpendicular to the film plane, since in this material the direction of easy magnetisation is along the c-axis.

Perpendicular Recording Applications

The potential of palladium/cobalt multilayers as a material for perpendicular magnetic memory storage was demonstrated in a paper by B. M. Lairson from Rice University, Texas, and J. Perez and C. Baldwin from Censtor Corporation, San Jose, California. They compared palladium/cobalt multilayers with conventional cobalt-chromium alloys and found that the palladium/cobalt multilayers had a number of advantages, including the larger signal which is read back from the information stored when using palladium/cobalt multilayers. The multilayer properties of palladium/cobalt can be easily modified to match a particular data recording head, and the multilayers do not require the use of a high temperature deposition process to produce the desired properties. Platinum-cobalt alloys were also reported to have potential as a future perpendicular recording media by T. Hikosaka, T. Komai and Y. Tanaka from Toshiba R. & D. Center, Kawasaki, who produced platinum-cobalt alloys with large perpendicular anisotropies and coercivities by sputter deposition. They obtained these properties by adding oxygen to the high pressure (30 mTorr) sputtering gas to produce a material in which the platinum-cobalt alloy grains were separated by amorphous oxide boundaries. The oxygen rich boundaries magnetically help to isolate the grain, which produces the large perpendicular anisotropy and coercivity of the material.

Conclusions

The results presented at this conference showed that both platinum- and palladium-containing materials have potential applications as magnetic data storage materials, in both magneto-optical and perpendicular recording applications. The publication of the full conference proceedings will be split between the Journal of Applied Physics and the IEEE Transactions on Magnetics later this year.

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Pretreatment of Titanium for Platinum Plating

A variety of electrochemical processes make use of platinum plated titanium electrodes. Before an adherent coating can be deposited onto the titanium, however, the tenacious oxide layer must first be removed, this being especially important if the thickness of the platinum deposit is to be greater than 2 to 3 micrometres, as is generally required for industrial use.

In a recent article M. Pushpavanam and S. R. Natarajan of the Central Electrochemical Research Institute, Karaikudi, India, describe experiments carried out to identify a titanium pretreatment procedure that would facilitate the direct electrodeposition of platinum from a dinitro sulphato platinous acid (DNS) system at pH 2–3 (Met. Finish., 1994, 92, (6), 85–87, 157). Eight different etchant compositions were considered in the experimental programme and their performance assessed in terms of deposit appearance and adhesion, performance under corrosion conditions and the initial substrate metal weight loss. Adherent platinum coatings up to 8 micrometres thick, with good corrosion resistance, were produced by direct deposition after the titanium substrate had been treated in a solution of sodium fluoride, hydrochloric acid and acetic acid; the optimised conditions being identified in the article.

P.E.S.
An Interfacial Mediator Interpretation of Noble Metal Electrocatalysis

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Electrocatalysis is of considerable interest in many areas, such as in energy conversion and storage, electroanalysis, water purification and electroless metal deposition, and some of the most active materials in this area are the noble metals and their oxides, for example platinum and ruthenium dioxide. It is widely accepted that (even in heterogeneous catalysis in general) there is a wide gap between theory and practice: most industrial catalysts are developed by repetitive testing techniques. It has been proposed by the author that the fundamental problem in this area is the fact that the active interfacial mediators in electrocatalysis, which are the adatoms and incipient hydrous oxide species, reside virtually outside the solid lattice and exhibit chemical – and especially redox – behaviour very different to that of well embedded surface species. There is an urgent need to develop and apply highly sensitive techniques to investigate the behaviour of such quite low coverage reactive surface/interfacial species.

Electrocatalysis is concerned largely with methods – usually based on the choice and state of the electrode material – for increasing the rate of a desired electrode reaction at a specific potential or, alternatively, lowering the overpotential (and hence the energy requirement) for a given rate of reaction (1–3). As in all forms of catalysis, the operation of an electrocatalyst is based on the provision of an alternative route for reaction, one that has a lower energy of activation than that of the same process in the absence of the electrocatalyst. Electrocatalysis may be viewed as a subsection of heterogeneous catalysis which currently has far more widespread applications and has been more extensively investigated. However, there are important differences (1), one of which is the fact that cell processes (electrode reactions always occur in pairs – oxidation at the anode and reduction at the cathode) are frequently “uphill” from a thermodynamic viewpoint, for example:

\[ \text{H}_2\text{O}(l) = \text{H}_2(g) + \frac{1}{2}\text{O}_2(g) \]
\[ \Delta G^\circ = +237.2 \text{ kJ/mol (T = 298 K)} \]  

[i]

The water electrolysis cell used to carry out such a reaction may be regarded simply as a convenient device for adding the extra energy (in electrical form) needed to convert the reactants to the higher energy products. Such a system based on the reaction shown in Equation [i] forms the basis of a very interesting future energy strategy. Solar energy may be converted (in photovoltaics) to electrical energy and then (in electrolysis cells) to chemical (that is, hydrogen) energy. The hydrogen may be piped elsewhere, stored, and then used on demand, with oxygen from the air, to produce electricity in a quite efficient manner in a hydrogen/oxygen fuel cell whose operation is based on the reverse of the reaction shown in Equation [i]. This intermediate production of hydrogen (or perhaps a metallic hydride) is the basis of a remarkably clean, carbon dioxide-free approach to future energy demand that is worthy of greater attention: a 350 kW energy conversion and storage system, based on this approach, is currently in operation in Saudi Arabia (4).

The role of electrocatalysts in such energy conversions systems is a crucial one as the processes involved in both the electrolyser and fuel cell must occur both rapidly (thus reducing plant size and capital cost) and efficiently – with minimum
energy loss. The demands on the electrocatalysts, in terms of activity, long term stability and cost, are quite severe and platinum metals play a vital role in several of the processes involved.

In-situ Changes in Surface Activity

An important factor with regard to the operation of an electrocatalyst is that these materials usually operate in contact with an electrolyte. A solvent such as water is not inert, it frequently interacts not only with the other reactants or intermediates at the interface but also with the electrode (or the electrocatalyst) itself. It is well established for instance that with platinum (an efficient electrocatalyst for many reactions) in aqueous media (5) hydride (or H$_{ads}$) or oxide (OH$_{ads}$ and O$_{ads}$) films are formed on the metal surface over certain ranges of potential, see Figure 1. It is generally accepted that, as is clear from Figure 1, oxygen gas evolution at a platinum anode surface (which usually occurs well above the reversible potential for this reaction, 1.229 V(RHE) at T = 298 K) occurs not at the metal but at the oxide-coated metal surface (1). The solvent is not the only species that can react with, and modify the reactivity of, the surface of the electrocatalyst - so also can electrolyte anions such as Cl$^{-}$, SO$_{4}^{2-}$ or HSO$_{4}^{-}$, adventitious impurities and organic reactants. For example in the oxidation of methanol, at the anode of a direct methanol/air fuel cell, at low pH the process of interest is complete conversion according to the following reaction:

$$\text{CH}_3\text{OH} (l) + \text{H}_2\text{O} (l) = \text{CO}_2 (g) + 6\text{H}^+ (l) + 6\text{e}^- \text{ [ii]}$$

However, this process tends to be severely inhibited due to the accumulation of a CO$_{ads}$ poisoning species produced at the interface via the following type of side reaction (6):

$$\text{CH}_3\text{OH} (l) = \text{CO}_{ads} + 4\text{H}^+ (l) + 4\text{e}^- \text{ [iii]}$$

Other alterations in the electrocatalyst that may occur in practice include dissolution - resulting (with multicomponent systems) in surface enrichment phenomena - and sintering (which results in loss of true surface area and surface density of active sites).

The Gap between Theory and Practice

A rather disconcerting feature in the area of heterogeneous catalysis in general is the presence of a wide gap between theory and practice.
Thus, Bond has pointed out recently that “Reflections on the research carried out in the field of heterogeneous catalysis over the last four decades will show not so much a catalogue of problems solved as of problems shelved” (7). At approximately the same time Schlogl claimed that “All the catalytic processes vital to industry were developed by purely empirical methods and countless screening experiments” and “Our understanding of the relationship between structure and reactivity is inadequate” (8). The situation with regard to electrocatalysis is not different; the empirical nature of this area was pointed out earlier by Pletcher who also stated that “there remains a gulf between those who developed electrode materials and those who seek to understand the physical chemistry of electrocatalysis” (9).

A major factor contributing to the lack of understanding may well be insufficient attention devoted to defect centres or active sites at solid surfaces. A typical bulk metal such as platinum or gold has a well characterised 3-dimensional lattice structure – and the surface is frequently envisaged as a planar termination of such a lattice. Such a surface is easier to comprehend and model (as compared with its defect counterpart) and considerable attention has been devoted in recent years to producing, and investigating the activity of such single crystal plane electrode surfaces (10). They are obviously excellent substrates for investigation by newly developed high resolution microscopy (for example scanning tunnelling and atomic force (11)) techniques. The problem is the major gap (discussed by Schlogl (8)) between single crystal plane surfaces and those used in practice, for example platinum dispersed at quite low coverage, as an electrocatalyst, on carbon at the cathode of a fuel cell. The ill-defined surface of the metal in such a state is not easily modelled and as is clear, for instance from a recent conference proceedings on electrode/electrolyte interfaces, the role of defects, at a fundamental level, is widely ignored at present (12). This is quite surprising as the “active site” concept, originally proposed by Taylor, has been well established in the empirical interpretation of heterogeneous catalysis for many years (13).

A further complication in electrocatalysis is the possibility that low co-ordination surface metal atoms exhibit significantly different redox behaviour as compared with their high co-ordination equivalents at the same surface. The basis of this approach, which was discussed in some detail in a recent controversial paper from this laboratory (14), is supported by the following statement by Adamson (15):

“Not all atoms on the surface [of a solid] are equivalent in nature; those present at ragged asperities are more energy-rich than those with a normal number of nearest neighbours and possess a higher than average surface energy and surface mobility”.

Low co-ordination, energy-rich, surface metal atoms are unusual in several respects. Firstly, because of the lack of crowding at the surface, these atoms react with solvent molecules (or other species) in an unusually rapid manner. Secondly, these less crowded atoms, on oxidation, can co-ordinate more oxygen or hydroxide species and hence may form hydrous, rather than anhydrous, oxides. Finally, because the reactive metal atoms (the reduced form of the couple) are energy (or activity)-rich, they generally oxidise at a lower potential than high co-ordination surface metal atoms in a process known as premonolayer oxidation. As already discussed earlier (14) anomalous oxidation is an independently established feature of the reaction of supported platinum clusters with gaseous oxygen (16). The formation of low coverage hydroxy species on gold in base at premonolayer potentials has already been established using Surface Enhanced Raman Spectroscopy (SERS) (17). Unfortunately, SERS does not yield precise information as to the identity of the product and the technique is applicable, to a large extent, only to the Group I(b) metals (gold, silver and copper).

A Revised View of Noble Metal Electrochemistry

As pointed out in an earlier review, hydrous oxides are now known and have been investigated for most of the noble, and several non-noble, metals (18). They are best regarded as
a distinct series of compounds (14) that differ from their regular, anhydrous, oxide or hydroxide equivalents in that they frequently exhibit poor structural regularity combined with high redox activity; the latter is particularly evident in systems such as iridium, rhodium, iron and nickel hydrous oxides (18) where intermediate redox transitions, for example those between the II/III or III/IV oxidation states (of the same cation), are involved.

It is assumed that all real metal surfaces contain poorly stabilised, high energy, atoms; these may be concentrated at unusual sites, such as tips of asperities, or occur in a random manner (due to thermal vibrations) on the surface. Normally the coverage of such species is quite low and both the electrochemical and spectroscopic responses due to their oxidation is usually quite weak. As mentioned here earlier there is spectroscopic (SERS) evidence for the formation of hydroxy species on gold in base at low potentials. All noble metals are assumed to exhibit such premonolayer oxidation behaviour and – although the evidence is not yet conclusive – the correlation (as discussed here below) between hydrous oxide electrochemistry and the electrocatalytic behaviour of the noble metals, both with regard to oxidation and reduction processes, is impressive.

