UK ISSN 0032-1400

PLATINUM METALS REVIEW

A quarterly survey of research on the platinum metals and of developments in their application in industry

VOL. 39 **OCTOBER 1995** **NO. 4**

Contents

Ruthenium, Nitric Oxide and Disease	150
Platinum and Palladium Convert Biofuel By-product	159
Fourth Grove Fuel Cell Symposium	160
Osmium, the Densest Metal Known	164
New Materials for Fuel Cell Systems	165
Microstructure and Properties of Some Dispersion Strengthened Platinum Alloys	167
Modelling Techniques for Catalyst Development	171
Routes to Useful Products and Processes	172
Platinum Metals in Electrochemistry	173
Ruthenium Effect on the Transformation in Equiatomic Titanium-Nickel Alloy	174
Noble Metals Utilised in Drugs and Healthcare	179
Abstracts	180
New Patents	186
Index to Volume 39	191

Communications should be addressed to
The Editor, Susan V. Ashton, Platinum Metals Review
Johnson Matthey Public Limited Company, Hatton Garden, London EC1N 8EE

Ruthenium, Nitric Oxide and Disease

A NOVEL INORGANIC CHEMISTRY APPROACH TO DRUG DESIGN

By S. P. Fricker
Johnson Matthey Technology Centre

Recent discoveries in the biological sciences have revealed that nitric oxide has a number of important physiological functions and is also implicated in a number of diseases. This realisation has provided a stimulus for nitric oxide related drug research and development. In this review new work aimed at the development of potential therapeutic use of ruthenium compounds, particularly ruthenium(III) polyaminocarboxylate, JM1226, is presented and discussed in the context of the chemistry and biology of nitric oxide. Based on these studies, prospects for the further development of JM1226 appear promising.

Nitric oxide (nitrogen monoxide, NO) is commonly viewed as being a toxic environmental pollutant. This has been the major motivation for research into both its chemical reactivity and biological activity. Nitric oxide is one of the major emissions from car exhausts and for many scientists the co-ordination chemistry of the platinum group metals and nitric oxide is synonymous with the development of the automobile catalytic converter. However, new developments in the biological sciences have now allowed us to look at some of the well known chemistry of transition metals and nitric oxide from a different perspective.

Nitric Oxide in Mammalian Cells

A major conceptual change has taken place in the biological sciences following the recent discovery that nitric oxide is synthesised and secreted by a number of mammalian cells (1, 2). Nitric oxide has been found to be an essential component of many physiological processes, such as the regulation of cardiovascular function, signalling between nerves in both the peripheral and central nervous system and mediating host defence against microorganisms and tumour cells. The biological activity of nitric oxide has been shown to be mediated by the nitrosylation of iron in iron-containing proteins. Many fundamental biological processes, such as regulation of blood pressure, learning and memory, defence against microorganisms and tumours, and penile erection, are now known to be dependent upon the formation of metal-nitrosyl complexes. A breakdown in the regulation of nitric oxide metabolism has been implicated in a number of diseases, including hypertension, epilepsy, diabetes, arthritis and septic shock.

The Biomedical Technology Group at Johnson Matthey has made a major contribution to the research and development of metal-based drugs, most notably in the field of the platinum anticancer drugs (3, 4). Recently, we have adopted a novel approach to the problem of nitric oxide-mediated disease, by viewing nitric oxide as a ligand for transition metals, in particular ruthenium. This paper presents the background to this approach, together with a brief review of the chemistry of nitric oxide and an historical account of the discovery of the biological action of nitric oxide. The role of nitric oxide both in maintaining normal function and in the pathogenesis of disease is also reviewed. The mechanism by which nitric oxide exerts its biological effects is discussed, based upon our knowledge of its chemical reactions in a biological environment, and the application of this knowledge in the search for new drugs to treat nitric oxide-mediated diseases is described. New data from our laboratory are presented, demonstrating the potential therapeutic use of ruthenium

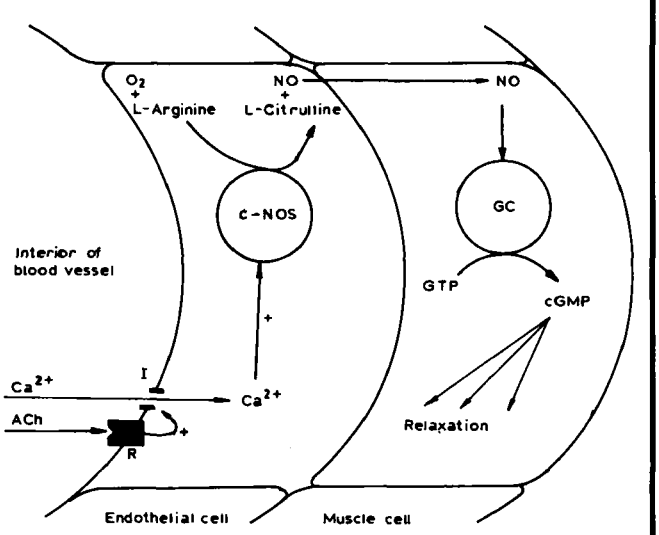


Fig. 1 A cross-section through an artery, showing the processes occurring in an internal endothelial cell and an adjacent muscle cell. Nitric oxide is synthesised in response to stimuli such as the neurotransmitter acetylcholine (ACh). Acetylcholine binds to a receptor (R) on the surface of an endothelial cell. This opens an ion channel (I) to allow calcium to enter the cell. This causes an increase in intracellular calcium which activates the constitutive nitric oxide synthase (c-NOS). The nitric oxide produced diffuses out of the endothelial cell into the muscle cell. Nitric oxide activates the enzyme guanylate cyclase (GC) which synthesises cyclic guanosine monophosphate (cGMP). The cGMP in turn activates a series of events leading to muscle relaxation, vasodilation of the blood vessel and a lowering of blood pressure

complexes as nitric oxide scavengers in septic shock, and possible future developments are discussed in the light of progress made to date.

The Chemistry of Nitric Oxide

Nitric oxide is a colourless gas at room temperature and is soluble in water. It has an electronic configuration of $(\sigma_1)^2(\sigma_1^*)^2(\sigma_2, \pi)^6(\pi^*)$ (5). The unpaired electron means that nitric oxide is formally a radical and is responsible for the unique properties of that molecule. Unlike most radicals, nitric oxide does not readily form dimers. This is because the unpaired electron cancels out the effect of the bonding electrons, giving a bond order of 2.5, which in a dimer would remain unchanged.

Nitric oxide is very reactive and in the gas phase will react very rapidly with oxygen to form nitrogen dioxide (NO_2). The mixture of nitrogen oxides (NOx) emitted from the exhaust of internal combustion engines which are not cleaned up by catalytic converters, is of course, a major contribution to environmental pollution. Nitric oxide is paramagnetic but does not have an electron paramagnetic resonance (EPR) spectrum in solution. However, it does form paramagnetic metal complexes and this property has been used to study haem iron in haemoglobin and more recently the interaction of nitric oxide with metalloproteins in biological environments (6).

The co-ordination chemistry of nitric oxide is similar to that of carbon monoxide, since both are π-acceptor ligands; however, nitric oxide has one more electron than carbon monoxide and this occupies a π^* orbital. The existence of metal nitrosyl complexes has been known for over a century but they have not been so extensively studied as their carbonyl counterparts. One reason for this is that the M-NO bond (M is metal) is very stable in most cases, which results in the metal nitrosyls being generally unreactive compared with M-CO complexes. Nitric oxide can form three types of metal-nitrosyl complex with:

(i) linear, terminal, M-N-O groups
(ii) bent, terminal, M-N-O groups and
(iii) bridging NO groups.

Nitric oxide can lose the electron in the π^* orbital to form the nitrosonium ion, NO^+. This will form linear NO complexes where the ligand is formally NO^+.

In the bent, terminal complexes, having bond angles of 120 to 140°, the ligand can be

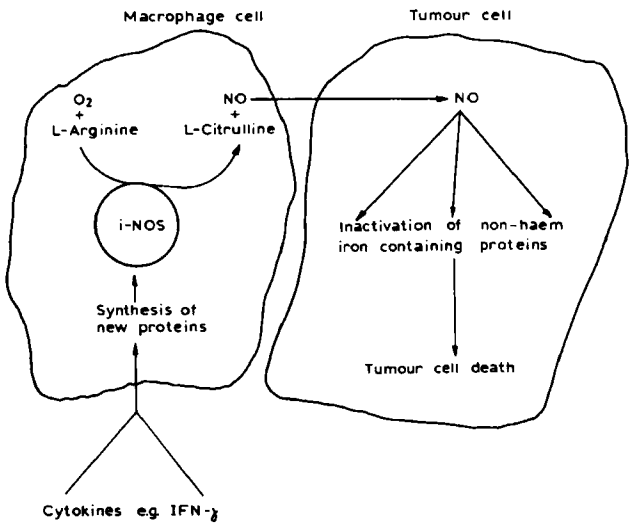


Fig. 2 The processes which occur in the blood when a macrophage cell (left) attacks a tumour cell (right). The macrophage cell is an important component of defence against tumour cells. The macrophage is activated by cytokines, such as interferon-γ, (IFN-γ). It responds by synthesising the inducible nitric oxide synthase enzyme (i-NOS). The nitric oxide produced by i-NOS diffuses out of the macrophage and into the adjacent target cell, where it kills the target tumour cell by inhibiting key enzymes which contain non-haem iron centres. A macrophage cell line, RAW264, has been used at the Johnson Matthey Technology Centre to evaluate new nitric oxide scavenging compounds

represented as $NO^{\cdot}$. This is an oversimplification of the situation (7, 8) but it provides us with a useful way of discussing the reactivity of nitric oxide with metals.

In subsequent sections we will look at the mechanism by which nitric oxide exerts its biological effects, by the nitrosylation of iron centres in proteins, and at the application of ruthenium compounds as scavengers of nitric oxide in disease.

The Biology of Nitric Oxide

The realisation that nitric oxide could have a positive biological function resulted from several convergent lines of research carried out in laboratories throughout the world (2).

Organonitrate compounds such as glyceryl trinitrate (nitroglycerin) have long been used in the treatment of angina. These compounds cause relaxation of arterial blood vessels (vasodilation) and act by releasing nitric oxide. A number of compounds which occur naturally in the body, such as the neurotransmitter acetylcholine (a chemical signalling molecule), also cause vasodilation. Arteries can be thought of as two concentric tubes, see Figure 1. The outer tube consists of muscle which is responsible for constriction and dilation of the artery. The inner tube, the endothelium, consists of a layer of cells called endothelial cells.

In 1980 Furchgott demonstrated that for acetylcholine to function as a vasodilator the artery must have an intact endothelium (9). The implication was that acetylcholine acted on the endothelial cells, these in turn produced a second chemical signal which triggered the relaxation of the muscle layer. This chemical was called endothelium derived relaxing factor (EDRF). Two independent groups (those of Furchgott and Ignarro) proposed that EDRF was actually nitric oxide (2) and in 1987 Ignarro's laboratory and a research group at the Wellcome laboratories confirmed this hypothesis (10, 11).

Functions of Nitric Oxide Within the Body

It is now known that nitric oxide plays a key part in the regulation of blood pressure as a component of an integrated control mechanism.

In 1988 it was found that nitric oxide could also function as a neurotransmitter (1, 2). The two major neurotransmitters in the peripheral nervous system are acetylcholine and noradrenaline. These chemicals act as messengers at nerve/nerve and nerve/muscle junctions. However, some peripheral nerves were known

to use neither noradrenaline (nonadrenergic, NA) nor acetylcholine (noncholinergic, NC), and these were named NANC nerves.

NANC nerves are found in many of the bodily tissues including gastrointestinal tract, respiratory tract, cardiovascular muscle and the urogenital system. Nitric oxide was discovered to be the neurotransmitter for NANC nerves.

The involvement of nitric oxide in penile erection has received much attention. This is mediated by NANC nerves which release nitric oxide causing relaxation of the smooth muscle of the corpus cavernosum and increased blood flow leading to penile erection.

Nitric oxide is also a neurotransmitter in the brain. Its exact function in the brain is unknown but one hypothesis is that it may be involved in long-term experience and memory. All previously known chemical signalling molecules, such as neurotransmitters and hormones, were either small organic molecules like acetylcholine, or peptides and proteins. The discovery that a small, diatomic, inorganic molecule is a biological signalling agent has completely changed the way in which we now think about the mechanism of regulation of many vital bodily functions.

The study of the immune response (the body's defence against foreign cells such as bacteria, viruses and tumours) led to the discovery of yet another role for nitric oxide (12). It was known that the urinary excretion of nitrite and nitrate, which are the end products of the oxidation of nitric oxide in an aqueous biological environment, increased during infection. Other studies had demonstrated that the mechanism by which macrophages (one of the cells of the immune system) killed cells was by targeting intracellular iron. This effect was dependent upon the presence of L-arginine (an essential amino acid) but it could be reproduced by nitric oxide. It was concluded that the macrophages were using nitric oxide to kill the target cells, see Figure 2.

Nitric Oxide Synthase (NOS)

These findings also enable us to account for the biological source of nitric oxide. Nitric oxide is synthesised in cells by the enzyme nitric oxide synthase (NOS) which catalyses the oxidation of L-arginine to L-citrulline and nitric oxide, see Figure 3(a). There are a number of known inhibitors of nitric oxide synthase, many of which are substrate analogues of L-arginine, for example N^{ω}-monomethyl-L-arginine (L-NMMA), see Figure 3(b). These inhibitors have been used extensively as tools in the study of the biological action of nitric oxide, as discussed below.

The unique enzyme, NOS, has a complex reaction mechanism and many of its details are still unknown (13, 14). There are a number of isoforms of nitric oxide synthase and the simplest classification divides them into two main classes: the constitutive and the inducible forms.

The constitutive enzyme, c-NOS, as its name suggests, is always present in the cell. It is dependent upon calcium for its activity and it is

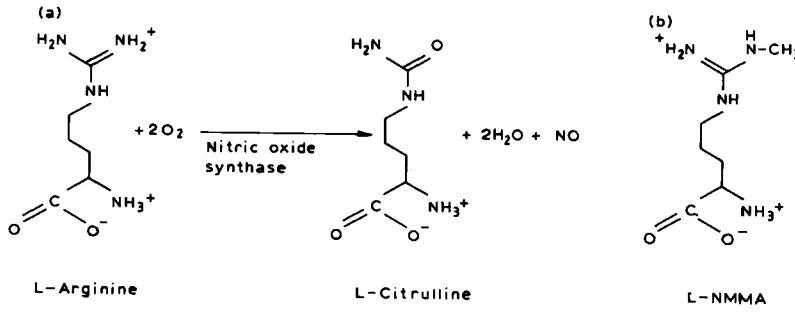


Fig. 3(a) Nitric oxide synthase (NOS) produces nitric oxide by the oxidation of L-arginine; (b) NOS can be inhibited by arginine analogues such as N-monomethyl-L-arginine (L-NMMA)

regulated by intracellular calcium concentrations. As an example, the neurotransmitter acetylcholine causes a transient increase in the calcium concentration in endothelial cells which activates c-NOS, leading to a burst of nitric oxide production. The local concentration of nitric oxide produced by c-NOS is low (of the order of nM), which is compatible with the function of nitric oxide as a chemical messenger.

The second form of the enzyme is the inducible form, i-NOS. This isoform is calcium independent and is synthesised by cells, for example macrophages, in response to external stimuli. It is regulated by turning on protein synthesis (transcription). The synthesis of i-NOS by macrophages is stimulated by components of the bacterial cell wall (lipopolysaccharide and endotoxin) and by cytokines (peptides that regulate the immune response) such as interferon-γ. Once i-NOS has begun to produce nitric oxide it will continue to do so for several hours and at concentrations (of the order of μM) that are high enough to be toxic to the target cell.

Diseases Caused by Dysfunction in Nitric Oxide Metabolism

Since it is now known that nitric oxide has this multifunctional role in the human body, it is not surprising that dysfunctions in nitric oxide metabolism have been found in a number of diseases (1, 2). For example, it has been proposed that an impairment in c-NOS activity in endothelial cells is a contributory factor in essential hypertension.

Hypertension can be treated clinically with nitric oxide donor drugs, such as the organonitrates. An inorganic nitric oxide donor drug, sodium nitroprusside, is used in emergency cases. However, the overproduction of nitric oxide is toxic to the body. The production of excessive, toxic quantities of nitric oxide is a major contributory factor in diseases such as diabetes, arthritis, inflammation, epilepsy and septic shock.

The disease known as septic shock is caused by very high levels of bacteria circulating in the blood. This triggers the immune response, including the stimulation of macrophages and other cells to synthesise i-NOS, which leads to an increase in the concentration of nitric oxide. This has a two-fold effect. First, the toxic levels of nitric oxide can cause tissue damage. Second, and more important, the nitric oxide also causes vasodilation, which leads to a severe drop in blood pressure and vascular collapse. This situation is made even worse by the fact that such patients also fail to respond to the vasoconstrictor drugs which are normally used to raise blood pressure. The lack of response to these drugs is also believed to be due to nitric oxide. Septic shock is fatal in more than 50 per cent of cases, therefore the search for new drugs that can reduce nitric oxide levels in this and in other diseases is a major challenge for medicinal chemists and is a potentially profitable area for the pharmaceutical industry.

The Biological Chemistry of Nitric Oxide

Nitric oxide mediates these multiple and diverse biological events by the nitrosylation of iron. However, the control of biological systems at the molecular level is worth considering, in order to put our understanding of the biological actions of nitric oxide into a wider context.

A mammalian cell receives an external signal, such as a hormone, for example adrenaline, and the result of this is seen as a biological event, in this case an increase in the metabolism of carbohydrate to provide energy for the "fright, fight or flight" response. There is a sequence, or pathway, of intracellular biochemical events between receipt of the external signal and the response. The study of the biochemistry of cell-signalling pathways is an area of intense activity, but in spite of this only some of the steps in the sequence are known.

A key step in a number of cell-signalling pathways is the formation of the second messenger molecule, cyclic guanosine monophosphate (cGMP) from guanosine triphosphate (GTP); cGMP then goes on to activate other biochemical actions in the signalling sequence.

This biochemical reaction (GTP to cGMP) is catalysed by the enzyme guanylate cyclase (GC)

see Figure 1. One of the significant observations made in the early stages of the research into nitric oxide was that nitric oxide increased the activity of guanylate cyclase in the arterial smooth muscle cells.

It is notable that this enzyme contains haem (1, 2). Haem is a complex of the tetradentate protoporphyrin ligand with Fe(II) and is found in a number of enzymes and the oxygen carrier protein haemoglobin.

Nitric Oxide Reactions in the Body

Nitric oxide will form complexes with Fe(II) haem and Fe(III) haem (6, 15). In haemoglobin (Hb) the normal oxidation state is Fe(II) (d^6) and in this case nitric oxide acts as a two electron donor to form Hb(Fe(II))NO. The remaining unpaired electron makes the molecule paramagnetic, which allows it to be detected by EPR. This has been exploited in the investigation of the biological properties of nitric oxide. The HbNO can be further oxidised in the presence of oxygen to methaemoglobin (HbFe(III)). Nitric oxide will also bind loosely to HbFe(III) (d^5) and reduce it slowly to Hb(Fe(II))NO.

Haem-ligand interactions are influenced by the local environment provided by the host protein. The important conditions are hydrophobicity/hydrophilicity of the surrounding amino acids, steric effects and the axial ligands. The latter may be particularly important for the activation of guanylate cyclase. It is known that both oxygen and carbon monoxide bind more strongly to haem when a basic ligand, histidine in haemoglobin, occupies the fifth co-ordination position, whereas nitric oxide binding to haem is enhanced when this position is empty. One possible explanation for the activation of guanylate cyclase is that when nitric oxide binds to the iron haem the result is an out-of-plane movement of the iron to give a haem core similar to that of a free porphyrin (15). There are still many questions to be answered concerning the mechanism of activation of guanylate cyclase by nitric oxide, not least the oxidation state of the iron in the haem group of guanylate cyclase.

A knowledge of the interaction between nitric oxide and haemoproteins is important for our understanding of the aqueous chemistry of nitric oxide in a biological environment. The gas phase chemistry of nitric oxide is well documented but extrapolation to the aqueous phase is misleading. It is now known that nitric oxide reacts with oxygen in an aqueous environment to give nitrite (16). Nitric oxide will also react with oxyhaemoglobin to give methaemoglobin and nitrate.

The nature of the oxidation products of nitric oxide is therefore dependent upon the oxygen status of the environment (6). In venous blood nitric oxide is converted primarily to NO_2^-, whereas in arterial blood (where oxyhaemoglobin is present) the main product is NO_3^-. These reactions of nitric oxide account for the raised levels of nitrate and nitrite seen in patients with bacterial infections (due to the elevated levels of nitric oxide produced by cells, such as macrophages).

Nitric Oxide Effects on Tumours

The toxicity of nitric oxide towards bacteria and tumours can also be explained by the formation of metal-nitrosyl bonds. In tumour cells the intracellular targets that macrophages attack have been identified (12). Three key proteins involved in energy metabolism were shown to be selectively inhibited; these were: aconitase, complex I and complex II. All contain non-haem iron as iron-sulphur clusters, for example Fe_4S_4 in aconitase. Nitrosylation of the iron in these enzymes has been demonstrated by EPR. Ribonucleotide reductase, a controlling enzyme in DNA synthesis, was also inhibited. This enzyme contains an Fe_2O centre, and the nitrosylation of this iron centre may be one mechanism by which nitric oxide inhibits this enzyme.

Ruthenium Complexes as Nitric Oxide Scavengers

The realisation that nitric oxide is involved in disease has provided a new focus for pharmaceutical research. The traditional approach to research by a medicinal chemist is via organic chemistry, and many researchers are at present engaged in investigating the use of inhibitors of the nitric oxide synthase enzyme.

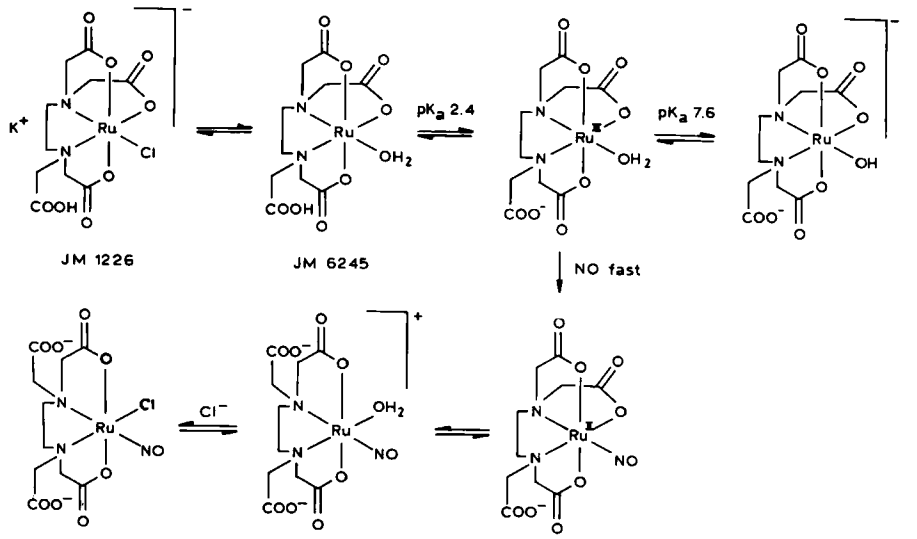


Fig. 4 The proposed mechanism for the reaction of K[Ru(Hedta)Cl], JM1226, with nitric oxide involves the formation of the aqua complex, [Ru(Hedta)(H_2O)], JM6245. This is followed by associative ligand substitution with nitric oxide to give the nitrosyl. The chloro and aqua species exist in equilibria in water

Septic shock is being studied in a number of laboratories and the arginine analogue inhibitors of NOS have been studied clinically against this disease (17). However, they have a number of side effects, mainly affecting the local blood circulation within organs, particularly the lungs (18). This is because in addition to inhibiting the formation of the undesirable excess quantities of nitric oxide produced by i-NOS, they also inhibit the production of nitric oxide by c-NOS of endothelial cells. Many commercial and academic laboratories have attempted to produce selective inhibitors of i-NOS but to-date there has been little success reported.

However, in the Biomedical Technology Group at Johnson Matthey we have pursued a different approach to the problem by exploiting our knowledge and expertise in co-ordination chemistry and inorganic pharmaceuticals. Armed with the knowledge that nitric oxide can act as a ligand for transition metals, we have examined metal complexes as possible scavengers for the therapy of nitric oxide-mediated disease.

Ruthenium has a rich co-ordination chemistry (19) and complexes containing nitric oxide have been known for well over a hundred years; $K_2[Ru(NO)Cl_5]$, for instance, was isolated in the mid-nineteenth century. Ruthenium readily forms nitrosyls and there are more known nitrosyl complexes of ruthenium than of any other metal (7). The Ru-NO bond is generally very stable and as a ligand nitric oxide is not easily displaced, persisting through a variety of substitution and redox reactions.

Ruthenium (III) (d^5) will react with nitric oxide to form six co-ordinate mononitrosyl complexes with a linear Ru-N-O group. The Ru(III) is reduced to Ru(II) with the ligand being formally NO^+ (as mentioned earlier this is an oversimplification and ignores the structural problems associated with nitrosyl chemistry). Therefore ruthenium appeared to be a good candidate as the basis of a nitric oxide scavenger.

Drug Design

When designing drugs a number of factors have to be taken into consideration (20). These include the necessity that the chosen compounds

must be of low toxicity and that the distribution of the drug within the body and its excretion from the body must be controllable (pharmacokinetics). Toxicity and pharmacokinetics are interrelated and both depend upon the chemical properties of the compound, such as its solubility and its chemical reactivity.

The chemical properties of the transition metals are well suited to deal with the problems of drug design: transition metals have variable oxidation states, ligands are co-ordinated in a precise spatial arrangement and can be chemically modified so enabling the properties of the complex to be fine-tuned to control the pharmacological interactions in a biological system. For a nitric oxide scavenger we require a ligand set which is itself stable but which promotes specific binding of nitric oxide. Generally ligands around ruthenium(III) are kinetically inert and there is another benefit in that the formation of the Ru-NO bond further stabilises the *trans* ligand in the resulting ruthenium(II) complex.

Ruthenium(III)polyaminocarboxylates

One class of ligand that satisfies most of these requirements is the polyaminocarboxylates (21). The parent compound K[Ru(Hedta)Cl] (JM1226) has emerged as the potential front runner in the search for a metal-based nitric oxide scavenger, see Figure 4. The ligand, ethylenediaminetetraacetic acid (edta), is pentadentate leaving one co-ordination position available for substitution by nitric oxide. The complex is water soluble and should therefore remain in the blood and not cross lipophilic cell membranes.

This has two important consequences: it should have a good pharmacokinetic profile, such as: be rapidly excreted in the urine, only have access to the excess nitric oxide in the bloodstream, and not be available to the nitric oxide produced by endothelial cells responsible for regulating blood pressure.

Initial evidence for the nitric oxide binding ability of this compound was provided by a chemical study in which nitric oxide gas was introduced above a stirred solution of the test compound in a closed apparatus. A decrease in pressure was measured and taken to indicate that nitric oxide had been removed. At the end of the experiment the reaction mixture was freeze dried and analysed by infrared spectroscopy. A peak at 1897/cm, which is characteristic of the linear Ru-N-O bond, was indicative that nitric oxide had been bound and that the ruthenium(II) nitrosyl compound had been formed.

The proposed mechanism for this reaction involves the formation of the aqua species [Ru(Hedta)(H_2O)], JM6245, which takes place readily at physiological pH (22), see Figure 4. This is followed by associative ligand substitution with nitric oxide to give the nitrosyl. The pendant carboxylate group may facilitate this substitution (23), since if the carboxylate is replaced by an alcohol group there is a reduction in the activity which is observed during the biological tests (see below).

Kinetic studies performed at the University of Essex, using stopped-flow equipment, indicate that the rate of formation of the nitrosyl is so fast that the reaction takes place within the dead time of the instrument (> 2 ms) at room temperature. Measurements made at 6.5°C give a rate constant of 2.6×10^7/Ms.

JM1226 Pharmacological Activity

The next step was to investigate the ruthenium compound in a simple biological system. We exploited the fact that macrophage cells produce nitric oxide in response to the bacterial cell wall component, lipopolysaccharide, and to interferon-γ. We used a macrophage cell designated RAW264 which can be cultured in the laboratory (24). The nitrite in the culture medium was assayed as a measure of the amount of nitric oxide produced by the cells. It was found that the level of nitric oxide could be reduced by the i-NOS enzyme inhibitor L-NMMA (the control experiment) and also by JM1226, see Figure 5(a).

In order to confirm the binding properties of JM1226 for nitric oxide in our biological system, we also made use of the ability of macrophages to kill tumour cells. We demonstrated that RAW264 cells could kill the mouse tumour cell P815 and that this was mediated by

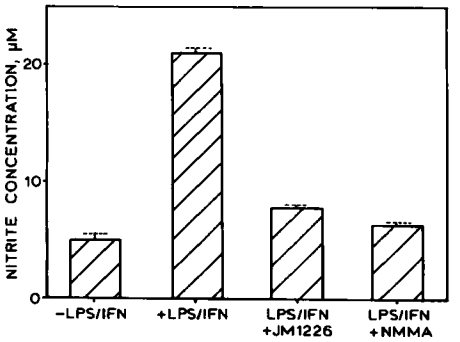
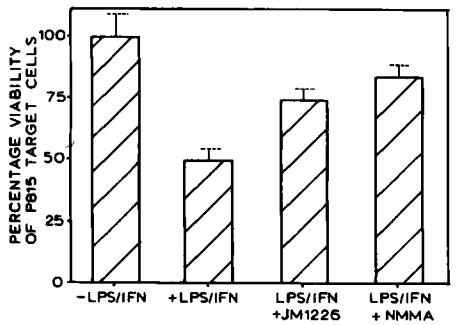


Fig. 5 The RAW264 macrophage cell line used as a biological system for testing the ability of ruthenium(III) compounds to scavenge nitric oxide. RAW264 cells produce nitric oxide when activated with lipopolysaccharide and interferon-γ (+LPS/IFN).
(a) JM1226, K[Ru(Hedta)Cl], at a concentration of 100 μM can reduce the level of measurable nitrite, produced by oxidation of nitric oxide in the cell culture medium, showing the potential to scavenge nitric oxide in a biological environment. Background levels were determined in the absence of activators (–LPS/IFN). The nitric oxide synthase inhibitor, L-NMMA, a positive control at a concentration of 250 μM, also reduced nitrite levels. Error bars represent a standard error of mean n = 3



(b) JM1226, K[Ru(Hedta)Cl], can protect against nitric oxide-mediated cell killing. The nitric oxide generator cell was cocultured with the P815 tumour cell. Activated RAW264 cells killed 50 per cent of the P815 cells. Viability in the presence of 100 μM JM1226 was raised to 75 per cent. Error bars represent a standard error of mean n = 6

nitric oxide. The removal of nitric oxide should have a protective effect, and in the control experiment the enzyme inhibitor L-NMMA inhibited cell killing. More importantly JM1226 was also able to protect the P815 cells against RAW264 nitric oxide-mediated cell killing, see Figure 5(b). Similar results were obtained with the aqua species [Ru(Hedta)(H_2O)].

Having demonstrated that we had a potential nitric oxide scavenger we then needed to get closer to the real life situation. Collaborators were using isolated rat tail arteries to investigate the vasodilatory properties of nitric oxide donors (25). One commonly used nitric oxide donor is the nitrosothiol S-nitroso-N-acetylpenicillamine (SNAP). This compound will break down in water to release nitric oxide. The addition of SNAP to an isolated artery preparation was found to cause it to relax or vasodilate in a dose-dependent manner with an ED50 (the concentration giving a 50 per cent relaxation) of 6.0 μM. Haemoglobin, which forms an iron-nitric oxide complex, will attenuate this response.

When JM6245, the aqua derivative of JM1226, was tested at a concentration of 10^{-4} M in the isolated artery model the SNAP response was attenuated, giving an ED50 of 1.8 mM, which is a 300-fold inhibition in the response of the artery. Using the isolated artery model, it has also been shown that JM6245 will reverse the poor response of the artery to vasoconstrictor drugs, which is a major clinical problem when trying to treat patients with septic shock. We have gone further with this work, demonstrating that JM1226 has a positive benefit in two models of nitric oxide-mediated septic shock (26). In these models of disease the activity displayed by JM1226 is indicative of the potential therapeutic efficacy of the ruthenium(III) polyaminocarboxylates.

Conclusion

The use of inorganic nitric oxide scavengers is a novel approach to the therapy of diseases mediated by excess production of nitric oxide. We have discovered a class of compounds, the ruthenium(III) polyaminocarboxylate complexes, which have pharmacological activity in biological systems ranging from cultured cells through to sophisticated disease models. The project has progressed rapidly through the early stages of pre-clinical research and development

since our patent was filed in 1993 (21). There are many obstacles still to be overcome on the road to clinical success but the indications are positive.

Preliminary studies suggest that these compounds possess low toxicity and many of the desired pharmacokinetic properties. There is plenty of scope for ligand modification and an extensive synthetic programme is enabling new compounds with the potential for better activity to be identified.

Minor chemical modifications are also known to affect activity, thus giving scope for the design of further ruthenium compounds which might be used in the many diverse nitric oxide-mediated diseases. Indeed inorganic medicinal chemistry may provide the key to success in this field of study, where the traditional organic chemistry approach to drug design appears to be struggling; and future prospects appear very encouraging for this potential new addition to the inorganic pharmacopoeia.

Acknowledgements

The success of a major project is the result of teamwork. My fellow members of the project team are Drs. Elizabeth Slade, Barry Murrer and Nigel Powell at the Johnson Matthey Technology Centre and Dr. Jean Vollano at Johnson Matthey Biomedical Research, U.S.A. Thanks are due to Dr. F. W. Flitney, University of St. Andrews, Professor M. T. Wilson, University of Essex, and Professor F. Y. Liew, University of Glasgow, and to their colleagues.

References

1 S. Moncada, R. M. J. Palmer and E. A. Higgs, *Pharmacol. Rev.*, 1991, **43**, 109

2 C. Nathan, *FASEB J.*, 1993, **6**, 3051

3 C. F. J. Barnard, *Platinum Metals Rev.*, 1989, **33**, (4), 162

4 M. J. Abrams and B. A. Murrer, *Science*, 1993, **261**, 725

5 F. A. Cotton and G. Wilkinson, in "Advanced Inorganic Chemistry", John Wiley and Sons, Inc., New York, 1980, pp. 423–425

6 Y. Henry, M. Lepoivre, J.-C. Drapier, C. Ducrocq, J.-L. Boucher and A. Guissani, *FASEB J.*, 1993, **7**, 1124

7 F. Bottomley, *Coord. Chem. Rev.*, 1978, **26**, 7

8 J. A. McCleverty, *Chem. Rev.*, 1979, **79**, 53

9 R. F. Furchgott and J. V. Zawadzki, *Nature*, 1980, **288**, 373

10 R. M. J. Palmer, A. G. Ferrige and S. Moncada, *Nature*, 1987, **327**, 524

11 L. J. Ignarro, G. M. Buga, K. S. Wood, R. E. Byrns and G. Chaudhuri, *Proc. Natl. Acad. Sci. U.S.A.*, 1987, **84**, 9265

12 J. B. Hibbs, in "Iron in Central Nervous System Disorders. Key Topics in Brain Research", eds. P. Reiderer and M. B. H. Youdim, Springer Verlag, Vienna, 1993, pp. 155

13 B. S. S. Masters, *Ann. Rev. Nutr.*, 1994, **14**, 131

14 R. G. Knowles and S. Moncada, *Biochem. J.*, 1994, **298**, 249

15 A. Tsai, *FEBS Lett.*, 1994, **341**, 141

16 D. A. Wink, J. F. Darbyshire, R. W. Nims, J. E. Saavedra and P. C. Ford, *Chem. Res. Toxicol.*, 1993, **6**, 23

17 A. Petros, D. Bennet and P. Vallance, *Lancet*, 1991, **338**, 1557

18 F. M. Robertson, P. J. Offner, D. P. Ciceri, W. K. Becker and B. A. Pruitt, *Arch Surg.*, 1994, **129**, 149

19 E. A. Seddon and K. R. Seddon, "The Chemistry of Ruthenium", Elsevier, Amsterdam, 1984

20 C. F. J. Barnard, S. P. Fricker and O. J. Vaughan, in "Insights into Speciality Inorganic Chemicals", ed. D.T. Thompson, Royal Society of Chemistry, Cambridge, 1995, pp. 35–61

21 M. J. Abrams, S. P. Fricker, B. A. Murrer and O. J. Vaughan, *World Patent Appl.* 95/5814A; 1995

22 T. Matsubara and C. Creutz, *Inorg. Chem.*, 1979, **18**, 1956

23 A. A. Diamantis and J. V. Dubrawski, *Inorg. Chem.*, 1981, **20**, 1142

24 S. P. Fricker, E. Slade and N. A. Powell, *Biochem. Soc. Trans.*, 1995, **23**, 231S

25 F. W. Flitney, I. L. Megson, D. E. Flitney and A. R. Butler, *Br. J. Pharmacol.*, 1992, **107**, 842

26 F. Q. Cunha, J. Assreuy, D. W. Moss, D. Rees, L. M. C. Leal, S. Moncada, M. Carrier, C. A. O'Donnell and F. Y. Liew, *Immunology*, 1994, **81**, 211

Platinum and Palladium Convert Biofuel By-product

The search for non-polluting automotive fuels has encouraged a growth in alternative fuels, including biofuels such as ethanol and biodiesel. Several countries already use biofuels and in Europe biodiesel is produced from rapeseed oils, yielding up to 14 per cent of potentially valuable glycerol. Now, R. Garcia, M. Besson and P. Gallezot (*Appl. Catal. A: Gen.*, 1995, **127**, (1–2), 165–176) report that they can orientate the selectivity of glycerol oxidation to oxidation of the primary or secondary alcohol function. A 77 per cent selectivity at 90 per cent conversion to glyceric acid on palladium catalysts, and a 55 per cent selectivity to glyceric acid on platinum catalyst were achieved. A bismuth-platinum catalyst achieved a 37 per cent yield in dihydroxyacetone.

Fourth Grove Fuel Cell Symposium

FROM TECHNICAL SUCCESS TO THE CHALLENGES FACING COMMERCIALISATION

"Opportunities, Progress and Challenges" was the theme chosen for the Fourth Grove Fuel Cell Symposium, held at the Commonwealth Institute, London, from 19th to 22nd September 1995. Some 250 delegates from 23 countries heard that fuel cells, used for clean and efficient power generation, had made tremendous technical progress over the two years since the last Grove conference. Most advances had been made with the phosphoric acid fuel cell (PAFC) and the proton exchange membrane fuel cell (PEMFC), both of which operate at low temperatures and employ platinum-catalysed electrode materials.

The growing acceptance that fuel cell technology is now proving itself in use was demonstrated by the considerable attention paid at this conference to cost reduction, market entry opportunities and the issues surrounding fuelling and infrastructure.

Fuel Cell Technology Status

The PAFC is the fuel cell closest to widespread commercial exploitation. The leading world developer is ONSI, a joint venture between International Fuel Cells (IFC) and Toshiba. Their fleet of fifty-six PC25A 200 kW co-generation power plants have been successfully operated by their owners over the past three years. H. D. Ramm of IFC reported that the PC25A units have now accumulated 750,000 fleet hours of operation, with a remarkable worldwide average availability of 94 per cent and a mean time interval between power plant down time of 2,200 hours. This unprecedented reliability is already significantly better than the conventional mature co-generation technology.

The next generation PC25C system is one third smaller and lighter than the PC25A, and costs half as much to manufacture. The plant is available at $3,000/kW and ONSI already has buyers for two-thirds of the 50 plants it intends to build over the next two years.

The PEMFC can operate at higher power densities than other fuel cell types and, because of this and its intrinsic simplicity, it is considered suitable for both stationary and transportation applications. Progress by Ballard Power Systems of Canada, in the development of a commercial product for both applications, was described by K. B. Prater. A prototype stationary 250 kW power plant, operating on natural gas and producing grid quality AC power, is due for completion in early 1996, with a demonstration of pre-commercial units in a utility environment being on schedule for field trials in 1997 to 1999.

A more tangible indication of the potential of this fuel cell was demonstrated by its application in powering transit buses. Following the first phase feasibility demonstration in 1993, Ballard have now produced the pre-commercial prototype of a fuel cell powered zero emission transit bus. In this full sized 40 ft commercial bus, a PEMFC engine comprising twenty Ballard second generation stacks, produces a total of 200 kW (275 hp) – the same power as the diesel engine normally installed in the bus.

Further evidence of the commercial viability of this application is the fact that the fuel cell engine occupies the same space as the diesel engine, see Figure 1, and provides at least the same performance. The fuel cell supplies the entire motive power for the bus, and also the power for lighting and air conditioning. The buses are powered by hydrogen stored in compressed gas cylinders in the roof space, and have a range of 400 km (250 miles). Refuelling with hydrogen at the bus depot is expected to take only minutes and is seen as a workable fuelling option for fleet vehicles.

These second generation stacks produce 13 kW under standard operating conditions at an average cell voltage of 0.58 V. The power density output of 300 W/l is double that of the original 5 kW stacks employed in the first bus.

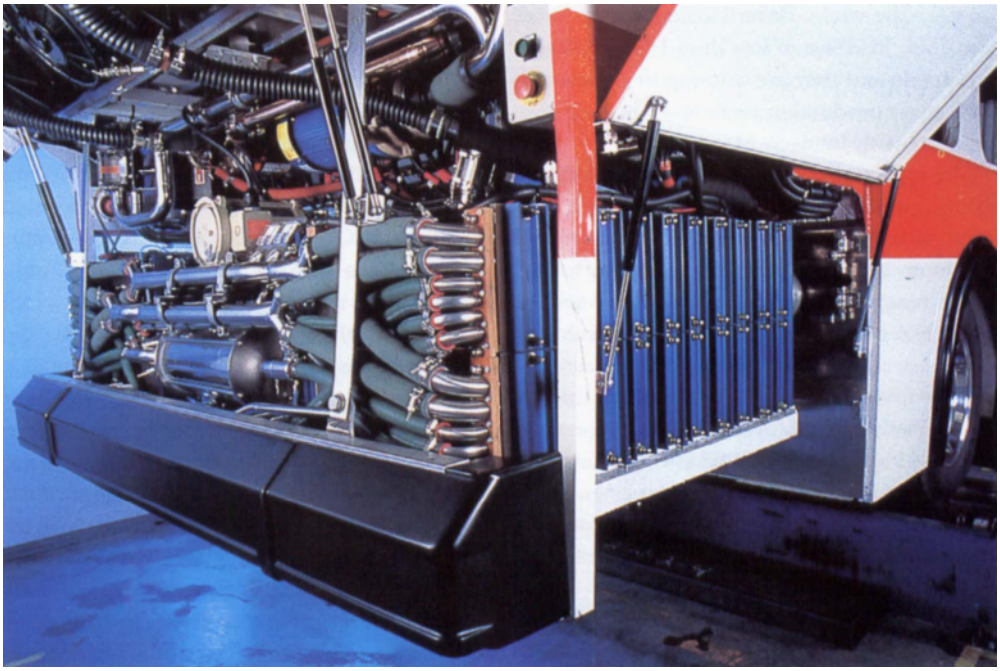


Fig. 1 The prototype Ballard commercial zero emission transit bus is powered entirely by a compact 200 kW PEMFC engine which occupies the same space and volume as the conventional diesel engine powered versions. The fuel cell provides all the power, heating and lighting required by the bus

Ballard also reported that the third phase in the commercialisation of the transit bus involves fleet trials by transit companies in routine operation. The first of these, to start in 1996, has recently been announced by the Chicago Transit Authority. The scheduled date for full bus commercialisation, powered by a third generation stack, currently under development, is 1998. These buses will be designed to have a range of 560 km (350 miles).

Progress was also reported between Ballard and Daimler-Benz on the development of stacks with very high power density for use in small passenger vehicles. The target power density for this, the most demanding application, is usually regarded as 800 to 1000 W/l. Ballard used this conference to announce that they had produced a stack with a volume of 31.9 litres delivering a continuous output of 32.3 kW at a high average cell voltage (thus high efficiency) of 0.68 V. The stack operates at lower-than-standard operating pressures to increase efficiency further, and easily meets the 1000 W/l target. This stack exceeds the power density targets identified in the U.S. programme – "Partnership for a New Generation Vehicle" (PNGV). Recent progress has been so successful, that even for this application, the emphasis will shift away from the achievement of key performance criteria, towards maintaining this performance in stacks manufactured in high volumes at costs comparable to those of the present day internal combustion engines.

Optimising Platinum Use

An example of the progress being made in cost reduction is shown by the requirement of the platinum electrocatalyst. The early generation PEMFC stacks use high platinum loadings of around 4.0 mg/cm^2 of electrode area. This is economically unfeasible for most applications. The PNGV programme is aiming to achieve loadings of 0.1 mg/cm^2 by the year 2004, and although loadings of less than 0.5 mg/cm^2 have frequently been demonstrated in small laboratory fuel cells, this now needs to be confirmed

on full scale stacks. Ballard believe that total cell platinum loadings of less than 1.0 mg/cm^2 are attainable and they are working to achieve this with mass production techniques in their programme with Johnson Matthey.

The low operating temperature fuel cells (< 200°C) of the PAFC and PEMFC types, continue to use exclusively platinum or promoted platinum based electrocatalysts for both electrode reactions. The technical poster session highlighted some of the current research into new electrocatalytic materials. Many researchers are modifying platinum so it is able to tolerate trace levels of carbon monoxide, present in reformed hydrogen, for PEMFC applications. Promising initial results using tungsten oxide promoted platinum/ruthenium alloys were described by A. C. C. Tseung, K. Y. Chen and P. K. Shen of Essex University.

Fuelling Fuel Cell Powered Vehicles

It is presently anticipated that small vehicles, unlike buses, will have to be fuelled with a high energy density liquid fuel, since it is unlikely that hydrogen storage technology will advance sufficiently for them to be able to store on-board adequate quantities to give acceptable vehicle ranges. To-date the favoured option has been to reform liquid methanol on-board the vehicle in order to produce a hydrogen-rich fuel for the fuel cell stack.

This approach has been adopted by Daimler-Benz in their fuel cell vehicle programme, as reported by T. Klaiber, and also by General Motors in their U.S. Department of Energy/PNGV programme. Although steam reforming is the most highly developed process, there is growing interest in partial oxidation reforming, which, because it is an exothermic reaction, can achieve a more rapid start up and response under dynamic conditions. The intrinsic simplicity of the latter approach and potential lower cost is viewed as the most important factor at this stage in the commercialisation of fuel cell powered vehicles.

The most elegant solution to the technical challenge of on-board reformer development is the direct use of liquid methanol oxidation in the fuel cell stack (DMFC). Current work on this technology was described by M. Waidhas, W. Drenckhahn, K. Mund and W. Preidel of Siemens. They reported considerably improved levels of cell performance when a polymer membrane, similar to that used in the hydrogen fuelled PEMFC, was employed as the electrolyte (SPE-DMFC). Previous cell current densities of 50 mA/cm^2 at 0.4 V have been too low to be of practical use, due to poor kinetics of the methanol electro-oxidation reaction, but Siemens have now been able to achieve current densities of up to 400 mA/cm^2 at 0.5 V and Faradaic efficiencies of over 90 per cent. Better kinetics at the platinum based catalyst/membrane interface may contribute to this improvement, although the best results have been obtained at 140°C using pure oxygen, which is impractical for most high volume applications.

In the United States the Jet Propulsion Laboratory is at the forefront of renewed interest in DMFCs, and in a poster presentation (H. Frank, S. R. Narayanan, W. Chun, B. Nakamura, T. Valdez, S. Surampudi and G. Halpert) on the SPE-DMFC programme, reported that platinum/ruthenium remained the electrocatalyst of choice for methanol electro-oxidation, and that performances on air operation of up to 300 mA/cm^2 at 0.4 V were being achieved.

Although these performances are creating greater interest, there is still need for further improvement, through advances in the catalysis of both the methanol oxidation and oxygen (air) reduction reactions.

Diesel/Gasoline Fuel

The growing maturity of fuel cell stack technology was demonstrated by discussion of the key issue of fuel infrastructure, particularly for mobile applications. C. Borroni-Bird of Chrysler strongly advanced the view that the preferred choice of fuel should not be methanol but existing fuels such as gasoline/diesel. This is due to a belief that existing oil pipelines cannot be used for distributing methanol, due to its highly corrosive nature.

Additional factors, such as the high cost of investing in new methanol plant, the cost of

methanol and its lower energy density were cited by others supporting this stance. It was suggested that the very low efficiency of reforming petroleum based fuels, for example diesel fuel, if used in a partial oxidation reactor, would be offset by the much higher efficiency of diesel production, relative to that of methanol.

The U.S. Department of Energy (DoE) is supporting a programme being undertaken by Arthur D. Little, that has a target of a 50 kW gasoline fuelled partial oxidation reformer by 1997. Laboratory results have shown that gasoline can be successfully reformed to a hydrogen containing fuel.

High Temperature Fuel Cells

The most advanced high temperature fuel cell is the ERC (Energy Research Corporation) 2 MW molten carbonate fuel cell (MCFC) demonstration at Santa Clara, California. This system, which was described by D. R. Glenn of Fuel Cell Engineering Corporation, is due for completion and start up in early 1996. The higher intrinsic efficiency of this fuel cell (design target is > 52 per cent) gives it the potential to compete with existing generating technologies in the multi-megawatt power generation range. A further key advantage is its fuel versatility, since it can operate on, for example, natural gas, landfill gas, biogas or fuel obtained from coal gasification.

Stacks of the type to be used in the plant have successfully accumulated 100,000 hours of operation in controlled environments, and ERC are confident of their performance capability. A market entry for a 2.8 MW power plant is targeted for 1999.

The success of both this and the other significant MCFC demonstration – M-C Power's two 250 kW power plants – will be critical to the future of this fuel cell technology.

The even higher temperature operated (~ 1000°C) solid oxide fuel cell (SOFC) can be designed with either tubular or planar cell geometries. A 25 kW unit of the former type, is being developed by Westinghouse and was reported to have now achieved over 7,000 hours of operation, whereas the development of a planar 10 kW type as a mobile electric power generating system was described by L. J. Frost, R. M. Privette and A. C. Khandkar of SOFCo.

Market Opportunities

Reducing cost was the key topic for discussion and in particular how to reduce production costs to enter the market; however, in order to achieve the necessary lower costs, volume manufacturing resulting from market penetration is first needed!

Many speakers, including H. D. Ramm of IFC, emphasised the targeting of **high value niche applications**; such as reliable power for hospitals, high quality power for computer, telecommunications and data centres, and as alternatives to centralised power generation where transmission, distribution and the provision of new lines is a contentious issue. The entry market has to be specialised and clearly focused on applications where the benefits offered by fuel cells can be fully valued.

Indeed, for stationary applications the real cost of fuel cell power generation should be assessed against the complete life-cycle costs, which should include capital cost, installation, operation costs (maintenance and fuel) and overhaul. Ramm reported that the PC25C were now approaching a figure of 1.5 cents/kWh over a 20 year life cycle.

The cost issue was taken a step further by P. Bos of Polydyne, who suggested that minimising the financial risk was critical to fuel cell commercialisation. The cost of commercialising a 2 MW utility system was estimated to be 200 times larger than that of a 2 kW system. As fuel cell use in transport is unlikely to provide an early commercial market, due to the low market value caused by the low cost of the internal combustion engine, he identified the stand-alone **micro-co-generation residential application** as a high value entry market. A consortium of 12 major utilities have formed the "Small Scale Fuel Cell Commercialisation Group" to demonstrate 50 to 100 2 kW units per utility, probably based on PEMFC technology, by 1998.

The opportunity offered by the residential market was identified by other groups, including

B. Barp, R. Diethelm, K. Honegger and E. Batawi of Sulzer Innotec, who are working on developing the SOFC for this application.

For **transportation**, heavy-duty vehicles such as transit buses or trucks represent the best opportunity for early market entry. The U.S. DoE figures show that in North America the current annual demand is for 25,000 buses and 900,000 trucks (> 10 klbs). S. Chalk, of the U.S. DoE, reported that if the forthcoming zero emission regulations were adopted by California and the North Eastern states, there would be a total requirement of 353,000 zero emission vehicles (ZEVs) in the year 2003.

In the near term these will be geared to battery cars, and the DoE predict that fuel cell cars will not enter the market until 2007, and will attain 8 to 10 per cent of new annual sales by 2030 (currently 16 million new vehicles per year in North America). The DoE model makes the assumption that fuel cells and all other competing new technologies would be equally successful in meeting technical and economic goals.

Since cost was viewed by several speakers as the most critical factor influencing the rate of commercialisation, they believed that stack developers should not put undue emphasis on factors such as stack efficiency at this stage. For example, the much simpler partial oxidation now appears the more acceptable fuel processing route despite the slightly lower system efficiency projected by most model analyses.

Conclusions

The PAFC co-generation plants continue to demonstrate highly efficient and reliable operation, but large markets are needed before a fully cost effective product can become widely available. The PEMFC system has made rapid progress with the development of high power density stacks which meet targets for transportation applications. Early market opportunities lie with fleet vehicles, such as transit buses, which can tolerate larger sizes, higher costs, and on-board hydrogen fuel storage and depot refuelling. Commercialisation is on schedule for the end of the decade. Opportunities for light-duty passenger cars have been provided in the United States by the zero emission regulations, to be enacted in 1998, and the programme to improve vehicle fuel economy.

The technical progress over the past three years is such that attention is moving away from fuel cell stack technology to issues of cost, market entry opportunities and the fuelling infrastructure. These are the key challenges for the latter half of the 1990s, in the development of a commercial market for power generation based on fuel cell technology. G.A.H.

Osmium, the Densest Metal Known

Until recently much confusion existed in the literature as to which is the densest metal, osmium or iridium. Crabtree reviewed the experimental data, but his calculated densities of 22.59 ± 0.02 g/cm^3 and 22.57 ± 0.02 g/cm^3, respectively, led to an overlap in the uncertainties and a suggestion that the problem had not been solved (1). However, in a similar review by the present author, calculated densities at 20°C of 22.588 ± 0.015 g/cm^3 and 22.562 ± 0.009 g/cm^3, respectively, suggested that the problem just may have been resolved in favour of osmium (2).

Although the uncertainties calculated for the densities are usually dominated by the accuracies assigned to the lattice parameters, the accuracy of the atomic weight can also contribute significantly – if it is poorly known, as was the case for osmium until quite recently. However with newly accepted atomic weights of 190.23 ± 0.03 for osmium and 192.217 ± 0.003 for iridium the contribution to the uncertainties of the densities is now minor (3).

Using the lattice parameters selected previously by the present author (2), the calculated density of osmium is revised to 22.587 ± 0.009 g/cm^3 while that for iridium remains the same. On these grounds it is suggested that osmium can now unambiguously be considered to be the densest metal at 20°C. J.W.A.

References

1 R. H. Crabtree, *J. Less-Common Met.*, 1979, **64**, (1), 7

2 J. W. Arblaster, *Platinum Metals Rev.*, 1989, **33**, (1), 14

3 Commission on Atomic Weights and Isotopic Abundances, *Pure & Appl. Chem.*, 1994, **66**, 2423

New Materials for Fuel Cell Systems

A REPORT OF THE FIRST INTERNATIONAL SYMPOSIUM

The first of an intended biennial symposium, The First International Symposium on New Materials for Fuel Cell Systems, was held at the Montréal Bonaventure Hilton, Canada, from 9th to 13th July 1995. The symposium, which was organised by the Laboratoire d'Électrochimie et de Matériaux Énergétiques, École Polytechnique de Montréal, concentrates on the material science of fuel cell systems, rather than on applications. As such, all aspects of the fuel cell system, namely catalyst, electrolyte and fuel processing components were dealt with. The meeting attracted some 120 delegates, including a large number of participants from industry.

The keynote address was delivered by A. J. Appleby from Texas A & M University, who discussed "New Materials for Fuel Cell Systems". He stressed the importance of the electrolyte, since it determines the properties required for the other materials in the system. In practice, only a limited choice of materials is available: strong acids, strong aqueous alkalis, molten alkali carbonates and solid oxides.

Appleby pointed out that there are gaps in the operating temperature ranges of fuel cells due to a lack of suitable electrolytes; for example there is a gap between the upper operating temperature of phosphoric acid fuel cells (PAFCs): 210°C, and the lower operating temperature for molten carbonate fuel cell (MCFC): 625°C; and similarly between the upper temperature for the MCFC: 675°C, and the lower temperature for solid oxide fuel cells (SOFCs): 900°C. The temperature windows, in which fuel cells are operated, are set by their performance characteristics at the lower temperature and by material characteristics (stability and resistance to corrosion) at the upper temperature.

Electrolytes

The proton exchange membrane fuel cell (PEMFC) operates at the much reduced temperatures of 60 to 100°C and has excellent performance characteristics; however, the expense of the membrane itself – presently costing some $\$700/m^2$, is a considerable drawback. At present, the membrane component of a PEMFC fuel cell stack accounts for 20 to 30 per cent of the total cost of the materials. Accordingly, there is a considerable incentive to develop other membrane materials which can be prepared by simpler and less expensive chemistry than the currently used perfluorinated sulphonic acid polymers.

This latter point was discussed further by A. E. Steck of Ballard Advanced Materials, Canada, who described the development of ion exchange membranes beginning with the early work done at General Electric in the 1950s, to the perfluorinated membrane materials presently used in PEMFC, which are manufactured by Du Pont (Nafion) and Dow. Although these materials are noted for their stability and good performance, the current cost is prohibitively high. In order for PEMFCs to be commercially viable for the automotive market, the membrane cost will need to be reduced to between $\$50/m^2$ and $\$150/m^2$. Steck then went on to describe work being done at Ballard on the development of a low-cost membrane. This third generation membrane, BAM3G, appears close to achieving the goals of performance, stability and cost, which are required for commercialisation of PEMFC.

Fuel Processing

As well as the fuel cell stack, the symposium also dealt with aspects of fuel processing. The keynote speakers in this session were R. Kumar and S. Ahmed from the Argonne National Laboratory, U.S.A., who presented work on fuel processing for transportation fuel cell systems. They discussed the various means of producing hydrogen from fossil fuels (primarily methane and methanol) and described the comparative merits of each, using calculations of overall system efficiency. It was concluded that while all fuel processor designs are driven by some performance criteria, transportation applications

using low temperature fuel cells, especially the PEMFC, set the most demanding constraints. In this case the fuel processing is best served by partial oxidation systems as they appear simpler, compact and more responsive.

Catalysts

Carbon supported platinum, usually in combination with one or more other metals for both anode and cathode reactions, remain the materials of choice for new electrocatalysts for low temperature fuel cells. H. A. Gasteiger and P. N. Ross from the Lawrence Berkeley Laboratories, U.S.A., discussed the differences between platinum-ruthenium and platinum-tin alloys for both methanol and carbon monoxide oxidation, using results obtained with bulk metal samples. It was found that while ruthenium can adsorb both carbon monoxide and water, tin can only adsorb water. Thus in catalytic reactions involving carbon monoxide, platinum-tin displays superior activity.

A complementary piece of work was described by J. Stumper, D. Olligs and U. Stimming from the Institut für Energieverfahrenstechnik, Jülich, Germany, in which the optimum surface composition of platinum and ruthenium in platinum-ruthenium alloys for carbon monoxide electro-oxidation was probed using *in-situ* infrared spectroscopy. Only one type of carbon monoxide species was found on platinum-ruthenium surfaces, suggesting that atomic mixing occurs between platinum and ruthenium at the surface.

The use of platinum-ruthenium catalysts in the form of supported materials was discussed further by M. P. Hogarth, P. A. Christensen and A. Hamnett from Newcastle University, who presented encouraging results, discussed elsewhere in this journal on page 173, of a methanol vapour fuelled PEMFC single cell which achieved a power density of 0.2 W/cm^2.

The addition of tungsten to supported platinum and platinum-ruthenium catalysts was the subject of several presentations. A. R. J. Kucernak, C. J. Barnett, G. T. Burnstein and K. R. Williams, from Cambridge University, showed that the electrodeposition of "WO_3" onto platinum and platinum-ruthenium catalysts modestly enhanced the methanol oxidation activity. They also showed that the addition of $H_4SiW_{12}O_{40}$ to the electrolyte improved the methanol oxidation performance of a supported platinum-ruthenium catalyst. It is likely that the adsorption of tungstic acid from solution onto the catalyst was responsible for the enhanced performance.

The chairman of the symposium, O. Savadogo from the École Polytechnique de Montréal, discussed the potential promotion of supported platinum catalysts, used for oxygen reduction, by H_2WO_4 in both PAFCs and PEMFCs. It was found, especially with low platinum loaded catalysts, that the addition of H_2WO_4 gave enhanced oxygen reduction kinetics for PAFC conditions.

The last session of the Symposium was devoted to new catalysts. Of particular interest was the presentation by N. Alonso-Vante from the Hahn-Meitner Institut, Berlin, who discussed novel ruthenium-based materials for oxygen reduction in acid electrolytes; the semiconducting transition metal selenides of general formula, $(Ru_{1-x}Mo_x)_y SeO_z$ ($0.02 < x > 0.04$; $1 < y > 3$; $z \approx 2y$). At present, their oxygen reduction activity is somewhat poorer than platinum, but unlike platinum cathode catalysts they have the advantage of being tolerant to the presence of methanol. The operation of Direct Methanol Fuel Cells usually leads to methanol being transported to the cathode through the electrolyte, where cathode depolarisation takes place. A methanol tolerant cathode catalyst would be a significant technological breakthrough. This was examined further during the poster session with Newcastle University describing work on the sulphur analogues of the selenium material.

In view of the importance of material science to improvements in fuel cell technology, this symposium was a welcomed addition to fuel cell and electrochemical related conferences. It is hoped that the planned 2nd Symposium will take place in 1997. Copies of the proceedings of this symposium are available in North America from COOPOLY l'École Polytechnique de Montréal, and in Europe from Technique et Documentation–Lavoisier, Paris. D.A.L., D.T.

Microstructure and Properties of Some Dispersion Strengthened Platinum Alloys

THE INFLUENCE OF YTTRIUM AND ZIRCONIUM ADDITIONS

By Qiaoxin Zhang, Dongming Zhang and Shichong Jia
Advanced Materials Institute, Wuhan University of Technology, Wuhan, China

and Wulin Shong
Department of Materials Engineering, Huazhong University of Science and Technology, Wuhan, China

The effect of adding very small amounts of yttrium and zirconium to platinum alloys has been investigated. The results indicate that a platinum alloy which contains both elements has a higher recrystallisation temperature and superior mechanical properties than a platinum alloy containing only zirconium. In addition, the platinum alloy which contains both yttrium and zirconium has a stable structure in which regular second phases have been found both in the grains and on the grain boundaries.

Platinum has excellent properties when used at high temperatures in oxidative atmospheres, although its industrial application is restricted by its relatively low strength. In order to improve its strength, rhodium was initially used as a strengthening element at contents less than 20 to 25 per cent (1). Since the 1970s, ZGS platinum (2) and ODS platinum have been developed; these being strengthened by well dispersed additions of zirconium oxide, ZrO_2 and yttrium oxide, Y_2O_3, respectively. The ZGS platinum and ODS platinum alloys have much improved properties, but their processing technologies have to some extent limited their possible applications.

For this reason, we have studied the effects that two alloying elements, yttrium and zirconium, have on the properties of platinum. The alloys were made by the metallurgical method described below and the results were encouraging.

Alloy Preparation and Experimental Methods

A mixture of platinum with yttrium and zirconium, having purities of 99.95, 99.9 and 99.9 per cent, respectively, were electron-beam melted in vacuum. The total weight fraction of zirconium, or of yttrium and zirconium, was less than 0.7 weight per cent.

The ingot sized platinum-zirconium and platinum-yttrium-zirconium alloys were cold forged and rolled into sheets suitable for microstructural examination and also drawn into wires for mechanical testing. No annealing was done during these forming processes. However, to facilitate rolling it may be better to include an anneal.

The alloys were then annealed at various temperatures and later etched in a mixture of hot hydrochloric and nitric acids for measurement of the grain diameters.

Microstructure and Stability of the Materials

The properties of these materials are determined by their microstructures. As shown in Figure 1, which is typical of many metals, the hardness of the platinum, platinum-zirconium and platinum-yttrium-zirconium alloys varied with the annealing temperature (annealing lasted for 0.5 hours) and decreased rapidly over the temperature range in which recrystallisation took place.

The hardness and also the recrystallisation temperature of the platinum-yttrium-zirconium

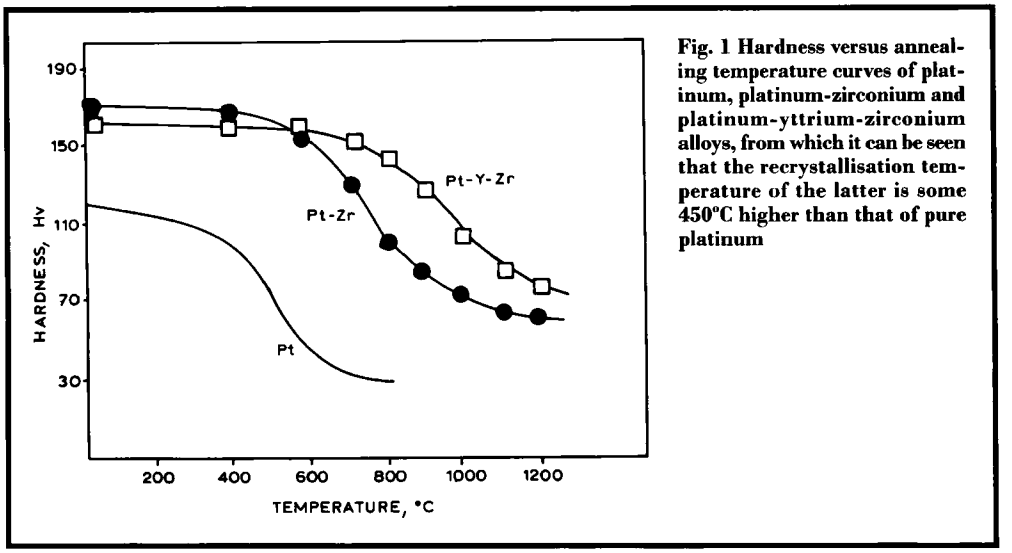


Fig. 1 Hardness versus annealing temperature curves of platinum, platinum-zirconium and platinum-yttrium-zirconium alloys, from which it can be seen that the recrystallisation temperature of the latter is some 450°C higher than that of pure platinum

alloy have higher values than those of platinum-zirconium. The hardness, Hv, of the platinum-yttrium-zirconium alloy annealed at over 1200°C is 72, and its recrystallisation temperature is approximately 450°C higher than that of pure platinum.

Microscopical analysis indicates that after annealing at 800°C for 0.5 hours recrystallisation of the platinum-zirconium alloy occurs, with a very small grain size but with the elongate structure resulting from rolling still visible in some areas; the platinum-yttrium-zirconium alloy does not show any recrystallisation. After annealing at 1000°C for 0.5 hours, the grain size in the platinum-zirconium has grown significantly, and the platinum-yttrium-zirconium alloy has begun to recrystallise, but its grain size is still relatively small, see Figure 2.

When annealed at 1200°C for longer periods, the grain size of the platinum-zirconium changes substantially while the platinum-yttrium-zirconium grain size is little changed, as shown in Figure 3.

Therefore, it can be deduced that alloying platinum with both yttrium and zirconium gives superior structural stability compared with alloying platinum with zirconium alone. This is very important for materials employed at high

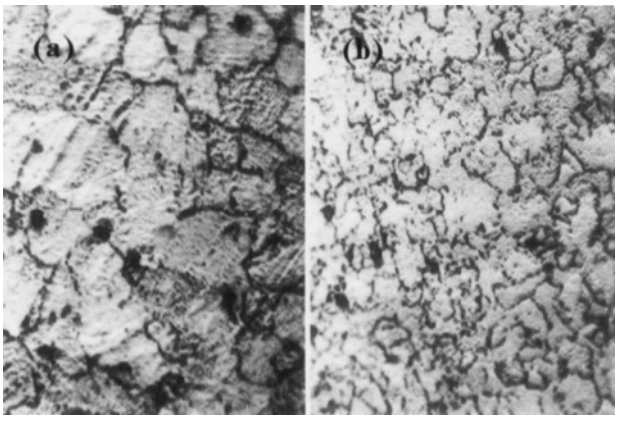


Fig. 2 Photomicrographs for platinum-zirconium and platinum-yttrium-zirconium after annealing at 1000°C for 0.5 hours. The grains of the latter are smaller:
(a) platinum-zirconium
(b) platinum-yttrium-zirconium
Magnification of (a) and (b) × 450

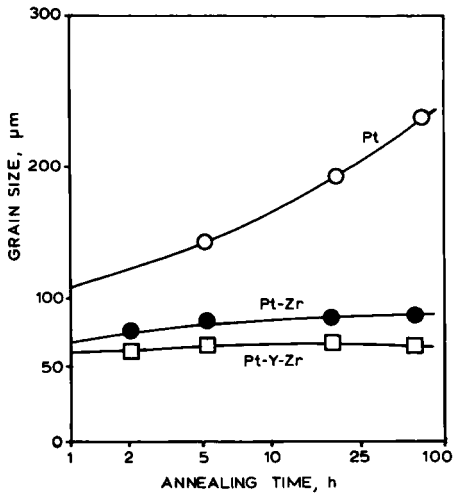


Fig. 3 After annealing at 1200°C the relationship between grain size and annealing time shows that the alloy containing yttrium and zirconium is superior to that containing only zirconium, and in both the grain growth is less than occurs in platinum. The same working procedure was used for all three materials

temperature. Additionally, it is considered that platinum-yttrium-zirconium is more stable than platinum-zirconium; the initial tendency to change is apparent in platinum-zirconium, but not in platinum-yttrium-zirconium.

The distribution of a second phase in platinum-zirconium and platinum-yttrium-zirconium alloys annealed at 1200°C is illustrated in Figure 4. The second phase in the platinum-zirconium, which exists mainly on the grain boundaries, was analysed using an Energy Analysing Electron Microscope and found to be a zirconium compound. The main compounds in the platinum-zirconium alloy system are PtZr, Pt_2Zr and Pt_3Zr, and these are formed when the platinum alloy contains more than 3 per cent zirconium (4).

However, as the amount of zirconium in the platinum-zirconium alloy which we were investigating was less than 0.7 per cent, the compound was not likely to be any of these three platinum-zirconium compounds. It may be reasonable to deduce that the zirconium compound in our platinum-zirconium alloy is zirconium oxide formed during processing. In addition to this zirconium oxide on the grain boundaries, the platinum-yttrium-zirconium alloy also has some regular shaped particles of an yttrium and zirconium compound distributed within the grain.

These particles, which are only tens of nanometres in size, have not yet been studied, but are likely to improve creep resistance and high temperature stability. This is to be the next step of our work.

Physical Properties of the Materials

The resistivities of platinum-yttrium-zirconium and platinum-zirconium alloys are a little higher than that of pure platinum, while their elongations are slightly less. However, their hardnesses and strengths are greatly improved compared to platinum, especially the high temperature strength and the creep resistance of the platinum-yttrium-zirconium alloy, see the Table.

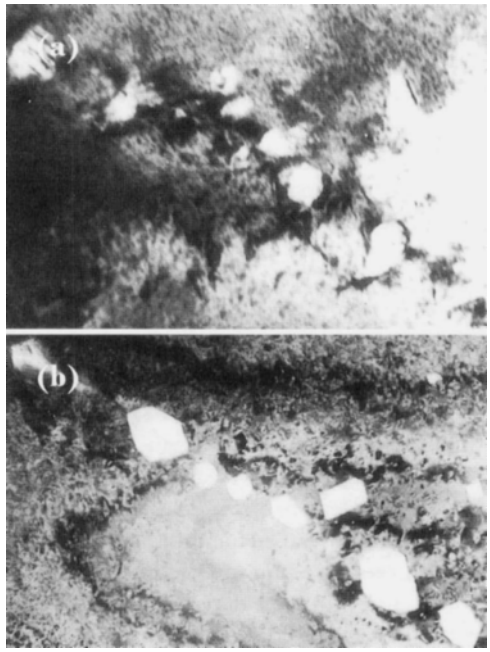


Fig. 4 Distributions of the second phase in platinum-zirconium and platinum-yttrium-zirconium alloys after annealing at 1200°C:
(a) platinum-zirconium alloy × 60,000
(b) platinum-yttrium-zirconium alloy × 72,000

Properties of Platinum, Platinum-Zirconium, Platinum-Yttrium-Zirconium and Platinum-10 per cent Rhodium Alloys (3, 5)

	Pure Pt	Pt-Zr	Pt-Y-Zr	Pt-10%Rh
Resistance at 20°C, μcm	10.6 (3)	12.46	12.42	18.4 (3)
TCR*/ °C; mean 1~100°C	0.0039 (3)	0.0017	0.0011	0.0017 (3)
Tensile strength, UTS, MPa (annealed)	124 (3)	278	283	330 (3)
Elongation, per cent, (annealed)	40 (3)	36	35	35 (3)
Hardness, Hv (annealed)	40 (3)	65	72	75 (3)
UTS at 1200°C, MPa	35.2 (5)	40.0	44.6	58.8 (5)
Rupture time, at 1200°C, 25 MPa, h	11.5 (5) (at 4.9 MPa)	3	7.6	307 (5) (at 4.9 MPa)

* TCR: Temperature coefficient of resistance

The values for hardness given in the Table were measured on sheet; all the other values in the Table were determined using wire samples. The strength of the alloys increases with increases in the total volume fraction of yttrium and zirconium, but the elongation decreases.

The stress-rupture life for platinum-yttrium-zirconium at 1200°C and 25 MPa is similar to that of platinum-10 per cent rhodium alloy at 1000°C. Further work on stress rupture and creep data is presently being undertaken.

The following three factors are believed to result in the properties of the platinum-yttrium-zirconium alloy being superior to those of platinum-zirconium.

[a] Solution Strengthening

The difference in the atomic radii between platinum (1.38Å) and zirconium (1.579Å) is less than that between platinum and yttrium (1.797Å), so the platinum-yttrium-zirconium lattice is more distorted than the platinum-zirconium lattice, which results in increased hardness.

The difference in electronegativity between platinum (2.2) and zirconium (1.4) is less than that between platinum and yttrium (1.2), so the bond forces and the polarisation effect in platinum-yttrium-zirconium are greater; this improves the high temperature strength (6). This is a special effect that occurs in alloys containing very small additions of alloying elements.

The interaction between zirconium and rare earth yttrium dissolved in platinum increases the alloy strength more than yttrium alone in the platinum-yttrium alloy.

[b] Dispersion Strengthening

The second phase in platinum-yttrium-zirconium, distributed on the grain boundaries and also in the grains, improves the high temperature strength and the creep resistance.

[c] Boundary Strengthening

Compared with zirconium, yttrium is more inclined to deposit on the grain boundary, causing impaired boundary diffusion and migration (7). Therefore, it is more effective for platinum to be alloyed with small amounts of zirconium and the rare earth yttrium, than it is to be alloyed with the same amount of zirconium alone.

Conclusions

The addition of very small amounts of yttrium and zirconium to platinum makes the platinum alloy structure more stable and greatly improves the recrystallisation temperature. The second phase distributed on the grain boundaries and within the grains improves the high temperature strength and creep resistance.

These additions of yttrium and zirconium improve the properties of platinum at both room and elevated temperatures, and alloying with the two elements is more effective than alloying only with zirconium.

References

1 A. S. Darling, G. L. Selman and A. A. Bourne, *Platinum Metals Rev.*, 1968, **12**, (1), 7

2 G. L. Selman, J. G. Day and A. A. Bourne, *Platinum Metals Rev.*, 1974, **18**, (2), 46

3 G. L. Selman and A. A. Bourne, *Platinum Metals Rev.*, 1976, **20**, (3), 86

4 Chunxiao He and Guangchen Ma, "Equilibrium Diagram for Precious Metal Alloys", Metallurgical Industry Press, Peking, China, 1983

5 Y. Ning, *Precious Met. (China)*, 1984, **5**, (2), 42

6 T. T. Kou, Wenhui Shu and Shouyu Dai, *Acta Sci. Nat. Univ. Jilinensis*, 1962, (1), 177

7 Kunyu Zhao and Dingxin Li, *Precious Met. (China)*, 1993, **14**, (2), 9

Modelling Techniques for Catalyst Development

Computer-Aided Design of Catalysts

EDITED BY E. ROBERT BECKER AND CAMO J. PEREIRA, Marcel Dekker Inc., New York, 1993, 640 pages, ISBN 0–8247–9003–0, U.S.$195.00

This book is the 51st in an occasionally excellent series on the chemical industries, and while it has its limitations it is nevertheless a valuable addition to the collection. The series consists of assembled chapters on a theme contributed by distinguished professionals. As such the volumes often lack coherence and stand or fall on the excellence of the contributions and the timeliness of the theme. This book is certainly timely as the use of computing methods in catalysis is growing rapidly. Computer aided design can mean different things; here the editors define it as "the process of selecting catalyst properties that ..... optimise the reactor performance". The emphasis on choosing catalyst properties means that there is very little on the design of new catalysts in this book. Rather the chapters deal with the methods for the measurement and modelling of catalyst parameters and the application of these methods in various industrial processes. Also missing is any attempt to discuss the modelling and economics of entire processes and plants; the emphasis is firmly on the performance of the reactor section.

The early chapters deal with modelling methods, such as: selectivity patterns in methane partial oxidation; modelling complex mixtures in catalytic cracking using carbon centre methods; Monte Carlo simulations for complex hydrotreating mixtures; pore diffusion models; catalyst pellet impregnation profiles and catalyst wetting effects on multiphase reactions. Later chapters concentrate on particular applications, such as Fischer-Tropsch catalysts, automobile catalysts including transient behaviour in monolith reactors; polymerisation catalysts; membrane reactors and petroleum refining. Platinum group metals feature here most directly, particularly platinum, palladium and ruthenium.

The chapter on the design of Fischer-Tropsch catalysts by E. Iglesia, S. C. Reyes and S. L. Soled, compares cobalt and ruthenium catalysts in the context of models which combine transport processes and elementary kinetics, and concludes that selectivity is dominated by the transport processes rather than by the nature of the active sites.

Chapters on modelling for automotive emission control by S. H. Oh, and design of monolithic catalysts for improved transient reactor performance by K. Zygourakis, use platinum catalysts as the basis for a discussion of modelling in car exhaust systems. Oh reviews his outstanding work and shows that even with many simplifying assumptions useful predictions as to catalyst loadings and performance may be obtained. The application of this approach to heated catalysts was discussed at the recent North American Catalysis Society meeting. The importance of 2-dimensional modelling for problems such as flow maldistribution and other transient effects is dealt with at greater length by Zygourakis.

Palladium features most extensively in a chapter on catalytic membrane reactors by T. T. Tsotsis, R. G. Minet, A. M. Champagnie and P. K. T. Liu. This topic has a long history and remains popular due to the inherent elegance of controlling reactant addition or product removal by a selective membrane. However large scale applications await the development of membranes that are thin enough and robust enough for the demanding conditions of most petrochemical processes.

This book is a useful contribution to bridging the gap between chemical engineers and chemists in the field of catalyst and reactor design. While individual chapters may disappoint specialists on any given topic, together they provide a valuable introduction to the area and can be read profitably by non specialists; the book will be of use in advanced education. J.C.F.

Routes to Useful Products and Processes

Insights into Speciality Inorganic Chemicals

EDITED BY D. T. THOMPSON, The Royal Society of Chemistry, London, 1995, 505 pages, ISBN 0–85404–504–X, £39.50

The needs of graduates contemplating industrial research are addressed in this important book covering the major industrial applications of inorganic chemicals. Its eighteen chapters are written by authors with wide experience of their topics. About half the chapters feature the platinum group metals, giving a fair indication of their relevance to industry.

In the chapter on refining J. Hill describes the occurrence of the platinum group metals, their extraction, including chemical processes based on precipitation/filtration, and improved processes using solvent extraction and ion exchange. There is a good critique of the drawbacks to the classical processes, and it is emphasised that a major disadvantage to all the processes is that rhodium is extracted last.

A chapter on the medical applications of inorganic chemicals, by C. F. J. Barnard, S. P. Fricker and O. J. Vaughan describes platinum anticancer drugs and the development of cisplatin and carboplatin. Structure activity studies and the mechanism of action of these drugs are considered, but there is still much to find about the molecular basis of their action.

Heterogeneous catalysis is considered by G. C. Bond in a chapter on inorganic materials as catalysts for chemical processes. This subject is extensive, but refers to the importance of the platinum group metals only in hydrogenation, dehydrogenation, dehydrocyclisation, hydrogenolysis and Fischer-Tropsch chemistry.

The use of homogeneous catalysts in large scale industrial processes is described by A. Parkin. He discusses three processes employing platinum group metal complexes: the carbonylation of methanol by rhodium iodide based catalysts, the hydroformylation of alkenes by rhodium carbonyl phosphine complexes and the Wacker process for alkene oxidation to acetaldehyde using palladium where the catalyst is regenerated by a copper redox system.

The increasingly important topic of catalysts for stereospecific synthesis is examined by J. M. Brown. Here platinum group metals find particular use in reductive processes. There is reference to rhodium catalysts used for the preparation of L-DOPA, and rhodium systems based on bis(phospholane) designed by Du Pont. The versatility of ruthenium binap complexes in alkene double bond hydrogenations is shown in the syntheses of citronellol and vitamin E, and in a potential route to isoquinoline alkaloids. These ruthenium catalysts can also hydrogenate ketones with a high enantioselectivity; the rhodium analogues have commercial potential in vitamin B5 synthesis. Osmium tetroxide is mentioned for Sharpless dihydroxylations.

Automobile catalysis, a major use for platinum and rhodium, is addressed by M. Bowker and R. W. Joyner. The development of three-way catalytic converters, the principles of catalyst operation and surface chemistry are described. Future developments include enhanced durability, which can be provided by palladium only catalysts. The inventiveness of industrial scientists will be challenged by legislation imposed to reduce carbon dioxide emissions; when the zero emission legislation comes into force non-carbonaceous fuels may be necessary.

Other applications which involve the platinum group metals include the electronics industry, where ruthenium dioxide and bismuth ruthenate are used as thick film resistors and where palladium is used as a leaching inhibitor of silver from thick film conductors. Additionally, tris(bipyridyl)ruthenium catalysts are being used in solar energy conversion.

This volume thus provides a valuable overview of the industrial applications of inorganic materials. Each chapter has a useful list of specific and general references and key journals, thus providing the reader with an easy means to acquire further information. M.J.H.R.

Platinum Metals in Electrochemistry

FURTHER WORK ON ELECTROCATALYSTS REPORTED

The Electrochem '95 Conference, organised by the Society of Chemical Industry and the Royal Society of Chemistry was held at the University of Wales, Bangor, from 10th to 14th September 1995. During the week, parallel mini-symposia covered the topics of: structure and reactivity at interfaces, electrochemical processing, polymers and novel materials, fuel cells and electrocatalysis, corrosion, solid state ionics and batteries, semiconductor electrochemistry, electroanalytical chemistry and environmental electrochemistry. Of the approximately 260 delegates, less than 10 per cent were from industry, which must be a cause for concern. Not surprisingly then, developments in new instrumentation dominated much of the proceedings, and the latest advances in techniques, such as FTIR, EXAFS, STM and AFM, are certainly striking. However, one felt occasionally that some simple "wet chemistry" would have given just as much, if not more, insight into the fundamental science in question.

Technical Presentations

The group at Bath University lead by Professor L. M. