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Communications should be addressed to
The Editor, Platinum Metals Review
Johnson Matthey Public Limited Company, Hatton Garden, London EC1N 8EE
Platinum in High Temperature Superconductor Technology

LITERATURE SURVEY SUGGESTS POTENTIAL USES

By E. F. Maher
Johnson Matthey Technology Centre

High temperature superconducting oxides are being subjected to intensive investigation, designed to establish the basic mechanisms governing their superconductivity and to enable their electrical and mechanical properties to be optimised and commercial applications developed. Chemical composition, crystallography, microstructure and the concentration of point defects are all factors that have a crucial bearing on superconductivity. Progress in fabrication and thermal processing would elevate these high temperature superconducting oxides from laboratory curiosities to a position where widespread commercial use could be envisaged. Much has already been published on the use of the platinum group metals with the new superconductors. This article has been compiled from a search of the literature and indicates some of the applications that are, or could be, of commercial significance.

The phenomenon of superconductivity, that is the total absence of electrical resistance in a material when it is maintained below a critical temperature, has found limited commercial application. For example, body scanners used for medical imaging make use of conventional niobium-tin superconductors. However the requirement for liquid helium cryogenic cooling systems, which hold the temperature below the critical temperature, restricts the use of conventional low temperature superconductors.

Applications for superconducting materials would be expected to increase very significantly if their critical temperatures were higher, and therefore easier to achieve. Progress towards this is being made following the discovery and development of so-called high temperature superconductors. These are complex oxide materials that have critical temperatures above the boiling point of liquid nitrogen (77K). The processing of these materials, in order to improve both their mechanical and electrical properties, and hence their performance, is being studied in laboratories all over the world.

Superconductivity is dependent upon many factors including chemical composition, crystallography, microstructure and point defect concentration, and for virtually any application the stability of the superconducting property is crucially important. The superconducting phase in the new materials is thought to be inherently thermodynamically unstable, and thus any thermal treatment will play a vital role, particularly for power applications where the material would be used in bulk form.

The published literature on high critical temperature superconducting oxides amounts to tens of thousands of papers and patents, many referring to the use of platinum group metals. Indeed, over one hundred papers have been published specifically on the use of noble metals with the new superconductors, mostly on aspects of high temperature processing. One critical factor for the successful production of high temperature superconductors is the oxygen defect concentration. This is neither easy to measure nor control. The simple exclusion of oxygen during processing is not sufficient to
Principal Uses of Platinum in Superconductivity

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control the oxygen defects, which from thermodynamic considerations must exist in the superconducting oxide materials; but a reduction in the number of extraneous perturbing influences on the oxygen content must contribute to improved materials. Thus the use of noble metals as containers, diffusion barriers and electrical contacts, for example, can assist in improving process control.

The driving force behind research and development of these superconducting materials is their potential application in areas such as high power magnets and high speed switches for computers. At this early stage it is not clear which application areas will emerge as the dominant ones, and hence the specific technologies required cannot yet be identified. However by making comparisons with the semiconductor industry it may be possible to make some general predictions on how the technology and application areas will develop, and the roles which platinum will play.

Overview of High Temperature Superconductivity

The advent in 1987 of the new high temperature superconducting materials, such as YBaCuO (YBCO), was hailed as a major step forward in the development of superconductors. Some applications for conventional superconductors—such as high power magnets—were already developed and commercially viable, despite needing liquid helium cooling. Until 1986 the critical temperature had risen by only about 20°C since the first observations of superconductivity were made by Onnes in 1911 (1). Within weeks of the disclosure by Bednorz and Muller of a new class of superconducting material based on copper oxides containing barium and rare earth elements (2), critical temperatures as high as 100 K were being reported. For nearly two years a new high temperature superconducting material or variant was being reported weekly, but relatively little progress was made in understanding the phenomenon. In some respects, the classical superconductivity theory (3) is inadequate to describe the new superconductors, but even now there is no universally accepted replacement. Certain parts of the theory, including Cooper pairs of charge carriers, are retained by most newer theories.

The main drawback arises when attempting to explain the pairing interaction and how it can survive to much higher temperatures than the classical phonon coupling mechanism allows.
Frantic formulation, patenting and publicising of new combinations of materials with superconducting properties at temperatures above 77 K has now been replaced by an alternative approach driven by potential applications. Investigators were initially obsessed with raising the critical temperature ever higher, but it became clear that once critical temperatures substantially above 77 K had been reached, further increases would not be of great significance, unless room temperature could be achieved. Indeed, for most applications the most important parameter is the critical current—the maximum current that can be attained until the self-induced magnetic flux associated with this current causes the system to become unstable and collapse due to interactions between nearby superconducting regions. The low critical currents observed were the major barrier to commercialisation, and to a large extent this is still the case, although progress has been made. The same was true of the classical Type I superconductors, for example niobium, until Type II superconductors such as niobium-tin, were discovered.

The increase in critical current in Type II superconductors depends on the recognition of the phenomenon of flux pinning. Essentially, flux pinning ensures that the magnetic flux associated with localised high current densities of superconducting regions does not interact with the flux due to neighbouring regions in such a way as to exceed the critical magnetic flux density and thereby collapse the superconducting currents. A modern Type II superconductor is an inhomogeneous system by design, with the discontinuities serving to stabilise the system, and effectively prevent instabilities from escalating and destroying the system via a domino effect. Clearly, any region which becomes even momentarily non-superconducting will give rise to a Joule heating effect, which, if the heat is not conducted away rapidly, will result in other regions exceeding the critical temperature, losing their superconductivity, and precipitating further thermal runaway. Thus the thermal design of superconducting systems with, for example, copper sheaths around niobium-tin wire, was the key to establishing the very high critical currents now possible in conventional superconductors.

Successful commercialisation of many new materials has generally depended to a large extent on the recognition of the role of inhomogeneities. In the broadest possible sense we can regard any departure from perfect crystallinity, or a local departure from a single phase amorphous material, as an inhomogeneity. Deliberately introduced inhomogeneities have been used to enhance, and frequently stabilise, the properties of materials. Thus while extremely high purity levels are essential for growing single crystal semiconducting materials, regions deliberately doped with controlled amounts of impurities are used to produce, for example, the pn junctions which are the basis of many electronic devices. The same is true of the mechanical properties: the work hardening of metals leads to the interaction and entanglement of dislocations such that further deformation becomes progressively more difficult. Similarly, the stabilisation of grain boundaries in materials, such as ZGS platinum, gives enhanced properties. Furthermore mechanical damage on the back of silicon wafers is used to “getter” unwanted impurities from the bulk material during quenching after high temperature diffusion processes.

The role of inhomogeneities in the new superconductors is also crucial to their operation, if only because they are Type II superconductors. Different thermal treatments of these materials give rise to widely differing microstructures and electrical properties. Inhomogeneities can be regarded as real and possibly essential parts of superconducting behaviour, rather than as unwanted artefacts. In fact the occurrence of the higher critical temperatures seems to be associated with “dirty” specimens (4).

**Comparison of Semiconductor and Superconductor Development**

Certain parallels can be drawn between the development of semiconductor materials, as a part of the electronics industry (5), and the new superconductors which may help to predict
major applications for the latter, and identify technological goals that will have to be achieved before commercialisation can take place. The new superconductors are generally semiconductors above the critical temperature, and their discovery was also driven by the same requirement for high speed solid state switching.

Another reason for comparing semiconductors and superconductors is that the required performance of the latter is only likely to be attainable, at least for the foreseeable future, using techniques which give very close control over material properties, such as crystallinity and chemical composition. Single crystal growth and thin film deposition are currently able to give higher performance characteristics than, for example, ceramic processing, and the former techniques are more likely to be used in the first commercial applications. The semiconductor industry is skilled in such matters and much information is available on the techniques for depositing thin films on single crystal substrates, and so on.

There are likely to be problems in processing superconductors but, except for applications needing bulk materials, the techniques used in the electronics industry are immediately relevant. This is also true of many of the analytical methods, such as secondary ion mass spectroscopy and X-ray scanning auger microanalysis, that are necessary to achieve the required control. Thus, there is not the same learning curve, which compensates for the greater complexity of chemical composition and microstructure of the materials. Fortunately it appears that chemical purity of itself is not as essential as it is with semiconductors.

**Growth in Literature on Superconductors**

Superconductivity was first reported in 1911 (1). Coincidentally, the first element Onnes investigated was platinum, which does not exhibit superconductivity. Now there are over 46,000 publications on superconductors. Commercial applications for the "old" superconductors are still growing, mostly for applications requiring high power magnets, but there has been a massive upsurge in effort since 1987 when the new high temperature superconductors were discovered.

**Platinum in High Temperature Superconductors**

At temperatures as low as two millionths of a degree Kelvin and magnetic fields as low as two milli Gauss, no superconductivity was observed in platinum, palladium and rhodium, according to a study in 1978 (6). However, a number of alloys of platinum have been found to be superconducting, such as UPt (7) and MoPt (8), but with one possible exception these have all been low temperature superconductors. The possible exception is CuPt, which a recent patent suggests is superconducting at temperatures as high as 200K (9)! This work has not been confirmed, however, and no other reference to it has been found in the literature.

Over 100 papers and patents have been published specifically mentioning platinum in connection with high temperature superconductivity in either the title or the abstract, and in addition many more papers refer to platinum and its uses in the text. These can be divided into several main groups, in terms of: the final form of the superconducting materials, the techniques used for production and the application areas.

In this way, we can attempt to predict the application areas that may be commercially viable first, the form these superconducting materials will take, the materials processing technologies which will be most relevant and finally what the uses of the platinum are likely to be. It is assumed here that a high level of activity relates to a market need, and that such activity is likely to lead to the first commercial products.

**Electrical Contacts**

Good electrical contacts for superconductors are of importance, since there is no point in having high critical currents if contact resistance precludes their use because of Joule heating effects. Platinum, gold and silver are the best materials for making contact to the YBCO ceramics (10, 11), since other metallic films...
interact with the oxide materials to produce alloys with semiconducting behaviour. Such contacts are usually sputter deposited, but can also be formed by pressing (12). Platinum powders and pastes have been successfully used for fabricating terminal electrodes to superconducting ceramics with high critical currents \(1000 \, \text{A/m}^2\). As with semiconductors, ohmic contacts are not the only ones of use. A platinum-aluminium alloy has been used to produce a tunnel junction on a Josephson junction single crystal YBCO device (13).

**Containers**

An obvious use of platinum is as a containment vessel during high temperature processing of oxide superconductors. Single crystals of these materials are frequently grown in platinum or iridium crucibles (14, 15, 16), which are also used during the preparation of melts prior to tape casting and wire drawing operations (17). Oxide powders have been sintered on platinum substrates (18) or occasionally in platinum pipes, foils and capsules (19–25), and sometimes the powders are quenched on platinum plates (26). Clearly the high melting points, general chemical stability and non-magnetic qualities of the platinum group metals are ideally suited to thermal processing in oxidising environments. Containers made from materials other than platinum metals are used, frequently with a platinum coating (27).

**Ceramic Processing**

In addition to containers and substrates, there is another potentially significant use for platinum. A number of reports refer to the use of platinum powder as a densifying agent during sintering, and for improving the mechanical properties of the new superconductors (28–30). Indeed in one case (28), it is claimed that the superconducting properties were enhanced when finely divided platinum was used at a loading below 0.2 per cent. Platinum deposition on the oxide powders during thermal processing is also reported (31). Fired superconducting thick films have been produced from solutions containing noble metals (32). Studies of the chemical reactions of platinum group metals additions during sintering of YBCO have highlighted their importance in high temperature processing of the superconducting oxides, although an additional thermal treatment is needed for optimum properties (33).

**Electrochemical Uses**

In a number of publications electrochemistry is specifically involved in the preparation or characterisation of superconducting material. Platinum electrodes are extensively used both for the synthesis of material (34, 35) and during its analysis by electrochemical techniques (36, 37). Electrophoretic deposition on a roughened platinum substrate is reported (38) and various superconducting articles have been fabricated by electrodeposition (39).

There have been novel schemes for controlling the oxygen content of the materials, even during active service, using platinum electrodes and solid state electrolytes, which allow transport and control of oxygen ions. For example hot isostatic pressing in a partial pressure of oxygen (with electrically biased electrodes to control oxygen migration) has produced a mechanically strong superconductor (40). A similar process has been reported to produce a thin film superconductor device (41).

**Wires**

Frequent use is made of platinum wires during the processing of the oxide superconductors, because of their stability at high temperatures and their resistance to oxidation. On passing platinum wires through a melt of oxide materials, superconducting coatings are deposited (42–45); single crystal coatings of superconducting material have also been produced (46). Platinum grids have acted as supports for silicon nitride membranes prior to deposition of YBCO for in-situ studies of thermal processing by electron microscopy (47). Ceramic composites of platinum wires and oxide superconductors have been fabricated (48, 49). Fibres and ribbons of superconducting materials have been produced using the laser heated pedestal technique in combination with
platinum wire (50). Platinum has also been used during the fabrication of wires of superconducting material. Platinum and platinum alloy substrates have been employed when powders or oxide layers have been melted by laser beam, and subsequently solidified, so forming wires of superconducting material (51, 52). Superconducting wires have also been fabricated from mixes of oxides and noble metal powders (53) or by lining a metal tube holding oxide powder with silver, gold or platinum powders and then sintering (54). Platinum barriers have been used around superconducting material contained in a copper sheath, when drawing wires (55, 56), and for cladding oxide preforms prior to wire drawing (57). Base metal wire with a platinum diffusion barrier and a magnesium oxide intermediate layer has been a substrate for fabricating superconducting wire (58).

Composites

Superconducting composites comprising oxides, metallic and even glass components of vastly differing shapes and structures have received much attention. The most obvious composite structure, that of a container with the superconducting oxide inside, has already been referred to above. If the container remains in place as a sheath of metal after the contents have been sintered or processed, then the resulting structure is clearly composite, with the inner core being the superconducting component. Apart from the use of platinum barrier layers for the processing of powder compacts (59, 60), such diffusion barrier coatings have been used on the inside of base metal container sheaths (61, 62).

There have been a number of composites based on platinum fibres (48, 63, 64), and dispersed metal phases giving additional mechanical strength (65, 66). Platinum coatings on superconducting oxide fibres in a solder matrix have been proposed (67). Platinum stabilisation layers for wire strips and tapes are reported (68, 69), and there have been examples of laminated structures, both planar (70) and concentric (71) with alternate layers of oxide and metal alloys surrounding a superconducting oxide core. In one instance, the superconducting core was surrounded by a glass envelope with a platinum barrier layer at the interface (72). A laminate structure with glass has also been used in the fabrication of a device (73).

Superconducting Thin Films for Devices

Probably the most commonly cited application of platinum to date has been in connection with thin film electronic devices. Platinum has been used extensively in thin film form as a barrier diffusion layer with three major objectives:

(i) to maintain and control the oxygen stoichiometry
(ii) to prevent chemical impurities diffusing from the substrate and contaminating the superconducting layer
(iii) to orient the oxide film crystallographically. Thus the commonly used substrates for devices, namely silicon, gallium arsenide, sapphire, alumina and zirconia, have all been used to support superconducting oxide films, very often with platinum buffer layers to minimise substrate interactions and provide orientation.

For optimum superconducting properties, the thin oxide film needs to be preferentially aligned with the c-axis vertical. Platinum buffer films have been shown to have an orienting effect on the oxide film, even for amorphous substrates such as alumina (74) or zirconia (75, 76). Although there have been many reports of single crystal strontium titanate and magnesium oxide substrates being used, thin films of these materials on amorphous substrates have also been used with platinum buffer layers to give superconducting oxide films with high critical current density (77). Clearly, the practicality of electronic devices using new superconductors will depend to a large extent on the film-substrate compatibility (78).

Conclusions

High temperature superconductors show every promise of being a commercial success despite their technical complexity. Potential application areas, currently unsatisfied, abound. Academic institutions are striving
to unravel the complexities of materials and mechanisms and major companies are investing substantially in research and development. Never have so many different technologies and analytical techniques been applied to the understanding and advancement of a class of materials. This is partly the result of the proliferation of the new techniques and analytical instrumentation available, and partly because of the wide range of potential applications.

As with semiconductor materials, thermal processing will be important and there are numerous opportunities here for platinum to assist in the achievement of the desired degree of process control and material stability. The exclusion of ferromagnetic materials during processing is particularly important, as is controlling oxygen migration.

High temperature superconductivity will have an impact on power applications, such as for transportation and energy storage devices (79). However, of the many potential applications for the new superconductors, magnetic and optical detectors, satellite communications, magnetic screening, and magnet/motor technology may be among the first to be commercialised. In terms of volume of platinum, the use for superconducting magnets is likely to be the dominant one, but critical current densities will need to be substantially increased. The use of thin films rather than wire in this application warrants serious study, since in thin films the critical currents can be much larger than in bulk material.

Electronic device applications, using thin films, will probably be commercialised sooner than high temperature superconducting magnets. Specialised detectors (such as antennas) and superconducting interconnects on silicon are emerging as likely applications in the short to medium term. In the long term, the high speed switching application may compete with advances in optical computing for the next generation of electronic devices.

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Polymetallic Activation

A REVIEW OF THE INTERNATIONAL SYMPOSIUM

By P. Braunstein
Université Louis Pasteur, Laboratoire de Chimie de Coordination, Strasbourg, France

An International Symposium on Polymetallic Activation was held at the Università di Parma, Italy, from the 13th to 15th September 1990, as part of a collaboration, supported by the European Commission, involving university laboratories at Strasbourg, Freiburg, Torino and Parma which carry out research on diverse aspects of polymetallic activation. An international panel of speakers presented plenary lectures giving the state of the art in their area, discussing and evaluating the results of this initiative and suggesting future actions aimed at developing and strengthening the links between European laboratories performing complementary research.

Polymetallic activation occupies a central position in organometallic and co-ordination chemistry as it has frontiers with the synthesis of new materials, with the study and applications of pure metals and metal particles, and brings an enormous insight into how organic substrates can interact with metal atoms and surfaces and undergo coupling/or decoupling reactions. The dynamics of clusters and of their ligands have also shown how uniquely an ensemble of atoms behave. The development of new catalytic processes requires a fundamental understanding of the elementary steps responsible for molecular activation and transformation. The desired high chemo-, regio- and enantioselectivity, essential for the manufacture of fine chemicals and pharmaceuticals, necessitates the development of more complex and sophisticated catalysts of a tunable nature. Molecular design and polymetallic activation thus become central themes. They need to be studied in greater depth and in a multidisciplinary manner, using the different techniques which are now available, but the costs of which require optimum utilisation of the equipment and co-operative research.

Professor A. J. Carty of the University of Waterloo, Ontario, Canada, presented the structural chemistry, hydrogen activation and substitution reactions associated with a series of tetracyan clusters of ruthenium or osmium, such as $\text{Ru}_4(\text{CO})_{11}(\mu_1\text{PPh})$ and $\text{Ru}_4(\text{CO})_{11}(\mu_2\text{PPh}_2)_2$. The latter undergoes reversible

![Fig. 1 A reversible hydrogen activation of $\text{Ru}_4(\text{CO})_{11}(\mu_1\text{PPh})$ under photochemical conditions leads to the static tetrahedral 60-electron cluster $\text{Ru}_4(\text{CO})_{10}(\mu_1\text{PPh})_2(\mu_1\text{H})_2$. This can be reversed under carbon monoxide](image)
hydrogen activation under photochemical conditions leading to \( \text{Ru}_4(\text{CO})_{10}(\mu-\text{PPh}_3)_2(\mu-\text{H})_2 \), a static tetrahedral 60-electron cluster, see Figure 1. This net 4-electron change on metal-metal bond formation is reversed under an atmosphere of carbon monoxide (1).

The role of the ligands (carbonyls, phosphido, phosphinidene ...) was shown to be very important for the chemistry of these and related clusters, and the wide variety of structural types encountered in the regime of \( M_n \) clusters having a 62-64 electron count was illustrated by X-ray diffraction results.

The theoretical nature of the metal-metal bonding in clusters of low nuclearity was discussed by Dr. C. Mealli, C.N.R., Florence, Italy. A number of systems were presented where the distance between the metal atoms cannot be used as a sufficient criterion for deciding about the bonding between the metals. Valuable pieces of information can however be obtained from the nature and energy levels of the molecular orbitals involved. It was also emphasised that a negative Overlap Population is not always in conflict with the existence of a direct \( \sigma \) bond (2).

The synthesis and co-operative reactivity of unsaturated heterobimetallic complexes containing early and late metals zirconium, hafnium, rhenium, and ruthenium, rhodium, iridium, palladium, platinum, respectively, were described by Dr. R. T. Baker, E.I. Du Pont de Nemours, Wilmington, U.S.A. Their synthesis involves metal complexes containing multiply-bonded terminal \( (\text{PR}_3)^- \) ligands which lead to built-in electronic unsaturation at the early metal centre, see below:

\[
\begin{align*}
[M] + M'[L]_{n+z} & \rightarrow 2L

\end{align*}
\]

\( [M] = (\eta^5-C_5\text{H}_5)_2\text{Zr}, (\eta^5-C_5\text{H}_5)_2\text{Hf} \)

\( [M'] = \text{Ru, Rh, Ir, Pd, Pt} \)

Reactivity studies have demonstrated the importance of the bridging ligands in allowing, amongst other things, different core structures (planar, bent, with metal-metal interactions) to be stabilised. For example, the \( d^2-d^8 \) complex \( (\eta^5-C_5\text{Me}_5)_2\text{Ta}(\text{PPh}_3)_2(\mu-\text{PPh}_3)_2\text{Rh}(\text{PMe}_3)_2 \), adds hydrogen across the \( \text{Ta} = \text{Rh} \) double bond, forming \( (\eta^5-C_5\text{Me}_5)_2\text{TaH}(\mu-\text{PPh}_3)_2\text{RhH}(\text{PMe}_3)_2 \) (3).

Professor E. Sappa of the Università di Torino, Italy, one of the partners in the European programme, presented reactions of homo- and heterometallic carbonyl clusters of iron, ruthenium and cobalt with functionalised alkynes and dialkynes. The flexibility of the metal core allows unusual bonding modes of the organic fragments to occur and the resulting clusters often display novel features of catalytic relevance (4). For example, the nucleophilic reactivity of acetylides co-ordinated to many metal centres represents a model of related behaviour on metal surfaces, where formation of new carbon-carbon, carbon-nitrogen or carbon-sulphur bonds may occur, see Figure 2. Some clusters have been found to catalyse selectively the homogeneous hydrogenation of dienes and alkynes (5) or represent possible models, isolable in the case of ruthenium, for the intermediates involved in the cobalt mediated co-oligomerisation of functionalised alkynes leading to heterocyclic products.

The construction of new bridging ligands in dinuclear and trinuclear cobalt complexes was presented by Dr. M. J. Mays of the University Chemical Laboratory, Cambridge, U.K. The coupling of small molecules or fragments such as \( \text{Ph}_2\text{P}, \text{RC=CR}' \), \( \text{CH}_2=\text{C}=\text{CH}_2 \) and \( \text{CO} \) may follow different pathways, and a high regio...
selectivity has been observed, depending on the
nuclearity of the initial cobalt complex, the
nature of the R or R' groups and the order of
addition of the ligands. Inorganic units may serve
as unique templates for the coupling of organic
moieties (6a). A different chemistry will take
place at a dimolybdenum centre (6b).

Professor K. Vrieze of Van't Hoff Instituut,
Amsterdam, The Netherlands, described the ac-
tivation of metal cluster-co-ordinated enamine by
hydrogen and carbon monoxide, see Figure 3. A
sequence of isomerisations which took place
about a Ru, chain of atoms was carefully
monitored. The diastereoselectivity of the reac-
tions was emphasised, illustrating the importance
of introducing chirality in such molecular
systems. Two processes were observed in an un-
precedented interconversion between
diastereoisomers of a linear tetraneuclear
ruthenium complex: a mdical mechanism and an
intramolecular conversion induced by carbon
monoxide addition.

The chemistry of carbon-carbon, carbon-
nitrogen and nitrogen-nitrogen multiple bonds
on clusters was described by Professor H.
Vahrenkamp of the Universität Freiburg, Ger-
momany, another member of the four-party joint
research project. By varying the ligands and the
metals in a systematic way (isoelectronic and
isolobal relationships) he described the basic
aspects of the cluster-surface analogy and various
substrate interconversions in the ligand sphere
(7), see Figure 4. The key influence of the
substrate bonding mode on its reactivity is il-
ustrated, for example, by the fact that the \( \mu_2\)–
\( \eta^1\)-C=CH unit is electrophilic at the outer
carbon atom, in contrast to vinylidene ligands in
mono- or dinuclear complexes. Selected examples
illustrated the pathway from the fundamental
study of cluster-ligands interactions to cluster-
mediated organic synthesis. The reversible and
diastereospecific insertion of the prochiral alanine
precursor, 2-acetamidoacrylic methyl ester, into
the metal-hydrogen function of the chiral clusters
HCoMM'\((\mu_2,-CR)Cp(CO)_3\), see Figure 5,
(where M = Ru, Os; \( M' = Mo, W; R = Me, Ph \))
was shown to be of the Markovnikov-type.

The diastereospecificity observed illustrates the
transfer of chiral information from a cluster to an organic substrate (8).

The preparation of unusual clusters, organophosphorus and organoboron cage compounds, and organic cyclic addition products of alkynes and alkenes by using the highly reactive intermediates generated in metal vapour reactions was described by U. Zenneck of the Universität Heidelberg, Germany. Mild reaction conditions may thus be used, owing to the enhanced reactivity which characterises bare metal atoms (9).

Professor L. A. Oro of the University of Zaragoza, Spain, presented a number of multinuclear rhodium and iridium complexes whose structures are largely controlled by binucleating N, N, N, O or N, S ligands. The stabilisation provided by these ligands enables different arrangements of metal atoms to be characterised. Their flexibility allows, in many cases, the promotion of intra- or intermolecular interactions. A linear tetrairidium complex was
Platinum Group Metals-Based Bimetallic Couples Used in Heterogeneous Catalysis

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<td>Hydrocarbon skeletal rearrangements</td>
<td>Cr-Pd, W-Ir, Re-Pt, Fe-Ru, Ru-Ni, Co-Rh, Rh-Ir, Ir-Pt</td>
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<td>Hydrogenation/isomerisation of carbon-carbon multiple bonds</td>
<td>Ru-Os, Ru-Ni, Os-Ni</td>
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<td>Hydrogenation of CO and CO₂</td>
<td>Mo-Fe, W-Os, Mn-Co, Fe-Ru, Ru-Co, Os-Rh, Co-Rh</td>
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<td>Hydroformylation of olefins</td>
<td>Fe-Rh, Ru-Co, Co-Rh</td>
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<td>Reductive carbonylation of nitro derivatives</td>
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</table>

shown to be an intermediate in the transannular oxidative addition of I₂ to an Ir₂ complex (10). Oxidative addition of I₂ to the triply heterobridged complex [Ir₂(μ-pz)(μ-SBu)(μ-MeO₂-C-C=CCO₂-Me)(CO)₂{P(OMe)₃}] (pz = pyrazololate), as shown in Figure 6 results in a remarkable change in the Ir-Ir distance from 2.614(2) to 3.626(2) Å (11).

Professor G. Predieri of the Università di Parma, Italy, presented some recent results obtained during the course of the joint research project on the use of homo- and heterobimetallic carbonyl clusters as precursors of heterogeneous catalysts. This important area of catalysis has been recently reviewed and the Table indicates the major role played by the platinum group metals in such mixed-metal cluster-derived heterogeneous catalysis (12). The pentanuclear cluster [NiOs₅(η-C₃H₅)(μ-H)₂{μ-Cu(PPh₃)}(CO)₅], supported on

Chromosorb and thermally activated under hydrogen, forms a heterogeneous catalyst for the hydrogenation-dehydrogenation of several substrates, in particular alcohols. It shows higher dehydrogenating ability than the systems derived from the parent cluster \([\text{NiOs}_8(\eta^2-C_2H_2)(\mu-H)(CO)_8] \) or from \([\text{NiRu}_8(\eta^2-C_2H_2)(\mu-H)(CO)_8] \) (13). The latter cluster has also been supported on alumina in the presence of potassium hydroxide and thermally decomposed, with the aim of preparing catalysts for ammonia synthesis which would work under milder conditions than the current industrial catalysts. Bimetallic particles were generated, as shown by energy-dispersive X-ray analysis. Although it was found that the \(\text{Ru}_2(CO)_6\)-derived catalyst was more than twice as active as the \(\text{NiRu}_2\)-derived catalyst for the same metal loading and at 400°C, the addition of small amounts of cobalt (0.1 per cent) or copper (0.05 per cent) to the 5 per cent ruthenium catalyst resulted in an increased productivity at lower temperature (14). It is known that ruthenium, promoted by alkali metals, is much more active than iron in ammonia synthesis and is less affected than iron by the poisoning effects of water and carbon monoxide but suffers much more from the inhibitory effects of hydrogen.

Finally, Dr. P. Braunstein, the co-ordinator of the European research project, described heterometallic complexes held together by diphosphine or phosphido bridges and which are good candidates for the study of site selectivity in heterometallic systems. The first complexes containing an alkoxysilyl ligand which forms a \(\eta^2-\mu_2\)-SiO bridge, where \(M\) is palladium or platinum were discussed, where the unexpected interaction between the oxygen donor and the soft metal centre was demonstrated by X-ray analysis and \(^1\text{H}\) NMR spectroscopy (15).

The unprecedented structure and topology of an octanuclear \(\text{Pd}_4\text{Mn}_4\) cluster containing bridging cyanide ligands was discussed. The highly symmetrical structure of this molecule constituted of two helices of opposite chirality (16) prompted its use as the "logo" for the Symposium, Figure 7.

The excellent local organisation by Professor A. Tiripicchio of the Università di Parma, Italy, who is a participant in the joint project and who has determined crystal structures for many of the speakers at this Symposium, and the limited number of participants, facilitated numerous excellent discussions.

The synergy between the different studies performed by the research groups represented at this Symposium was very obvious and was emphasised during the round-table discussion at the end of the meeting. Among the conclusions reached were that concerted European actions, which are also increasingly needed in industry, are essential to successfully perform competitive fundamental research; and that the high-level teaching facilities available in various Centres of Excellence must be optimised by encouraging the mobility of post-graduate and post-doctoral students and staff, and by co-ordinating complementary expertise.

It was felt that the areas covered by this Symposium are more topical than ever, and that continuity in performing such studies and training post-graduate students constitute major priorities. Initiatives were taken to promote these ideas, particularly at the European level.
Advances in the Study of Platinum Group Elements

Progress in the understanding of the mineralogy of platinum group metals worldwide is reported in The Canadian Mineralogist, 1990, 28, (3). Of the twenty-one papers included, twelve were presented at the annual meeting of the Geological and Mineralogical Associations of Canada (GAC-MAC) which was held in Montreal, in May 1989. The remainder are new papers, all relevant to the theme of the above title.

The section on occurrences consists of nine papers, commencing with the 1990 MAC Presidential address given by J. M. Duke on the implications of magmatic segregation process models for Kambalda-type nickel sulphide deposits. A unifying model of the magmatic mineralisation process in layered intrusions is proposed by A. J. Naldrett, G. E. Brügmann and A. H. Wilson. This attempts to account for the various platinum group metal concentrations found in different deposits of apparently similar genesis.

As these magmatic processes become better understood, the apparent exceptions to the rule, such as the Alaskan-type Tulameen deposits in British Columbia, attract greater interest. There, as discussed by G. T. Nixon, L. J. Cabri and J. H. G. Laflamme, platinum-iron-copper alloys and osmium-iridium-ruthenium minerals appear to have crystallised directly from a silicate magma. This paper serves as a link to the next section, which includes discussions on ophiolite deposits containing platinum group metals. It is suggested that sulphur concentration is the factor controlling mineralisation in a silicate matrix.

Hydrothermal processes for the transport and deposition of platinum group metals are also considered, including a study by J. H. Crocket of platinum group metal mineralisation in sulphide-rich deposits near to sub-sea hydrothermal vents on ocean ridges. For surface deposits, the importance of ground water transport involving fulvic acid and simple organic analogues is discussed by S. A. Wood.

A mineralogical study of the system platinum-antimony-tellurium has been carried out by W.-S. Kim and G. Y. Chao, and a new palladium-copper-tellurium-sulphur mineral species, Vasilite, is reported by A. V. Atanasov. While some of the deposits considered may never be economically viable, either for platinum group metal or base metal exploitation, the implications of the work reported for the overall understanding of the subject cannot be over-estimated.

J.H.F.N.
A Means to a Cleaner Environment

ENERGY EFFICIENT PLATINUM-CONTAINING FUEL CELLS TO BE INTRODUCED COMMERCIALLY IN THE EARLY 1990s

The twelfth National Fuel Cell Seminar held in Phoenix, Arizona, U.S.A. from 26th to 28th November 1990, was attended by some 450 delegates from 17 countries, representing both developers and potential users worldwide. "Fuel Cells – An Answer to a Cleaner Environment" was the key theme running throughout the conference. This was strongly linked to the firm belief that fuel cells would make an important contribution to the world’s energy needs over the next ten years as economically viable fuel cell power plants become commercialised. The conference heard that platinum containing phosphoric acid fuel cells (PAFC) are soon to be produced on a commercial basis. Both Fuji and Toshiba announced that they had opened PAFC production facilities in Japan during 1990. The key progress regarding development of Proton Exchange Membrane Fuel Cells (PEMFC) was the announcement of a U.S. Government sponsored programme, to be led by General Motors, to produce a PEMFC powered motor vehicle.

The conference reflected the growing extent of the multi-national collaborations that are now underway to develop fuel cell technologies. The Seminar Organising Committee comprised the United States Department of Energy, the Electric Power Research Institute, the Gas Research Institute, the National Aeronautics and Space Administration, and, for the first time, the Commission of the European Communities and the Fuel Cell Development Information Centre, Japan. Over half of the attendees were from Japan or Europe.

An Environmental Overview

The “Keynote Address” was given by J. Lents of South Coast Air Quality Management District (SCAQMD). Focus was directed towards the recently approved new U.S. Clean Air Act which will enforce ever more stringent emissions standards over the next 20 years. In Los Angeles in particular, the regulations will require 40,000 zero emission motor vehicles by 1998, increasing to 200,000 by 2003. This will provide a major incentive for the development of fuel cell powered vehicles. The SCAQMD is working with the U.S. Department of Energy to promote development of a viable fuel cell system. The new standards will also require greater efficiencies from the electricity generation industries. This will present further opportunities for the fuel cell developers.

The growing concern regarding environmental problems has accelerated Japan’s fuel cell research and development programme, according to T. Sugimoto from the New Energy Development Organisation (NEDO). Coupled with the increasing pressure to produce more efficient energy generation technology, this has led the Japanese Ministry of International Trade and Industry to expect fuel cell plants to be generating 1.9 million kW of power by the year 2000, and 8.3 million kW by 2010.

It was predicted by K. Joon of the Netherlands Energy Research Foundation that in Europe too, current energy generating technologies would not be able to comply with future emission standards. With the imposition of carbon dioxide constraints, he forecast that fuel cells would achieve 10 per cent penetration of the Dutch combined heat and power (CHP) market by the year 2010. In Europe the PAFC is generally regarded as the market opener for the higher temperature molten carbonate and solid oxide fuel cell systems. K. Seip of the Centre for Industrial Research, Norway, reported on his work using a model to quantify the benefits of fuel cells versus coal- and gas-fired electricity generation plants in terms of their effects on the natural environment, buildings and materials, socio-economic, and health and safety impacts. His model predicted that on health costs alone, it would be cost
effective to switch from coal produced to fuel cell produced electricity.

**Phosphoric Acid Fuel Cells for Stationary Applications**

Evaluation of PAFC demonstrator plants, both in the 50–200 kW CHP and multimegawatt utility power generation modes, and the progress being made towards commercialisation of the technology, were reviewed by several speakers from Japan, Europe and the U.S.A. In recent years progress has been greatest in Japan.

Activities at Fuji were described by R. Anahara. Following the successful demonstration of a 50 kW on-site cogeneration plant by Tokyo Gas Company, Fuji have now received orders for 31 of these units with options on another 50. Seven sets of 100 kW have also been ordered. Although mostly destined for Japanese gas companies, four of the 50 kW units will be supplied for demonstration programmes in Europe. Based on the experience gained of a 1 MW power plant during the Moonlight Project, Fuji is now planning to construct 5 MW plants suitable for electric utilities, in association with Kansai Electric Power Company. Compactness is seen as a key design feature that will be a requirement for urban installation. Fuji opened a semi mass production facility in November 1990 to meet the early demand for 50 kW and 5 MW power plants. The current production capacity is 15 MW per year. Improved cell performance, principally through improved catalysis by the platinum based electrocatalysts, was seen by Fuji as critical to the reduction of both the cost and the size of the entire plant. Current power densities had improved to 160 mW/cm², from 80 mW/cm² in 1986. The target performance was cited as 230 mW/cm² by 1992. Fuji were confident that these targets would be met.

Progress by Toshiba in commercialising the PAFC for both electric utility and on-site use, was discussed by T. Matsushita. Toshiba intend to commence production of the 11 MW units during 1995–96. Plant size would be about one third of the current size of the prototype nearing completion at Tokyo Electric Power’s Goi Thermal Power Station. Plant costs of $2000/kW were said to be competitive in Japan, although the fully commercialised target cost would be $1000/kW. For on-site systems Toshiba have supported the formation of a subsidiary company to International Fuel Cells (IFC), known as ONSI. Fifty-three 200 kW units have been ordered for U.S., Japanese and European customers. Toshiba also has its own programme for cogenerators in the 50–200 kW size range. They anticipate entering commercial production of these units in 1993. Matsushita reported that Toshiba had also opened a PAFC production plant during 1990, with current capacity of 10 MW/year. Although Toshiba are also working on molten carbonate electrolyte fuel cells (MCFC), they believe that it would be sometime into the 21st century before this technology could be commercialised. They saw the PAFC and MCFC playing a role alongside each other, rather than competing, from about the year 2010 onwards.

Progress on the 11 MW PAFC plant at Goi was outlined in more detail by N. Kato of Toshiba. The bulk of the plant has been installed, and process and control tests are currently ahead of schedule. The final fuel cell stack assemblies, being manufactured by IFC, are due to be installed early in 1991 with the plant becoming operational by the spring of the same year. Demonstration objectives will be to run for over 10,000 hours, with 3000 hours of uninterrupted operation, with electrical and heat efficiencies of 41.1 and 31.6 per cent, respectively. Several poster presentations described the operation of IFC’s pre-production 200 kW cogeneration plants in office and hotel situations. Several thousand hours of operational experience has now been gained by both the gas and electricity power companies in Japan.

In the United States, the major customer for the ONSI 200 kW units is Southern California Gas Company who will start taking delivery of the first of their ten units in 1992. David Moard reported that customer interest had been very high; he commented that...
of Partial Energy Service (PES), fuel cells would be a profitable business for Southern California Gas. In this scenario the gas company purchases the fuel cell, and installs and maintains the unit on the customer's property while the producer is responsible for performance guarantees, provision of spare parts, etc. The customer has no primary responsibility for the fuel cell or its operation, nor direct investment in the capital equipment.

Westinghouse Electric Corporation are proceeding with the development of their air cooled PAFC system. With improved cell and stack technology they have now achieved cell performance of 702 mV, with a decay of only 6mV per 1000 hours. The 2.5 kW demonstration stack has so far achieved 5300 hours of operation. The ultimate Westinghouse product will be a 400 kW module, and the first demonstration will be at Norsk Hydro in Norway. This plant will be fuelled with by-product hydrogen from the chloralkali process. The demonstration, currently at the design stage, is intended for start-up in mid 1992. Westinghouse see a niche market for the PAFC in industrial applications.

In Europe the major PAFC demonstration is currently the 1 MW plant being built into a new civic centre development in Milan. The plant is being installed by Ansaldo using fuel cell stacks supplied by IFC. Site work is nearly finished with installation of the fuel cell system due for completion in September 1991. It is intended to commence power generation by mid 1992. Westinghouse see a niche market for the PAFC in industrial applications.

Platinum Catalysts for Phosphoric Acid Fuel Cells

A paper on high stability platinum alloy electrocatalysts was presented by K. Tsurumi of Tanaka Kikinzoku Kogyo. He reported cell performances of 780 mV with the latest alloy material, compared to 680 mV with pure platinum systems. Using base metal dissolution as a guide to long term stability, this alloy showed very little decay in comparison to prior art alloys of platinum-vanadium, platinum-chromium, platinum-cobalt-chromium and platinum-nickel-cobalt. Platinum alloy electrocatalysts were also shown to have high activity for hydrogen oxidation in the presence of trace levels of carbon monoxide. At platinum loadings of 0.1 mg/cm² and with 2 per cent carbon monoxide in hydrogen, an alloy catalyst exhibited minimal over-potential at 200°C, although this performance declined as the temperature was reduced to 160°C.

A poster presentation by T. Ito of NE Chemcat Corporation, Japan described the production of a higher power density fuel cell system with improved cost performance by the use of platinum alloy catalysts with higher loadings of platinum than the conventional 10 per cent platinum supported on carbon. Platinum-iron-cobalt catalysts at 10, 20, 30 and 35 weight per cent platinum loadings gave performances of 734, 752, 765 and 769 mV, respectively, at 200 mA/cm². At 700 mV, this translated into 21, 36 and 39 per cent more power output with the higher loading materials compared to the conventional 10 per cent alloy catalyst. It was calculated that these increased power densities can lead to benefits which outweigh the extra cost of the catalyst.

Work at the Institute CNR-TAE in Italy on the influence of particle size of platinum catalysts in PAFCs was presented by N. Giordano. Catalysts with particle sizes ranging from 15–125 Å exhibited a particle size effect, as previously demonstrated by other groups, in which the smaller particles possessed intrinsically lower activity. Giordano believed that this was related more to a change in the proportion of specific crystal faces at the surface as the particle size changed, rather than to the influence of inter-crystallite separation as proposed by other workers.

Fuel Cells for Transportation Applications

Over the past two years there has been increased interest in the potential application of fuel cells to vehicular transportation. This has arisen due both to increased concern about, and regulation of, vehicle emissions in the United
States, and the recent technical advances in the performance of Proton Exchange Membrane Fuel Cells. For the first time, this year's seminar attached major importance to transportation applications.

Details of a major new programme, sponsored by the U.S. Department of Energy, to build an advanced reformate/air PEMFC power plant were revealed at the conference. The project will be led by the Allison Gas Turbine Division of General Motors, which will co-ordinate the effort between General Motors, Los Alamos National Laboratory, Ballard Power Systems, Dow Chemical Company and the South Coast Air Quality Management District. The overall aim of the six and a half year programme is an actual fuel cell/battery hybrid vehicle demonstration. Although it is intended that the fuel cell will take as much of the load as possible, batteries are included in the system to cope with part of the power surge demands. Target performances of the demonstration vehicle include fuel economy improvements of 60 per cent over conventional engines, a 40 per cent reduction in carbon dioxide emission, and a 90 per cent reduction of the emissions currently regulated in the U.S.A. A contract has been awarded for the first phase of the programme, which has the objective of producing a 10 kW power source system evaluator over a 24 month period. Component research and development will be carried out in this initial phase and will include studies to improve the efficiency of the platinum based electrocatalyst.

One of the greatest challenges in this programme will be the development of suitable methanol reformer technology. Several papers addressed reformer concepts. N. E. Vanderborgh of Los Alamos outlined the components of a reformer operating via the steam reforming route. For use with a PEMFC it is necessary to have three reactors in the fuel processing stage. After the initial fuel converter and shift reactors the hydrogen stream still contains 1 per cent carbon monoxide. To avoid severe poisoning of the platinum catalyst the reformate is passed through a preferential oxidation reactor, into which small quantities of oxygen are injected to selectively oxidise the carbon monoxide (in the presence of hydrogen) to the required levels of less than 10 ppm.

The benefits of a partial oxidation of methanol reforming process were outlined by R. Kumar of Argonne National Laboratory. Although less efficient than steam reforming, the direct heat transfer characteristics of this type of reformer facilitates good transient response to fluctuating load demands. This property is seen to be very important for a fuel cell automotive power system.

Ballard Power Systems of Canada will be producing the fuel cell stacks for the vehicle programme sponsored by the U.S. Department of Energy. In addition, D. Watkins reported that further applications for their PEMFC stacks include a 100 kW unit for a British Columbia bus programme, with an on-the-road demonstration by the end of 1992. Military and utility applications of the PEMFCs are also being considered. Demonstrations in small two-man submarines and at the Dow chloralkali plant in Sarnia, Canada, are currently underway.

Other fuel cell types being evaluated for transportation applications were also reported at the seminar. In particular, PAFCs have an application in the 50–120 kW range for buses, trucks and heavy duty vehicles. R. Kevala of Booz, Allen and Hamilton, and K. Okano of Fuji presented updates on the Department of Energy funded PAFC/battery hybrid bus project. A 25 kW brassboard design has been successfully evaluated against typical bus driving cycles. The next phase of the project will address the design of the test buses incorporating both a 50 kW fuel cell and a 132 amp-hour lead acid battery.

Submarine and Space Applications

Fuel cells continue to be developed for the more specialised space power requirements, and certain marine applications. In particular there were several presentations on the use of PEMFCs as air-independent submarine propulsion systems. W. Bette reported that Siemens are currently developing a 34 kW laboratory
module for this application. Performance targets are 540 mA/cm² and 684 mV per cell, with a cell active area of 1180 cm². Small single cells operating under 2 bar pressure of hydrogen and oxygen have exceeded this target and shown excellent stability up to 18,000 hours, with only 2 μV per hour decay. The cells comprised DuPont Nafion membranes and 4 mg of platinum/cm² electrode loading. Recent improvements in cell construction and water management have increased the current density to 700 mA/cm² at the rated cell voltage.

Emphasis on fuel cells for manned space missions is presently focused on the development of regenerative fuel cell systems, as evidenced by presentations from NASA, Los Alamos and the Hamilton Standard Division of United Technologies Corporation. The use of electrolyzers powered from solar arrays in conjunction with either alkaline or PEM fuel cells, to provide power during dark orbiting periods, offers the best opportunity as energy storage systems for the long duration space missions being planned for Mars and beyond. PEMFCs appear to be attracting favour due to their potential for longer term catalyst stability compared to the alkaline systems.

Conclusions

“Fuel cells are five years from commercialisation” has been a frequently used phrase for many years! We now, however, appear to have reached the time when this phrase can be stated more in truth than in false hope. Led by the Japanese companies, Fuji and Toshiba, the phosphoric acid fuel cell will soon become a practical reality for 50–200 kW combined heat and power applications. Worldwide concerns about pollution and global warming continue to increase, and in the coming years this will serve to broaden further the scope for commercialisation of these fuel cells. Similarly, a major new opportunity for the Proton Exchange Membrane Fuel Cell has opened up, with the start of programmes to build fuel cell/battery hybrid power systems for transportation, which could lead to the development of pollution free motor vehicles. As noted by several speakers, “the future for fuel cells is brighter now than ever before.”

Quasicrystals in Rapidly Solidified Alloys

Five-fold electron diffraction patterns were found in a rapidly solidified aluminium-palladium alloy in 1978. Although a number of quasicrystals have since been identified in particular alloys of aluminium with a platinum metal, no systematic study has been made.

Now a series of papers on the topic, reporting work carried out in the P. R. China, has been published in the J. Less-Common Met., 1990, 163, (1). An overview of quasicrystals in aluminium-transition metal alloys in general, and aluminium-platinum group metals in particular, is presented by K. H. Kuo (Pages 9–17). Aluminium-ruthenium and aluminium-osmium alloys have been studied by Zhong-Min Wang, Yi-Qun Gao and K. H. Kuo, mainly by transmission electron microscopy. They observed icosahedral quasicrystals in melt-spun ribbons of Al,Ru, but not in Al,Os. Decagonal quasicrystals form readily in the latter, but only rarely in the former (Pages 19–26).

Rong Wang, Lina Ma and K. H. Kuo have discovered decagonal quasicrystals in both rapidly solidified Al,Rh and Al,Ir, and in addition have found two new hexagonal aluminium-rhodium phases (Pages 27–35). L. Ma, R. Wang and K. H. Kuo confirm the presence of decagonal quasicrystals in rapidly solidified Al,Pd, but not in Al,Pt (Pages 37–49).

Grove Fuel Cell Symposium

The successful First Grove Cell Symposium, held in London, England during September, 1989, was reviewed here immediately after the conference (D. G. Lovering, Platinum Metals Rev., 1989, 33, (4), 169–177). A second meeting is now planned, and this will again be held at the Royal Institution, London, from 24th to 27th September, 1991.

In addition to those already engaged in fuel cell technology, the Symposium is expected to be of particular importance to people involved with advanced energy systems, and those responsible for energy and environmental policy making.

Further information can be obtained from: Kay Russell, Elsevier Seminars, 256 Banbury Road, Oxford OX2 7DH, England.

The Photogeneration of Hydrogen

EFFECTIVE PLATINUM-GOLD COLLOIDAL CATALYSTS

By Anthony Harriman
Center for Fast Kinetics Research, University of Texas at Austin, Texas, U.S.A.

Bimetallic colloidal particles, comprising variable mol fractions of platinum and gold, function as effective catalysts for the photochemical production of hydrogen under sacrificial conditions. With increasing mol fraction of gold there is a significant decrease in the rate of hydrogenation of the reactants such that higher yields of hydrogen are attainable.

Colloidal dispersions of platinum, stabilised with various surfactants, have been used as catalysts for the photoreduction of water to hydrogen as a means of storing solar energy in the form of chemical potential (1, 2). Hydrogen evolution can be extremely efficient over short irradiation periods but, unfortunately, the colloids catalyse hydrogenation of unsaturated bonds as the reaction proceeds (3). The total yield of hydrogen is limited, therefore, by the susceptibility of the reactants towards hydrogenation. Often, the performance of a catalyst can be improved markedly by forming an alloy with a compatible metal and it is known that adding small amounts of gold to macroscopic platinum catalysts inhibits alkane hydrogenolysis while increasing the rate of dehydrogenation (4). Preliminary studies have suggested that this approach may be applied to highly dispersed catalysts supported on graphite (5), and we have shown recently that bimetallic platinum-gold colloids can function as efficient hydrogen-evolving catalysts in solar energy storage devices operated under ambient conditions (6).

Results and Discussion

Colloidal dispersions of platinum and gold were prepared by γ-radiolysis of mixtures of Na₂PtCl₄ and NaAuCl₃ in nitrogen-saturated water at pH7 containing Carbowax 20M (1 x 10⁻³ mol/dm³) (1, 2). The total metal concentration was fixed at 5 x 10⁻⁴ mol/dm³ and the mol fraction of each metal was varied from 0 to 1. The actual composition of each colloidal dispersion, after treatment with ion-exchange resins, was determined by atomic absorption and the average particle sizes were established by high resolution transmission electron microscopy. X-ray emission spectroscopy carried out in conjunction with scanning transmission electron microscopy confirmed that individual particles contained both platinum and gold but their relative intensities, compared to the atomic absorption results, suggested segregation with surface enrichment of gold.

The platinum-gold colloids were used to catalyse hydrogen-evolution from a well-established sacrificial photosystem using zinc tetrakis(N-methyl-4-pyridinium)porphyrin as photosensitiser, methyl viologen (MV₂⁺) as electron relay, and dihydronicotinamide adenine dinucleotide (reduced form) as sacrificial electron donor in nitrogen-saturated water at pH4 (7). Upon illumination of this photosystem with visible light, the reducing radical MV⁺· is formed in high yield and it persists for many hours in the absence of oxygen. Photolysis in the presence of a colloid ([metal] = 2 x 10⁻⁴ mol/dm³) resulted in evolution of hydrogen. As the mol fraction of gold increases, there is an increase in the rate of evolution of hydrogen (RH₂) until an optimum value is reached at about 20 to 30 per cent gold after which RH₂ decreases. There is also a progressive increase in the total yield of hydrogen on exhaustive photolysis ([H₂]) as the mol
fraction of gold increases. Overall, the optimum composition for the catalyst appears to be about Pt₆Au₄.

The increased yields of hydrogen obtained with increasing mol fraction of gold are attributed to inhibition of hydrogenation of the reactants by surface gold atoms. With mol fractions of gold exceeding 20 per cent, hydrogen is not consumed upon prolonged irradiation although this is a serious problem for colloids containing little or no gold. Many of the platinum atoms on the colloid surface are prevented from functioning as active catalytic hydrogen evolving sites because of specific adsorption. The adsorbate may be H⁺ atoms, MV²⁺, MV⁺⁺ or surfactant used to protect the colloid against flocculation. Incorporating gold atoms into the colloid surface dilutes platinum-platinum co-ordination sites where specific adsorption occurs, allowing surface platinum atoms to operate as active hydrogen sites.

In hydrogen-saturated aqueous solution at pH4 containing colloidal platinum (2 x 10⁻⁴ mol/dm³), hydrogenation of MV²⁺ occurs very slowly. The reducing radical MV⁺⁺, however, is hydrogenated readily under ambient conditions and it is apparent that this reaction is responsible for consumption of hydrogen during photolysis. The rate of hydrogenation of MV⁺⁺ (Rᵥ₅⁴), as catalysed by the various colloids, was measured by electrochemical methods. It was found that Rᵥ₅⁴ decreased significantly with increasing mol fraction of gold. The inhibition of hydrogenation of MV⁺⁺ on the bimetallic particles is a consequence of the decreased mobility of H⁺ atoms (8) and the increased energy of adsorption of H₂ (9, 10).

This study has shown that the use of bimetallic platinum-gold colloids can improve the rates and yields of hydrogen evolution from photosystems in which one or more of the reactants is susceptible towards hydrogenation. This arises because gold atoms at the surface of the colloidal particle inhibit specific adsorption and hydrogenation of the reactants. This behaviour, which is well known for macroscopic catalysts (11, 12), shows the advantages that may be gained by using alloys in place of pure metals.

Acknowledgements

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Cleavage in Iridium Crystals

As the only metal with good mechanical properties in air at temperatures above 1600°C, iridium is used for the crucibles in which presintered mixed oxides are melted during the growing of high purity single crystals for electronic applications. Fabrication techniques have been developed to enable these crucibles to be manufactured to the required high standard, none-the-less the factors that govern the deformation of iridium are not yet fully established.

Metal-Hydrogen Systems

A REVIEW OF PALLADIUM AND PALLADIUM ALLOYS

The second International Symposium on Metal-Hydrogen Systems, Fundamentals and Applications, was held from the 2nd to 7th September 1990, in Banff, Canada. This survey outlines a selection of the papers presented at the conference on work involving hydrogen interaction with the platinum group metals.

The chairman of the organising committee, Professor F. D. Manchester, opened the conference by commenting on the many new developments that have arisen within the field of metal-hydrogen studies since the 1988 Symposium in Stuttgart — perhaps most notably as a consequence of the "cold fusion" controversy which has brought many aspects of metal-hydrogen research to world attention.

Cold Fusion

As a reflection of this particular area of interest, a significant proportion of the papers were concerned with various aspects of cold fusion.

A group from Japan, K. Tsuchiya (Tokyo National College of Technology), K. Ohashi (Tamagawa University), Y. H. Ohashi and M. Fukuchi (Keio University) approached the question by estimating the nearest neighbour distance between two deuterium atoms in a f.c.c. palladium lattice using the Schrödinger equation, taking into account the electronic screening cloud. They estimated the D-D distance to be 0.66 Å, which is smaller than the molecular value of 0.74 Å.

Several researchers tackled the question of electrolytically induced cold fusion by using various techniques to determine the maximum possible deuterium content of palladium.

An in-situ X-ray diffraction observation of a palladium foil cathode during electrolysis of heavy water solution, particularly concentrating on the nature of the transformation into the deuteride (β-PdD₂) phase, was reported by T. Yamamoto, T. Oka and R. Taniguchi from the Osaka Prefectural Radiation Research Institute, Japan. The lattice constants observed were converted into deuterium concentrations and potentials by the use of known data on the phase relation. A maximum deuterium content, expressed as an atomic ratio, D:Pd = 0.80 at room temperature was reported.

A limiting concentration of D:Pd = 0.78 was reported by P. R. Stonadge, M. J. Benham, S. M. Bennington, J. P. A. Fairclough and D. K. Ross from Birmingham University, who used time-of-flight neutron diffraction and concurrent resistivity measurements to investigate electrochemical charging of palladium rods.

On a positive note, an alternative approach taken by researchers H. Uchida, Y. Matsumura, T. Hayashi and M. Kawachi (Tokai University, Japan) was the use of GM- and NaI-scintillation counters to measure γ- or X-ray emissions from an electrolytically deuterided palladium electrode. They reported 20 to 35 per cent excess radiation during deuteriding of palladium wire in KOD solution at greater than 600 mA/cm² and 20 V but no excess radiation on hydriding of palladium in KOH at similar current and voltage input.

Negative results were again however reported by Y.-Q. Lei, Y.-L. Chen, D.-L. Sun, J. Wu and Q.-D. Wang from Zhejiang University, China; no excess heat or γ-ray emission higher than background were detected during a 290 hour electrolysis of deuterium oxide using a palladium bar cathode.

The subject of cold fusion was raised in debate again at the conclusion of the conference. Despite the huge number of negative results, and apparent irreproducibility of the effect, some delegates cautioned against complete dismissal of the phenomenon.

Electronic Structure

Electronic band structure calculations featured in several of the reported theoretical studies of metal hydride systems. In work motivated once

again by interest in cold fusion possibilities, A. C. Switendick from the Sandia National Laboratories in New Mexico, reported on the use of band structure and density of state calculations to determine the stability of the palladium deuterides PdD, PdD₂, and PdD₃. The only stable system was concluded to be PdD.

The use of density of state calculations to analyse the Pd-H, alkali metal-H and H-H interactions in the recently synthesised hydrides Na₃PdH₁₃ and Li₃PdH₁₃, was reported by M. Gupta (Université Paris-Sud, France) and W. M. Temmerman (Daresbury Laboratory, Warrington, UK). Since the pure intermetallic compounds cannot be synthesised in the absence of hydrogen, such calculations have provided a valuable insight into the role of hydrogen atoms in the lattice.

**Order-Disorder Transformations**

An area of study in which the platinum group metals featured prominently was that of order-disorder transformations. Professor T. B. Flanagan of the University of Vermont opened a session on this topic by reviewing literature evidence and presenting recent observations of how hydrogen can induce lattice mobility in metals, and lattice changes in disordered alloys. There is segregation of palladium-nickel alloys into palladium- and nickel-rich regions under conditions of ultra high hydrogen pressure and temperatures greater than 493 K, and there is also evidence that the palladium-rhodium-hydrogen system may be subject to segregation on a small scale. Under high pressures of hydrogen, disordered Pd₀.₅Cu₀.₅ and Pd₀.₅Ag₀.₅ transform to ordered tetragonal structures. At $P_{H_2} > 1$ MPa and $T > 450$ K, disordered Pd₀.₅Mn transforms to an ordered form which has an increased hydrogen solubility. This can be seen as a variation on Le Chatelier’s Principle; if a disordered alloy can dissolve more hydrogen by either ordering or segregating then the stress is reduced.

Two papers contributed by researchers B. Sobha, B. Coluzzi, C. Costa and F. M. Mazzolai of the University of Perugia, Italy, reported on a combined study of long range and short range diffusion relaxation processes, by Gorsky relaxation and internal friction measurements, respectively, designed to compare the local motion of hydrogen in the ordered and disordered Pd₁Mn system. It was concluded that the relaxation processes appear to be due to stress assisted hydrogen interstitial reorientation processes.

A comprehensive study of hydrogen induced ordering in palladium-manganese alloys over the wider composition range 10 to 31 per cent manganese, investigated by metallography, X-ray and electron diffraction studies, and by electrical resistance measurements, was presented by K. Baba, Y. Niki and Y. Sakamoto from Nagasaki in collaboration with T. B. Flanagan.

**Hydrogen Solubility and Diffusivity**

The wide range of papers reporting on aspects of hydrogen solubility and diffusivity in palladium and palladium alloys again reflects continued special interest in the properties of this element among its congener elements in the platinum group, and indeed among other metals.

A paper by American workers, G. J. Thomas, S. E. Guthrie, (Sandia National Laboratory), R. W. Siegel and J. A. Eastman (Argonne National Laboratory) reported pressure-composition measurements on nanophase palladium, investigating the effects of high surface:volume ratio on hydrogen-metal interactions. It was found that in comparison with coarse grained materials, there is an increase in the α-phase solubility, but that the β-phase hydrogen:palladium solubility limit is decreased.

Thermodynamic parameters of hydrogen and deuterium absorption and desorption by palladium as derived by calorimetry were reported in a paper by W. J. Luo, J. D. Clewley and T. B. Flanagan of the University of Vermont. It was found that, within the limits of experimental error, the enthalpies of protide (deuteride) formation and decomposition were equal, and further that there is no evidence of any anomalous excess heat evolved in the PdD system as compared to PdH.

Although the stability of palladium hydride itself tends to be too high for convenient kinetic
study of its formation and decomposition, Z. Gavra, J. R. Johnson and J. J. Reilly of Brookhaven National Laboratory, New York, reported the use of \( \text{Pd}_{8.80} \text{Ni}_{8.15} \) as a suitable substitute. Experiments carried out with the hydride particles suspended in \( \eta \)-undecane revealed the decomposition kinetics to be in accord with a phase controlled boundary model in which the rate limiting process is the phase transformation taking place at the interface between the unreacted hydride core and a hydrogen saturated metal product layer (shrinking core model). The model is to be tested in the future with other systems.

A poster by H. Züchner and T. Rauf from the University of Münster, Germany, reported derivation of pressure-composition isotherms for the palladium-hydrogen and palladium-silver-hydrogen systems by using an electrochemical bielectrode charging method. This was found to be a simple and convenient technique provided certain specific conditions, such as using thin foils and low charging current densities, are adhered to in order to avoid anomalies in systems where phase transformations occur.

Solubilities and thermodynamic quantities of hydrogen in palladium-ytterbium solid solution alloys in the composition range 2.0 to 8.0 atomic per cent ytterbium, as determined from absorption pressure-composition isotherms between 273—473 K and hydrogen pressures up to 100 Torr were reported by F. L. Chen, M. Furukawa and Y. Sakamoto from Nagasaki University. Plateau pressures corresponding to the \( \alpha \beta \) phase equilibrium decrease with ytterbium content. Results were compared with previously studied palladium-rare earth alloy-hydrogen systems.

Pressure-composition and resistivity-composition relationships derived by an electrochemical technique at 298 K and 323 K for palladium alloyed with 1, 2 and 4 atomic per cent scandium were presented by R.-A. McNicholl and F. A. Lewis of the Queen’s University, Belfast. In accordance with palladium-scandium being an expanded alloy, the absorption plateau pressures decrease with increasing alloy content but a somewhat unique invariance of the desorption plateaux was observed.

Also dealing with the same alloy system, U.S. investigators, T. J. Udovic, J. J. Rush (National Institute of Standards and Technology, Gaithersburg) and H. Schone (College of William and Mary, Williamsburg) in collaboration with I. S. Anderson from the Paul Scherrer Institut, Switzerland, reported on the use of inelastic neutron scattering in studying the effect of scandium impurity atoms on the vibrational density of states of hydrogen absorbed in palladium. Preliminary analysis of spectra obtained at 296 K and 80 K with hydrogen concentrations of 2 per cent and below, suggested hydrogen trapping of less than 1 per cent by the scandium atoms in a 2 per cent scandium alloy, and the existence of clusters looking like \( \beta \)-phase but modified by having a central scandium atom.

In a further analysis of the palladium-platinum-hydrogen system F. A. Lewis, S. G. McKee and R.-A. McNicholl (Queen’s University, Belfast) reported that relationships between increment of specific resistivity and hydrogen content, \( n \), for the higher platinum content alloys seemed representable to a good approximation by a common curve of similar type to “Nordheim” forms of relationships between resistivity and composition appropriate to substitutional alloys. Assessments were made as to how far deviations from the common curve in the case of palladium and the lower platinum content alloys could be accounted for in terms of coexistence of phases with differing levels of hydrogen occupation.

A paper presented by R. V. Bucur and N. O. Ersson from the University of Uppsala, Sweden, with the help of X. Q. Tong (Belfast), reported work on \( \text{Pd}_{77} \text{Ag}_{23} \) and pure palladium samples designed to investigate the dual influence of foreign atoms and defects in a host palladium lattice on the diffusivity and solubility of hydrogen.

**Amorphous Alloys**

The work reported on amorphous alloys included a study by investigators K. Tanaka, T. Araki and T. Abe (Nagoya Institute of Technology, Japan) of thermal desorption spectra of hydrogen on glassy and crystalline \( \text{Zr}_2 \text{Pd} \) alloys. By simulation analysis using plural Gaussian curves to reproduce the different possible
site energy distributions of the hydrogen atoms (which are dependent on their metal atom environments), they deduced that in the glassy alloy, hydrogen atoms sit on Zr₁, Zr₁Pd and Zr₁Pd₂ type sites, whereas in the crystalline alloy, they sit only on the Zr₄ sites at low hydrogen contents.

O. Yoshinari from Nagoya Institute of Technology, Japan and R. Kircheim from Max Planck Institute, Stuttgart reported that the solubility of hydrogen in amorphous Pd₇₃.₁₇X₄.₈Si₈ (X = silver, copper, chromium, iron or nickel) alloys decreased in comparison with solubility in amorphous Pd₄₇Si₁₄. Diffusion coefficients were quite different in various ternary palladium-silicon alloys but this could be attributed to differing activation energies when a constant reference diffusivity was assumed.

Instrumental Techniques

A number of papers dealt with the use of various instrumental techniques for exploring aspects of metal-hydrogen interactions. A paper by D. H. W. Carstens and P. D. Encinias (Los Alamos National Laboratory, New Mexico) involved the use of Laser-Raman Spectroscopy for studying hydrogen isotopic exchange over palladium metal. A joint U.S. group from Washington University, St. Louis and Iowa State University, Ames (D. B. Baker, M. S. Conradi, R. E. Norberg, D. R. Torgeson and R. G. Barnes) presented a paper on novel measurements of nuclear spin cross-relaxation in metal hydrides using NMR. D. K. Ross, M. W. McKergow and D. G. Witchell (University of Birmingham) with J. K. Kjems (Riso National Laboratory, Denmark) reported the use of diffuse neutron scattering to monitor super lattice reflections as the deuterium atoms order at the 50 K anomaly in palladium-deuterium.

Applications

Promising practical applications involving the platinum metals were proposed in a number of papers presented. A group from the Max Planck Institute in Stuttgart (H. H. Uchida, H.-G. Wulz and E. Fromm) have observed remarkable enhancement of hydrogen dissociation if nickel, iron or palladium, acting as catalysts, are present on the surface of oxidised titanium or intermetallic storage materials. This may prove a significant advance in the development of poisoning-resistant hydrogen storage systems. A promising material for a hydrogen separation membrane was reported by M. Amano, M. Komaki and C. Nishimura (National Research Institute for Metals, Tokyo, Japan). Palladium plated vanadium-15 atomic per cent nickel alloy membranes show good resistance to hydrogen embrittlement while having superior hydrogen permeability compared to palladium.

Concluding Remarks and Future Developments

The conference concluded with a rapporteur session in which it was agreed that while some aspects of metal-hydrogen research have reached maturity, the future holds many openings and scope for development of new areas of study particularly, for example, examination of bonding theories including the idea of pairing interactions, and exploring the realm of new intermetallic materials.


R.-A. McN.

Palladium Membrane Reactors

The oxidative dehydrogenation of cyclohexane can take place with high yield when a palladium membrane is used to divide the reactor into reaction and separation sections. In order to establish the effect of the gas flow patterns when a sweep gas is used to remove the permeated hydrogen, five ideal flow models have been analysed and compared by N. Itoh, Y. Shindo and K. Haraya of the National Chemical Laboratory, Tsukuba, Japan (J. Chem. Eng. Jpn., 1990, 23, (4), 420-426).

Concurrent, counter current, plug-mixing, mixing-plug and mixing-mixing models were considered. It was found that the highest performance was shown by the second of these, where the feed gas on one side of the palladium membrane flows in the opposite direction to the sweep gas on the other.
Isomers of Platinum(II) and Palladium(II) Complexes

PREDICTING THE DIRECTION OF ISOMERISATION AND RELATIVE THERMODYNAMIC STABILITY

By Professor Yu. N. Kukushkin
The Lensoviet Institute of Technology, Leningrad

Geometrical isomers of platinum(II) and palladium(II) differ substantially in their chemical and biological properties. Under certain conditions one isomeric compound can transform into another. It is essential for chemists to be aware of the probable direction of the isomerisation process, and to predict which isomer is likely to be relatively more stable. The rules in this paper will permit such judgements to be made.

Complex compounds of platinum(II) have played an important part in the formation and development of co-ordination theory, and this has given a strong impetus to the growth of inorganic chemistry. The existence of two isomeric forms for the PtX₂ₐ compounds (where A is amine, and X is anion) allowed Werner to conclude that platinum(II) complexes have square-planar structures (1). These isomeric forms are a result of the cis- and trans- locations of ligands A and X.

Later, the conclusion about the square-planar structure of platinum(II) complexes was repeatedly confirmed by various physical and chemical methods of investigation.

Isomeric compounds of platinum(II) differ significantly in their reactivities, and many of the chemical methods used for the identification of individual forms are based on this (2). Different rates of substitution of ligands often result in a substantial difference in the catalytic properties of two isomeric complexes. A remarkable discovery was made twenty years ago when it was found that cis-[PtCl₂(NH₃)₂]₁ had clearly pronounced anti-cancer properties, while its trans-isomer was completely inactive (3,4). The same picture could be observed for other diaminedihalogen complexes of platinum(II). This discovery was used as a basis for a perceived application in medicine; namely, the use of co-ordination compounds for the chemical treatment of cancer.

Isomeric compounds are often different in their thermodynamic stabilities. Thus, Chernyaev and his co-workers established that the total energy of trans-[PtCl₂(NH₃)₂]₁ is about 13 kJ/mol less than that of the cis-isomer (5). Thus, under certain conditions, it can be expected that cis-[PtCl₂(NH₃)₂]₁ will undergo isomerisation into trans-[PtCl₂(NH₃)₂]₁. The existence of isolable isomeric pairs is caused by the inertness of platinum(II) complexes. Square-planar complexes of nickel(II) are more labile than platinum(II) complexes; for this reason, cis- and trans-isomeric pairs are almost unknown for nickel(II) complexes. Palladium(II) complexes have intermediate lability. Therefore, isomeric cis- and trans-pairs of palladium(II) are fewer in number than for platinum(II), but are more numerous than for nickel(II).

Experimental evidence shows that the isomeric complexes of platinum(II) and palladium(II) interconvert, often spontaneously or in the presence of catalytic agents. Sometimes, trans-configuration complexes transform to their respective cis-configuration complexes, but more
frequently this occurs the other way round, that is the \textit{cis}-form being less stable converts to the \textit{trans}-form. These conversions can be observed both in the solid phase and in solution. For example, the complex [PtBr$_2$(NH$_3$)$_2$] isomerises into \textit{trans}-[PtBr$_2$(NH$_3$)$_2$] at 25$^\circ$C (6), while with \textit{trans}-[PtCl$_2$(py(Et,SO)] (where py is pyridine and Et is ethyl), the reverse takes place, and it isomerises into \textit{cis}-[PtCl$_2$(py(Et,SO)]) at 134$^\circ$C (7).

Predicting the direction of isomerisation is very important for chemists. If such a prediction can be made, then the relative thermodynamic stabilities can be predicted simultaneously for individual isomeric complexes.

Different approaches can be used to explain the direction of isomerisation. Many facts about the isomerisation of platinum(II) and palladium(II) complexes have been considered by the author with regard to the \textit{trans}-effect of the ligands (2). As a result, a substantial amount of experimental data has been explained and the direction predicted for yet unknown isomerisation processes (8, 9).

The \textit{trans}-effect phenomenon has kinetic and static aspects. In a study of the kinetic and static aspects of the phenomenon, two respective series of ligands are obtained.

Since isomerisation is connected with the dynamic side of the said phenomenon, then for the most common ligands the \textit{trans}-effect series can be written as follows: H$_2$O $<$ NH$_3$, amines $<$ Cl$^-$ $<$ Br$^-$ $<$ NO$_2^-$ $<$ PR$_3$, R$_2$SO $<$ CO $<$ CR$^-$... It should be noted that ligands are arranged in order of increasing \textit{trans}-effect. The more to the right a ligand is in the \textit{trans}-effect row, the greater its lability-producing action will be.

In order to predict the direction of geometric isomerisation for platinum(II) and palladium(II) complexes, it is necessary to select a neutral ligand with the lowest \textit{trans}-effect to use as an indicator. The isomerisation goes in the direction which results in the formation of a complex where that ligand will be located opposite another ligand with the smallest \textit{trans}-effect. If, in the complex in question, the indicator ligand is located opposite a ligand with the next smallest \textit{trans}-effect, then such a compound should not isomerise.

As was noted above, the following process takes place in the solid phase at 25$^\circ$C:

\[
\begin{array}{c}
\text{NH}_3, \text{Br} \\
\text{Pt} \\
\text{NH}_3, \text{Br}
\end{array}
\xrightarrow{\text{cis}}
\begin{array}{c}
\text{NH}_3, \text{Br} \\
\text{Pt} \\
\text{Br}, \text{NH}_3
\end{array}
\]

In the initial compound, the ammonia molecule has the lowest \textit{trans}-effect and the bromide ion has the greatest. Thus, in the initial compound, both of the ammonia molecules will be prone to isomerisation. Isomerisation takes place in the direction of formation of the \textit{trans}-[PtBr$_2$(NH$_3$)$_2$] complex wherein the ammonia molecules are located opposite the ligand having the lowest \textit{trans}-effect, (that is \textit{trans} to themselves).

In contrast, \textit{trans}-[PtCl$_2$(py(Et,SO))] isomerises into the \textit{cis}-configuration compound:

\[
\begin{array}{c}
\text{py} \\
\text{Cl} \\
\text{Pt} \\
\text{Cl}, \text{Et,SO}
\end{array}
\xrightarrow{\text{trans}}
\begin{array}{c}
\text{Cl} \\
\text{py} \\
\text{Pt} \\
\text{Cl}, \text{Et,SO}
\end{array}
\]

In the initial complex the pyridine molecule has the lowest \textit{trans}-effect, while the greatest \textit{trans}-effect is exhibited by the diethyl sulphoxide molecule co-ordinated to platinum(II) by its sulphur atom. Thus, in the initial complex, pyridine is labilised by the \textit{trans} diethyl sulphoxide ligand with its strong \textit{trans}-effect and so isomerisation takes place. The molecule of pyridine in \textit{cis}-[PtCl$_2$(py(Et,SO)]) is less labile, and this complex happens to be more stable thermodynamically.

Two more examples from numerous experimental results will now be considered. Thus, it has been established that the following process takes place in the solid phase (10):

\[
\begin{array}{c}
\text{Me} \\
\text{PMe,Ph} \\
\text{Pt} \\
\text{Cl}, \text{PMe,Ph}
\end{array}
\xrightarrow{\text{cis}}
\begin{array}{c}
\text{Me} \\
\text{PMe,Ph} \\
\text{Pt} \\
\text{PhMe,P}
\end{array}
\]

Since in these complexes the methyl ligand has the greatest \textit{trans}-effect, the phosphine molecule...
is labilised and hence isomerisation occurs. The process occurs in the given direction despite the fact that the other phosphine molecule is moving from the position trans to the chloride ligand into a trans-position relative to the phosphine ligand, that is from a ligand with a somewhat greater trans-effect towards a ligand having the greatest trans-effect. The important thing is that the phosphine molecule moves away from the ligand having the greatest trans-effect.

It has been established that the use of sulphamic acid to remove two nitro-ligands from the \( \text{[Pt(NO}_2\text{)}_2\text{(H}_2\text{O)}_2\text{]} \) complex in a water medium leads to the formation of cis-\( \text{[Pt(NO}_2\text{)}_2\text{(H}_2\text{O)}_2\text{]} \), which would then isomerise into trans-\( \text{[Pt(NO}_2\text{)}_2\text{(H}_2\text{O)}_2\text{]} \) (11). Both of these processes are caused by the high trans-effect of the nitro-ligand, with isomerisation proceeding in accordance with the rule.

Isomerisation of complexes in the solid state can be clearly demonstrated using differential thermal analysis (DTA) curves. In many cases, isomerisation is accompanied by an exothermic peak, as for example, for cis-\( \text{[PtBr}_2\text{(NH}_3\text{)}_2\text{]} \). Frequently, isomerisation shows on the DTA curve as coupled endo- and exothermic peaks, as for example, for trans-\( \text{[PtCl}_2\text{py(Et}_2\text{SO)}\text{]} \). The endothermic peak corresponds to the melting of the initial complex, while the following exothermic peak reflects two processes: isomerisation of the complex and crystallisation of the isomerisation products from the melt. Identical coupled endo- and exothermic peaks can also be observed during isomerisation of cis-\( \text{[PtMeCl(PMe}_2\text{Ph)}_2\text{]} \) (10). Thus, the presence of an exothermic peak and, especially, of characteristic coupled endothermic and exothermic peaks (without any change in mass in both cases) can point to the isomerisation process.

Since in many cases, platinum(II) and palladium(II) complexes isomerise without any change in mass, it may be concluded that, in the absence of a solvent, isomerisation proceeds without loss of ligands, that is in an intramolecular manner. Probably, a complex of tetrahedral type is an intermediate in the isomerisation process (2).

Thus, using the rule described, it becomes possible to explain comprehensively the isomerisation processes which take place both in the solid phase and in solution.

A Russian proverb states that: "There are no rules without exceptions", and this rule also has exceptions. In particular, the rule does not describe all of the experimental facts for the isomerisation of \( \text{[PtX}_2\text{(PR)}_2\text{]} \)-type phosphine-halogenide complexes. On the other hand, it is quite possible that this rule holds true not only for platinum(II) and palladium(II) complexes, but also for the square-planar complexes of nickel(II), rhodium(I), iridium(I) and gold(III), that is for complexes with a \( d^1 \)-electron configuration of the central atom. As was noted previously, the square-planar complexes of nickel(II) are rather labile, and for this reason both cis- and trans-isomeric forms are extremely unlikely to be encountered for \( \text{[NiX}_2\text{L]} \)-type compounds. However, if we want to see which of the two possible forms exists, then it will be the particular form in whose direction the isomerisation process should be taking place.

No doubt there are different approaches which could be used to explain the direction of isomerisation processes in square-planar complexes. Thus, Jørgensen has formulated the ligand anti-symbiosis principle which enables a judgement to be made about the relative thermodynamic stability of isomeric complexes (12). However, this principle does not describe all of the known experimental facts, either. For example, in a recent paper it was shown that \( \text{[PtCl}_2\text{L}y \text{]} \)-type complexes (where \( L \) is pyridine and its derivatives, and \( Y \) is a ligand with a donor atom of oxygen), always have the form of a trans-isomer (13). Such a situation cannot be explained using the anti-symbiosis principles (13). It is worth mentioning that the same experimental facts can, however, be explained by the rule described in this paper.

In conclusion, we must note that in addition to the trans-effect of inner-sphere ligands, the nature of the solvent and the steric difficulties created by large ligands can be important factors which sometimes influence isomerisation. Naturally, these could complicate the predictions for the direction of the isomerisation process.
Magneeto-Optical Recording Materials

In 1989 the attention of readers of this Journal was drawn to research work being carried out at the Philips Research Laboratories and at E. I. du Pont de Nemours on layered cobalt and platinum structures, which were considered to have potential for meagno-ocptical recording. In the same issue an abstract of a paper from the Sony Corporation Research Center describing some magno-optical properties of ultrathin cobalt-platinum and cobalt/palladium layers, also indicated the potential of these materials for high density recording. Continuing interest was demonstrated during 1990 by further reports from these organisations, and from elsewhere.

Progress continues to be made in the subject, as can be gathered from the recent literature which includes, among others, papers from the three establishments named earlier.

According to a combined paper from the first two establishments, large magnetic anisotropy and coercivity in platinum/cobalt multilayers is dependent on sharp interfaces between the layers. Krypton and xenon are better mass-matched to the platinum sputtering target than argon, and their use results in less energetic bombardment by reflected gas neutals during the film growth. Thus interfacial mixing of the platinum and cobalt films is reduced, and magnetic properties improved. Another way to reduce the mixing of the platinum and cobalt layers, caused by energetic reflected argon atoms, is to sputter at high pressure; this increases the number of collisions that the atoms make before arriving at the substrate, and so reduces their energy (P. F. Garcia and W. B. Zeper, *IEEE Trans. Magn.*, 1990, 26, (5), 1703–1705).

A further paper from the Sony Corporation gives a review of previous studies on the magnetic properties of cobalt-platinum and cobalt-palladium systems, before going on to describe and discuss current work on cobalt/platinum and cobalt/palladium multilayers. Magnetic hysteresis of the multilayers, their magno-optical properties, and the effect of sputtering conditions and underlayers on the coercivity, were considered. With large Kerr rotation at shorter wavelengths, and high resistance to corrosion, ultrathin multilayers of both pairs of materials are considered to be promising candidates for high density magno-optical recording. An examination of dynamic read/write characteristics of the materials was made, with ultrathin multilayers deposited on photo-polymerisation glass substrates, pre-grooved with 1.6μm pitch. Carrier-to-noise ratios of 53 and 46 dB, at 780 nm, were seen for cobalt-platinum and cobalt/palladium, respectively. A higher ratio will be achieved by refining the noise level and optimising the disc structure (S. Hashimoto and Y. Ochiai, *J. Magn. Magn. Mater.*, 1990, 88, (1&2), 211–226).

Osmium and Ruthenium Complexes

Recent work on organic oxidations by osmium and ruthenium oxo complexes has been the subject of review No. 22 in the TMC Literature Highlights series (W. P. Griffith, *Trans. Met. Chem.*, 1990, 15, (3), 251–256).

The most important osmium oxidant is OsO₄, which, when functioning catalytically, is one of the most effective, selective and efficient organic oxidants. Ruthenium complexes in the higher oxidation states are more powerful oxidants than their osmium analogues. While ruthenium(VI) complexes are mild, effective oxidants, osmium(VI) complexes have virtually no oxidative properties. (71 Refs.)
ABSTRACTS

of current literature on the platinum metals and their alloys

PROPERTIES

Electrical Properties, Stability, and Applications of Ultrathin Porous Pt Films on SiO₂


The morphology of 25 Å porous Pt films deposited on thermally grown SiO₂ at room temperature and 250°C is presented. The impedance was measured over the range 100 Hz to 1 MHz. At 1 kHz, the impedance was measured in electric fields up to 250 V/cm at temperatures –192 to 140°C. The AC impedance of the 25 Å Pt film deposited at room temperature decreased by 25% in 21 days at 150°C in room air, but the AC impedance of the Pt film deposited at 250°C did not change.

Volatilization of Pt-Rh Alloys at High Temperature


Studies of the volatilisation of Pt-7Rh and Pt-Rh-Au alloys at high temperature showed that the volatilisation loss of the alloys at 1200–1350°C obey a parabola-straight line rule, and the transposition time from the parabola loss to straight line loss decreased with increasing temperature. The volatilisation loss increased with increasing Rh content and by addition of Au to Pt-Rh alloys. The activation energy of volatilisation of Pt-7Rh-3Au alloy is 167 kJ/mol.

Columnar Epitaxy of PtSi on Si(111)


Columnar grains of PtSi surrounded by high quality epitaxial Si were obtained by ultrahigh vacuum codeposition of Si and Pt in an 8:1 ratio on Si(111) substrates heated to 610–810°C. The areal density of columns varied from 120 to 3.8/μm², and layers with thicknesses from 100 nm to 1 μm were displayed. The PtSi grains are also epitaxial and have one of three variants of the relation defined by PtSi(010)∥Si(111), with PtSi(001)∥Si(110).

Properties of a Platinum-Yttrium-Boron Alloy

K. SCHWARZ and W. MOLLE, Neue Hütte, 1990, 35, (10), 391–393

The properties of a Pt-0.03Y alloy were improved by adding a small amount of B. The addition of B resulted in an increase in the rate of internal oxidation and a fine dispersion of the Y oxide particles was obtained. High creep rupture strength, a high creep resistance and a decreased grain growth were found.

Magnetic and Transport Properties of the UTIn Series (T = Rh, Pd and Pt)


Magnetic susceptibility, magnetisation, electrical resistivity and magnetoresistivity measurements have been performed for the U(Rh, Pd, Pt)In series crystallising in the hexagonal Fe₂P type structure. Results for URhIn are reported for the first time. Antiferromagnetic ordering in URhIn and UPtIn with a Néel temperature of 7 and 22 K and metamagnetic transitions in fields of ~1.5 and 3.5 T at 4.2 K have been observed, respectively. Resistivity anomalies at low temperatures have been observed. UPdIn was antiferromagnetic with a Néel temperature of 20 K.

Effects of High Concentration CO and CO₂ on Hydrogen Permeation through the Palladium Membrane


The effects of high concentrations of CO and CO₂ on the H permeation characteristics of a Pd membrane 0.7 mm thick, 12 mm diameter cut from cold-rolled Pd plate, followed by annealing were investigated using pure H₂, H₂-CO (10%, 50%), and H₂-50%CO₂ at 423–723 K and pressures 0.9–250 kPa. Deterioration in H permeability and diffusivity in the Pd membrane occurred for H₂-CO(10%, 50%) gas below 523 K with a concentration dependence on CO, while only slight deterioration occurred for H₂-50%CO₂ gas below 473 K. Results are explained by different adsorption energies of CO and CO₂ at the Pd surface. Deterioration in H₂ permeability is attributed to a decrease in effective area for H₂ dissociation by the weak adsorption of CO.

Kinetic Description of the Transition from a One-Phase to a Two-Phase Growth Regime in Al/Pd Lateral Diffusion Couples


The kinetics of the solid-state reaction between Al and Pd is studied in the geometry of a lateral Al-Pd diffusion couple at 250–430°C. The first reaction phase is the crystalline Al₇Pd₃(6) phase and after its growth to a critical length, the quasicrystalline decagonal Al₇Pd(γ) phase starts to grow in between the Al and the Al₇Pd₃ phases. The first-phase Al₇Pd₃ and second-phase Al₇Pd₃ grow simultaneously. Excellent agreement between the data and the model is found. From the analysis the effective interface growth constant for the Al₇Pd₃ is extracted as a function of temperature.
Electrical Resistivity Changes Due to Interstitial Hydrogen in Palladium-Rich Substitutional Alloys


The changes in electrical resistivity of Pd solid solution alloys, alloyed with Ag, Au, Cu, Y, Ce, Ti, Zr, V, Nb and Ta, with H concentration were measured at 301 K up to t(WM)=1.5 K. BABA, Interstitial Hydrogen Electrical Resistivity Changes Due to Internal Oxidation of Pd-40Ag-1RE 3910-3916

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The internal oxidation of Pd-40Ag-1RE (RE = Sm, Eu, Gd) alloys and their properties were studied in air at 800–1200°C. For the alloys containing Sm or Gd, the oxidation rate along the grain boundaries was higher than that of grains in some parts. It is concluded that the internal oxidation of Pd-40Ag-1RE alloys is controlled by volume diffusion.

Microstructural Stability of Diluted Pb-Cu-(Sn-Se-Pd) Alloys

A. De La Torre, P. Adeya, G. Caruana and M. Aballe, Z. Metallkd., 1990, 81, (8), 594–600

The evolution of microstructure was followed in homogeneous, fine grained Pb-Cu, Pb-Cu-Sn-Se and Pb-Ca-Sn-Se-Pd alloys optically, by SEM and by microanalytical identification of phases and measurement of several microstructural parameters, at temperatures between 323 and 423 K for 4 to 700 h. Small Cu and Se additions substantially reduce Pb grain size; Pb acts as a grain stabiliser during heat treatments. Grain size distributions in one or two dimensions are lognormal and invariant with treatment temperature and time. The Pb containing alloys have high microstructural stability at the temperatures studied, making them suitable for chemical plant application.

Magnetic Properties of Nonequilibrium Fe-Pd Alloys Produced by DC Triode Sputtering


Sputter-deposited Fe-x-Pdx alloys of ~100μm thickness were prepared by DC triode sputtering. The single b.c.c. phase was obtained for x = 0–0.25 in contrast to the narrow single b.c.c. of x = 0–0.03 in the equilibrium phase diagram. The lattice constant and the magnetisation increased by annealing below 500 K and decreased by annealing above 500 K.

The (α + β) Hydrogen Miscibility Gaps in Hydrogenated Palladium-Rich Pd-Y(Gd)-Ag Ternary Alloys


Pd-rich Pd-Y(Gd)-Ag ternary alloys were investigated as possible diffusion membranes for H purification, and their alloying behaviour and the extent of (α + β) H miscibility gaps in hydrogenated alloys were studied. Metallographic and X-ray studies of annealed Pd0.99−x−y(Y(Gd))0.01(x+y)Ag, alloys with a Ag content y of 5–24 at.% and x in at.% giving the value of the content of Y and/or Gd, indicate that every one of these alloys forms as a single α-Pd phase. It was found that the (α + β) H miscibility gaps in the hydrogenated alloys with any given Ag content decrease gradually as the content of Y and/or Gd increases, and the critical compositions for the disappearance of the miscibility gaps are approximately isoelectronic.

Do Thermal Spikes Contribute to the Ion-Induced Mixing of Ni into Zr, Ti, and Pd?


Low-temperature ion beam mixing rates for Pd-Ni, Ni-Ti and Zr-Ni bilayers greatly exceeded binary collision estimates, and appeared quite sensitive to thermodynamic driving forces. In the absence of a temperature dependence such a behaviour is usually ascribed to interdiffusion within thermal spikes. It is suggested that interdiffusion within a thermal spike of the Vineyard-Johnson type is not the dominant mechanism.

On the Constitution of the Pd-Te System up to 28 at.% Te


The constitution of the Pd-Te system was completed in the Pd-rich range up to 28 at.% Te and at >600°C. The solid solution between Pd and Te has a maximum Te content of 16.3 at.% at ~770°C. The system shows a eutectic with 23.0 at.% Te at 773°C. Three phases Pd1Te, (19 at.% Te), Pd5Te, (26 at.% Te) and dimorphic Pd3Te (25 at.% Te) were observed in the subsolidus region.

Structure Changes on Relaxation of Differently Cooled Pd4.83Si0.165 Alloy Glass


The radial distribution function (RDF) of X-ray diffraction was studied for liquid-quenched Pd4.83 Si0.165 alloy glasses in relation to cooling conditions. The atomic distance (r1), total co-ordination number (n) and volume (V) were obtained by a first peak of RDF. The faster the cooling rate, the larger the r1, n and V become. Based on the relaxation theory, it is shown that linear changes in r1, n and V with the thickness (D) indicate the reciprocal cooling rate.
High-Temperature Oxidation of Rhodium

The oxidation kinetics of Rh were measured in air at 1 atm at temperatures 600–1000°C. The oxidation weight gain proceeds logarithmically at 600–650°C, followed by power law behaviour at >800°C. The logarithmic growth kinetics comes from thickening of hexagonal Rh₂O₃ scales. The transition reflects a thickening of hexagonal and orthorhombic Rh₂O scales. Over 800°C the growth kinetics result from thickening of a predominantly orthorhombic Rh₂O₃ scale. At 1000°C the oxide becomes volatile.

The Controlled Oxidation of the High Chromium Steel Alloys Fe₄₀Cr and Fe₄₀Cr₃Ru

Fe₄₀Cr steel with and without 3% Ru added were exposed to O₂ at different temperatures in a UHV system to find out how the Ru enhanced the corrosion resistance of the alloy. Cr was oxidised before Fe in both Fe₄₀Cr and Fe₄₀Cr₃Ru, but only in the Ru alloy did the Cr also enrich the surface, at temperatures over 275°C, to form a substantial oxide, possibly because of an attractive interaction between Fe and Ru in the bulk.

New Compounds in the 30–40 at.% Ru Range of the Rare Earth-Ruthenium (R-Ru) Systems

New compounds were prepared and identified in the rare earth-Ru (R-Ru) systems and a complete compound formation scheme was constructed. Two new crystal structures were found and completely resolved. Y₃Ru₇ and Er₃Ru₇, while for a third one (RRu₇) the complexity of the structure prevented any structural determination.

CHEMICAL COMPOUNDS

Complex Formation of Platinum with Tin(II) in Aqueous Solution of Malic Acid

Studies of the interaction of K₂PtCl₆ with SnCl₂·2H₂O in 1 M malic acids at 20°C showed the formation of bimetallic Pt(II) complexes of anion type with maximum content of SnCl₂·H₂O⁻ ligands, with the molar ratio = 5. Chloride ions in [Me₆N⁺][Pt(SnCl₂)₄⁻] and [Me₆N⁺][Pt(SnCl₂)₄] dissolved in the malic acid were completely replaced by malate-ânions, thus preserving the Pt-Sn bond. During heating, Pt-Sn complexes undergo intermolecular conversion, which result in the formation of bimetallic compounds with Pt oxidation order −1.

Synthesis and X-Ray Crystal Structure of Trimesitylrhodium(III)

The first neutral homoleptic aryl of Rh(III), Rh(2,4,6-Me₃C₆H₂), was prepared by interaction of RhCl₃(C, H, S) and mesitylmagnesium bromide. X-ray crystal studies showed that there was “agostic” interaction between Rh and an ortho-CH₃ group in a distorted fac-octahedral geometry but no evidence for agostic H bonding was found. 1H NMR spectra over a temperature range indicate synchronised rotation of the mesityl group about the Rh-C bond.

A Novel Zwitterionic otho-Metallated Ruthenium(II) Phenolate

Decarbonylative metallation of the dialdehyde by [Ru(PPh₃)₂Cl₂] produced the unusual complex [Ru(MeL)(CO)(PPh₃)₂(Cl)]. X-ray crystallographic studies showed that the Ru⁺⁺P₃C₆O-chelated phenolato function with a neighbouring Ru(MeL) fragment incorporates a four-membered C₆O-chelated phenolato function with a neighbouring monoprotonated azomethine moiety.

Preparation of Uniform Colloidal Metallic Ruthenium and Its Compounds

Colloidal spherical particles with narrow size distribution of a Ru double salt, (NH₄)₂[Ru¹¹⁺O(NO)₂Ru¹⁰⁺O(OH)₂]·2RuIVO₂CO₃·8H₂O were obtained by ageing solutions of RuCl₃ containing K₂SO₄ and urea at elevated temperatures. The amorphous product was readily converted to RuO₂ by calcination at 400°C. The same original powder, dried and heated at 250–300°C in a stream of H₂ yielded metallic Ru.

ELECTROCHEMISTRY

Electrochemical Behaviour of Basal Single Crystal Pt Electrodes in Alkaline Medium

The electrochemical behaviour of basal single crystal Pt electrodes in 0.1 M NaOH has been studied. The voltammogram for the Pt(111) surface orientation shows two clearly defined zones; one corresponds to weak H adsorption states and the other could tentatively be assigned to strong H adsorption states. The voltammogram for a Pt(100) surface shows four different H states while for the Pt(110) orientation only one H state is obtained.
Electrochemical Oxidative Cleavage of the Platinum-Hydrogen Bond in trans-[PtHCl(PEt₃)₂]
The electrochemical oxidation of the Pt(II) hydride, trans-[PtHCl(PEt₃)₂], in CH₃CN containing NBu₄ClO₄ at a Pt gauze electrode produces almost exclusively Pt(II) complexes as products, none of which contain Pt-H bonds; trans-[PtCl(solvent) (PEt₃)₂]+ is the major oxidation product. Titrations on the electrochemically oxidised solutions show that Pt-H cleavage occurs with H⁺ formation. The overall oxidation process is therefore: H⁺ → H²⁺ and not Pt(II) → Pt(IV).

Reactor Control and Reaction Kinetics for Electrochemical Urea Oxidation
The electrochemical oxidation of urea on anodic Pt surfaces to NH₃ and CO₂ was studied in the range 0.5–1.1 V relative to Ag/AgCl to develop a model to mimic the experimentally observed phenomena. The model indicates maximum urea current utilisation can be achieved by appropriately controlling the applied current density in the system. The absolute urea conversion rate can be maintained by increasing the available Pt surface area.

A New Fluoride Resistant Ceramic Electrode for Electrochemical Effluent Treatment Processes
The effect of fluoride ion on two inert anode materials, Pt-clad Nb and Ir oxide-coated Ti, and a new Ir oxide-coated Ti suboxide ceramic electrode was determined to find its effect when used for treating electrolyte effluent. The materials were tested under laboratory conditions in a H₂SO₄ acid-based fluoride containing solution. The ceramic material had superior corrosion resistance and hence longer life than either of the metal oxides.

Corrosion Resistance and Electrochemical Behaviour of Platinnised Porous Titanium Electrodes in Acid Media during Water Electrolysis
Studies were performed of the corrosion resistance of plated porous Ti electrodes with a Pt layer deposited either galvanically or by ionic coating using a magnetron, on thin (0.5 mm) porous (30%) Ti base during polarisation by a high density current of up to 1.0 A/cm² in 10% H₂SO₄ solution. Cumulative data of tested electrodes in a compartment with solid polymeric electrolyte are given.

Rectifying Bilayer Electrodes: Layered Conducting Polymers on Platinum
The preparation of sequential bilayer structures made from any pair of polybithiophene, (I), polypyrrole, (II) and poly(3-bromothiophene), (III) by anodic electropolymerisation on Pt electrodes is described, and the electrochemical properties of the junction between the two conducting polymers are discussed. The polymers in the outer layers of the electrodes Pt/I/II and Pt/III/II can be trapped in the oxidised state for several hours and charge can be released from the outer layers via an appropriate redox couple in solution.

Hydrochloric Acid Electrolysis Using Solid Polymer Electrolytes. II. Gas Purity and Current Efficiency
Current efficiencies and purities of H and Cl in HCl acid electrolysis by membrane-electrocatalyst composites of Ir-Pt/Nafion 117/Pt-Ir prepared by chemical plating were investigated over the range 1.7–12 mol/kg HCl concentrations, and temperatures 25–75°C and current densities up to 100 A/dm². Cathodic current efficiencies of 97–98% were found.

The Electrowidation of Methanol in the Potential Region of Platinum-Oxygen Layer
Methanol oxidation at a Pt electrode in 0.5 mol/dm³ H₂SO₄ at high potentials was retarded by the formation of an O layer and a new type of retarding substance from MeOH. During retardation due to the formation of O layer, the rate of MeOH oxidation decreased and increased with increasing O coverage and potential, respectively. Reverse effects in O coverage and potential concurrently occurred when the potential was variable. At low O coverage, the decreased effect from O coverage was more notable than the increased effect from the potential, but this reversed at medium coverages.

Electrochemical Activity of Silicides of Some Transition Metals for the Hydrogen Evolution Reaction in Acidic Solutions
The H evolution reaction was examined on silicides of transition metals in H₂SO₄ solutions. The highest rates were observed on Pt and Pd silicides, followed by those of Cu, Cr and Ni. If Fe silicides are used as typical transition metal silicides their electrocatalytic activity for the H evolution reaction is enhanced considerably by electrodepositing traces of Ru, and especially Pt on their surfaces.

Morphological Changes in Silver Colloidal Particles during Oxidative Treatment in Complex Solutions of Gold and Palladium


The treatment of polychromatic imaging Ag particles in H2PdCl4 and H2AuCl4 solutions resulted in a change in the spectral and colour properties of an image. During the process, the spectral Ag particles transform to Ag shells with Pd and Au particles being ultradispersed on a surface.

Poly(pyrrole-2,2'-bipyridyl) Rhodium(III) Complexes: Modified Electrodes


The synthesis and electropolymisation of new [RhIII(L2Cl4)]*BF4- complexes, where L = 2,2'-bipyridine bearing pendant pyrrole units, and the electrochemical behaviour of the resulting polymers are examined. Films of this material are highly stable for bulk electrocatalytic reactions, especially for efficiently reducing water to H2 and for the hydrogenation of cyclohexanone to cyclohexanol.

The Electrochemical Reduction of Cp*Rh Complexes


The electrochemical reduction of [Cp*RhCl2](1) or [(Cp*Rh)(μ-Cl)]PF6(2) in methylene chloride and acetone and of [(Cp*Rh)(μ-OH)]PF6 and Cp*Rh(acetone)2+ in acetone was investigated by cyclic voltammetry and coulometry. An involved stepwise reduction sequence with electron transfer, Cl- loss and disproportionation from (1) or (2) produces the novel blue, air-sensitive, binuclear RuII species [Cp2RuCl2].

Application of Ion Implantation/RBS to the Study of Electrocatalysis


Ir-implanted Ti near-surface alloys were prepared by ion implantation, characterised by Rutherford backscattering (RBS) and subsequently anodically oxidised to form electrocatalytically active Ir2Ti1-xO2/Ti electrodes, and their electrochemical behaviour in acidic chloride, sulphate and perchlorate solutions was studied. The specific catalytic activities (rate per catalyst surface site) of Ir2Ti1-xO2/Ti and Ru2Ti1-xO2/Ti and their relative catalytic activities were evaluated. Ir2Ti1-xO2/Ti was only 45% as effective a catalyst for Cl2 evolution as Ru2Ti1-x/Ti, but it was far more stable, with a corrosion rate of only 5% that of Ru2Ti1-xO2/Ti.

Catalytic Oxidation of Methanol by Ruthenium Oxides


The electrocatalytical behaviour of Ru oxide/C electrodes for O evolution and MeOH oxidation in acid solutions is reported. The electrodes were characterised by various techniques which showed the Ru to be present as a mixture of RuV oxides, including the stable rutile phase. Electrochemical studies show that a RuVI species promotes the catalytic oxidation of MeOH, while surface-bound RuO2 is involved in the O evolution reaction.

Topotactic Two-Phase Reaction of Ruthenium Dioxide (Rutile) in Lithium Nonaqueous Cell


Electrochemical and X-ray diffraction studies were performed for the reduction of RuO2 with rutile structure in 1M LiClO4 propylene carbonate:1,2-dimethoxyethane (1:1) solution. RuO2 was topotactically reduced to Li2RuO2, which is orthorhombic via an intermediate phase having a tetragonal lattice. The reaction was reversible. Although three phases coexisted during the reduction of RuO2, oxidation of LiRuO2, the reaction was classified as a topotactic two-phase reaction where an intermediate phase existed between the RuO2 and Li2RuO2 phases.

PHOTOCONVERSION

An Ultramicrostructured Photocathode System Composed of TiO2 Single Crystal and Layered SiO2 and Pt Thin Film


An ultramicrostructured photocathode system composed of a TiO2 single crystal and thin films of SiO2 and Pt was prepared by exposing the vertical section of the layered SiO2 and Pt film. The SiO2 layer is ~140 nm thick. The electrode showed photoresponse under irradiation in the presence of NH3, water vapour, EtOH and acetone. This may be the first microphotoelectrode system which can work in the gas phase.

Photocatalytic One-Step Syntheses of Cyclic Imino Acids by Aqueous Semiconductor Suspensions


Photocatalytic cyclisation using aqueous suspensions of TiO2 or CdS loaded with Pt oxides under Ar at room temperature was applied to the one-step synthesis of optically active cyclic imino acids, pipercolin acid and proline from the α,ω-diamino carboxylic acids and their Nα-substituted derivatives.

A Direct Absorber Reactor/Receiver for Solar Thermal Applications


A novel catalytic reactor concept of 3.5 kW is described where concentrated radiant solar energy is directly absorbed on Rh/Al₂O₃, thus avoiding the heat-transfer limitations of conventional tubular reactors for high-flux conditions.

Photocatalytic Asymmetric Reduction of 3-Methyl-2-Oxobutanoic Acid with Chiral Rh(II) Complexes and Powdery Semiconductors


Photocatalytic asymmetric reduction of the title acid giving 2-hydroxy-3-methylbutanoic acid has been performed at up to enantiomeric excess of 60% in aqueous MeOH with chiral BINAP-Rh(II) complexes and semiconductor photocatalysts, TiO₂ or CdS. The efficiency of the asymmetric reduction is still low, but the asymmetric hydrogenation of α-ketocarboxylic acid has been obtained without using H₂.

Simultaneous Photodissociation of H₂ and PMe₃,Ph from OsH₂(PMepy,Ph)₂: Production of Dimeric and Paramagnetic Osmium Polyhydrides


Concurrent photodissociation of H₂ and PMe₃,Ph (= P) from OsH₂(PMepy,Ph)₂ in benzene, THF and EtOH has been proved by chemical trapping. It is the first polyhydride to undergo two distinct photoprocesses with comparable efficiencies. The final products observed on photolysis of OsH₂(PMepy,Ph)₂ under vacuum is an equilibrium mixture of Os₂H₃P₉ and Os₃H₃P₂. The former is also photosensitive, leading to products of P-CH₃ cleavage (Os₂H₃(PMepy,Ph),₉(P-MepyPh)₂), as well as to a product of Os-H heterolysis, [Os₂H₃P₂]₁ (trans-OsH₂P₉), which contains a unique paramagnetic polyhydride anion.

Spectral, Photophysical and Photochemical Properties of Ru(bpy)₃⁺ on Porous Vycor Glass


The properties of Ru(bpy)₃⁺ adsorbed on porous Vycor glass have been characterised. The complex is immobilised on the glass surface and can be quenched by O₂, N₂O and SO₂. Other forms of quenching are discussed, as are the few differences in behaviour due to the Ru being on a solid support and not in a fluid medium. The net photoredox chemistry initiates with a two-photon ionisation of Ru(bpy)₃⁺. Electron conduction may occur by a surface mechanism.

A Luminescence Quenching Study on the Localization Problem of Ru(bpy)₃⁺ in Micelles and Hemimicelles


Quenching studies on the luminescence emission of compound Ru(bpy)₃⁺ with ferrocyanide ion, 9-methylnaphthalene and dioxystearic acids were carried out in hemimicellar and micellar aggregates to gain insight into the location of this Raman and luminescence probe. Ru(bpy)₃⁺ is bound to a more nonpolar hemimicellar hydrophobic region. Stern-Volmer constants for the dioxystearic acid quenching of its luminescence in micelles indicated that the optical electron in the metal-ligand charge-transfer state of the probe molecule resides in a bipyrildyl ring which appears to be close to position 7 of the stearic acid chain.

Conversion of Light into Electricity with Trinuclear Ruthenium Complexes Adsorbed on Textured TiO₂ Films


A series of CN-bridged trinuclear Ru complexes of structure [RuL₃,(μ-(CN)Ru(CN)L₃)₁]₂, where L=2,2'-bipyridine, 4,4-dicarboxylic acid and L' = 2,2'-bipyridine (1), and other bipyridines, etc, have been synthesised. The two carboxylic functions act as interlocking groups through which the dye is attached at the TiO₂ film surface. The interlocking groups provide strong electronic coupling, allowing charge injection to proceed at quantum yields close to 100%. Monochromatic incident photon-to-current conversion efficiencies are >80% in some cases. Regenerative cells with these trinuclear complexes and ethanolic triiodide/iodide redox electrolyte have optimal results with (1), giving a fill factor of 75% and a power conversion efficiency of 11.3% at 520 nm.

Design of Antenna-Sensitizer Polynuclear Complexes. Sensitization of Titanium Dioxide with [Ru(bpy)₂(CN)₂]₂[Ru(bpy(COO)₂)]₂⁻


The use of antenna-sensitiser molecular devices is proposed as a possible strategy to increase the light harvesting efficiency of sensitised semiconductors. The cyanido-bridged trinuclear complex [Ru(bpy)₃]₂(CN)₂,Ru(bpy(COO)₂)]₂⁻ was prepared and studied. The complex adsorbs on TiO₂ via the negatively charged -Ru(bpy(COO)₂)]₂⁻ central unit. Photophysical and photoelectrochemical studies were performed and emission and excitation spectra showed that in this complex the light energy absorbed by the terminal Ru(bpy)₃[CN]₂ (antenna) groups is efficiently funnelled to the central -Ru(bpy(COO)₂)]₂⁻ (sensitiser) fragment.

ELECTRODEPOSITION AND SURFACE COATINGS

Deposition of Transition Metal and Mixed Metal Thin Films from Organometallic Precursors

Y.-J. CHEN, H.-J. MÜLLER, H. D. KAESZ, R. S. WILLIAMS, R. F. HICKS, J. I. ZINK.

High purity films of Pt, Ir, Rh and Ni and Re have been grown by organometallic chemical vapour deposition OMCVD (a), while thin films of Pt, Rh or Ir have been grown by photo-assisted OMCVD of volatile hydrocarbon precursors, but these contained more C than films grown under (a). Short-path OMCVD for organometallic precursors of limited volatility was used to deposit films of intermetallic compounds, PtGa, and CoGa. Substrates to be coated are placed in the reaction tube at the temperature needed for controlled decomposition of the precursor complexes. The various hydrocarbon derivatives, carrier gases, substrates, light sources, temperatures and means of producing thin films are discussed.

Preparation of Thin Palladium Films by Use of an Electroless Plating Technique


An electroless plating technique was used to prepare thin Pd films permeable only to H. Before plating, Pd nuclei were deposited on the outer surface of a porous tube by sensitisation and activation treatments with Sn(II) chloride and Pd(II) chloride solutions, respectively. The rate of Pd deposition during plating was related to the Pd nuclei concentration, which increased with repeated number of treatments. Sn deposition retarded Pd deposition, but treating with AgNO3 solution before activation promoted the formation of Pd nuclei. An alkaline solution was used to plate the Pd on the porous glass tube, twice as fast as conventional plating methods.

APPARATUS AND TECHNIQUE

An Oxygen Sensor Composed of Tightly Stacked Membrane/Electrode/Electrolyte


An O2 sensor which operates at room temperature has been constructed using Nafion, a porous Pt cathode directly deposited on Nafion and a polyethylene (PE) film directly covering the cathode surface. The sensor is amperometric and all the components are tightly stacked. The O2 reduction current is limited by the O2 diffusion rate through the diffusion-limiting PE film and it changes in proportion to O concentration of gases up to 100%.

Platinum Metal Etching in a Microwave Oxygen Plasma


The etching of Pt foils in an O plasma generated in a flow-type microwave system was studied as part of a general effort to understand the etching of metals in both plasma and chemical systems. It was found that very rapid etching (−6 Å/s) took place even at low power inputs of 200 W. The principal plasma parameters, including oxygen atom and ion concentrations, and electron temperature, were measured as a function of distance below the microwave coupler. Etching of Pt in an O plasma jet resulted from the concomitant action of O atoms and high energy electrons.

Use of Oxide Electrodes for Proton-Conductor Gas Sensor

N. MIURA, K. KANAMARU, Y. SHIMIZU and N. YAMAZO, Solid State Ionics, 1990, 40/41, (Part I), 452–455

An amperometric proton-conductor CO sensor operative at room temperature was developed by using a Pt/SnO2 and a Pt/WO3 electrode. The CO sensitivity of this sensor was about 7 times higher than the H2 sensitivity and the 90% response time was ~ 3 minutes. The sensor became H2 selective when a Pt-black electrode was combined with a Pt/WO3 electrode. Sensing mechanisms are discussed.

The Hydrolysis Products of cis-Dichlorodiammineplatinum(II). 3. Hydrolysis Kinetics at Physiological pH


The rate of hydrolysis of cis-PtCl2(NH3)2 has been measured in non-buffered aqueous solutions at I = 0.2 M NaClO4 and T = 45°C at constant pH over the range 4.0–8.5; the reverse reaction was also monitored. This allowed models for the hydrolysis of cis-PtCl2(NH3)2 under physiological conditions to be tested, and shows that the Rosenberg model for Pt(II) transport in vivo may need modification.

Study by UV-Visible Potential-Modulated Reflectance Spectroscopy of the Chemisorption of CO, Methanol and Ethanol on Several Noble Metal Electrodes


The title method has been used as a technique to determine the energy of electronic transitions in chemisorbed carbonyls and the type of bonding of CO. This was used to examine the electroadsorption of CO, MeOH and EtOH on Pt, Pd, Rh, Ru and Au electrodes. A maximum is reported, which depends only on the type of bonding of CO to the surface, i.e. linear, bridge-bonded or multiply bonded.

The Use of RuO, in Studies of Polymer Blends by Scanning Electron Microscopy
Flat samples of blends of polypolyene (PP) and styrene-ethylene-butylene-styrene (SEBS) were contrasted with RuO, and studied by SEM having a back-scattering electron (BSE) detector. The SEBS phase had bright areas with dark dots and the PP phase was dark. The dots were unstained EBDomains of the triblock SEBS polymer. This method gave high resolution images due to the intrinsic electrical conductivity on the surface from the deposited Ru species; the RuO, vapour gave electrical conductivity to the stained areas. This method allows a BSE detector to be used in morphological studies.

HETEROGENEOUS CATALYSIS
A Heterogeneous “Ligand-Accelerated” Reaction: Enantioselective Hydrogenation of Ethyl Pyruvate Catalyzed by Cinchona-Modified Pt/Al,O Catalysts
The effect of low modifier concentrations on the rate and enantioselectivity of ethyl pyruvate hydrogenation catalysed by Pt/Al,O, modified with 10,11-dihydrocinchonidine (HCD) was studied in order to test the concept of “ligand-accelerated” catalysis for a modified heterogeneous system. The reaction mechanism was found to be in complete agreement with a simple two-cycle mechanism. The adsorption of HCD on the Pt surface must be reasonably strong and/or only a small fraction of the surface Pt is modifiable. Simple geometric considerations indicate that a modified ensemble should be one adsorbed cinchona molecule and 10–20 Pt atoms.
Molecular Die Catalysis: Hexane Aromatization over Pt/KL

Studies of n-hexane aromatisation over 0.6–0.8% Pt/KL, prepared by exchanging zeolite L powder with Pt(NH₃)₄Cl₂ solution at room temperature for 20 h, and 1%Pt/SiO₂ catalysts were performed at 510°C, 100 psig pressure, with a H₂/hexane mole ratio of 6. Pt/KL catalysts showed a much greater selectivity for hexane aromatisation than Pt/SiO₂ catalysts and a strong preference for cracking the terminal C-C bond as opposed to interior bonds.

Preparation of Platinum Cluster Catalyst Supported on Porous Chelate Resin-Metal Complexes for Hydrogenation of Olefin and Diene

Catalysts of Pt clusters/chelate resin-metal complexes of Na(I), Mg(II), and Al(III) were prepared by reduction of Pt ions immobilised on the high porosity supports. The catalytic activity of the supported clusters increased in the order: Na(I)<Mg(II)<Al(III), which is consistent with increase in surface area of the resin.

Kinetics of Liquid-Phase Hydrogenation of Cinnamaldehyde over a Pt-Sn/Nylon Catalyst

The kinetics of liquid-phase hydrogenation of cinnamyl alcohol and cinnamaldehyde over Pt/nylon and Sn-Pt/nylon catalysts were studied. The kinetics of cinnamaldehyde hydrogenation over Sn-Pt/nylon at 10–60°C were interpreted on the basis of a two-site model, where B sites, associated with Sn, were involved in hydrogenation of cinnamaldehyde and hydrocinnamaldehyde, whereas A sites, associated with Pt, catalysed cinnamyl alcohol hydrogenations. The results show strong adsorption of cinnamyl alcohol on Pt sites, which also explains the apparent negative activation energies of some rate constants.

Carbon Monoxide Restructuring of Palladium Crystalites Surfaces

Six Pd/Al₂O₃ catalysts, with dispersions ranging from 3 to 86% were studied during repeated cycles of exposure to CO at 25°C and reduction at 300°C. CO cycling lowers the dispersion of all the samples to 20 to 50%. The loss of surface sites was higher on the small crystalites. The adsorption capacity recovered with oxidation at 550°C and reduction at 300°C. The H₂ solubility in the bulk of the Pd crystallites was not affected by CO cycling. Surface restructuring may be used to enhance the catalytic activity of Pd.

Selective Acetylene Hydrogenation in Mixtures with Ethylene in the Presence of a Palladium Catalyst

Studies of hydrogenation of C₂H₂-C₂H₆ mixture on Pd/γ-Al₂O₃ catalyst performed at 311–373 K in a wide range of reagents concentrations showed the formation of C₂H₆ from the intermediate compound systems ZH₂-C₂H₄ (where Z are new active centres of the catalyst) which proceeds in two parallel routes. It is shown that in the case of C₂H₂-C₂H₆ interaction, the mechanism of ethylene and acetylene with H₂ is the same as that during hydrogenation of individual hydrocarbons.

The Effect of Bismuth on the Selective Oxidation of Lactose on Supported Palladium Catalysts

The selective oxidation of lactose by O₂ has been studied in a batch reactor containing an aqueous slurry of 0.5 kmol/m³ and 1.0 kg/m³ of Pd/C promoted by Bi. This resulted in 100% selectivity to Na lactobionate up to conversions of 95% in the pH 7–10 range and at up to 333 K. A maximum initial reaction rate of 0.47 mol/kg s occurred at molar Bi:Pd of 0.5–0.67. Other aldoses could be oxidised with similar selectivities.

Activity and Selectivity of 1-Hexene Conversion on SAPO-11 and Pd/SAPO-11

The activity and selectivity patterns for 1-hexene reactions were compared at 150–450°C for four different kinds of acidic zeolites (H-mordenite, HZSM-5, SAPO-11 and Pd/SAPO-11) with different acid properties and geometric structure. The Pd/SAPO-11 catalyst gave enhanced double bond shift (DBS) selectivity and less cracking at higher temperatures in comparison to unloaded SAPO-11. There was a strong correlation between the shift from DBS to cracking with total acidity.

An Infrared Study of the Hydrogenation of Carbon Monoxide and Carbon Dioxide at High Pressure over Pd/La₂O₃

A new high-pressure IR cell reactor has been used to study the reactions of CO and CO₂ with H₂ over Pd/La₂O₃ films at a pressure of 8300 Torr. The activation energy for the CO₂ hydrogenation (25.1 kcal/mol) which produces MeOH is higher than that reported elsewhere for the analogous CO hydrogenation reaction. The CO₂ reaction may proceed through hydrogenation of adsorbed CO, rather than by direct hydrogenation of CO₂, over Pd/La₂O₃.
Structure-Sensitivity of the Deactivation of Pd/SiO2 for Methylcyclopropane Hydrogenolysis by CO


Pd/SiO2 catalysts with 5–80% metal exposed have been characterised for reactivity for methylcyclopropane hydrogenolysis as a function of CO concentration. The CO surface coverage and metal crystallite size are important in the deactivation behaviour of the catalyst. Pretreatment conditions help to determine reaction and deactivation structure sensitivity patterns. As CO coverage increases a monotonic decrease in activity occurs for large Pd particles, while catalysts with >40% metal exposed have a near-step drop in activity between 20–30% coverage.

Effects of Promoters of Palladium/Silica Catalysts for the Synthesis of Methanol


Methanol synthesis from syngas on promoted Pd/SiO2 catalysts was carried out at 1–20 atm (H2:CO = 2) and 220–310°C. The effects of Ca, K or La promoters on the activity and selectivity for methanol formation were studied. The highest methanol activity was achieved with 0.5wt.% Ca promoted Pd/SiO2 catalysts and was about four times that of non-promoted catalyst.

Effects of Cerium Addition on the CO-NO Reaction Kinetics over Alumina-Supported Rhodium Catalysts


Laboratory reactor studies showed that the addition of Ce to a low-loaded Rh/Al2O3 catalyst resulted in changes in CO-NO reaction kinetics, mainly suppression of N2O formation, decreased apparent activation energy, and a shift to a positive-order dependence of the rate on NO partial pressure. The Ce-induced modification of the kinetics leads to increases in the NO reduction activity at low temperatures.

Effect of Potassium on the Formation of Isocyanate Species in the NO + CO Reaction on Rhodium Catalyst


Adsorption and IR spectroscopic studies of the effect of K on the formation of isocyanate species in the NO + CO reaction on supported Rh catalysts showed that the addition of K to 5% Rh/Al2O3 significantly decreased the uptake of H2, CO and NO at 300 K. Presorbed K caused a significant increase in the formation of the NCO complex, with the maximum intensity obtained for a sample containing 2.5% K. The same effect was observed on Rh/SiO2 catalyst where two NCO species were identified (2180 cm⁻¹ for Rh-NCO and 2310 cm⁻¹ for Si-NCO).

CO Adsorption on Rhodium(I) and on Metallic Rhodium Supported on Titanium Dioxide


The interaction between a cationic organometallic Rh(I) compound and TiO2 in acetone leads to Rh(I)/TiO2. The reduction with H2 at atmospheric pressure and ambient temperature yields a supported metallic Rh catalyst which is active in 1-hexene hydrogenation. The precursor and catalyst have been characterised, and the predominant species is dicarbonyl on both. Dissociative CO adsorption is discussed.

Selectivity Changes in the Ring-Opening Reaction of Methylcyclopentane over Rhodium Catalysts Caused by the Addition of Silver and Metal-Support Interactions


The hydrogenolysis of methylcyclopentane (MCP) was studied over Rh-Ag/TiO2 catalysts after various reduction/oxidation treatments. The addition of Ag resulted in a decrease in activity, accompanied by an increase in the selectivity toward n-hexane (n-Hx). This increase in selectivity was enhanced when Ag and Rh are impregnated simultaneously and when the catalysts are reduced at 773 K. The selectivity changes can be interpreted in terms of a shift in the ring-opening mechanism. This shift is caused by a blockage of large ensembles required to constitute the multi-site complexes. This blockage would be more effective when Ag and TiO2 species are simultaneously present on the Rh surface.

Carbon Dioxide Hydrogenation on Rhodium Supported on Transition Metal Oxides. Effect of Reduction Temperature on Product Distribution


Studies of the effects of metal reduction conditions during CO hydrogenation on Rh/TiO2 and Rh/Nb2O5 catalysts showed the presence of C1–C4 hydrocarbons which followed Anderson-Schulz-Flory statistics. For Rh/TiO2, the role of CO as an intermediate in CO2 hydrogenation was clearly evident. In both catalysts, the formation of the SMSI state (strong metal-support interaction) during high temperature reduction greatly affected catalytic activities and selectivities. The differences in the general behaviour of the two oxides as far as the reversibility of the SMSI in the reaction conditions was concerned was ascribed to thermodynamic and/or kinetic constraints in the formation of SMSI during high temperature reduction.
Synthesis of Hydrocarbons and Alcohols from CO and H₂ over Co-Rh Catalysts


Studies of synthesis of hydrocarbons and alcohols from CO and H₂ (CO:H₂ = 1:2) over Co catalysts promoted by addition of Rh and Cu were performed at 250–300°C and pressure of 0.1–6.0 MPa. The results show that 4.5% Co-0.1% Rh-5:10% Cu/TiO₂ at 250–300°C and pressure of 0.1–6.0 MPa. The acidic cation exchange resins immobilized by addition of Rh and Cu were performed with chiral cationic water soluble ligands, [(S,S)-2,4-bis[bis-[p-N,N-dimethylammonium]phenyl]phosphinolpentane]+, etc., were immobilized on cation exchange resins. All these supported complexes catalyze the asymmetric hydrogenation of dehydroaminoacid derivatives with no detectable loss of Rh into the substrate phase. Rates and enantioselectivities depend on the ligand and the nature of the exchange resin.

IR Study of CO Adsorption and Its Interaction with Oxygen over Ir/Al₂O₃ Catalyst


An IR study of the behaviour of CO adsorption and its interaction with oxygen over Ir/Al₂O₃ catalyst showed that CO adsorption on Ir/Al₂O₃ with high Ir loading was an activation process, and the intensity of the adsorbed CO band increased with the increase in adsorption temperature from ambient to 300°C. The amount of adsorbed CO at 150°C was approximately one half of that at the maximum. The migration of adsorbed CO and O was increased by increasing the temperature.

Zeolite A-Supported Ru Catalysts


A number of zeolite A-supported Ru catalysts were prepared either by addition of Ru precursor to the zeolite A synthesis gel (ZS) with resulting metal being dispersed intrazeolitically, although not uniformly, or by surface deposition of Ru on zeolite A with metal particles primarily on the external surfaces of the zeolite crystallites. With the exception of the strong molecular sieving effect on the reaction of cyclopropane found for RuNaA(1ZSi), the most important effect on the catalysis was Ru particle size.

Surface Structure and Catalysis for CO Hydrogenation of the Supported Ru Species Derived from the Ru₃(CO)₁₂ Inorganic Oxides


Supported Ru cluster particles were prepared by the surface reaction of Ru₃(CO)₁₂ with inorganic oxides followed by H₂ reduction at 723 K. On V₃O₅ the cluster was converted to three-atomic-layer Ru metal particles, while one-atomic-layer [Ru₆] clusters were formed on SiO₂ (n=12) and TiO₂ (n=6). Clusters [Ru₆(OZ)₆] (Z=Al or Mg) with Ru-O surface bonds were formed on Al₂O₃ (n=6), K-doped Al₂O₃ (n=6) and MgO (n=3). CH₄ was predominantly formed on [Ru₆]₆/SiO₂. The 6-Ru atom clusters with Ru-Ru distances of 0.262–0.265 nm had the highest selectivity for C₁–C₃ hydrocarbon formation. Metallic [Ru₆] clusters on TiO₂ had higher activity than [Ru₆(OAl₃)] clusters bonded to the surface through O atoms. The smallest surface-bound clusters on MgO produced mainly CH₄ and CO₂.

**HOMOGENEOUS CATALYSIS**

A New Platinum-Based Catalyst System for Olefin Asymmetric Homogeneous Hydroformylation


A number of Pt(II) diphosphino complexes in combination with SnCl₂ are known to be active in olefin hydroformylation. It is now reported that the complex [Pt(C₅H₅)(μ-H)(μ-Cl)][Pt(C₅H₅)(μ-H)(μ-Cl)] interacts with [PtCl₂(μ-Cl)(μ-DIOP)] to give catalysts active in the hydroformylation of styrene and 1-hexene. The activities of the systems depend upon the molar ratio of the two Pt complexes and the nature of the substrate. The systems display good chemoselectivity and induce asymmetry in the branched aldehydes formed. Z-Phenylpropanal can be isolated in ~27% optical purity from styrene hydroformylation.

Evidence for a Bis(alkylidene) silacyclobutene Intermediate in the Platinum-Mediated Formation of a Silacyclobutene


The treatment of Ph₃Si(C≡CCMe₃) with a cationic Pt-H reagent resulted in the formation of a 4-alkylidene-1-silacyclobutene ring system. Acetic acid cleaves at Pt-C bond to yield alkenylsilanes products, showing the intermediate formation of a Pt-Si μ-alkenylidene complex. ROH reagents react with a proposed bis(alkylidene) silacyclobutene intermediate to initiate ring opening and to form R=R=Si μ-alkenylidene complexes (where R=H, Me, Et or Ph). The R=H complex ion structure was confirmed.
Hydroformylation with Platinum Phosphinito Complexes


Pt complexes containing phosphinito ligands afford active hydroformylation catalysts at 30–100 bar and 80–100°C. The hydroformylation rates for α-alkenes are the same as those obtained with Pt-trichlorostannate catalysts. Products are a mixture of alcohols and aldehydes with linearities in excess of 90%. Internal alkenes can also be hydroformylated with linearities as high as 70%.

Homogeneous Catalysis of Platinum Blue Related Complexes in Photoreduction of Water into Hydrogen


The evolution of H₂ is reported on dissolving platinum blues [Pt₂(NH₃)₃(C₂H₄NO₂)(PF₆)[PF₆]2, 1-2] in water. The H₂ seems to be due to an interaction between [Pt₂(NH₃)₃(C₂H₄NO₂)][PF₆]2 and H₂O, etc. in water. A homogeneous photochemical H₂-producing catalyst system is made with (1) or [Pt₂(NH₃)₃(C₂H₄NO₂)][PF₆]2, 3H₂O, etc. as electron relay. Quantum yields for their H₂ production are 0.022 and 0.11, respectively.

Palladium-Catalyzed Hetero- and Carbanoannulation of Vinylic Cyclopropanes and Cyclobutanones

R. C. Larock and E. K. Yum, *Synthesis,* 1990, 9, 529–530

ortho-Functionally substituted aryl iodides react under mild conditions with vinyl- and isopropenylcyclopropane and isopropenylcyclobutane in the presence of Pd(II) acetate and an appropriate base, K acetate, triethylamine or Na carbonate to give 2-(1-alkenyl)-substituted 2,3-dihydrobenzofurans, indolines and indans in good yield. This gives a novel versatile route to a variety of heterocycles and carbocycles, amenable to unsaturated cycloalkanes, 1,2-, 1,3- and 1,4-diienes as well as alkynes.

Carboxylic Acid Transvinylization as Catalyzed by Complexes of Palladium Acetate with Phenanthroline-Like Ligands


The complexing of Pd acetate with di-imine ligands results in a promotion effect on the vinyl exchange processes and ensures excellent selectivity and stability of the catalysate under reaction conditions. Vinylation of both saturated and unsaturated carboxylic acids by vinyl acetate proceeds smoothly even at an increased concentration of H₂O in the mixture.

Heteropoly Anion-Modified Palladium Catalyst for Reductive Carbonylation of Nitrobenzene


An efficient catalyst system of PdCl₂ and Keggin-type heteropoly anions containing Mo and V which had a noticeable promoting effect on the Pd, were used in a reductive carbonylation of nitrobenzene to form N-phenylcarbamate in the presence of alcohol in dimethoxyethane solvent. Turnover numbers were 98 and 196 in terms of moles of Pd and heteropoly anion.

ζ-Olefin-Palladium-Copper Complexes as Intermediates in Formation of Propylene Glycol Monoacetate during Oxidation of Propylene in the System PdCl₂/CuCl₂/HOAc


Studies of the kinetic and physical-chemical mechanisms during propylene oxidation by O₂ in the system PdCl₂/CuCl₂/HOAc were performed by various electron spectroscopic techniques. The contact of propylene-oxygen gaseous mixture with acetate solutions of PdCl₂, CuCl₂, LiCl and LiOAc resulted in a catalytic reaction yielding propylene glycol monoacetate and acetone.

Phase Transfer Pd(0) Catalyzed Polymerization Reactions. III. Polymerization by Cross-Coupling of Alkyl-Boron Compounds and Aromatic Halides Catalyzed by PdCl₂(dppf) and Bases


A novel one flask polymerisation of a sequence of hydroboration of a diol with 9-borabicyclo[3.3.1]nonane followed by the intermolecular cross-coupling of the resulting α-ω-bis[Balkane-diyi]-9-borabicyclo[3.3.1]nonanes with dihaloarenes is described. The reactions are catalysed by PdCl₂(dppf) and a base and are performed in a two-phase (organic liquid-liquid or solid-liquid) phase transfer catalysed system. This provides unique synthetic routes to the preparation of functional polymers containing C–C bonds in the main chain.

Hydrodechlorination of CCl₄ in the Presence of Pd(OAc)₂


Methane was produced by the reaction of H₂ on CCl₄ in acetic acid in the presence of Pd(OAc)₂, catalyst under 0.1 MPa and at 20–80°C. In the presence of aliphatic alcohols, CH₃OH content in the reaction products decreased sharply yielding chloroform and ethyl chloride as main hydrodechlorination products.
Synthetic Methodology Involving the Carbopalladation of Allenes


Carbopalladation of allenes by vinyllic or aryllic Pd species (vinyllic or aryllic halides + Pd(0)/L₅ catalyst) gives new 2-substituted η-allyl Pd complexes, which have interesting stereoc hemical properties due to the conjugated unsaturated system on the central C atom of the η-allyl ligand, and react with high regio and stereoselectivities with delocalised car boxynucleophiles. The overall process creates two new C-C bonds in a single reaction and leads to functionalised 1,3-dienic (or styryl) compounds of known stereochemistry.

Expanding Industrial Applications of Palladium Catalysts

J. TSUJI, Synthesis, 1990, (9), 739–749

A review of Pd in industry as homogeneous and heterogeneous catalysts classifies them into having oxidative reactions with olefins and aromatic compounds and oxidative carbonylation, by Pd(II) salts and appropriate reoxidants; and Pd(0) complexes for reactions of organic halides and reactions via π-allylPd complexes. Careful selection of reaction conditions, solvents, choice of ligand and catalyst modifiers are necessary to achieve long catalyst life and high selectivity. (89 Refs.)

Rhodium Phosphine Complexes as Acetalisation Catalysts


Complexes containing Rh(III) triphos moieties as catalyst precursors have been studied for acetalisation and trans-acetalisation reactions. The complexes are reactive under mild conditions and give a high turnover rate and induce interesting diastereoselectivities. For methyl-substituted acetals and trans-acetalisation reactions. The complexes give high selectivity. (89 Refs.)

Optically Active Phenanthrolines in Asymmetric Catalysis. III. Highly Efficient Enantioselective Transfer Hydrogenation of Acetophenone by Chiral Rhodium/3-Alkyl Phenanthroline Catalysts


The in situ catalysts prepared from [Rh(Diol)Cl]₂ (Diol = 1,5-hexadiene or 1,5-cyclooctadiene) and 3-alkylphenanthrolines display extremely high catalytic activity in the transfer hydrogenation of acetophenone. Turnover rates up to 10,000 cycles/h have been recorded in 2-propanol solution at 83°C, with KOH as promoter. Asymmetric inductions up to 65% e.e. have been obtained, using a ligand with a chiral trimethylpropyl substituent. In the asymmetric process the most active and stereoselective catalytic species might be a Rh hydride complex containing two phenanthroline ligands in a chiral C₂ array.

An Experimental and Modelling Study of Polybutadiene Functionalization to Polyaldehydes Using a Homogeneous Rhodium Catalyst


The liquid-phase hydroformylation of a polybutadiene containing 1,2 and 1,4 olefin units can be performed using a homogeneous Rh-phosphine ligand catalyst (Wilkinson’s) with excess phosphine ligand at mild reaction temperatures. The product is a polybutadiene whose degree of olefin unit functionalisation can be controlled through use of proper reaction conditions. The olefin units in the polybutadiene are selectively hydroformylated to the 1,2 terminal branched and 1,4 internally branched aldehyde products. The aldehyde addition is reasonably uniform in the range of polymer molecular weight.

Unusual Activity and Selectivity in Alkyne Hydroisilylation with an Iridium Catalyst Stabilized by an O-Donor Ligand


Studies of alkyne hydroisilylation by Ir in the O-donor ligand environment of Grim’s triso ligand (=tris(diphenyloxophosphoranyl)methanide) showed that the reaction is selective for 1-alkynes and regioselective for β-products. However, it gave the thermodynamically less favoured cis-vinylsilane products by an unexpected anti addition of Si-H to the triple bond. Mechanistic studies suggest that the alkyne first inserts into the M-Si, not the M-H, bond and that a trans to cis rearrangement occurs via an η₁-vinyl intermediate before reductive elimination. A number of Rh and Ir complexes of the type [(triso)ML₂] are prepared.
Selective Oxygenation of Aliphatic Ethers Catalyzed by Ruthenium(II) Complexes


Studies of selective and fast conversions of primary ethers to esters (or lactones) were performed using Li hypochlorite in the presence of catalytic amounts of Ru(II) complex catalysts RuX_L, (L is (CH3)2SO and (L) is 1,3-bis(diphenylphosphino)propane). Isopropyl ether undergoes oxidative cleavage to acetone, while secondary ethers bearing methylene groups in the β-position are converted into β-keto ethers. Methyl ethers are unaffected by the oxidation.

A New Ruthenium(VI) Oxidant: Preparation, X-Ray Crystal Structure, and Properties of (Ph₄)[RuO₂(OAc)Cl₂]


The title compound was obtained by the addition of RuO₂ in CCl₄, to a slight excess of PPh₃ and glacial acetic acid in acetonitrile, followed by recrystallisation from dichloromethane-CCl₄. The compound has a quasi-trigonal bipyramidal structure with a symmetrically bound acetato ligand and cis-dioxo ligands in the trigonal plane. It is an effective oxidant for halides, alcohols, sulphones and phosphines, functioning catalytically in the presence of N-methylmorpholine-N-oxide.

Autocatalysis and Free Radical Mechanism in a Ruthenium Cluster Catalysed Hydrogen Transfer Reaction


The mechanisms of the [(Ph₄)₅Ru][H₂Ru₂(CO)₁₀] (1) catalysed disproportionation and transfer-hydrogenations of cyclohex-2-en-1-one have been shown to involve free radicals. In the latter reaction (1) is converted to other carbonyl species via autocatalysis. Spectroscopic analyses at the end of a catalytic run at 82°C and 5h, and > 100 turnovers of cyclohexanol with (1) as the pre-catalyst showed that all of (1) was converted into a mixture of soluble carbonyl and hydridic species.

Ruthenium-Catalysed C-H Bond Activation. Evidence for a Concerted Mechanism in Oxyfunctionalization of Cyclic Saturated Hydrocarbons


Oxidation of bridged polycyclic alkanes with in situ generated RuO₂ occurred by a concerted mechanism involving interaction of the highly electrophilic oxo Ru species with tertary unhindered C-H bonds. However, it is not yet clear whether an alkoxo-hydroxy- or alkoxo-hydroxy-oxo Ru species was involved as a key intermediate.

Oxo Transfer and Metal Oxidation in the Reaction of [Ru(PPh₃)₃Cl₂] with m-Chloroperbenzoic Acid: Structure of [Ru(PPh₃)₃(m-CICO₂H₃CO)Cl₂]


One mol and 0.5 mol of peracid were consumed for oxo transfer to PPh₃ and oxidation of metal, respectively, in the reaction of [Ru(PPh₃)₃Cl₂] with m-CICO₂H₃COH. X-ray studies of the product [Ru(PPh₃)₃(m-CICO₂H₃CO)Cl₂] showed that after oxo transfer the oxo-carboxylate residue remains chelated to the metal centre. The trans,cis,cis-RuO₂Cl₂O group has a two-fold symmetry. The complex undergoes one-electron quasi-reversible reduction but only at low potentials.

FUEL CELLS

“Development of Advanced Noble Metal-Alloy Electrocatalysts for Phosphoric Acid Fuel Cells (PAFC)”


Highly dispersed Pt and Pt alloys for PAFC electrocatalysts of crystallite size 12 Å diameter are discussed. For the cathodes advanced alloys have been developed of higher performance than Pt. For anodes diluting the Pt with less expensive materials gives a superior performance to Pt alone. For O reduction modifications to produce ordered alloys have given stability for over 9000 hours in the hot PAFC environment, as have alloys of Pt-Co and/or Cr containing Ga additions. For H oxidation Pt-Pd alloys show greater tolerance to poisoning and greater stability against crystallite growth. For successful commercialisation fuel cells must achieve high performance, low cost and long life.

ELECTRICAL AND ELECTRONIC ENGINEERING

Display of Wide Dynamic Range Infrared Images from PtSi Schottky Barrier Cameras


Twelve-bit digitised infrared images taken with PtSi Schottky barrier detector arrays have been processed on work stations. Two techniques for 8-bit global display are compared. The projection technique gives superior results based on an extensive set on indoor, day and night imagery. The new projection algorithm can be used as a powerful and robust local contrast enhancement technique. A real-time implementation of the projection algorithm is now incorporated into a specially designed camera and gives a very satisfactory automated alternative to the offset/gain controls.
Temperature Dependence of the Resistance in the Pt/Ti Nonalloyed Ohmic Contacts to p-InAs Induced by Rapid Thermal Processing


The temperature dependence of the resistance in the Pt(60 nm)/Ti(50 nm) nonalloyed ohmic contacts to p-InAs (Zn doped 1 × 10^{18} to 1 × 10^{19} cm^{-3}) induced by rapid thermal processing at 300–600°C was studied. The ohmic nature of these contacts was attributed to both the low metal-semiconductor interfacial barriers and to the heavily doped semiconductor contacting layers. The results showed conversion from thermionic emission as the dominant carriers transport mechanism across the interfacial barrier for the as-deposited sample to a combination of thermionic and field emission mechanisms for the heat-treated samples.

Electrical and Structural Properties of Pt/Ti/p+-InAs Ohmic Contacts


The thermally stable Pt/Ti metallisation scheme was applied to Zn doped p+-InAs layers to evaluate the influence of the outstanding electrical properties of the p+-InAs, such as the narrow band gap and the surface Fermi level pinning in the conduction band on the ohmic contact performance. Zn doping was 1 × 10^{18} to 1 × 10^{19} cm^{-3}. After rapid thermal processing for 30 s the specific contact resistances were lowered to <6 × 10^{-1} Ωcm for a 450°C anneal. This heat treatment enhanced limited reactions in both the Pt/Ti and Ti/InAs interfaces, but did not degrade the stable microstructure.

Hole Trap Level in Pt-Ti/p-InGaAs/n-InP Heterostructures Due to Rapid Thermal Processing


Deep level transient spectroscopy and I-V-T measurements were performed on Pt-Ti/p-InGaAs/n-InP heterostructure mesa diodes annealed by rapid thermal processing (RTP). Four electron trap levels with activation energies of 0.61, 0.45, 0.35 and 0.30 eV were observed which are believed to be native defects in InP, and they were independent of RTP conditions. A new hole trap level, with an activation energy of 0.89 eV was found only for samples annealed at >500°C and thought to be introduced by Ti diffusion at high temperature. I-V-T data were consistent among all samples, indicating that the hole trap level is not dominant in the current mechanism.

Stability of Amorphous Ir-Ta Diffusion Barriers between Cu and Si


Thin film amorphous Ir-Ta (a-IrTa) was tested as a diffusion barrier between (100) Si and Cu. Sandwich structures of (100) Si/a-IrTa/Cu/a-IrTa were stable during annealing in vacuum up to 700°C. At 750°C interdiffusion of Cu and Si occurred. The crystallisation temperature of thin film a-IrTa was reduced from 900 to 750°C in the presence of Cu. The high stability of the metallic a-IrTa buffer layer makes it useful for application in miniaturisation of very large scale integrated electronics.

MEDICAL USES

Metal Complexes as Anticancer Agents. The Future Role of Inorganic Chemistry in Cancer Therapy


A review of the background and reasons for the success of cisplatin in the treatment of various tumours is discussed. Other metal complexes with cancer inhibiting properties for chemotherapy are examined; these include Ru compounds, Ti compounds and possibly Au and Sn compounds; as well as drug targeting with Pt complexes showing affinity to hormone receptors and osteotropic properties. (77 Refs.)

[Bis(aminomethyl)dimethylilalane] platinum(II)dichloride: A Potential Antitumor Agent


The title compound was synthesised by a three-step procedure and its anti-tumour activity was investigated against L1210 leukaemia in mice. With suitable dosing it extended the life span by at least 100% and resulted in 40–50% survivors (day 30) in two experiments. It appeared to be as least as active as cisplatin under these conditions.

Effect of Palladium Addition on the Tarnishing of Dental Gold Alloys


Tarnishing tests were performed on Au-Cu-Pd and Au-Cu-Ag alloys. Tarnish resistance was almost perfect for the alloys with nobility of >50%, but it seemed to relate to the Pd:Cu atomic ratio for the alloys with low nobility. Pd inclusion reduced the tarnish susceptibility up to ~ 10 at.%. Tarnishing of the alloy with low nobility was very sensitive to its microstructure. Pd-bearing alloy showed no increase in the degree of tarnishing by phase separation. This may be attributed to the enrichment of Pd in the Cu-rich phase.
NEW PATENTS

METALS AND ALLOYS

Gold Based Alloy for Jewellery

LENGD. RUSKIE SAMOT. Russian Patent 1,498,809

A Au based alloy contains 58.0–59.0 wt.% Au, 3.5–4.5 wt.% Pd, 7.5–8.5 wt.% Ag, 0.7–1.5 wt.% In, 0.5–1.2 wt.% Mn and balance Cu. The alloy has improved ductility and is used for jewellery.

ELECTROCHEMISTRY

Oxygen Generating Electrode for Electromagnetic Propulsion Vessel

M. MUROYA Japanese Appl. 2/77,394

An O2 generating electrode consists of a Ti base material coated with at least one oxide of RuO2 or IrO2, on which is a Mn oxide layer. The RuO2 and/or IrO2 layer promotes the O2 generating reaction, prevents dissolution of the Ti, and attaches the Mn oxide layer. The electrode has good O2 generating efficiency, is used for electromagnetic propulsion vessels, and generates less chlorine, thus reducing environmental pollution.

Electrochromic Material Containing Rhodium

OSAKA GAS K.K. Japanese Appl. 2/86,683

An electrochromic material consists of a viologen Rh complex prepared by reaction of Rh chloride and 4,4′-dimethyl-2,2′-bipyridine by heating so that they dissolve in a solvent such as dimethyl formaldehyde. The complex shows an electrochromic phenomenon of red coloration to decoloration by electrochemical oxidation/reduction.

Electrolysis Electrode Manufactured Using Ion-Beam Mixing

LIMES K.K. Japanese Appl. 2/88,785

An electrode is manufactured by using an ion-beam mixing method to form an amorphous alloy layer consisting of at least one Fe group element, at least one platinum group element, and at least one of Ti, Zr, Nb and Ta, on the surface of a metal substrate, and treating the alloy film with acid. This provides an electrode material with an irregular surface suitable for electrolysis of brine water.

Activating Titanium Anodes for Electrochemical Processes

VER. CHEM. BITTERFELD East German Patent 273,364

A Ti anode is activated by anodising in an electrolyte containing sealing components, fluoride and 0.01–2.0 mol/l Ru chloride. Oxidising is by spark discharge under a direct voltage of 10–200 V, followed by optional treatment with platinum group metal chlorides, and tempering.

ELECTRODEPOSITION AND SURFACE COATINGS

Non-Corrosive Palladium Electroplating Solution

AT. & T. BELL LAB. U.S. Patent 4,911,798

Electroplating of Pd and Pd alloys uses a bath containing 0.0001M to 0.1–0.5M (saturated) Pd, an alloying metal from Pt, Rh, Ir, Ru, Ag, Cu, Ni, Co, Cr, and Mn, an alkylhydroxyamine as complexing agent, and a buffer system. A corrosion resistant coating with high electrical conductivity is produced, for example, for connector pins.

Palladium Electroplating Bath

AT. & T. BELL LAB. U.S. Patent 4,911,799

A novel electroplating process uses a bath of pH 6.0–13.5, containing a Pd source, an alkyl ammonium chloride surfactant with 4–35C, and a specified brightener, for example o-benzaldehydesulphonic acid. The process is used for electrical contact surfaces in contact devices or electrical connectors. The plated films have excellent adhesion and ductility, are crack-free, have a bright finish, and show excellent electrical contact and wear properties.

Electroplating Process for Through Hole Circuit Boards

SHIPLEY CO. U.S. Patent 4,919,768

A non-conductive body is electroplated by treating the surface in sequence with a >0.01 M Sn2+ salt solution, a 0.00001–1.0 M sulphide solution, a 0.001–0.01 M Pt or Pd salt solution, and electroplating the resulting surface with Cu or solder.

Erosion Resistant Coating with Platinum Layer

AVCO CORP. U.S. Patent 4,919,773

A coating used to impart erosion resistance to a stainless steel or Ti alloy substrate has 3 layers: a ductile barrier layer of e.g. Pt of 0.1–1.5 mils thickness, a layer of pure metal selected from Groups III–VI of thickness 0.2–1.5 mils, and a layer of a boride, carbide, oxide or nitride element from the above Groups of thickness 0.2–2.5 mils. The coating may be used for components of a gas turbine engine, and gives improved erosion resistance without degradation of the mechanical properties of the substrate.

Addition of Palladium Solution to Copper Plating Liquid

TOYAMA NIPPON DENKI Japanese Appl. 2/70,069

A Pd solution is added quantitatively to a Cu plating liquid extracted into a reaction cell, while the Cu ion concentration is measured continuously by colorimeter. This determines the time period until the concentration reaches a set value, and a deficient amount of stabiliser is added to the plating bath.
Ground Coating Conductive Paint Composition
SUMITOMO METAL MINI K.K.
A paint composition contains 50–80 wt.% metallic powder which is either Ag powder or a mixture of 90–99 wt.% Ag powder (0.5–3.0 μm) and 10–1 wt.% Pd powder (up to 0.3 μm), acid-proof glass powder, PbO/ZnO/B₂O₃/SiO₂ glass powder, and an organic vehicle. The composition is used prior to metal plating on the terminal electrodes of laminated composition 90–99 powder which is either Ag powder or a mixture of.

Two-Tone Coloured Metal Plating for Watch Casings
CASIO COMPUTER CO. LTD. Japanese Appl. 2/111,537
A two-tone coloured metal plated synthetic resin product is produced by coating the surface of a moulded synthetic resin product with an underplating metal, plating with Pd metal, plating with Au metal, partly masking the Au layer, releasing the unmasked Au layer to expose Pd, and releasing the mask to reveal the Au plated portions. This method has high plating workability, and is used for making aesthetic watch casings.

Improved Rhodium Deposition on Disks
AUTOM. ELEMENT CONS. Russian Patent 1,507,878
Improved electroplating of discs with enhanced uniformity is achieved using a unit including a drive for lifting and lowering the disc, a shaker mechanism and a vibrator attached to rigidly tied screens. The unit gives improved Rh film deposition on working faces of discs, and eliminates coat porosity.

APPARATUS AND TECHNIQUE
Carbon Monoxide Gas Sensor with Platinum Coils
SEIKO CO. LTD. European Appl. 358,925A
A catalytic combustion type CO gas sensor includes a gas sensotimeter to determine the CO concentration, based on the difference in resistance of two Pt coils on the catalytic combustion of CO, one in the active section and the other in the compensating section. The device has low cost, high reliability and provides easy handling, and may be used to detect CO emitted from domestic gas appliances due to incomplete combustion.

Rapid Oxygen Sensing Device
NAT. AERO & SPACE ADMIN. U.S. Patent 4,911,890
A device for sensing the amount of molecular O₂ in a gas includes a heated ceramic electrolyte disc coated with Pt electrodes, which generates a voltage output proportional to the partial pressure difference of the O₂ in the product gas and the reference air. The amount of O₂ in a combustion product gas is quickly sensed, to control the amount of O₂ in the gas, in order to maximise efficiency and minimise pollution.

Gas Sensor with Stable Properties
FIGARO GIKEN K.K. Japanese Appl. 2/28,548
A gas sensor has a heat resisting insulating substrate, a RuO₂ heater and a metal oxide semiconductor membrane, with a region of potential gradation between the RuO₂ heater (low potential) and the membrane (high potential). Contamination of the metal oxide semiconductor with alkali metal ions such as Na by migration from the RuO₂ heater can be prevented, and stabilised characteristics are maintained for a long time.

Responsive Oxygen Sensor with Thin-Film Platinum Electrode
TANAKA KIKINZOKU KOGYO Japanese Appl. 2/38,964
A solid electrolyte type thin-film O₂ sensor has a porous thin-film Pt electrode formed from an organic Pt ink and a thin-film zirconia solid electrolyte formed from an organic Zr ink. The organic Pt ink consists of 20% Pt resinate, 3% Bi resinate, 1% Pb resinate, 2% Si resinate, 1% Sb resinate, 53% gum resin, and 20% terpineol. A small-sized inexpensive, and highly responsive O₂ sensor is obtained.

Adsorbing Plate for Collection of Evaporated Platinum Particles
TANAKA KIKINZOKU KOGYO Japanese Appl. 2/83,291
When melting ferrite blocks or rods in a Pt or Pt alloy crucible for growing a ferrite single crystal, a Pt or Pt alloy adsorbing plate is placed above the crucible at a lower temperature, and Pt evaporating from the crucible is collected. The amount of Pt particles floating in the growth furnace environment is reduced, giving rise to a very pure ferrite single crystal.

Platinum Crucible for Preparation of Sample Glass Bead
NIPPON STEEL CORP. Japanese Appl. 2/83,431
A sample for use in fluorescent radiation is prepared by fusing a powdery sample in a Pt crucible to form a glass bead. Oxidant, sample, flux, and separating agent are put in the Pt crucible, oxidised at 800–900°C for 5–15 minutes, and fused at 1050–1200°C for 3–10 minutes. The glass bead can be prepared automatically in a short time, and can be analysed with high accuracy without damaging the Pt crucible.

Enzyme Sensor with Precious Metal Substrate
TERUMO CORP. Japanese Appl. 2/87,056
An enzyme sensor has a conductive substrate of Ir, Ru or Pd-oxide, Pt or Au, preferably in thin membrane shape, and an enzyme fixed membrane. The enzymes, for example glucokinase, are obtained from a thermophilic organism and can be grown at, and do not lose activity at >40°C, so heat and solvent resistance are improved, and life is extended. The sensor can be easily used in mass production processes, and storing is easy.
Apparatus for Determination of Acid Concentration in Fluids
SUMITOMO ELEC. IND. K.K.

*Japanese Appl. 2/122,249*

Apparatus used for determination of acid concentration in fluids consists of a measuring vessel, a graphite anode, a Pt cathode, a DC current supply unit, and a conductivity measuring unit. The acid concentration can be found with high sensitivity. The apparatus is easy to handle, has good chemical resistance, and corrosion and breakdown of the electrodes do not occur.

Long Life Gas Concentration Sensor
FUJIKURA CABLE WORKS K.K.

*Japanese Appl. 2/126,149*

A gas concentration sensor with long life consists of porous Pt electrodes on either side of a solid electrolyte plate, with a cap covering the electrode and forming an internal chamber between the electrode and partition. Each electrode has a porous protective layer which is a mixture of Al₂O₃ and Au. The Al₂O₃ has a good Au adsorption, hence there is no decrease in electrode efficiency, and the electrodes are protected from SO₂.

Sensor for Controlling the Level of Liquid Coolant
VEB. HOCHVAK DRESDEN East German Patent 274,757

The level of low boiling point liquid is controlled by a Pt resistance wire resistor covered with a ceramic protection tube. A heating current of 50-90 mA is applied to the Pt resistor which is part of a Wheatstone bridge unit. The sensor can distinguish between liquid or gas which avoids false recordings, and is used to control the level of liquid coolant, especially liquid N₂.

Higher Quality Selective Electrode for Lactose Determination
AS. LITH. BIOCHEM. INS. *Russian Patent 1,502,995*

An electrode with increased selectivity for determination of lactose consists of a Pt electrode coated with a 5μm thick separating membrane, and then with a bi-enzyme membrane containing co-immobilised glucooxidase and β-galactooxidase, with a microporous film on top. The current is measured versus a reference electrode, giving a linear current versus lactose content relationship up to 3.0 wt.%.

Carbon Monoxide Thick Film Sensor
D.-W. LEE
*South Korean Patent 89/2,572A*

A CO thick film sensor has a diffused resistor layer deposited between the Si base plate and SiO₂ layer, with vacuum deposited electrodes on the layer, an auxiliary layer coated above the electrodes, followed by the CO sensing layers and electrodes formed in sequence. The CO sensing material consists of 0.3–0.7 wt.% of Pt and 99.3–99.7 wt.% of TiO₂ or ZnO.

JOINING

Brazing Alloy for Joining Superalloy Metals
GET PRODUCTS CORP. *U.S. Patent 4,839,141*

A brazing alloy with good gap filling and high temperature properties consists of 15–35 wt.% Pd, 5–30 wt.% Au, 10–30 wt.% Ni, 20–48 wt.% Cu, and 5–25 wt.% Mn, and has a brazing temperature of 1025–1080°C, a solidus temperature above 1000°C and a liquidus temperature above 1018°C. The brazing alloy is used in joining superalloy metals.

HETEROGENEOUS CATALYSIS

Production of a Hydrocarbon White Oil
UOP

*European Appl. 360,010A*

A hydrogenation catalyst, consisting of 0.05–5 wt.% of a platinum group metal on a refractory oxide support, is used in the production of a hydrocarbon white oil by hydrogenating a feed stream of 15–30°C hydrocarbons obtained from an aromatic alkylation process. A white oil product is obtained.

Novel Catalyst for Ally1 Acetate Preparation
SHOWA DENKO K.K. *European Appl. 361,484A*

A novel catalyst for allyl acetate manufacture consists of a carrier impregnated with 0.3–1.0 wt.% Pd, 0.2–1.0 wt.% of Cu, Pd, Rh and/or Ru, and an alkali metal acetate. The catalyst is used for the gas phase reaction of propylene, acetic acid and O₂ at 140–170°C and 2–10 atm, giving high relative activity and selectivity, long life, and enabling a lower reaction temperature to be used, which reduces the corrosive effects of the acetic acid.

Hydrogen Production by Shift Reaction Process
IMPERIAL CHEM. INDNS. P.L.C.

*European Appl. 361,648A*

Catalysts showing good activity for the shift reaction process contain a metal such as Pd and preferably an alkali metal oxide or an alkaline earth metal oxide. A H₂ containing gas stream is produced from a carbonaceous feedstock by forming a gas stream containing H₂, CO and steam at >700°C, cooling to 550–650°C, passing over the Fe-free catalyst (no methanation activity) to catalyse the shift reaction, and cooling to <500°C.

Platinum Hydrogenation Catalyst for Preparation of Photostabilisers
CIBA GEIGY A.G. *European Appl. 363,318A*

The preparation of 2-(2-hydroxyphenyl)-2H-benzotriazoles is carried out by catalytic hydrogenation of a nitrobenzene (2-azo-2) phenol compound in the presence of a supported 0.1–3 wt.% Pt hydrogenation catalyst and an organic amine.
Platinum Based Knitted Fabric Catalyst
JOHNSON MATTHEY P.L.C. European Appl. 364,135A
A knitted precious metal fabric for use as a catalyst consists of a metal from the platinum group, Au and Ag; particularly Pt or Pd. The fabric is made by knitting the metal fibre with a supplementary fibre which is later removed. The fabric is used as a catalyst for NH₃ oxidation, and results in increased conversion efficiency—90 to 95% compared with 90% for a conventional material—when tested in an NH₃ oxidation reactor at medium pressure.

Catalytic Production of Hydrogen Peroxide in an Aqueous Medium
ATOCHEM. European Appl. 364,374A
A catalytic process for production of H₂O₂ involves reacting H₂ with O₂ at above atmospheric pressure in an aqueous medium free from organic compounds and containing a platinum group metal catalyst, especially Pt or Pd. The aqueous medium is first contacted with H₂, and then with O₂. The process is safe to operate, allows any chosen proportions of H₂ and O₂ to be used, and allows unused H₂ and O₂ to be recycled.

Laminated Combustion Catalyst Element
GENERAL ELECTRIC CO. European Appl. 370,244A
The element has a metal alloy substrate, an oxidation resistant layer of Pt, Pd or Ru <0.0001 inches thick, and an Al₂O₃ washcoat layer containing Pt, Pd, Rh or metal oxide as combustion catalyst. The element can be used in an oxidising atmosphere at high temperatures for an extended time, for example at 1800–2500°F, with a service life up to 8000 h. It is used as a combustion catalyst to reduce exhaust emissions from gas turbines.

Three-Way Catalyst with Suppressed Hydrogen Sulphide Emissions
NIPPON SHOKUBAI KAGAKU EUROPEAN APL. 372,156A
An exhaust gas purification catalyst consists of activated Al₂O₃, supporting 5–30 wt.% Pt and/or Pd, 1–20 wt.% Rh, Ce oxide, activated Al₂O₃, and optionally an alkali metal and/or Ni oxide; all coated on a honeycomb monolith carrier. The catalyst removes CO₂, hydrocarbons and NOₓ from the exhaust gases of vehicle engines, while suppressing H₂S emissions.

Palladium Catalyst for Hexamethylenimine Preparation
DU PONT DE NEMOURS CO. European Appl. 372,492A
A gaseous mixture containing hexamethylenimine vapour, water vapour and H₂ is contacted with a solid catalyst of 0.1–10 wt.% Pd on Al₂O₃ spheres, at 160–260°C and 0–100 psig, to prepare hexamethylenimine. The mixture may also contain at least one of NH₃, CH₄, or N₂, which are believed to increase catalytic activity. High conversion of the diamine and high yields of the hexamethylenimine are obtained in the process.

Catalytic Removal of Carbon Monoxide and Hydrocarbons from Waste Gases
JOHNSON MATTHEY INC. World Appl. 90/5,579A
A catalyst having good activity, durability, long life and resistance to S oxides consists of 0.005–2 wt.% Pt, Pd, Rh, Ir, Os and/or Ru on a SiO₂, ZrO₂, TiO₂, zeolite and/or α-Al₂O₃ support material, which may be applied to a ceramic or metallic monolith. The catalyst is used below 500°C in an oxidising atmosphere to treat waste gas from engines burning fossil fuels, and gives above 90% conversion for CO and above 50% for C₂H₄, C₃H₈, and so on.

Preparation of Mixture of Paraphenylenediamines
MONSANTO CO. U.S. Patent 4,900,868
Preparation of a mixture of 2 or more different N,N'-disubstituted paraphenylenediamines is by reductive alkylation of a N-containing compound such as 4-nitrodiphenylamine, with 2 or more ketones in sequence, in the presence of H₂ and a Pt/C catalyst. The cost effective, mixed ketone process is problem-free; a single ketone is recovered, a desired ratio of paraphenylenediamines is achieved, and less ketone is hydrogenated to alcohols.

Preparation of Polymethylene in High Yield
U.S. DEPT. OF ENERGY U.S. Patent 4,904,700
Polymethylene is prepared by contacting a H₂/CO or water/CO mixture in a solvent with catalyst slurry of at least 1 wt.% Pt and/or Pd on a support having a deposit of Fe. The catalyst can operate under mild pressure and temperature conditions (100–300°C), and can be used in slurry form with dilute reactant concentrations to obtain high yields of the product. The polymer materials produced are useful as diesel or jet fuels.

One Step Preparation of 2-Pyrrolidone
PHILLIPS PETROLEUM CO. U.S. Patent 4,904,804
Preparation of 2-pyrrolidone is effected by contacting a 1–10 molar excess of NH₃, with succinic acid or anhydride and H₂, in the presence of at least one diluent and a Pd/Al₂O₃ catalyst, with a molar ratio of succinic acid or anhydride/Pd of 1–1000. Reaction is at 200–300°C and at least 1000 psig for 0.5–18 h. The process enables a one step preparation of 2-pyrrolidone in higher yields than prior art processes.

Catalyst Panels for Stationary Power Plant Exhaust Purification
W. R. GRACE CO. U.S. Patent 4,916,001
Removal of pollutants from the exhaust of hydrocarbon-fuelled power plants is achieved using rectangular unitised monolithic honeycomb catalyst panels, with a catalyst of Pd-V₂O₅ on Al₂O₃-ZrO₂. Less structural material is required in the panels, which allows more catalyst to be exposed to exhaust gas, and reduces the pressure drop through the unit.
Three-Way Automotive Exhaust Catalyst  
W. R. GRACE CO.  
U.S. Patent 4,916,105  
The catalyst has a substrate, to which is applied a washcoat slurry consisting of water; 0.2–7 wt. % of a metal ferrite of formula $\text{MFe}_2\text{O}_4$, where $\text{M}$ is Co, Ni, Cu, Zn, Mn or Fe; and 20–50 wt.% of catalysed $\text{Al}_2\text{O}_3$, having 0.1–7.5 wt. % Pt, Pd and/or Rh (individually not above 2.5 wt. %), and 0–50 wt. % rare earths; followed by drying and calcining. The catalyst controls emissions of hydrocarbons, CO and NOx, individually not above 2.5 ppm, by the action of the zeolite embedded in the catalyst. The catalyst is used to remove hydrocarbons with higher efficiency at lower temperatures, even from fuel-rich combustion exhaust, by the action of the zeolite embedded in the catalyst.

Hydrocarbon Reforming Process with Dual-Zone Catalyst  
UOP  
U.S. Patent 4,929,332  
Gasoline range hydrocarbons are reformed in two sequential catalyst zones; the first having a catalyst composite with 0.01–2 wt. % Pt, 0.05–5 wt. % Ge, Ag, Al, Si, and/or Rh (in this catalytic system having the same components, plus a promoter from Rh, Ir, Ru, Re, Co and/or Ni. This system gives improved yield of petroleum aromatics or gasoline products compared with a single catalyst system.

Catalyst for Methanol and Formaldehyde Vapour Oxidation  
FORD MOTOR CO.  
U.S. Patent 4,919,903  
A dispersed catalyst consisting of Pd with Rh and/or CeO$_2$, with an Al$_2$O$_3$, at a Rh/Pd wt. ratio of 0–0.3 and a CeO$_2$/Pd wt. ratio of 0–50, is used for complete oxidation of CH$_3$OH and/or HCHO vapour at 85–200°C, in the exhaust from a CH$_3$OH fuelled I.C. engine calibrated for stoichiometric air/fuel mixtures. Gases having 0.01–1% CH$_3$OH vapour and 0.001–0.05% HCHO vapour are more efficiently converted than by prior art Ag/CeO$_2$-catalysts.

Platinum Catalyst for Preparation of N-Alkyl-Anilines  
CIBA-GEIGY CORP.  
U.S. Patent 4,921,980  
N-alkyl-anilines are prepared by reacting an aniline with an alcohol in the presence of H$_2$ and a catalyst at 150–300°C and 0.5–6 bar pressure. The catalyst consists of 0.2–10% Pt, 0.05–3% of a Group Ia and/or IIa metal compound, and at least one other compound on a SiO$_2$ gel carrier. The reaction can be continuous and gives high conversion and selectivity.

Platinum or Palladium Catalyst for Wax Isomerisation  
EXXON RES. & ENG. CO.  
U.S. Patent 4,923,588  
A wax isomerisation catalyst consists of Pt or Pd and 0.1–1.5 wt. % fluoride on an Al$_2$O$_3$, or Al$_2$O$_3$-containing support in the form of 1/20 inch trilobes. Waxes are isomerised into hydrocarbons by passing over the catalyst in the presence of H$_2$. The method is used for conversion of slack waxes from dewaxing hydrocarbon oils, or synthetic waxes from the Fischer-Tropsch process into liquid hydrocarbons boiling in the range 370°C.

Naphtha Reforming to Improve Gasoline Octane Value  
UOP  
U.S. Patent 4,923,595  
Naphtha is reformed by contacting it with H$_2$ and a catalyst consisting of an Al$_2$O$_3$ support with 0.05–1 wt. % Pt, uniformly dispersed; 0.1–2 wt. % Ge, Pd or Sn, uniformly dispersed; 0.1–2 wt. % Rh, Ir, Ru, Co or Ni, which is surface impregnated; and 0.5–1.5 wt. % Cl. The catalyst has dual hydrocarbonation/dehydrogenation and cracking functions, and is highly active, selective and stable.

Palladium Catalyst for Dimerisation of Aromatic Halogen Compounds  
MITSUBISHI KASEI CORP.  
Japanese Appl. 2/53,742  
Aromatic halogen compounds having one or more halogen atoms on aromatic ring carbon(s) are dimerised by heating at 20–250°C, under ordinary pressure of 100 kg/cm$^2$, with reducing agents, halogen absorbers, surfactants, water, and a supported Pd catalyst present at 0.1–30 mg Pd per mol of starting material. Aromatic dimers are used for various chemicals, for example, 3,4,3',4'-biphenyltetracarboxylic acid is useful for polyimide resins.

Noble Metal Three-Way Catalyst with Zeolite Layer  
TOYOTA JIDOSHA K.K.  
Japanese Appl. 2/56,247  
A three-way catalyst consists of a support having a zeolite coating, and an Al$_2$O$_3$ coating loaded with (for example) 1.5 g/l Pt, 0.3 g/l Rh, 0.03 mol/l La, and 0.3 mol/l Ce. The catalyst is used to remove hydrocarbons, CO and NOx from combustion exhaust, and can remove hydrocarbons with higher efficiency at lower temperatures, even from fuel-rich combustion exhaust, by the action of the zeolite embedded in the catalyst.

Preparation of Carbamic Acid Esters  
BABCOCK-HITACHI K.K.  
Japanese Appl. 2/56,458  
Carbamic acid esters are prepared by reaction of amines or amino acids with CO, organic nitro compounds and organic hydroxyl compounds, at 60–230°C, using a catalyst of Pd, Rh or Ru on SiO$_2$ or Al$_2$O$_3$ and an aqueous solution of hydrogen halides. The esters are prepared under mild conditions, in high yield, without using phosgene, and are useful for pesticides, isocyanates, and so on. Less catalyst is used and it is readily recovered.

Combustion Equipment with Two Types of Rhodium Catalyst  
TANAKA KIKINZOKU KOGYO  
Japanese Appl. 2/57,808  
Fuel such as town gas is fed into combustion equipment having an upstream catalyst with 5–50 nm grain diameter Rh, and a downstream catalyst having Rh of 0.05–2 μm grain diameter and 0.1–10 wt. % Ce to prevent Rh deactivation, with the catalyst dispersed on a stabilised-oxide coated support. The upstream catalyst promotes improved ignition performance.
Exhaust Gas Purification Catalysts
MITSUI MINING & SMELTING

Exhaust gas purification catalysts with good catalytic properties are prepared by immersing ceramic supports in Pt salt solutions prepared by adding dinitrodiamino Pt to a HNO₃ solution, under pressure at 100–160°C. The Pt salt solutions are adsorbed efficiently on the supports and then reduced.

Oxidation Catalyst for Exhaust Purification
MATSUSHITA ELEC. IND. K.K.

The catalyst consists of a honeycomb structure, a perovskite structure composite oxide of formula ABO₃, where A is at least one of La, Ce and Sr, and B is Ce and/or Ni, mixed with an inorganic binder, and at least one of Pt, Pd and Rh. The catalyst carrier produced has a larger surface area, enabling the catalytic substance to be homogeneously dispersed and tightly held. The catalyst is used to oxidise CO and hydrocarbons in exhaust gas to CO₂ and water.

Particulate Oxide Catalyst Filter for Diesel Exhaust
SAKAI CHEMICAL IND. K.K. Japanese Appl. 2/102,315

A particulate oxide catalyst filter is obtained by supporting Pt, Pd, Mn oxide, Cr oxide or Fe oxide on a thin metal netting or plate which may be of stainless steel, and has many small holes of diameter ≥30 μm. Waste gas from diesel engines is forcibly passed through a number of filters; particulates are stably removed over long periods, and an increase in pressure loss of the filter is prevented.

Three-Way Catalyst with Improved Durability
TOYOTA JIDOSHA K.K. Japanese Appl. 2/102,735

A catalyst for purification of exhaust gas consists of a heat resistant carrier coated with an Al₂O₃ layer containing Pd-Nd and Rh-La composite oxides obtained by coprecipitating Pd-Nd and Rh-La, respectively. The catalyst is used for simultaneous removal of CO, hydrocarbons and NOx from car exhaust gases, and has improved activity and durability, resulting in effective utilisation of the noble metals.

Rhodium Solutions for Exhaust Catalyst Preparation
CATALER KOGYO K.K. Japanese Appl. 2/102,736–37

Rh-containing solutions are prepared by mixing Rh hydroxide crystals with either (a) weak basic nitrates selected from ammonium nitrate and rare earth metal nitrates, or (b) a water soluble organic acid having at least one carboxyl group, and dissolving in HNO₃, crystallising the HNO₃ solution, and dissolving the resultant crystals in water or HNO₃. The Rh solutions are used to prepare waste gas purification catalysts, with higher efficiency.

Exhaust Purification Catalyst with No Hydrogen Sulphide Generation
TOYOTA JIDOSHA K.K. Japanese Appl. 2/107,334

An exhaust gas purification catalyst consists of Pt, Pd or Rh supported on a metal oxide layer where Ce oxide exists on the surface of Al₂O₃, and a Ni-Ba composite oxide, with the oxide layer formed on a heat resistant substrate. The catalytic activity of the Ni is increased, and H₂S generation is prevented. In an example the catalyst showed 98%, 100% and 97% removal of hydrocarbons, CO and NOx, respectively.

Ruthenium Catalysts for Preparation of Perfumed Products
KAO CORP. Japanese Appls. 2/108,642 and 2/121,938

Catalysts consisting of 5 or 7% Ru on active C are used in hydrogenation reactions for the production of (a) 2-cyclohexylpropanol from 2-phenylpropanol or 2-phenylpropanal, or (b) a substituted cyclopentane-2-ol. A basic aqueous solution of pH 8.0–10.5 is added to the reaction medium or is used to wash the Ru catalyst. Product (a) can be used as a perfume and can be obtained in high yields, while product (b) has a woody odour, and can be produced industrially in high yields, in a short time.

Platinum-Loaded Catalyst Supports for Combustion
TANAKA KIKINZOKU KOGYO

Japanese Appl. 2/115,040

Catalyst supports for combustion are prepared by immersing Al₂O₃ fibre laminated supports in an HNO₃ solution of dinitrodiamine Pt to which reducing agent is added, fixing Pt, drying and firing. Small Pt particles are loaded uniformly on the catalyst supports, which can be used for burners in which gas fuels or vapourised liquid fuels are burnt at low temperatures.

Production of Hydrogen-Containing Gas for Car Fuel
MITSUBISHI HEAVY IND. K.K. Japanese Appl. 2/116,603

H₂-containing gas is produced by reacting CH₄ and O₂-containing gas at 100–600°C, using a catalyst of Pt and/or Pd on a support preferably containing 10–98 wt.% of rare earth element oxides, selected from La₂O₃, CeO₂, Nd₂O₃ or mixtures. The gas can be produced at low temperature, with good selectivity, and stability over a long time.

Production of Nucleosides
AJINOMOTO K.K. Japanese Appl. 2/117,689

Production of 2',3'-dideoxynucleosides is effected by converting a nucleoside into an intermediate compound, and then reducing in an aqueous organic solvent in the presence of a Pd catalyst and a base, under an atmosphere of H₂. The products are prepared in high yield with high selectivity using this process.
Curable Fluorosilicone Composition
SHINETSU CHEM. IND. K.K. *Japanese Appl.* 2/123,163
A curable fluorosilicone composition consists of 100 parts wt. of an organopolysiloxane, an organohydrogensiloxane, 0.01-10 parts wt. of another organopolysiloxane, and a catalytic amount of Pt, Pd or Rh series compound. The composition has high heat resistance, and is used for potting and coating of electric and electronic parts.

Preparation of Aromatic Urethanes
SUMITOMO METAL IND. K.K. *Japanese Appl.* 2/124,865
Aromatic urethanes are prepared by reaction of an aromatic nitro compound with CO and a hydroxy-containing organic compound, in the presence of a Pd or Ru catalyst fixed in a reactor, a Lewis acid promoter such as FeCl₃, and a N-containing heteroaromatic compound as ligand. Aromatic urethanes can be prepared without use of phosgene, without recovery, drying and reactivation of the platinum group metal, and with little metal loss.

Ammonia Converter with Increased Reliability
TEKHENERGOKHIMPROM. *Russian Patent* 1,493,303
An NH₃-air mixture is fed to an NH₃ converter having a vertical cylindrical body and containing a Pt catalyst mesh. Oxides of nitrogen are formed, which are fixed by cooling, and used to make dilute HNO₃ with increased reliability.

HOMOGENEOUS CATALYSIS
Visible Radiation Activated Hydroisilylation Reaction
MINNESOTA MINING MFG. CO. *European Appl.* 358,452A
A hydroisilylation process comprises reacting an unsaturated aliphatic compound and a composition containing at least one Si-bonded H in the presence of a Pt complex and a sensitizer. The sensitizer absorbs visible light on exposure and transfers energy to the (η¹-cyclopentadieny) tri-(α-aliphatic) Pt complex so that reaction is initiated. The method is used for visible light curable impression material for dental applications, and enables use of a heat-sensitive substrate, and safer visible radiation.

Alkadienol Production with Recirculating Palladium Catalyst
MITSUBISHI KASEI CORP. *European Appl.* 361,304A
Alkadienols are produced by reaction of a conjugated alkadiene and water in the presence of CO₂ and a catalyst consisting of a Pd compound and a phosphine or phosphite. The method efficiently separates high boiling point by-products from the Pd catalyst, which is then recirculated into the reaction system with higher activity. Alkadienols are produced, which are hydrated dimers of a conjugated alkadiene.

Homogeneous Rhodium Hydrogenation Catalyst
RANBAXY LAB. LTD. *U.S. Patent* 4,902,447
β-Deoxytetraacycline derivatives are prepared by hydrogenation of substituted methylenetetrayclines in the presence of a bis(triphenylphosphine) (hydroxylamine hydrohalide) dichloro Rh catalyst. The products are obtained in high yields and purity, and include the known antibiotic doxycycline. The process is more economical than known processes as less Rh is used for the catalysts.

Preparation of α-Phenyl Propionic Acid Derivatives
DAICEL CHEM. IND. K.K. *Japanese Appl.* 2/48,544
α-Phenylpropionic acid derivatives are prepared by reacting an α-phenylethyl alcohol derivative with CO, at 30-130°C, in a mixture of a hydrocarbon and an α-phenylpropionic acid derivative, in the presence of a Pd, Co or Ni compound as catalyst, and preferably a cocatalyst such as I, HI, or alkyl iodide. The products have analgesic, anti-inflammatory and anti-pyretic activities, and can be produced in high yield by this process.

Preparation of Indole-Carboxylic Acid Esters
NIPPON STEEL CHEM. K.K. *Japanese Appl.* 2/73,060
Indole-7-carboxylic acid esters are prepared by reaction of dihydro-indolyl thallium bis-trifluoroacetate with CO in a lower alcohol in the presence of Pd acetate. The indole esters are useful as intermediates in the preparation of drugs and agrochemicals, and can be produced from indolines in high yield and regiospecifically by this short process.

Palladium Catalyst for Preparation of Indole Compounds
NIPPON STEEL CHEM. K.K. *Japanese Appl.* 2/73,061
Indole compounds are produced by reacting a halogeno-indole with an olefin in the presence of 0.3-50 mol.% of a Pd catalyst such as Pd acetate or Pd chloride, a triarylporphine and a base. The reaction is carried out in a solvent at 80-140°C, for 0.5-48 h. The process produces indole compounds easily with low cost; which are useful as a starting material for pharmaceuticals or agrochemicals.

Rhodium Complex Catalyst for Selective Preparation of Silanes
TOSHIBA SILICONE K.K. *Japanese Appl.* 2/96,583
Aminoalkyalkoxysilanes useful as glass-plastics binders are prepared by reaction of silane compounds with allylamines in the presence of a Rh complex catalyst having N and/or S containing heterocyclic compounds as ligands. The products are prepared selectively using the Rh complex catalyst, which can be prepared readily from the Rh complex and ligands in situ. An example of the Rh complex is bis(1,5-cyclooctadiene) Rh(1) tetrafluoroborate.
Palladium Catalyst for Preparation of Polymerisable Monomers

MITSUI PETROCHEM. IND. K.K.

*Japanese Appl. 2/111,767*

Preparation of 1,3-dioxolen-2-one derivatives is by hydrogenation of 4,5-dihalo-1,3-dioxolan-2-one derivatives at 20–70°C, under atmospheric pressure to 10 kglcm², in the presence of a Pd catalyst (Pd at 0.1–3 wt.% of starting material), aliphatic tertiary amines and alkali metal compounds.

Palladium Complex Carbynlolation Catalyst

NIPPON PETROCHEM. K.K. *Japanese Appl. 2/117,636*

A mixture of two or more unsaturated hydrocarbons is reacted with CO and water or a lower alcohol at 40–250°C, with 10–600 kg/cm² of CO pressure, in the presence of a carbynlolation catalyst such as bis(triphenylphosphine) dichloro Pd. Selective hydrocarboxylation or hydroesterification of the vinyl radical produces α-aryl propionic acid derivatives or their esters, which are intermediates for production of α-(4-isobutylphenyl) propionic acid (Ibuprofen).

Platinum Group Metal Hydrogenation Catalysts

CENTRAL GLASS K.K. *Japanese Appl. 2/121,952*

Halomethyl-nitrobenzenes undergo fluorination and hydrogenation by reaction with HF and H₂ in the presence of a hydrogenation catalyst, to give the 4-fluorosulinline derivative. The catalyst may be Pt, Pd, Rh, Ir, Os or Ru in the form of metals, oxides, halides or hydroxides. The reaction yield and position-selectivity are high, giving products useful as intermediates for bactericides, herbicides and medicines.

Improved Preparation of Phthalides

MITSUBISHI KASEI CORP. *Japanese Appl. 2/121,976*

Phthalide(s) are prepared by hydrogenation of aromatic ortho-dicarboxylic acid(s) or their anhydride(s) in the presence of a catalyst of Ru, organophosphines, and conjugated bases. The phthalides are prepared under mild conditions in high and steady yield (60–90%), and are useful as intermediates for naphthalenes, anthracenes and certain alkaloids. The catalyst does not cause corrosion of the apparatus and shows steady, high activity for a long time.

Hydrogenolysis of Carbonyl Protective Groups on Peptides

BERLIN CHEMIE VEB. *East German Patent 274,822*

Carbonyl protecting groups on amino acid and peptide derivatives can be removed by hydrogenolysis without affecting sensitive histidine and tryptophan components. Hydrogenolysis is in an organic solvent, under a H₂ pressure of 1.5–50 bar, with a Pd catalyst present at 1–6 mg Pd per mmol of amino acid or peptide derivative; itself present at 200–600 mmol/l.

**FUEL CELLS**

Amorphous Alloys as Reversible Hydrogen Storage Media

STANDARD OIL CO. (OHIO) *U.S. Patent 4,923,770*

Amorphous alloys for reversible H₂ storage contain Pt, Ag and/or Hg; Ru, Fe, Ni, Al, Co, Mo, Mn and/or others; and Zr, Ti, Cd, Ca, Mg and/or others. A reversible H₂ storage electrode for use in alkaline or acid electrolyte can be formed using the alloy as a thin film or powder on a Ti or Ta substrate. The alloys can be repeatedly cycled without becoming embrittled or phase separated, oxidised or corroded.

Methanol Fuel Electrode Catalyst Containing Platinum and Ruthenium

MATSUSHITA ELEC. IND. K.K. *Japanese Appl. 2/51,865*

A new method for preparing a catalyst for the CH₃OH fuel electrode of a fuel cell involves attaching highly dispersed Pt and Ru on C fine particles. Suspended, highly dispersed C fine particles are ultrasonically blended into a colloidal liquid containing dispersed Pt and Ru, and then the catalyst particles are filtered, washed, dried, and heat treated at 200–500°C in air. An electrode with improved capability can be prepared by a simplified process.

Electrocatalyst for Methanol Fuel Cells

MATSUSHITA ELEC. IND. K.K. *Japanese Appl. 2/111,440*

An electrode catalyst for use in fuel cells is prepared by supporting noble metal particles (including Pt) on a C powder support using an alcohol as reducing agent, and 5–10% H₂O₂, as reaction promoter. The catalyst can be used for a CH₃OH fuel cell, in which case Pt and Ru are solid-melted to give an alloy on the C, giving improved CH₃OH oxidation potential.

Combustion Catalyst for Fuel Reformer

FUJI ELECTRIC MFG. K.K. *Japanese Appl. 2/111,601*

A fuel reformer has parallel tubes with a reforming catalyst such as a Ni system on the inner face and a combustion catalyst such as Pt or Pd on the outer face. In the reformer natural gas and CH₃OH are reacted with steam, and H₂-rich reformed gas is produced for use in a fuel cell.

**GLASS TECHNOLOGY**

Platinum Bushings for Glass Fibre Spinning

TANAKA KIKINZOKU KOGYO *Japanese Appl. 2/97,433*

Bushings for spinning glass fibre or continuous glass filament are made of Pt or Pt alloy, with the bushing plate being reinforcedly supported from the underside by a support of Si₃N₄, having a surface coating of Al₂O₃ or ZrO₂ film. This support has high material strength and excellent durability.
ELECTRICAL AND ELECTRONIC ENGINEERING

Corrosion Resistant Permanent Magnet
SUMITOMO SPEC. METAL K.K.
European Appl. 361,308A
A permanent magnet consists of a sintered body of 10–30 at.% rare earth metals, 2–28 at.% B and 65–85 at.% Fe, with the surface having a layer of Pt, Pd, Au and/or Ag, an electrolest layer of Ni, Cu, Sn and/or Co, and an adherent electroplated layer of Ni, Cu, Sn and/or Co. The magnet has high corrosion resistance and stability, showing up to 5% deterioration in properties after 500 h at 80°C and 90% relative humidity.

Thin Film Amorphous Alloy
MITSUI PETROCHEM. IND. K.K.
European Appl. 364,631A
A thin amorphous alloy film with a perpendicular axis of magnetisation consists of Fe and/or Co, Pt and/or Pd, and at least one other element from specified groups. The film has high oxidation resistance, high reflectance, and excellent magneto-optic properties, including high coercive force and large Kerr and Faraday angles.

Magneto-Optical Recording Element Having Palladium Layers
EASTMAN KODAK CO. European Appl. 367,685A
A magneto-optical recording element includes a substrate on which is a layer of magneto-optical medium consisting of alternating layers of Co and Pd >6 Å thick). The element gives an increased carrier to noise ratio, and requires less materials and manufacturing time than conventional magneto-optical recording elements.

Stable Electrolytic Capacitor Containing Palladium
MATSUSHITA ELEC. IND. K.K.
European Appl. 372,519A
A solid electrolytic capacitor includes a dielectric oxide film, a solid electrolyte layer, and a C layer, with a cathode layer and/or conductive adhesive consisting of a polymer and a Pd-containing electrically conductive powder. By using the Pd powder a small initial tan δ value is obtained which is stable at high temperatures and humidities, as well as a high resistance to short circuit failures.

Thick Film Thermistor Composition
DU PONT DE NEMOURS CO. U.S. Patent 4,906,406
The composition consists of an admixture of finely divided particles of a Ru based pyrochlore and a borosilicate glass or glass mixture which has a viscosity of 10–10000 poises upon firing at 700–1000°C. Novel compositions have a good temperature range, a high positive temperature coefficient of resistance, and give a wide range of resistance values.

Oxidation Resistant Rare Earth Permanent Magnet
TOHOKU METAL IND. LTD. Japanese Appl. 2/87,502
A rare earth permanent magnet consists of a matrix of a rare earth-Ru-transition metal phase, dispersed in which is a rare earth-transition metal-B tetragonal magnetic compound. The magnet is made by magnetic moulding a starting powder which is a mixture of the magnetic compound and the matrix.

Fine Ruthenium Oxide Particles for Resistance Pastes
TANAKA KIKINZOKU KOGYO Japanese Appls. 2/88,431–32
Ru oxide fine particles are prepared by neutralising an acidic aqueous solution of Ru chloride with aqueous NH₃ or ammonium solution, and converting Ru hydroxide into Ru oxide. The particles obtained have a spherical shape, and a sharp particle size distribution, with 70% having sizes 0.2–0.3 μm, and are used in resistance pastes for thick film circuits.

Ferromagnetic Thin Film for Magnetic Head
HITACHI K.K. Japanese Appl. 2/90,505
A ferromagnetic thin film consists of an Fe-B alloy containing 1 at.%<B<5 at.% and balance Fe, and preferably containing 0.5–1 at.% of at least one of Pt, Pd, Rh, Ir, Os, Ru, Au and Ag. The thin film is used for magnetic head core material of magnetic disk devices or VTR’s, having a low magneto-strain constant, high saturation magnetic flux density and high permeability.

Magnetic Recording Medium with Cobalt-Phosphorus-Platinum Layer
MITSUBISHI KASEI CORP. Japanese Appl. 2/108,221
A magnetic recording medium consists of a Co-P type magnetic layer which includes 0.01–10 wt.% Pt (with respect to the Co), on a non-magnetic substrate. Coercivity of the medium is enhanced, and high density recording can be obtained.

Catalyst Coated Plastic Fibre Mat for Screening
ASEA BROWN BOVERI A.G. German Appl. 3,840,200
Mats for screening and dissipating any static charges are made of non-metallic fibres, such as plastic fibres, which are at least partly coated with a Pd catalyst layer and lined with a Cu film 0.1 μm thick by a currentless technique.

Electroconductive Paste for Metallising Ceramics
V.S. KOSTROMAROV Russian Patent 1,485,315
An electroconductive paste contains 48–65 wt.% Pt-Pd alloy powder, 0.1–1.0 wt.% MnCo₂, ethyl cellosolve, ethyl cellulose, white spirit, pine oil and triethanolamine. The paste is used for metallising non-fired Bi containing ceramic articles.
MEDICAL USES

Stable Cisplatin Solution for Parenteral Administration
BRISTOL-MYERS SQUIB. European Appl. 369,714A
A stable aqueous solution of cisplatin in a sealed container contains up to 1 mg of cisplatin and a source of chloride ion equivalent to 20–100 mg of NaCl per ml of solution. It contains less aquated Pt species and is of pH 5–7.5 which is closer to physiological pH than known solutions. The cisplatin can be parenterally administered and is an important anti-neoplastic agent used for treating metastatic testicular, ovarian and advanced bladder cancer.

New Platinum Anti-Tumour Agent with High Therapeutic Index
S.S. PHARMACEUTICAL K.K. European Appl. 376,076A
A new Pt complex possessing excellent anti-tumour activity has 1,2-diaminocyclohexane as a ligand in the cis, trans-l-, trans-d- or trans-dl-configuration. The complex may be used in the treatment of genital cancer, bladder cancer, or head and neck cancer, and has a high therapeutic index, good water solubility, and may be administered as an anti-tumour agent at a daily dose of 1–50 mg/kg orally, or 0.5–18 mg/kg parenterally.

Polysaccharide Anti-Cancer Agent’ Containing a Platinum Complex
KURARAY K.K. World Appl. 90/3,402A
New derivatives of activated polysaccharides and their pharmaceutically acceptable salts consist of a polysaccharide containing -SO3H, -COOH, or -P(O)(OH)2 acidic groups, bound to which are complexed (trans-l,2-cyclohexanediamine) Pt groups. The derivatives are anti-cancer agents with a reduced tendency to cause vomiting.

Medical Preparation Prepared Using Palladium Complex Catalyst
YAMASA SHOYU K.K. World Appl. 90/5,526A
A pharmaceutical preparation contains as active component a 2-alkynyladenosine prepared by reaction of 2-bromo-adenosine or 2-iodoadenosine with a 2-alkyne in the presence of cuprous iodide and/or Cu, 1-15 wt.% of one or more of Ru, Ir and/or Re, 0-5 wt.% of one or more of Au, 0-5 wt.% of one or more Fe, 80-150 wt.% of cuprous chloride. The preparation is used in the treatment and prophylaxis of ischémic disease of the heart and brain.

Boron-Free Palladium Dental Alloy
PIERCE & STEVENS CO. U.S. Patent 4,917,861
A dental alloy having exceptional high temperature strength consists of 50–85 wt.% Pd, 5-40 wt.% of Co and/or Cu, 1-15 wt.% Ga, up to 5 wt.% of a modifier of Ru, Au, Ni, In, Sn and mixtures, 0.01–0.05 wt.% of an O2 scavenging component from Ge, Li and mixtures, and up to 0.5 wt.% of a grain refiner from Ir, Re and mixtures. The novel alloy can be used for dental restorations and has high tarnish resistance.

Novel Platinum Compounds with Potent Anti-Tumour Activity
TORAY IND. INC. Japanese Appl. 2/32,086
New Pt containing compounds may be prepared by reacting a compound such as dinitrato (1,2-diaminocyclohexane)Pt(II) and an alkali/alkaline earth metal hydroxide with another compound. The new compounds exhibit potent anti-tumour action in a test using mice inoculated with leukaemia L1210.

New Anti-Oncotics with Low Nephrotoxicity
TANABE SEIYAKU K.K. Japanese Appl. 2/67,217
New anti-oncotics contain an organo platinum complex, for example a substituted malonate trans-L-1,2-diaminocyclohexane Pt, as effective component. The anti-oncotics show good action against solid tumours, ascites hepatoma and leukaemia; inhibit propagation of tumour cells, and extend the survival period of animals with these tumours. The organo platinum complexes have a wide range of anti-oncotic effects for various tumours, and low nephrotoxicity.

Metal Material for Dental Use
TOKURIKI HONTEN K.K. Japanese Appl. 2/142,710
An alloy consisting of 10–25 wt.% Au, 15–35 wt.% Pd, 47–70 wt.% Ag and 0.1–5 wt.% of one or more of Sn and In is made into a plate 0.05–0.5 mm thick. Fe powder of diameter 0.04–0.8 mm is applied on one surface and pressed, and dissolved to make an uneven phase. The material has excellent adhesion strength, processability, support strength and durability, and is used for stabilising teeth with mobility and for supplementing front teeth with a defect.

New Platinum Complexes with Cytostatic Activity
BEHRINGWERKE A.G. German Appl. 3,834,098
New Pt complexes with a 1,3-diaminopropane derivative as ligand have cytostatic activity and low cytotoxicity. The Pt complexes possess cytostatic activity as shown in “in vivo” tests in mouse L1210 leukaemia cells, B16 melanoma, and M5076 reticulum cell sarcoma, and are also effective against resistant tumour cells.

Palладium-Silver Alloy for Dental Use
DEGUSSA A.G. German Appl. 3,905,987
A Pd-Ag alloy used as a tooth replacement consists of 45–80 wt.% Pd, 7–45 wt.% Ag, 6–2 wt.% Pt, 0–1 wt.% Ru, Ir and/or Re, 0–5 wt.% Au, 0–5 wt.% Sn, 0–5 wt.% In, 0–3 wt.% Zn, 0–2 wt.% Cu, 0–1 wt.% W, Mo and/or Ta, 0–7 wt.% Ga, 0–5 wt.% Co, and 0–3 wt.% Ge. The alloy can be fired with dental ceramics without colouring them.

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