From an historical viewpoint the conventional view of noble metal surface electrochemistry – hydrogen, double layer and oxide region in the case of platinum or double layer and oxide region in the case of gold – received early acceptance. However, while such an interpretation is evidently valid for the relatively well stabilised surface metal atoms (the vast majority of such atoms at the interface), it does not take into account the redox behaviour of the very minor coverage of energy-rich, poorly lattice stabilised, surface metal atoms. The low responses for the latter (as they undergo anomalous oxidation – at potentials well below that for the onset of regular monolayer formation) is evident in certain instances, for example silver (19) and gold (20); the premonolayer response for the latter is sometimes attributed (21) – incorrectly in the view of the author (and especially in view of the SERS data) – to the oxidation of impurities.

The recent claim (14) that premonolayer oxidation of platinum occurs within the hydrogen adsorption region may be controversial, but the observation of enhanced premonolayer oxidation of both platinum (22) and gold (23), plus charge displacement (24) from the hydrogen adsorption to the double layer region of platinum in acid (following prolonged polarisation at low potentials), clearly shows that the basic electrochemistry of the noble metals is more complex than is generally assumed.

**The Incipient Hydrous Oxide/Adatom Mediator Model of Electrocatalysis**

The Incipient Hydrous Oxide/Adatom Mediator (IHOAM) model of electrocatalysis (14) is based on the assumption that the low coverage (or incipient) hydrous oxide, M(OH)$_x$, formed in the premonolayer oxidation process, is the effective oxidant (or mediator) in electrocatalytic oxidation processes, see Scheme I, whereas the low co-ordination surface metal atom, M$^+$, is the effective reductant (or mediator) in electrocatalytic reduction processes, see Scheme II.

According to these schemes the mediator is restored to its initial state by externally supplied...
Fig. 2 Schematic outline of (a) the oxide electrochemistry (under cyclic voltammetry conditions) and (b) the electrocatalytic behaviour of gold in aqueous acid (—) and base (— —). The monolayer oxide formation/reduction region, above 1.1 V in (a), is generally one of low electrocatalytic activity. The data shown in (a) are from Refs. (34) and (35): the important point is the strong correlation, outlined by the dotted vertical lines, between the hydrous oxide reduction peaks in (a) and the regions showing dramatic current increase (and decreases) for the reaction of dissolved reagents in (b). The numbers in parenthesis in (b) denote references to original (more complete) data.

anodic ($i_a$) or cathodic ($i_c$) current, that is electrocatalysis involves an interfacial cyclic redox transition between two unusual states – the low co-ordination surface metal atom and the incipient hydrous oxide.

The above approach (which is controversial) has been outlined in considerable detail recently for both gold (25) and platinum (14). Significant support is provided by the data summarised in Figures 2 and 3. A schematic outline of the oxide (including the hydrous oxide) electrochemistry of gold in aqueous media is given in Figure 2(a); a more detailed account (including an explanation of the shift in the hydrous oxide/metal transition to a lower potential on increasing the solution pH) of the behaviour of this system has been published (14, 25). It is clear from Figure 2(b) that numerous electrocatalytic oxidation and reduction processes commence and terminate in the region of the active metal/hydrous oxide transition. Similar data is shown in Figure 3 for platinum – an account of novel aspects of the oxide electrochemistry of this metal has been published (26, 27).

Some general points concerning the data in Figures 2 and 3 are noteworthy:

[1] For many electrocatalytic oxidation processes the formation of the regular monolayer oxide deposit leads to inhibition of the reaction.

[2] In a given system, for instance gold in acid, there is a switch in the process being catalysed, for example from dichromate reduction at low potentials to hydrazine or oxalic acid oxidation at high potentials on sweeping through the active metal/incipient hydrous oxide transition region (28).

This is quite understandable in terms of a change in oxidation state of the interfacial mediator with potential: such results highlight the fact that the cessation of reaction of a bulk solution species, for example dichromate reduction on the positive sweep, is not due to surface...
deactivation – and only the IHOAM approach rationalises the changeover potential value and the variation of the latter with solution pH. Kinetic theories based on this approach have been developed for both metals (14, 19) and oxides (29).

[3] The region of onset of high electrocatalytic activity in the case of platinum (and gold) is far removed from that of monolayer oxide (or OH$_{ads}$ and O$_{ads}$) formation. In two of the cases shown here for platinum in acid, CO$_{ads}$ oxidation and Cr$_2$O$_7^{2-}$ reduction, there are two regions of significant current increase – coinciding approximately with the potentials for the two platinum hydrous oxide (HO2 and HO1 (26)) reduction processes, that is two distinct mediators (or inhibiting species) appear to be involved – again such a result is explicable only in terms of the IHOAM approach. The highly anomalous behaviour of the HO2 oxide of platinum in base was discussed at length in a recent publication (27). It is worth noting that the oxidation of a wide range of reactive organics also commences at around 0.2 V(RHE) on platinum in acid providing that steps are taken (for example use of a pulsing technique) to minimise the effect of deactivating CO$_{ads}$ species (30).

Conclusions

The major role of active sites or surface irregularities in determining both the catalytic and electrocatalytic activity of surfaces is widely accepted (31, 32). Such sites are frequently regarded in terms of co-ordinatively unsaturated
surface atoms (or groups (33)) but precise details with regard to structure and electronic properties of such species are generally not available (32). The novelty of the present approach is that it assumes (largely on the basis of the considerable knowledge now available on noble metal hydrous oxide behaviour, correlations between this and electrocatalysis – see Figures 2 and 3, and SERS data for gold (17)) that low co-ordination surface metals or groups exhibit a significantly different type of redox behaviour as compared with that of similar but high co-ordination number surface species.

A major practical problem in this area is the difficulty in detecting, and investigating the properties of, the quite low coverage, relatively labile, species involved. In addition, there is a range of practical considerations, for example it would obviously be useful to investigate methods for the optimisation of the activity, effective coverage (which is not necessarily the maximum coverage) and long term stability of a particular mediator.

Finally, the concept of activated chemisorption should not be discarded. In some instances, such as hydrogen gas evolution on platinum, this may well be the sole mechanism of reaction. In other cases, such as methanol oxidation at a platinum/ruthenium-activated anode (3), the electrocatalyst may operate in a bifunctional manner – the alcohol may be activated by chemisorption on platinum sites while the ruthenium functions as the oxygen transfer agent (to produce carbon dioxide). The active platinum atom may still undergo an intermediate redox transition in the course of the latter reaction, that is there may be an intermediate transfer of an oxygen species (derived from water) from a ruthenium to a platinum centre.

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Control of Emissions of Nitrogen Oxides

Environmental Catalysis: ACS Symposium Series 552

This volume contains papers given at a symposium sponsored by the Catalysis and Surface Science Secretariat at the 205th National Meeting of the American Chemical Society, held in Denver, Colorado, from 28th March to 2nd April 1993. Although the symposium covered a number of aspects of environmental gaseous pollution from mobile and stationary sources, the principal emphasis was on control of nitrogen oxide (NOx) emissions, and work was reported on platinum group metal based catalysts, notably containing platinum, palladium and rhodium.

Approximate molecular orbital computations of adsorption and nitric oxide (NO) reduction for rhodium, palladium and platinum monolayers on the (0001) faces of oxygen and aluminium of α-alumina, were reported by T. R. Ward, P. Alemany and R. Hoffmann (Cornell University) who concluded that the support significantly affects the Fermi levels of the composite system, which in turn affects the NO adsorption mode. They suggest that the platinum-oxygen interface is particularly suited for both dissociative adsorption and coupling of two adsorbed nitrosyls, yielding a reduced form of N₂O₃.

The state of platinum-rhodium catalysts during three-way catalysis continues to be important. B. E. Nieuwenhuys and J. Siera (Leiden University) and K.-I. Tanaka and H. Hirano (University of Tokyo) presented a joint paper on differences in behaviour of platinum, rhodium and platinum-rhodium catalysts in NO and sulphur dioxide (SO₂) mixtures. They concluded that the support significantly influences the reactions of NO with both carbon monoxide (CO) and hydrogen, since rhodium is generally a better catalyst than platinum for the CO/NO reaction, while platinum is better for the hydrogen/NO reaction. Thus the predominant mechanism for NO removal depends on catalyst surface composition.

Infrared studies performed by G. Srinivas, S. S. C. Chuang and S. Debnath (University of Akron) on the interaction of NO and CO on rhodium/silica and cerium-rhodium/silica clearly show the formation of rhodium-NO and silicon-NO as the predominant species during the CO/NO reaction at 723 K. However, isotopic studies under steady state conditions indicate that these species are “spectator” species rather than the principal reaction intermediates.

Palladium-only catalysts were compared with platinum, rhodium and platinum/rhodium systems for three-way control in closed loop controlled motor vehicles, by J. C. Summers and W. B. Williamson (Allied Signal). While palladium has significantly better hydrocarbon control, its NOx performance, especially under rich operating conditions, tends to be adversely affected by lead and sulphur. This can be overcome by developing palladium catalysts less sensitive to these poisons, or by combining separate palladium only and platinum/rhodium catalysts in multibrick systems, leading to converters containing varying amounts of all three metals, depending on car calibration and fuel quality.

While most papers discussed NO reduction, the effects of sulphated platinum/zirconia catalysts in NO and sulphur dioxide (SO₂) oxidations were reported by J. R. H. Ross and co-workers, (University of Twente). The sulphated catalyst had higher activity in both reactions, but increased selectivity for NO. A similar increase in NO selectivity occurred after ageing platinum/zirconia in a NO/NO₂/oxygen gas mixture, and sulphate could be detected on the aged catalyst. These effects are ascribed to changed surface acidity modifying adsorption strength.

Despite the papers being at least 18 months old, they are still a valuable addition for the design of catalytic systems to meet the emission limits set for the next decade.

D.E.W.
The Tenth World Hydrogen Energy Conference held at Cocoa Beach, Florida, U.S.A. from 20th to 24th June 1994, was the latest in a bi-annual conference series begun in the mid 1970s. This meeting provided an opportunity to bring together a gathering of technical, political, industrial and economic interests with the common goal of promoting hydrogen as a clean, versatile fuel and as an increasingly important chemical commodity. Some 612 participants included energy planners, environmentalists, industrial gas manufacturers, process chemists, chemical engineers, metallurgists and materials scientists presenting papers on topics ranging from hydrogen safety, storage, production and utilisation. Some 40 papers attested to the continued importance of the platinum group and rare earth metals in hydrogen storage, separation, catalytic and fuel cell technologies, and those papers which were related to the use of the platinum group metals are selectively reviewed here.

**Hydrogen Sensors**

The safe utilisation of hydrogen requires that proper account be taken of the potential hazards of an odourless, colourless and readily flammable gaseous element. During this conference assessments of some of these safety issues were presented. Clearly the detection and monitoring of hydrogen gas is an essential requirement for its safe handling in chemical, aerospace or other industry. Two papers focused on this need for cost effective and efficient methods of hydrogen detection.

A simple, low cost, hydrogen alarm system incorporating a palladium coated bimetallic coil was described by E. Szonntag, D. Woodbridge and T. Woodbridge of Aqua Magnetics Inc., Tampa, U.S.A. The device consists of two bimetallic temperature sensitive coils, one coated with finely dispersed palladium. With one end of both coils firmly fixed, exposure to hydrogen produces a rapid rise in temperature as the palladium on the coated coil absorbs the gas. The exothermicity of the reaction is enough to close the gap between the free ends of the bimetallic coils. When suitably configured with an alarm buzzer, battery and arc suppression circuitry the sensor is capable of responding to hydrogen concentrations significantly below the lower flammability limit of hydrogen (LFL 4 per cent). The second bimetallic coil ensures that the device maintains a constant sensitivity to hydrogen regardless of ambient temperature conditions. A solid state electronic design incorporating palladium was also discussed.

A NASA sponsored programme to develop new hydrogen detection systems for use during Space Shuttle ground support operations was described in a paper by R. Barile of I-NET Space Services and D. Bardel of the Florida Institute of Technology. The large quantities of hydrogen fuel required by the shuttle mean that conventional hydrogen detection methods (including 60 platinum wire catalytic combustion sensors located close to fuelling lines and valves in the launch pad) are widely used at the Kennedy Space Centre. However, certain locations and situations in, or near to, the Space Shuttle cause existing systems severe difficulties in terms of repeatability, accuracy, drift, response time, convenience and durability. As part of their studies, the authors examined the factors influencing the response of a group of solid state hydrogen sensors in which a catalytic film, of palladium or a palladium alloy, was employed to absorb hydrogen preferentially from the local gas. The film may be configured as a resistor, capacitor, transistor or thermistor, depending on the type of sensor. The response time of such sensors depends critically on the transfer of hydrogen from the ambient atmosphere to the film and subsequent transfer of hydrogen within the film. Calculations and experimental observations confirmed that the
rate of transfer of hydrogen within the solid phase was extremely fast, and several orders of magnitude more rapid than the gas-solid mass transfer. The relatively slow convective transfer of hydrogen in the boundary layer above the solid surface was the rate determining step for many of this type of sensor. Response times can thus be improved by aiding the transfer of hydrogen to the solid-gas interface. Typically a simple sampling device, such as a fan or pump, is used.

**Photoelectrochemical Hydrogen Production**

Over the past two decades a large body of work has been assembled on photoinduced hydrogen production. Whether the hydrogen is produced from water splitting or from a non-aqueous source the production mechanism is the same: light-driven electron transfer. Such systems rely on the use of a photosensitiser to effect the transformation of light energy into charge separation. One such group of photosensitisers, with particularly good properties, is the ruthenium polypyridinium complexes, such as Ru(bpy)$_2$Cl$_2$.

Photo-induced hydrogen production from aqueous solutions using a Ru(bpy)$_2$Cl$_2$ compound as a photosensitiser was described by C. Königstein and R. Bauer, of Vienna University of Technology. The paper also dealt with the use of rhodium compounds, Rh(I)Cl(dpm)$_2$ (Wilkinson’s catalyst) and Rh(bpy)$_2$Cl$_2$ as electron relay/homogeneous catalysts in light induced hydrogen forming reactions.

The performance and characterisation of surface modified platinum-coated p-silicon electrodes, for photoelectrochemical hydrogen production from water was reported by C. Maier and G. Bilger, of Stuttgart University, and M. Specht of the Solar and Hydrogen Energy Research Centre, Stuttgart. Semiconductors with a suitable band-gap for direct water splitting are handicapped because of their tendency to corrode in aqueous environments. The prevention of corrosion by coating the semiconducting material with platinum or other metals has been found to be effective. In addition, the platinum coating also acts as an excellent catalyst for H$^+$ reduction. In their study they examined in some detail the role of different platinum surface morphologies in determining hydrogen evolution efficiencies and the long term stability of silicon-based photochemical devices. Platinum was deposited on single crystal silicon by three methods: electron beam evaporation, magnetron sputtering and photo-assisted electrochemical deposition from a H$_2$PtCl$_6$ solution. While the physical vapour deposition techniques produced uniform and continuous platinum layers, the electrochemical procedure resulted in platinum island topographies which improved the photoelectrochemical properties. The electrochemical experiments showed that the platinum deposited via the electrochemical technique led to photocurrent-voltage characteristics capable of producing hydrogen at high conversion efficiencies (10 per cent in alkaline electrolytes).

Continuing the theme of photocatalytic hydrogen production using semiconductor technology, C. Linkous of the Florida Solar Energy Centre, Cape Canaveral, examined a platinum modified cadmium sulphide photocatalyst. Rather than deal with the aforementioned difficulties of aqueous electrolytes, Linkous chose to use hydrogen sulphide as a widely available hydrogen source. Platinisation of the cadmium sulphide particles was achieved by reduction of the chloroplatinate ion to the metallic state by photo irradiation in the presence of acetate ions. Photoreactor operation where hydrogen sulphide and light were the only inputs, and hydrogen and sulphur the only products, was demonstrated. The use of such a photoreactor system in the oil refinery industry was discussed.

Hydrogen photoproduction was demonstrated by K. Gurunathan, P. Maruthamuthu and M. Sastri, of the University of Madras, India, using a rarely studied wide band gap semiconductor, SnO$_2$, loaded with platinum and RuO$_2$ and sensitised with Ru(bpy)$_2$Cl$_2$. The maximum hydrogen production rate occurred at a [Ru(bpy)$_2$Cl$_2$] concentration of $3.75 \times 10^{-3}$ mol/l.

An alternative approach to the use of particulate systems for photoelectrochemical hydrogen generating processes was presented in two papers by S. Khare, N. Gontia and S. Nema,
of the University of Jabanpur, India. In the first paper, they examined photo-assisted hydrogen generation by an electroactive solid polymer electrolyte (SPE) membrane system. In this configuration TiO₂ particles and a platinum catalyst were incorporated into a Nafion membrane from TiCl₄/methanol and H₂PtCl₆/methanol solutions. The platinum loading was 0.05 mg/cm² of Nafion. A further preparative step involving the synthesis of an electroactive polymer: polypyrrole, within the Nafion membrane matrix was necessary to ensure that the membrane was both electronically and ionically conducting. Under irradiation the prepared membrane generated hydrogen at a level of 20 microlitres of hydrogen during a 10-hour period.

In the second paper, Khare, Gontia and Nema described the utilisation of a membrane system for hydrogen generation, this time with chlorophyll-platinum as the photoactive element. This was incorporated into a perfluoro-ionomer membrane matrix. A fine dispersion of platinum was prepared on a Nafion membrane prior to impregnation with chlorophyll derived from spinach. The light induced splitting of water by the platinised chlorophyll impregnated membrane was observed at a series of temperatures up to 160°C. Hydrogen generation continued for between 6 to 8 hours during photo irradiation with peak production at around 3 to 4 hours. The degradation in the water splitting ability of the membrane on prolonged irradiation was explained by the photolytic dissociation of the chlorophyll in the membrane.

A hydrogen generation system containing a platinum group metal was described by M. Gupta, M. Swarnkar and S. Nema also from the University of Jabanpur. In this system photo-induced water splitting was achieved by a 3-layer structure which utilised polyimide bound tris (2,2-bipyridine) ruthenium(II) complex and finely dispersed platinum.

Chemical/Fuel Applications for Hydrogen

A paper describing chemical hydrogen storage by synfuel production from electrolytically cogenerated hydrogen and carbon monoxide, was presented by M. Specht, A. Bandi and E. Mennenkamp-Iwer, of the Solar Hydrogen Research Centre, Stuttgart. In this work the reduction of a steam and carbon dioxide mixture was performed by high temperature electrolysis at 1000°C. An oxygen conducting, high temperature, yttria-stabilised zirconia ceramic, equipped with platinum electrodes, facilitated the oxygen removal necessary for the reduction process. The product of the electrolysis reaction was a syngas (hydrogen, carbon monoxide and carbon dioxide), which is useful as the basis for the production of a variety of synthetic fuels.

A noble metal catalyst, incorporated into a catalytic burner was described in a paper presented by P. Brockerhoff and B. Emonts, from the Institut für Energieverfahrenstechnik Forschungszentrum, Jülich, Germany. The catalytic burner comprised a cylindrical porous ceramic fibre through which the natural gas, hydrogen and air mixture flowed. The outside of the porous tube was treated with an alumina washcoat and a finely divided platinum catalyst. The paper describes the optimisation of the noble metal catalyst system and the performance of the system particularly in terms of low carbon monoxide and nitrogen oxides emissions. Carbon monoxide emissions were always below 100 mg/kWh over a wide range of operating conditions and as low as 3 mg/kWh at a power density of 120 kW/m². Emissions of nitrogen oxides were below 20 mg/kWh and sometimes as low as 6.7 mg/kWh depending on operating conditions.

A palladium based catalyst was employed in tests on a Hythane (natural gas/hydrogen mixture) fuelled internal combustion engine by V. Raman and J. Hansel, of Air Products and Chemicals Inc., Pennsylvania, and J. Fulton and F. Lynch of Hydrogen Consultants Inc., Colorado, and D. Bruderly of Bruderly Engineering Associates, Florida. It was found that the post catalyst emissions from burning either natural gas or Hythane were so low (under steady state conditions) that the effect of the added hydrogen could not be detected. However, under transient operating conditions,
such as specified in the Federal Light Duty Vehicle Testing Procedure, significant differences between natural gas and Hythane emissions, post catalyst, were observed.

Platinum Group Metals in Heat Pump Systems

A chemical heat pump system based on the reaction couple: 2-propanol dehydrogenation/acetone hydrogenation using ruthenium/carbon, ruthenium-platinum/carbon and ruthenium-palladium/carbon dehydrogenation catalysts was described by D. Taneda, I. Yasutomi, T. Imanishi, S. Shibata and T. Toida, of the JGC Corporation, Yokohama-shi, Japan. The heat pump system demonstrated an ability to upgrade low level heat at 353 K to temperatures of between 423 and 473 K. The effectiveness of the dehydrogenation catalyst was found to be highly significant in determining the efficiency of the overall system. The best catalyst was the ruthenium-palladium/carbon variant, with the pilot plant capable of giving coefficient of performance (COP) figures of 10 to 20. However the enthalpy efficiency remained low at only 10 per cent. The low efficiency was probably due to the limited dehydrogenation activity of the present catalyst. Improvements in the effectiveness of the dehydrogenation reaction would make the system a promising next generation heat pump.

A second paper, concerned with the chemical conversion of low quality heats via dehydrogenation using noble metal catalysts, was presented by Y. Saito and co-workers of the University of Tokyo. This group concentrated on the study of dehydrogenation catalysts for the 2-propanol-acetone and cyclohexane-benzene dehydrogenation reactions. Ruthenium, platinum, palladium and ruthenium-platinum composite catalyst systems were prepared for the dehydrogenation and dehydrogenation-dearomatisation reactions with particular emphasis on the characterisation of particle size and metal composition.

A chemical heat pump, containing a platinum/alumina catalyst, which utilised the cyclohexane-benzene dehydrogenation reaction was reported by K. Murata, K. Yamamoto and H. Kameyama from the Tokyo University of Agriculture and Technology. The platinum catalyst layer, of thickness around 270 μm, was incorporated into the inner wall of a double pipe heat exchanger of 10 mm diameter. In order to compare the tube wall reactor with other catalyst configurations, a fixed bed reactor was also tested by filling the tubes with pelletised catalyst. The results showed that the catalyst volume was reduced 4 times and the pressure drop at the reactor by 100 times when using the tube wall reactor catalyst. The development and optimisation of the tube wall reactor system should therefore enable more compact heat pump systems to be designed.

Palladium Based Membranes

A paper covering hydride phase miscibility gaps and inhomogeneities of hydrogen distribution within palladium based hydrogen diffusion membranes was presented by F. Lewis, R.-A. McNicholl and X. Tong, of Queen’s University, Belfast. The paper discussed the form of hydrogen absorption isotherms in two types of hydrogen diffusion membrane alloy (palladium-platinum and palladium-silver). One of the interesting observations involved the possibility that the position of the critical temperature may not be fixed, as was previously supposed. Hydrogen concentration inhomogeneities arising from strain gradient and ‘uphill diffusion effects’ may have a role in shifting formally accepted phase boundaries. This suggests the need for caution with regard to the proper assessment of hydrogen permeation through metal membranes under different pressure and temperature conditions.

Proton Exchange Membrane Fuel Cells

The development of a hybrid fuel cell battery powered electric vehicle, designated as the ‘Green Car’ was described by M. Nadal and F. Barbir of Energy Partners Inc., Florida, U.S.A. The ‘Green Car’ employs three platinum containing proton exchange membrane (PEM) fuel cell stacks, with each stack comprising 60 cells.
with a total power output of 19.2 kW. Hydrogen fuelling was achieved using a composite high pressure container made of aluminium and glass/epoxy resin. The total volume of stored hydrogen was 11,700 litres of pure gas at a pressure of 3000 psi. The vehicle was capable of a top speed of 60 mph and a range of 70 miles, with refuelling times between runs of only 5 to 10 minutes.

A paper on the internal humidification of PEM fuel cells was presented by D. Staschewski of the Karlsruhe Nuclear Research Centre, Germany. Platinum-carbon electrodes were hot pressed onto Nafion resulting in a platinum concentration of 2.5 to 2.8 mg/cm³. In order to improve electrical conductivity some of the experiments were performed with gold plated components. The monocell tests showed that the internal humidification worked well, up to 200 A or 0.5 A/cm².

The modification of electrocatalytic platinum bearing layers in solid polymer electrolyte systems was reported in a paper by V. Fateev, O. Archakov and E. Pivovarova, of the Kurchatov Institute, Moscow. Their study involved investigating the role of PTFE added to the catalyst layer in order to effect hydrophobisation.

The high parasitic power losses incurred by the use of compressors (particularly in vehicular applications) to provide pressurised gas to PEM fuel cells was the basis of work by C. Chamberlin, P. Lehman, R. Reid and T. Herron of Humboldt State University, California. Their work was directed to producing a hydrogen/air fuel cell which would be capable of operating at very low pressures (< 2 psig) and temperatures (41–42°C). To date this group have designed and fabricated 50 cm² and 150 cm² cells in 1, 2 and 4 cell stacks. The intention is to scale up to a 5 and 20 kW PEM fuel cell for incorporation into a vehicle.

A paper by N. Anand and co-workers of Texas A. & M. and H. Dhar of BCS Technologies Inc., Texas, described recent progress in PEM fuel cell technologies. In the last 6 years at Texas A. & M. platinum loadings have been reduced by a factor of 100. In addition, power density has tripled since the mid 1980s. A total platinum loading of 0.5 g/kW (cathode loading of 0.05 mg/cm²) gives a nominal 0.74 V at 0.3 A/cm² on non-humidified air and hydrogen at 1 atmosphere. Projections from this performance baseline, and assumptions regarding future advances, and cost reductions from mass production, predicted a platinum demand of around 10 tons for 1 million compact new cars per year.

In addition to the work on PEM fuel cell systems themselves, future low and zero emission vehicles will require efficient and cost effective methods of supplying pure hydrogen to the fuel cell. In a paper on hydrogen production in fuel cell vehicles, B. Hohlein, G. Colsman, R. Menzer, P. Brockerhoff, and E. Riedel, of Forschungszentrum Jülich G.m.b.H., Germany, and J. Hansen and I. Primdehl of H. Topsoe, Denmark, described the use of reformed methanol as a hydrogen energy carrier. The paper discussed the reforming process from the point of view of efficiency and balance of emissions. The paper concluded that the emissions of carbon monoxide, nitrogen oxides and volatile organic compounds would be very much less in a reformer/fuel cell than is possible with a conventional automobile drive system. The total emission balance for methanol produced from natural gas and consumed in a fuel cell vehicle will be 0.1 to 0.01 of the requirements for ULEV standards. This makes the indirect methanol fuelling approach for a fuel cell an attractive future option.

A paper covering on-board hydrogen purification for steam reformer/PEM fuel cell vehicles was presented by J. Amphlett, R. Mann and B. Peppley, of the Royal Military College of Canada, Ontario. This group examined various methods of hydrogen clean up, including pressure swing absorption, diffusion through metal membranes, polymer membranes, solvent absorption, low temperature shift, preferential oxidation (PROX) and internal oxidation within the anode compartment of the PEM fuel cell. Of these a PROX system based on a platinum catalyst and coupled with a shift reaction was preferred.

High temperature membrane separation of hydrogen using palladium membranes offers
the complete removal of all other contaminants, but suffers the drawback of excessive cost. It was concluded that the final choice of gas purification for a PEM fuel cell system working on reformed methanol may well depend on as yet unanswered questions regarding the possible secondary effects of impurities such as unreacted methanol and carbon dioxide. It is possible that these gases may react on the anode to form catalyst poisons, such as carbon monoxide or formic acid.

A concept hybrid vehicle, consisting of a battery recharged by a fuel cell, running on reformed compressed natural gas was described in a paper presented by K. Ledjeff, J. Gieshoff and G. Schaumberg, of the Fraunhofer Institute for Solar Energy Systems, Freiburg, Germany. The reforming reaction is promoted by a platinum catalyst operating at around 650°C. The experimental reformer was designed to produce hydrogen at a rate of 700 litres/hour which must then be purified by a medium and low temperature shift, using iron and chromium oxide and copper and zinc oxide catalysts, respectively, before admission to the PEM fuel cell.

Conclusions

The papers presented at the Tenth World Hydrogen Energy Conference reflect the general environmental thrust towards a more hydrogen-rich energy environment. Whether as a change to hydrogen combustion for automobiles or by the introduction of platinum containing fuel cells, hydrogen will clearly be an important element in a more environmentally sound future. The unusual hydrogen storage, hydrogen permeating and catalytic properties of the rare earth metals and platinum group metals ensure their role in a hydrogen-rich future.

The Conference proceedings, edited by D. L. Block and T. N. Veziroglu, have been published on behalf of the International Association for Hydrogen Energy. The next conference will be held in Stuttgart in 1996.

M.L.D.

High Temperature Platinum Selective Solar Surfaces

Spectrally selective coatings are used in solar collectors to concentrate the incident radiation. Their function is to enhance the operating efficiency of systems used for the production of electricity. These coatings have to be able to withstand high operating temperatures for long periods of time, and even higher temperatures for shorter times while the collectors are not in use.

Many materials and combinations of materials possess suitable optical properties and sufficient thermal stability for use at temperatures below 300°C. To improve the efficiencies of these systems, however, the coatings would be required to withstand significantly higher temperatures and few absorbers are stable in air at temperatures above 400°C.

For this reason researchers at the Universität Konstanz, Germany, have studied two systems, at temperatures up to 1000°C, for potential use as solar selective absorber surfaces, these being platinum on alumina and three molybdenum silicide modifications on alumina (J. H. Schön, G. Binder and E. Bucher, “Performance and Stability of Some New High-Temperature Selective Absorber Systems Based on Metal/Dielectric Multilayers”, Solar Energy Mater. Solar Cells, 1994, 33, (4), 403–416).

The optical properties of thin sputtered films of platinum on alumina were evaluated and found to agree with existing data. Thermal stabilities were tested for up to 400 hours at temperatures of 550 to 825°C. Platinum/alumina multilayers on quartz were stable in air up to approximately 700°C. The solar absorptance changed during a 300 hour experiment from \( \alpha = 0.92 \) to 0.90. On the actual metal used as a support in such collectors the coatings degraded faster, and at over 640°C the optical changes became more obvious.

Absorptances up to \( \alpha = 0.95 \) and emittances of \( E \approx 0.1 \) were achieved for platinum/alumina, and the coatings are thermally stable in air up to 600°C for a 400 hour testing period.

Strain Gauge Materials

Please note that the following alterations should be made to one of the figures in the paper entitled “Noble Metals Alloys as Strain Gauge Materials”, which appeared in Platinum Metals Rev., 1994, 38, (3), 98–108.

On page 106, in Figure 7, the data points have been displaced one position to the left. The density of state peaks should be at \( (d + s) \) numbers of 3, 5, 7 and 10, that is for Sc, V, Mn and Ni, respectively. Any confusion caused is regretted.
ABSTRACTS

of current literature on the platinum metals and their alloys

PROPERTIES

Antiferromagnetic Coupling in (111)-Oriented Co/Pt Superlattices


Antiferromagnetic (AF) coupling in molecular beam epitaxy grown (111)-oriented Co/Pt superlattices (1) was studied using NMR and low-temperature magnetisation. Spin-echo spectra and magnetisation results showed AF interlayer coupling in (1) with a Pt layer thickness of 18 Å. The coupling energy per unit area was ≤ 1 erg/cm². The structure of the Co films is mainly h.c.p. The model of separate regions of local interlayer AF coupling of different strengths was confirmed.

Coercivity and Microstructure in Co-Pt and Co-Pd Thin Films


Thin films of Co-Pt and Co-Pd were electrodeposited from alkaline baths based on Co amino-citrate and amino-nitrite complexes of the noble metal. Soft Co-Pd alloy films with coercivities of 3 kA/m were obtained. Co-Pt films had high coercivities ≤ 200 kA/m and high squareness. Ferromagnetism was found in Co-Pd alloy layers with low Co contents, below the known ferromagnetic limit for bulk samples.

Optical and Electronic Properties Modifications in Pd-Ni Multilayers


The effect on the optical properties and electronic structure of Pdₙ-Ni multilayers of the modulation period of ≤ 20 monolayers, was studied in the energy region 1.6-9.5 eV. A broad structure around 4.6 eV depended strongly on (m+n) whereas the plasma energy depended on both Pd-layer thickness m and modulation period. At 7 eV more features occurred in the dielectric function spectra, depending on m.

Electrical Transport and Impedance Spectra in NiO-Pd Composites


Transport properties of NiO-Pd composites were studied by measuring AC electrical conductivity at 700-1200°C in pure O₂, air and Ar. The electrical conductivity of the Pd-dispersed NiO composites under partial O₂ pressure decreased at first but then began to increase as a function of the volume fraction of dispersoid Pd particles. The overall resistivity of the composites was affected by both the bulk and the boundary effects, in contrast to that of the undoped poly-NiO.

Magnetic, Electrical and Thermal Properties of Heavy Fermion Superconductor UPd₃Al₅


Electrical resistivity, de Haas-van Alphen effect, specific heat and thermal expansion of UPd₃Al₅ are reported. The nominal composition was denoted by the formula UPd₃ₓAl₅₋ₓ. Samples with composition UPd₃₅Al₁₀ and UPd₃₋₅Al₁₀ revealed de Haas-van Alphen oscillations of the magnetic susceptibility. An anomaly was observed in the superconducting phase in the temperature dependence of the specific heat and thermal expansion of UPd₃Al₁₀.

CHEMICAL COMPOUNDS

New Platinum(II) Complexes with Schiff Base Ligands


Neutral Pt complexes [PtAXBX], [PtDₓJₓ], [PtDXₓ] where A, B = amines, D = Schiff bases, X = anionic ligand, were prepared. The reactions of [PtCl]⁺ with Schiff bases gave chelates which further reacted yielding cis-co-ordinated mixed N-donor ligand complexes. Pt methylglyoxal Schiff bases may cross cell membranes without difficulty.

Preparation and Characterization of Rhodium C₉₀ Complexes [Rh(acac)(Lₖ(C₆)ₘ)] (L = py, 4-Mepy, 3,5-Me₂py)


A series of new C₉₀ Rh complexes [Rh(acac)(Lₖ(C₆)ₘ)] (where L = pyridine, 4-methylpyridine, 3,5-dimethylpyridine, were prepared by the reaction of [Rh(acac)(C₆H₅)] with C₉₀ followed by treatment with pyridine or its derivatives. The molecular structure of [Rh(acac)(3,5-Me₂py)(C₆)ₘ](py)ₖ] was determined.

Reactions of RuCH(CO)(PPh₃)₂ with Allylic Amines: Insertions and an Unusual Carbon-Nitrogen Bond Cleavage of Allylic Amines


The title hydroxy-Ru(II) complex reacts with primary and secondary allylamines to give novel Ru(II) complexes Ru(CH₃CH₂CH₂NHR)Cl(CO)(PPh₃)₂, R = H, CH₃, CH₂CH = CH₂ and the corresponding enamines. These reactions result in the insertion of the allylic function into the Ru-H bond to yield the 5-membered aminopropyli chelate complexes. Tertiary allylic amines react with the hydroxy complex to give the corresponding (η-allyl)Ru(II) complexes.
Ruthenium Chromophores Containing Terpyridine and a Series of Polyazine Bridging Ligands


Ru complexes [Ru(tpy)(BL)Cl]⁺ containing the tridentate ligand tpy, where tpy = 2,2'-6',2''-terpyridine and BL = bridging ligand, were synthesised and characterised. The attached bidentate bridging ligands were 2,3-bis(2-pyridyl)pyrazine, 2,3-bis(2-pyridyl)quinoxaline and 2,3-bis(2-pyridyl)benzoquinoloxaline. All the [Ru(tpy)(BL)Cl]⁺ emitted in fluid at room temperature. The lowest energy adsorption was assigned as a Ru(δn)+BL(x*) transition. These Ru(tpy) compounds can be utilised for multimetallic systems capable of intramolecular electron transfer.

ELECTROCHEMISTRY

New Results in the Electro-oxidation of Formaldehyde on a Platinum Electrode in an Acid Medium


Studies of the oxidation of HCHO in perchloric acid on Pt electrodes showed the formation of a strongly bonded layer due to the hydration-dehydration equilibrium of HCHO. The presence of CH₃OH in HCHO solutions as stabiliser increases the rate of CO formation. Three structures were found for the adsorbed CO: the linearly bonded, bridge-bonded and multibonded forms. The adsorbed CO is responsible for blocking the surface, preventing the adsorption of reactive species.

Electrochemical Enhancement of a Catalytic Reaction in Aqueous Solution


Studies of the oxidation of H on a Pt/graphite electrode immersed in aqueous KOH solution showed that the application of a positive potential of 1–2 V to the Pt electrode increases the rate of H₂ oxidation by up to 500%. It is suggested that hydroxide ions are acting as promoters, with each ion supplied to the catalyst causing the oxidation of up to 20 H atoms.

Amorphous Ni-Nb-Pt Alloy Catalysts for Electro-oxidation of Ethylene


The catalytic activity for the electro-oxidation of C₂H₄ on HF-treated amorphous Ni-40Nb-xM-(1-x)Pt alloys was greatly increased after partial substitution (0.2 at. % M) of Pt by Sn or Ru. Additions of Mo and Mn slightly enhanced the activity, but W and Pd additions were ineffective. The highest activity was for Sn-containing alloy with Pt:Sn ratio of ~ 1:1. The binding energies of Pt 4f and Sn 3d electrons were independent of the Sn content of the alloy and the potential.

Temperature-Dependent Methanol Electro-oxidation on Well-Characterized Pt-Ru Alloys


The kinetics of CH₃OH electro-oxidation on well-characterised Pt-Ru alloy surfaces prepared in ultrahigh vacuum, were measured in H₂SO₄. The activity of Ru towards the dissociative adsorption of CH₃OH was a strong function of temperature. The optimum Ru surface concentration increased with increasing temperature, from ~10 at. % Ru at 25°C to ~30 at. % Ru at 60°C, and the apparent activation energies were consistent with this.

Anodic Film Growth on Ru/Pt Electrodes in HClO₄ and HCl Solutions


The potentiostatic growth of the anodic film on Ru/Pt electrodes in HClO₄, formed by a voltammetric run in the potential range of 0–1 V vs. SCE proceeded through the formation of two layers of different reduction reversibility at potentials below 500 mV vs. SCE. The outer layer grows more rapidly than the inner layer, up to 3 O monolayers in 7h. In HCl solution, Cl⁻ adsorption inhibits the formation of the anodic layer, decreasing its growth rate but reaching no limiting thickness for 7h. When held at potentials of > 650 mV, the initially homogeneous film converts into a bilayer where the outer layer becomes hardly reducible.

Methanol Oxidation on Carbon-Supported Platinum-Tin Electrodes in Sulfuric Acid


Electro-oxidation of CH₃OH in H₂SO₄ was studied on C-supported electrodes containing highly dispersed Pt-Sn bimetallic electrocatalyst which was prepared by an in situ potentiometric-characterisation route. The (3:2)Pt-Sn/C electrodes displayed the highest catalytic activity towards the electro-oxidation of CH₃OH giving maximum charge transfer from Sn to Pt. It is suggested that the charge transfer within this catalyst, together with the partial scavenging of oxidic impurities from Pt sites, are determining factors for the observed synergistic promotion of the CH₃OH oxidation reaction.

Novel Semiconducting Ternary Compounds: Ir₃Ru₃S₈ (0.005 < x < 0.5) for Oxygen Evolution Electrocatalysis


O₂ evolution occurred on degenerate Ir₃Ru₁₋ₓS₈ semiconductor electrodes. The Tafel slope showed a positive linear variation at 180–300 mV/dec with increasing Ir content of 0.5–50%. A higher Tafel slope and O₂ evolution occurred at an overpotential of 0.2 V, which is comparable to oxide electrodes. While O₂ evolves at low overpotentials, the higher Tafel slopes were due to a potential loss in the degenerate semiconductor.
PHOTOCONVERSION
Luminescent Donor-Acceptor Platinum(II) Complexes
The emission properties of the complexes [Pt{(dpm)(5,6-Me-phen)}(ClO₄)₂], [Pt{(phen)(C₆H₅)₂}(ClO₄)₂], [Pt{(5-Ph-phen)(CNCH₃)}(ClO₄)₂] (2) and [Pt{(N,N'-N-dpp)(NCCH₃)}(ClO₄)] were studied. The large percentage of metal-ligand charge transfer character was observed in the excited states of these Pt(II) complexes. The MLCT excited state of Pt(II) is very electrophilic as shown by the large kinetic isotope effect observed in the quenching of the photoexcited ground state to the excited state.

Pentane Carbonylation in the Photocatalytic System Bis(µ-chloroacarbonylrhodium)-Trimethylphosphine
The efficiency of the system containing Rh₂Cl₂(CO)₉ for pentane carbonylation was obtained with efficiency of 60 Ton.

Electrodeposition and Surface Coatings
Large Scale Two-Step Selective Aluminum CVD on Laser Patterned Palladium Lines
A maskless 2-step technology is described for writing Pd lines directly by laser onto a large uniform deposition of PdAc from acetone solution. The Pd lines are well resolved with good resistivity ~ 20 μΩcm and good adhesion to the SiO₂ substrate. A highly selective, second-step Al-CVD gave resistivities of ~ 6.5 μΩcm and 3000 Å thickness for a 7 min deposition.

Pyrophosphate Baths for Palladium-Nickel Alloy Coatings. Parts I and II
Concentration ranges of Na pyrophosphate for the primary bath used for Pd-Ni alloy coatings have been studied. Coating was carried out using a Pt sheet as an insoluble anode with the anode to cathode area ratio of 2:1. The operating conditions were selected with respect to repeatable deposition of 15–20% Ni-Pd alloy coatings. Plating solutions containing Na pyrophosphate, Pd and Ni compounds, can be used to deposit Pd-Ni alloy without using NH₄.

Ultrafast Optical Modulation of Quadratic Non-linearity from an Ru(II)-bipyridine Complex in Langmuir-Blodgett Assemblies
Alternate Langmuir-Blodgett (LB) films consisting of a Ru(II)-bipyridine complex and ammonium amphiphiles show a strong second-harmonic generation (SHG) on irradiation with nanosecond Nd-doped YAG 1064 nm laser pulses. The switching time for the optical modulation of SHG was determined to be < 2 ps from a sub-ps dye laser pump-probe SHG study. The mechanism for the optical modulation of SHG is ascribed to a change in the molecular hyperpolarisability of the Ru complex on going from the ground state to the excited state.

APPARATUS AND TECHNIQUE
Holographic Reconstruction of Pt(110) Using Multiple Wave Number Photoelectron Diffraction Patterns
The single wave number reconstruction and the multiple wave number phased sum reconstruction algorithms were used to obtain a 3D real space image of the Pt(110) surface from the Pt(110) surface of the Pt(110) surface of the Pt(110) surface (holograms) for six kinetic energies at 120–370 eV. The image quality depends on the photoelectron kinetic energy. The best quality reconstructed images were observed for single energy reconstruction at a kinetic energy of ~370 eV.
Static and Flow-Injection Voltammetric Determination of Periodate by Reduction at a Rotating Platinum Wire Electrode


The behaviour of periodate at a rotating Pt wire electrode was studied as a function of pH and concentration of periodate in two systems and a method for periodate determination was developed. In the static system, 4.0 × 10⁻¹–4.2 × 10⁻⁴ M periodate could be determined in the cell in a pH 7–7.5 phosphate buffer. In the flow-injection system periodate solutions of 20–100 μl were injected into the carrier stream of a phosphate buffer solution at pH 7. Periodate concentrations of 1.0 × 10⁻¹–1.0 × 10⁻³ M could be detected at a throughput of 15–40 samples/h.

Amperometric Enzyme Electrodes for Substrates of Immobilized Pyranose Oxidase


Two kinds of glucose biosensors for the determination of pyranose oxidase substrates have been developed based on detection of evolving H₂O₂ on a Pt or platinised graphite electrode at +650 or +400 mV, respectively. The biosensors detect H₂O₂ produced by pyranose oxidase bonded on an activated nylon net with about the same sensitivity to glucose as a similar sensor containing glucose oxidase. The lower selectivity allowed determination of saccharides, which are more difficult to detect, over a wide concentration by-product range from D-glucose by an enzyme pre-membrane with immobilised hexokinase. The sensor is stable in basic borate.

Comparison and Analysis of Pd- and Pt-GaAs Schottky Diodes for Hydrogen Detection


The H₂-sensing behaviours of Pd- and Pt-GaAs Schottky diodes, fabricated on the same GaAs substrate, were compared and analysed as a function of H partial pressure and temperature by I-V and Δt-t methods under steady-state and transient conditions. Adsorption activation energy of H and the heat of adsorption/H on the surface of Pd and Pt were studied and compared in both devices at 27–100°C. Pd-GaAs showed better performance for H₂ detection than Pt-GaAs under the same testing conditions.

Glucose Oxidation at Ruthenium Dioxide Based Electrodes


The oxidation of glucose at RuO₂–C paste composite electrodes in alkaline solution was examined. It is proposed that the catalytically active species are surface-bound oxy Ru groups which mediate substrate oxidation via a process of cyclic heterogeneous redox catalysis. The kinetics of glucose oxidation at RuO₂–C based composite materials are quite rapid, which suggests that conductive metallic oxides may used for the direct amperometric determination of glucose.

Novel Metal-Organic Ruthenium(II) Diimine Complexes for Use as Longwave Excitable Luminescent Oxygen Probes

I. KLIMANT, P. BELSER and O. S. WOLFBREI, Talanta, 1994, 41, (6), 985–991

Ru(II) diimine complexes with luminescence excitation maxima of 535–570 nm can be photoexcited by green LEDs and are found to be useful as luminescent O₂ probes. The probes were incorporated into organic polymers and the membranes were characterised with respect to O₂ sensitivity, luminescence intensity, response times and stability. The new probes can be used to optically sense O₂ over partial pressures of 0–200 Torr, with response times of ~1 min for aqueous samples but seconds for gaseous samples.

HETEROGENEOUS CATALYSIS

A Study of Platinum-Dysprosium-KL Zeolite Reforming Catalyst


The effect of Dy on the surface behaviour and catalytic properties of Pt-KL zeolite catalyst was studied in a pulsed micro-catalytic reactor. Pt-Dy-KL zeolite catalyst containing 0.1–0.5 wt.% Dy displayed higher activity for the aromatisation of either n-hexane or methylcyclopentane than unmodified Pt-KL catalyst. The stabilities of the Pt-KL and Pt-Dy-KL catalyst were studied using a poisoning method with CS₂.

Hydrogen Recovery from Hydrogen Sulfide by Oxidation and by Decomposition


Selective oxidation of H₂S to H₂ and S oxides in a two-step process and the catalytic decomposition of H₂S were studied at 350–650°C for the recovery of H₂ from H₂S. Pt/SiO₂ catalyst was effective in reacting with H₂S to produce H₂ and Pt sulphide at 500°C. The Pt was further treated with O₂ at 400°C to release S oxides and regenerate the Pt. Oxidation of SO₂, SO₃, retention of O by Pt, and adsorption of H₂S by SiO₂ also occurred and resulted in a minor loss in H₂ yield. It is suggested that H losses can be minimised by choice of operating conditions.

Reactions of n-Hexane over Pt-Zeolite Catalysts of Different Acidity


Pt/HY, Pt/NaHY, Pt/NaY and Pt/NaX catalysts, which are in order of decreasing acidity and increasing basicity, were tested at 603 K in n-hexane conversion as a model reaction. The acidic Pt/HY and Pt/NaHY catalysts were more active by ~ an order of magnitude than the two non-acidic catalysts. They produced mainly skeletal isomers, fragments, etc., whereas over Pt/NaY and Pt/NaX catalysts, metal catalysed C₉ cyclic isomerisation, ring closure and aromatisation prevailed. Pt/NaY showed a great aromatisation selectivity which can be attributed to the interaction of basic centres of the framework with the Pt particles.
Adsorption and Structural Properties of Heteropolyacid-Modified Pd/Al2O3 Catalysts: Effects on Hydrogenation Activity


The correlation between the adsorption properties of modified Pd + HPA/Al2O3 catalysts (HPA are heteropolyacids) and their activity in the hydrogenation of C=C and C=C bonds in but-2-yne-1,4-diol and oct-1-ene was studied. The modification of Pd/Al2O3 by HPA increases the number of adsorption sites by 2.5–3 times. The initial dimensions of the Pd catalysts by HPA reduces the number of adsorption anisotropy, which is an anisotropy that varies along the wave profile as changes in the adsorbate coverage generate different reconstructions of the substrate structure. This interplay between diffusional anisotropy and the state of the system may be general, causing new varieties of oscillatory patterning.

Square Chemical Waves in the Catalytic Reaction NO + H2 on a Rhodium(110) Surface


A transition from elliptical to square-shaped cross-sectional chemical waves in the catalytic reaction of NO and H2 on a Rh(110) surface is reported. The origin of the square pattern is attributed to a state-dependent anisotropy, which is an anisotropy that varies along the wave profile as changes in the adsorbate coverage generate different reconstructions of the substrate structure. This interplay between diffusional anisotropy and the state of the system may be general, causing new varieties of oscillatory patterning.

Stereoselective Hydrogenation of Allylphenols. II. Hydrogenation of p-tert-Butylphenol over Ruthenium Catalysts


 Hydrogenation of p-tert-butylphenol was studied over Ru/black or Ru catalysts supported on γ-Al2O3, SiO2, TiO2, sibunit and MgO. Two simultaneous reactions were observed over Ru/black: hydrogenation of p-tert-butylphenol and isomerisation of cis-4-tert-butyliclohexanol to trans-4-tert-butylclohexanol. Isomerisation was strongly suppressed over the Pt/support catalyst. Effects of solvents, pH and H2 pressure on stereoselectivity of hydrogenation were also studied.

Characterization and Catalytic Properties of Perovskites with Nominal Compositions La1−xSrAl1−xCuRuOy


Ru oxide catalysts were prepared by impregnating Al2O3, washcoats with H2O solutions containing La2+, Sr2+, Cu2+ and Ru3+ ions followed by calcination at 900°C. A perovskite phase of the nominal title composition was prevalent in samples with increasing Ru and Sr contents. The presence of Ru and Sr retarded the formation of La2CuO4 and promoted the formation of the perovskite phase. The light-off temperatures for NO reduction decreased from 534 to 335°C for the catalyst without Sr and with Ru.

HOMOGENEOUS CATALYSIS

Palladium Catalyzed Telomerization of Butadiene with Sucrose: A Highly Efficient Approach to Novel Sucrose Esters


A direct route for the telomerisation of butadiene with sucrose, catalysed by Pd(acac)2 and Ph3P ligand is reported. The reaction yielded the corresponding sucrose octadienyl ethers at high turnover numbers of 40,000. The products were clear, almost colourless liquids with a viscosity of 1500–2000 mPa s at 25°C and insoluble in H2O. The products are potential emulsifiers and defoaming agents.

A New Optically Active Monodentate Phosphine Ligand, (R)-(+)3-Diphenylphosphino-3'-methoxy-4,4'-biphenanthryl (MOP-phen): Preparation and Use for Palladium-Catalyzed Asymmetric Reduction of Allylic Esters with Formic Acid


(R)-(+)3-Diphenylphosphino-3'-methoxy-4,4'-biphenanthryl (MOP-phen) was prepared with (−)3,3'-dihydroxy-4,4'-biphenanthryl and used for the Pd catalysed asymmetric reduction of allylic esters with formic acid using Pd(OAc)2-dppp, PdCl2(η1,1-dimethylallyl)((R)-MOP) and trans-PdCl2([(R)-MOP]2 catalysts. The Pd-catalysed reaction yielded active olefins of ≤ 85 ee with monodentate optically active phosphate, which is a more enantioselective ligand than (R)-(−)2-diphenylphosphino-2'-methoxy-1'-binaphthyl, (MOP). The absolute configuration of (+)-(MOP-phen) was determined to be R.

Palladium-Catalyzed Cross-Coupling Reaction of Organometalloids through Activation with Fluoride Ion


A transient pentaco-ordinate silicate produced by activation of organosilicon compounds with fluoride ion was found to be capable of transmetalation with a catalytic organo-Pd complex in a cross-coupling reaction. Mono-, di- or trifluorosilanes can produce the alkenyl, aryl or alkyl group, respectively. The reaction which is highly chemo- and stereoselective, was successfully applied to synthesise HMG-CoA reductase inhibitor NK-104 and functionalised biaryls for liquid crystals.

Rhodium-Catalyzed Cross Coupling of Unactivated Allenes and 1-Alkynes


A mixture of HRh(CO)(PPh3)3 and Ph3P catalysed the cross-coupling reaction of unactivated allenes and 1-alkynes. C-C bond formation occurred regioselectively at the 2-position of allenes giving conjugated endo-(E)-enynes in high yields and selectivities. Added PEt3 improves the regio- and stereoselectivity.
Catalytic and Stoichiometric Hydroacylation of Olefin Derivatives with 8-Quinolinecarboxaldehyde by Rh(I)


Stoichiometric ligand-promoted hydroacylation of styrene and 2,3,4,5,6-pentafluorostyrene with [(C,H,)_3RhCl] resulted in a mixture of branched and linear alkyl ketones. Catalytic hydroacylation was obtained by the reaction of 8-quinolinecarboxaldehyde and vinyl derivatives, such as the above and vinylcyclohexane in the presence of Wilkinson’s complex, (PPh,P)RhCl, catalyst yielding 8-quinolinyls of 2-phenylethyl ketone, 2-pentafluorophenylethyl ketone and 2-cyclohexylketone ketone.

Efficient and Selective Catalytic Dehydrogenation of Alkanes Using Rhodium(I) Arsine Complexes


Arsine complexes of Rh(I), which are known to be relatively inactive homogeneous hydrogenation catalysts, efficiently catalysed the transfer dehydrogenation of alkanes in H₂ producing less ‘direct hydrogenated’ sacrificial olefins than similar phosphine-based Rh compounds. The Rh arsine catalysts were highly active in systems using simple alk-1-enes as sacrificial H acceptors. A heterogeneous arsine-based Rh catalyst which was synthesised by covalently grafting [RhCl(AsPh₃)], onto polystyrene beads also promoted the transfer dehydrogenation of alkanes.

Catalytic Activation of Carbon-Fluorine Bonds by a Soluble Transition Metal Complex

M. AZEINBERG and D. MILSTEIN, Science, 1994, 265, (5170), 359–361

Homogeneous catalytic activation of strong C-F bonds was achieved by Rh complex catalysts under mild conditions. Rh(I) silyle, L₂RhSiMe₃Ph (L = PMe₃), can easily cleave C-F bonds in CₓFₓ and CₓFₓH, even for the latter in preference to the CₓFₓ-H bond. The catalytic chemo- and regioselective reactions between polyfluorobenzenes and hydroxilanes result in substitution of F atoms by H. The catalytic cycles have high selectivity.

Hydroformylation of Alkenes and Alkynes Using a Heterobinuclear Rh-W Catalyst


Hydroformylation reactions of alkenes and alkynes were performed using the heteronuclear Rh-W catalysts, (CO)₆W(μ-PPh₃)₂RhH(CO)(PPh₃) (1) and [Rh(OAc)₂] (2). The catalytic reaction of styrene using (1) gave a very high yield of the branched chain aldehyde containing only a trace of the straight chain isomer. Reaction of the alkenyl dithiane, S(CH₂)₃SCH-CH₂CH=CH₂ with the (1) gave a higher ratio of linear to branched aldehydes than (2). Reaction of vinyl acetate with (1) gave a significant amount of linear aldehyde unlike (2), but reactions of allyl acetate gave similar products for both (1) and (2).

Direct Hydroesterification of Ethylene with Methyl Formate with the New System RuCl₃-NR₃-F-NR₃: An Example of Catalytic Activation of the CH Bond of Methyl Formate?


A highly reactive system was obtained for direct hydroesterification of C-H with methyl formate in the presence of RuCl₃-NR₃-F-NR₃, combined catalyst (where R = alkyl or aryl) using dimethylformamide as a solvent, in the absence of CO. The ratio of 1:2:5 for the Ru salt, NH₃ iodide and amine is particularly efficient, giving a turnover frequency of up to 2000/h. The excellent reactivity obtained was due to a direct activation of methylformate.

A Novel Perfluoroalkylation of Pyroles with Perfluoroalkanesulfonyl Chloride Catalysed by a Ruthenium(II) Phosphine Complex


Direct perfluoroalkylation of N-substituted pyroles with tridecafluorohexanesulfonyl chloride catalysed by a Ru(II) phosphine complex proceeded regioselectively in high yield. After temporary protection of the N-H function by a trimethylsilyl or triisopropylsilyl group, perfluoroalkylation using perfluorooalkanesulphonyl chloride and dichlororotriphenylphosphine(Ru(II)), followed by deisylolation, was found to be an excellent method for the regioselective synthesis of 2- and 3-perfluoralkylpyroles.

FUEL CELLS

Evaluation of an Effective Platinum Metal Surface Area in a Phosphoric Acid Fuel Cell


The effective Pt metal surface area in a real phosphoric acid fuel cell (PAFC) was evaluated by a new method, using in situ cyclic voltammetry. The electrochemical Pt surface area of a PAFC under real operational conditions was ~25 m²/g which was due to the isolation of the Pt particles from a C support.

ELECTRICAL AND ELECTRONIC ENGINEERING

Ruthenium Clusters in Lead-Borosilicate Glass in Thick Film Resistors


Diffusion behaviour of Ru ions in glass was studied in an interparticle glass matrix in RuO₂-based thick film resistors. The dissolved Ru ions form clusters <1nm in size in low-Pb glasses, which condense into Pb₂Ru₂O₇ crystalites in high-Pb glasses. A typical distance between Ru clusters in low-Pb glasses was 2–4 nm, which shows that the electrical conduction in TFR is sustained by the Ru crystallites in the glass.
NEW PATENTS

ELECTROCHEMISTRY

Highly Durable Electrodes for Electrolysis
DAIKI ENG. CO. LTD. European Appl. 593,372A
Highly durable electrodes, especially for electrolysis in sulphate baths, with high electrocatalytic activity for O₂ evolution, comprise Ti coated with Pt-group metal(s), such as IrO₂, diffused onto an intermediate Ti, Zr, Nb and Ta layer, which changes from a metastable β- to an α-phase by heat-treatment. Electrolysis is stable over long periods at low electrode potentials, by preventing the growth of Ti oxide.

Insoluble Electrode
NIPPON STEEL CORP. Japanese Appl. 6/81,198
The insoluble electrode comprises an electrode body, with a first coating of dense IrO₂ having a relative density of 90%, a second coating mainly of IrO₂ with a relative density of 90–50%. The first layer is formed by melting and evaporating metallic Ir in a closed O₂ atmosphere using the ion plating method. The insoluble electrode has excellent corrosion resistance even when undergoing a high current density electrolysis at ≥ 50 A/dm².

Reduction of Carbon Dioxide for Formic Acid
TANAKA KIKINZOKU KOGYO K.K. Japanese Appl. 6/93,485
The reduction of CO₂ is performed on opposing gas diffusion electrodes coated with Pt (alloy) and Pd catalyst with intermediate ion production exchange film connected by an aqueous carbonate solution and aqueous hydroxide salt solution. HCOOH is produced from CO₂ and H₂ by using energy of concentration difference after electrolysis. Increasing potential difference between the electrodes produces electric power.

ELECTRODEPOSITION AND SURFACE COATINGS

Selective Deposition of Platinum
U.S. SEC. OF NAVY U.S. Patent 5,320,978
Pt is selectively deposited on a (semi)conductive substrate such as Si, GaAs, etc., by applying a patterned polyimide mask layer and depositing Pt by CVD from Pt(PF₆)₃ onto exposed substrate only at a controlled pressure and temperature. The process is used in pattern metallisation of micro-electronic devices with Pt.

Organic Platinum Compounds for Plating
NISSAN CHEM. IND. LTD. Japanese Appl. 6/100,578
An organic Pt compound for plating Pt onto ceramics or metal is obtained by reacting dihalogeno(1,5-cyclooctadiene)Pt with a base in the presence of compounds containing H, HC groups of < 10 C, alkoxyl of < 10 C or 2–10 C alkoxyl, such as diphenyl ethylene. The organic Pt compounds show improved solubilities in terpene alcohol solvents and film-forming properties. Metallic Pt is formed after thermal decomposition giving uniform, continuous thin membranes.

APPARATUS AND TECHNIQUE

Image-Reflecting, Composite Mirrors
MONSANTO CO. World Appl. 94/9,180A
A composite mirror consists of ≤ 20 wt.% polymer and ≥ 80 wt.% metal clusters made of Pd, Au or Ag, of < 100 nm diameter, agglomerated on the surface of a substrate. When the metal is Pd or Ag the salt comprises anions selected from acetate, lactate, cyanate, etc. Composite mirrors are used to prepare image-reflecting holograms. The optically variable device can be printed on security documents.

Removing Chlorinated Lime from Tap Water
NIKKI UNIVERSAL CO. LTD. Japanese Appl. 6/39,378
An agent for removing chlorinated lime in drinking H₂O has Pt group metal, preferably Pt or Pd, on a porous support, such as Al₂O₃ or a ceramic honeycomb precoated with porous Al₂O₃ with ≥ 80% of the metal supported in depth from surface to 50 μm. The agent retains removal of high chlorinated lime even after repeated use and good quality drinking H₂O is obtained.

Solubility Measuring Sensor for Metal Oxide
NIPPON STEEL CORP. Japanese Appls. 6/50,929–30
A sensor for measuring solubility of a metal oxide in a molten chloride has a Ag electrode in AgCl-NaCl powder held in a protective tube made of Y₂O₃ and/or ZrO₂ with Al₂O₃ and SiO₂, and a Pt electrode immersed in a molten chloride outside the tube. Both electrodes are electrically connected to measure the potential difference between them. The potential corresponding to the amount of the metal oxide dissolved in the molten chloride can be measured over long periods, so can monitor material deterioration.

HETEROGENEOUS CATALYSIS

Production of Highly Pure Terephthalic Acid
MITSUBISHI KASEI CORP. British Appl. 2,271,568A
Highly pure terephthalic acid was produced by contacting an aqueous solution of crude acid with H₂ at 260–320°C in the presence of a Pt group metal catalyst, preferably Pd/C. Purification is initiated within 3 min after the aqueous solution reaches 250°C, at the total reaction pressure of 5–15 MPa. The process reduces the effective exposure to a high temperature so as to suppress thermal modification and formation of colouring impurities.

Catalyst for Hydrocarbon Conversion
SHELL INT. RESEARCH M.I.T., B.V. European Appl. 587,246A
Pd/SiO₂-Al₂O₃ catalyst is prepared by impregnation of a carrier with pore volume of ≥ 1.0 ml/g by contacting with Pd compounds in liquid. The catalyst is highly selective in hydroconversion of hydrocarbon products of Fischer-Tropsch synthesis or in alkane hydroisomerisation. The catalyst is useful in the preparation of middle distillates.
Purification of Oxygen Rich Exhaust Gas

CATALER IND. CO. LTD. European Appl. 589,393A CO, HC and NOx are removed from O2-rich exhaust gas, particularly from lean burn vehicle engines, by contacting with a catalyst comprising Pt and/or Pd; Ba; and Fe, Ni, Co, Mg and/or alkali metal supported on a porous carrier. The catalyst maintains high purification rates even after extensive use at high temperatures and when vehicles are used in city driving.

Difunctional Catalyst for Hydroisomerisation of n-Paraffins

ENRICERCHE S.P.A. European Appl. 590,714A A difunctional catalyst comprises an X-ray amorphous SiO2-Al2O3 gel with molar ratio of 30:1-300:1, a porosity of 0.3-0.6 ml/g, pore diameter of 10-30 Å and 0.05-5 wt.% Group VIII metal. The dual catalyst has both acidic and hydrogenation active sites, and high selectivity for n-paraffin hydroisomerisation to yield base oils for lubricants of low pour point and high viscosity index.

Catalytic Reforming of Naphtha

DEGUSSA A.G. European Appl. 601,398-99A Naphtha is catalytically reformed using a Pt group metal catalyst, such as Pt, and a Group IVB metal, optionally Sn, or halogen on a moulded oxide carrier as promoter, such as Zr. An example, a catalyst contains 0.05-2 wt.% Pt, 0.01-1 wt.% Sn, 0.05-5 wt.% Zr and 0.05-1.5 wt.% Cl, supported on Al2O3. The process produces high-octane hydrocarbons for gasoline, and also a high yield of BTX-aromatics, which are used as solvents.

Exhaust Catalyst

FORD FRANCE S.A. European Appl. 601,705A An exhaust catalyst is made by impregnating a support comprising ≥ 50 % γ-Al2O3 with an organo-noble metal compound such as Pt, Pd, Rh, in an organic solvent, followed by heating to remove solvent and organic residues. The organo group is dialkycarbonyl or 3-19 C carboxylate, preferably Pd2-ethyl hexanoate. Catalyst eliminates downstream corrosion by residual inorganics, such as Cl, NOx, and carrier degradation during impregnation using conventional acidic impregnants. The catalysts has improved light-off temperature, NOx reduction and longer life at high temperatures.

Preparation of Mixtures of Cyclohexanone with Cyclohexanone

BAYER A.G. European Appl. 602,499A Mixtures of cyclohexanone and cyclohexanol with predetermined ratios of 30-98:70-2 were prepared by hydrogenation of phenol with H2 using a Pd-carrier catalyst in the gas phase at 150-250°C and 0.8-8 bar. The catalyst is activated and regenerated by high temperature treatment with H2 and O2. In order to achieve the predetermined ratios, the specified time-temperature conditions must be maintained. The process requires only one catalyst and one reaction vessel. Cyclohexanone is useful for the preparation of adic acid and cyclohexanone is used to produce caprolactam.

Nitrogen Oxides Reduction Catalyst

AGENCY OF IND. SCI. & TECHNOL. European Appl. 602,602A A novel catalyst for reduction of NOx in vehicle exhaust emissions or factory waste gases, and using a hydrocarbon as a reducing agent, contains Pt, Ir, Rh and/or Ru plus some Au, and further contains Ce, La, Nd, Ge or Ga oxide in 10-10' by weight with respect to the weight of Pt group metal. The catalyst containing Pt or Ir, etc., is supported on a highly dispersed carrier such as Al2O3, SiO2, TiO2, zeolites, etc., via ion exchange, followed by deposition of Au or highly dispersed Au hydroxide on the carrier, then by optional reduction with H2. The catalyst is highly durable and does not require large amounts of hydrocarbon reducing agent.

Palladium Containing Metal Oxide Catalyst

JOHNSON MATTHEY PLC European Appl. 602,864A A Pd catalyst is prepared by co-precipitating metal oxide, such as Fe(III) oxide, Bi molybdate, Ce oxide, with Sb oxide, and Pd particles. The catalyst is used in a chemical reaction, particularly as a hazardous gas sensor. The sensor comprises: a means of contacting the gas with an Fe(III) oxide catalyst at ambient and an indicator for a temperature rise if gas is present. The catalyst is used in oxidative reactions, in sensors to indicate the presence of hazardous gas, such as those used in car exhaust systems to measure catalyst performance. The operating temperature of the reaction is reduced, saving energy and extending the life of the catalyst. The sensor has lower light-off temperature, and greater resistance to deactivation.

Catalyst for Oxidation of Carbon Monoxide

JOHNSON MATTHEY PLC European Appl. 602,865A Catalyst for oxidation of CO to CO2 comprises metal oxide particles of up to 250 Å in diameter among which are uniformly distributed noble metal particles of diameter < 10 Å. The catalyst is prepared by co-precipitating Pt, Pd, Rh and/or Au particles onto CeO2 particles and is calcined at 500-900°C. The catalyst is stable, does not need a reducing pretreatment and can be used without a carrier or supported on a monolith. Additionally, hydrocarbons are oxidised to CO2 and H2O, and NOx is reduced to N2, in the exhaust of vehicle engines, thus leading to less air pollution.

Reforming a Hydrocarbon Feed

CHEVRON RES. & TECHNOLOGY CO. World Appl. 94/2,438A A hydrocarbon feed for production of high purity benzene is reformed in the presence of a non-acidic catalyst comprising at least one Group VIII metal and a non-acidic support, such as Pt/zeolite. The reformate is separated into light (< 500 ppm wt. toluene) and heavy fractions, and the light fraction is separated into an aromatic extract stream and a non-aromatic raffinate stream. Catalyst has high selectivity for producing product streams containing 99.95 vol.% benzene. The process can reform a full boiling point hydrocarbon feed to enhance benzene purity, especially in the production of high octane hydrocarbon blending components for gasoline.

Platinum Metals Rev., 1994, 38, (4) 187
Three-Way Catalysts for Exhaust Gas

ALLIED-SIGNAL INC.

World Appls. 94/6,546A and 94/7,600A

Three-way catalysts for removing CO, HC and NOx from L.C.E. exhaust gas comprises first a Group VIII noble metal, such as Pt or Rh, dispersed on a first inorganic oxide support, preferably Al2O3, containing 5±% CeO2, and additional CeO2 as an O2 storage component. This three-way catalyst produced a better removal performance and minimum H2S. The second catalyst comprises a support containing La and Ce, and Al2O3 on a monolithic substrate with an effective amount of Pd. This catalyst performs as well as Pt/Rh containing catalysts.

Fluorinated Saturated Hydrocarbons

NIPPON ZEON K.K. World Appl. 94/7,829A

A fluorinated saturated hydrocarbon of formula R-CHR, R-CHR' is prepared by reacting a fluorinated unsaturated hydrocarbon, R-CF=CF-R' with H2 in the presence of a Pt catalyst. R, R' = perfluoroalkylene group, or R and R' can combine to form a perfluoroalkylene group. R and R' are preferably 1-4C. The catalyst contains 0.1-10 wt.% Pt on an activated C, Al2O3, or SiO2 support, or a Pt compound such as Pt oxide, colloidal Pt or Pt black. The fluorinated saturated HC is used as a cleaner, solvent, coolant, heating medium or even as an environmentally friendly spraying agent.

Catalysts for Production of Vinyl Acetate

HOECHT CELANESE CORP.

World Appl. 94/8,714-15A

A catalyst used for production of vinyl acetate from ethylene, O2 and acetic acid is prepared by impregnating a support with H2O-soluble Pd and Au compounds, converting them to H2O-insoluble compounds and precipitating them on a support, then reducing to form free Pt group metals. The catalyst contains a mixture of Au and Pd, using NaOH or KOH fixing solutions; or insoluble compounds are produced by immersing a support with H2O-soluble chloride salts of Pd and Au in a reactive alkaline solution. The catalyst is ducile and has high activity and selectivity.

Catalytic Production of Hydrogen Peroxide

SHOWA DENKO K.K. World Appl. 94/12,428A

A process for catalytic production of H2O2 from O2 and H2 in a reaction medium uses a catalyst made from a Pt group metal supported on Nb oxide, composite Nb oxide, Ta oxide or composite Ta oxide.

Piperazinylorgano-Silane Preparation

DOW CORNING CORP. U.S. Patent 5,300,641

Preparation of piperazinylorgano-silanes (1) at normal pressure comprises contacting an (aminoorganosilane) (2) with a piperazine compound (3) and Pd black catalyst at a concentration of 0.1-5 g/mole of (2), at 180-250°C, giving a final molar ratio for (3):(2) of 1.0-3.0. The reaction is carried out as a batch process in a stirred bed reactor with contact time of 5-1200 min, or as a continuous process with contact time of 0.2-120 min and does not require elevated pressure, nor additives, such as K2CO3 or Li.

Catalyst for Hydrogenation of Distillate Hydrocarbons

AMOCO CORP. U.S. Patent 5,308,814

Hydrogenation catalyst suitable for the hydrogenation of HC feedstock with a boiling point of 150-700°C comprises 0.1-2 wt.% each of Pd and Pt on zeolite Y which contains 1.5-6 wt.% Na. The Pd and Pt are incorporated onto the support in a weight ratio of 1:1 to 1:2. The catalyst has improved activity and life, and provides better distillate aromatics saturation, distillate desulphurisation and denitrogenation giving increased cetane number.

Preparation of 1,1,1,2,3-Pentafluoropropane

ALLIED-SIGNAL INC. U.S. Patent 5,315,048

Preparation of 1,1,1,2,3-pentafluoropropane (1) comprises reductive dechlorination of 1,2,3-trichloropentafluoropropane with H2 over an Al2O3 supported catalyst of Pd, Pt, Ru, Rh and/or Ir, preferably Pd or Pt, in the vapour phase at 140-300°C, with a contact time of 0.1 s to 2 min. (1) is used as a potential replacement for ozone depleting chlorofluorocarbons, as a blowing agent or propellant. High conversions are obtained by recycling at least part of the production stream through the reactor.

Preparation of Serinol or Its Derivatives

KAO CORP. Japanese Appl. 6/9,512

Serinol or its derivatives, which are useful as medical agents or aminoacid intermediates, are prepared by reductive amination of bihydroxy acetone in the presence of supported catalyst containing more than two kinds of catalysts selected from Pd, Pt, Rh, Ru and Ir, on active C, Al2O3, SiO2 and zeolite. The reaction is carried out in H2O at 0-150°C for 1-20 h. The ratio of Rh:Pd, Rh:Pt or Ru:Pt is preferably 10-0.0001. The amount of metal in the supported catalyst is 30-0.1 wt.%, preferably 10-0.5 wt.%. Serinol can be prepared in high yield under mild conditions.

Catalyst for Removing NOx from Combustion Exhaust

TOYO KOGYO CO. Japanese Appl. 6/39,292

A catalyst consists of a metal-containing silicate which is coated with an undercoat of Rh and a top coat of Pt and Ir. The catalyst is produced by loading Rh on the silicate by wash-coating and simultaneous impregnation of Pt and Ir into the support. The Rh catalyst layer is not directly exposed to high temperature exhaust, so that it is not easy to degrade; while the Pt and Ir catalyst layer is exposed directly to exhaust, giving a higher initial activity.

Catalyst for Purification of Exhaust Gas

TOYOTA Jidosha K.K. Japanese Appl. 6/99,072

The catalyst consists of Pt, Pd, Rh, Ir or Ru, and bimetallic silicate with Al and/or Ge in the crystal lattice. Preferably, transition metal, such as Cu or Co, is carried on the bimetallic silicate by ion exchange. NOx in exhaust gas with excess of O2 can be purified effectively at high temperatures of 250-400°C; the amount of HC adsorbed is increased and NOx decomposition is improved. By putting a Pt metal in the lattice, catalytic activity at 250-350°C is improved.
Neoalcohol Compound Production

HUELS A.G. German Appl. 4,230,565

Catalytic direct hydrogenation of 5–13C neo-carboxylic acids (1) to the corresponding neoalcohols of formula R,R,R-C(=O)-OH where R,R = 1–9C alkyl or 6–9C cycloalkyl (2), is carried out at 150–300°C and 50–350 bar at an LHHSV of 0.05–0.5 h over Re-Pd activated charcoal catalyst. The Re: Pd ratio is (1–30):1, especially 10:1. (1) are hydrogenated directly, without prior esterification, and 97% selectivity and high conversion are attained.

High Activity Oxidation Catalyst

DEGUSSA A.G. German Appl. 4,324,442

A highly active Pt/C catalyst containing Mo and/or Ce as a finely-divided modifier, is used for the oxidation of glyoxal to glyoxylic acid. The weight ratio Pt:Mo and/or Ce is 1:1–10, preferably 1:1–5. The catalyst is prepared by addition of H₂O-soluble Pt and compounds of Mo and/or Ce to an aqueous 5–30 wt.% activated C suspension, heating and simultaneously precipitating Pt with Mo and/or Ce followed by addition of a reducing agent. Improved activity, yield and selectivity are claimed.

Catalyst for Exhaust Gas Purification

MAZDA MOTOR CORP. German Appl. 4,333,343

Catalysts for engine exhaust gas purification comprise Pt together with Ir and/or a Group IIIIB and/or IVB metal on a support. The catalysts comprise Pt, Ir and optionally Rh, preferably (by weight) 45–92% Pt, < 50% Ir and < 15% Rh. The catalyst has high activity, especially for NOx reduction over a wide temperature range, and good thermal stability. Also claimed is a catalytic converter containing the above catalyst, where a part of the metal is in the binder.

HOMOGENEOUS CATALYSIS

Preparation of 1,3-Propanediol

SHELL OIL CO. U.S. Patent 5,304,691

1,3-Propanediol (1) and 3-hydroxy-propanal (2) are prepared by reacting ethylene oxide with CO and H₂ over promoted tert-phosphine-complexed Co carbonyl and Ru catalysts, using a CO:H₂ molar ratio of 4:1–1.6. The catalyst is preferably promoted using an acid chosen from metal salts of Groups IA, IIA or IIB, and rare earth elements. The Co:Ru atom ratio is 1000:1–1:100, and especially 50:1–1:5. (2) is a useful chemical intermediate, and can be readily converted into (1). Conversion of > 62 mol % is obtained.

Preparation of Triorganochlorosilane

DOW CORNING TORAY SILIC. U.S. Patent 5,312,949

Triorganochlorosilane (1) containing optionally substituted monovalent HC is prepared by reacting HCl with triorganohydrosilane, such as trialkylsilane, in the presence of Group VIII transition metal or complex. The process is carried out at 50–180°C in the presence of a Pt complex preferably Pt/divinyltetramethyldisiloxane complex or isopropanoic chloroplatinic acid hexahydrate. The process gives high yields of (1) without generation of by-products.

Aryl-Substituted Aliphatic Esters

ETHYL CORP. U.S. Patents 5,315,030 and 5,322,959

Aryl-substituted aliphatic esters or alkyl esters, especially ibuprofen ester, are prepared by treating an aryl compound and an alcohol or alkanol with CO₂ in the presence of a Pd catalyst under ≥ 1 atm pressure and 25–200°C, in the absence of O₂ and H₂O. The catalyst is Pd(0), Pd(I) or Pd(II) compound, such as PdCl₂, PdBr₂, etc., with optionally Cu compounds, and an acid stable ligand, such as triphenylphosphine.

Preparation of Propene Derivatives

KURARAY CO. LTD. Japanese Appl. 6/40,954

The preparation of a propene derivative (1) containing organic radical, H or lower alkyl, lower alkyl or aralkyl, uses a Pd catalyst consisting of a Pd salt and atrialkyl-phosphine in ratio 1:1–2 either in the conversion of formic acid ester or in the conversion of a carbonic acid ester, in the presence of HCOOH and a base. The Pd salt is Pd acetate, Pd acetylacetonate, and the trialklyphosphine is tributlyphosphine. (1) converts into vitamin D in high yield and high selectivity.

Preparation of Acetals

SAGAMI CHEM. Res. Centre Japanese Appl. 6/87,781

Acetals are prepared in high yields of 67–93% by contacting olefin with alcohol in the presence of Pd catalyst and Cu salt under a mixture of O₂ and CO. Pd catalyst, such as Pd metal or halide, is used at the ratio of 1/100–1 equivalent and Cu salt, such as Cu halide, Cu acetate, cuprous halide, at 1/100–1/2 equivalents. Acetals are used as a synthetic material or as intermediates for perfume, agricultural chemicals and medicines, and as organic solvents.

Preparation of Derivatives of Phenyl-Tetrazole

SYNTHELABO French Appl. 2,696,745

Phenyl-tetrazole derivatives containing 1–2C alkyl or aryl, aryl-naphthyl, pyridinyl-pyrimidyl, quinolinyl or imidazo-pyridinyl (all optionally substituted) were produced by reacting benzeneboronic acid derivative with aryl halide in a solvent of benzene-toluene, DMF etc., in the presence of a Pd catalyst and a base. The catalyst is Pd tetraakis (triphenylphosphine) and the base is preferably Na₂CO₃, K₂CO₃ or a tertiary amine. The reaction provides a method for obtaining direct aryl-aryl, aryl-naphthyl and aryl-heterocyclic couplings in the presence of a Pd catalyst.

FUEL CELLS

A Fuel Cell Cathode Catalyst

INT. FUEL CELLS CORP. World Appl. 94/10,715A

An alloy catalyst, especially for a fuel cell cathode comprises, in at. %: 40–60% Pt, 10–20% Rh and 20–50% Fe. The catalyst preferably maintains a mass activity for O₂ reduction of ≥ 40 mA/mg Pt at 0.9 V, at > 400°F and atmospheric pressure after ≥ 10,000 h of fuel cell operation at 300–400°F and 0.5–0.8 V. The catalyst is supported preferably on C and is 50–95 wt.% of the support. Catalyst has high physical and chemical stability as well as high activity.
Polycomponent Electrocatalyst
ECOLE POLYTECHNIQUE MONTREAL

U.S. Patent 5,298,343

A catalyst for a fuel cell cathode comprises Pt, Pd, Ru, Rh, Ir and/or Os mixed with tungstic or molybdate acid, Na tungstate or molybdate and/or NH₄ tungstate or molybdate, dispersed on a conductive carrier, preferably C of high surface area graphitized C particles of crystallite size 0.200–0.300 μm. A stable catalyst is produced with increased activity for electrochemical reduction of O₂.

Catalyst for Phosphoric Acid Fuel Cell
FUJI ELECTRIC CO. LTD. Japanese Appl. 6/124,712

The catalyst comprises fine particles of Pt, Au and Co alloy, supported on C material; preferably 3–25 wt.% Co, 8–40 wt.% Au and balance Pt. The catalyst is used for a phosphoric acid type fuel cell, having improved higher initial activity and stability. Output and life of the cell are also improved.

ELECTRICAL AND ELECTRONIC ENGINEERING

Interconnecting Via Fill Composition
E. I. DU PONT DE NEMOURS & CO. European Appl. 591,604A

Composition for manufacture of a fired multilayer electronic structure comprises (by wt. % of total inorganic solids) 90–100% Os, Ir, Ru and/or Rh (alloy) particles, preferably Ru, and 10–0% inorganic binder, preferably 0.5–10%, with softening point 400–1000°C. The mixture is dispersed in a liquid organic medium and conductive vias are formed by filling holes with the composition by screen printing and firing. Different metals, such as Cu and Ag, can be thus connected.

Magneto-Optic Recording Medium
TOSOH CORP. Japanese Appl. 6/60,448

Magneto-optic recording medium (1) has a recording layer of an artificial lattice of Co, Pt and/or Pd layers laminated alternately on a board. Part of the artificial lattice film on the board side has a shorter laminating period than the other part of the film and is 10–80% of the total film thickness, and consists of (in atomic layers) 0.5–1.5 Co and 1–6 Pt. The other part of the film consists of 1–2.5 Co and 2–8 Pt. (1) exerts a high magneto-optic effect and coercive force without raising the Curie temperature, giving high packing density recording and a high C:N ratio.

Magnetic Recording Medium
SONY CORP. Japanese Appl. 6/76,260

Magnetic recording medium (1) having formula (Co,Fe,Mn,M)ₓ(Fe,Pt,Al)ₓOᵧ, where (in at.%) a = 100–b–c, b = 0–50, c = 0.1–30 and x = 0–15, is an intermediate layer having f.c.c. crystalline structure. (1) relaxes the conditions of partial voltage of O₂ at the time of film formation to obtain magnetic thin films with a high perpendicular anisotropic magnetic field. (1) improves the output and overwrite characteristics of the magnetic recording without reducing the rectangular shape of the perpendicular magnetic curve.

Photomagnetic Recording Medium
MITSUI PETROCHEM. IND. CO. LTD. Japanese Appl. 6/76,379

The medium consists of a magnetic thin film (1) with perpendicular magnetic anisotropy, which is laminated on both sides of a magnetic thin Pt-Co film. Preferably (1) is a 30–500 Å thick composition modulation magnetic thin film of laminations of at least 1 layer each of 1–15 Å thick Co layers and 2–15 Å thick Pt layers. The medium has improved magnetic properties, and a larger Kerr rotating angle over a wavelength range of 400–850 nm.

Photomagnetic Recording Medium for Rewrite
SANYO ELECTRIC CO. LTD. Japanese Appl. 6/76,381

A photomagnetic recording medium has a recording layer comprising reciprocal laminate film with layers containing a transition metal and layers containing noble metal, and alloy layers containing rare earth metal and a transition metal. All being in close contact on a substrate. A photomagnetic recording disk of thickness 200–3000 Å was prepared from 5–20 Å Pt layers and ≤ 10 Å thick Co layers and Tb-Fe-Co alloy layers on a substrate. A smaller magnetic field allowed writing to disk.

Opto-Magnetic Disc with Improved S:N Ratio
HITACHI LTD. Japanese Appl. 6/103,623

The disc has three magnetic recording layers having different refractive indices or different vertical magnetic anisotropical energies on a substrate with an uneven guide groove. The optomagnetic effect is enhanced and S:N ratio is improved. In an example, a Tb-Co-Nb first magnetic layer (20 nm), Pt-Co second magnetic layer (10 nm), and Tb-Dy-Fe-Co-Ti third magnetic layer (50 nm) were successively applied on a SiN layer. In three magnetic layers, vertical magnetic anisotropy was highest in the third layer and lowest in the second layer.

Film Forming Method for Artificial Grid Multilayer Recording Medium
JAPAN ENERGY K.K. Japanese Appls. 6/111,403–04

A transition metal/Pt group metal, preferably Pt or Pd, artificial grid is formed by sputtering multilayers of film. The sputtering pressure for the Pt or Pd metal layer is kept higher, preferably at 0.5–5.0 Pa, than for the transition metal layer which is kept at 0.1–1.0 Pa. The medium has higher coercivity and improved corrosion resistance.

Magnetic Recording Medium with High Recording Density
TDK CORP. Japanese Appl. 6/124,832

Magnetic recording medium has a continuous thin film type magnetic layer comprising (by in.%) 5–40 Pd, 10–30 O, and balance substantially Co, on a nonmagnetic substrate. It is used for in-plane magnetic recording media capable of high density recording.

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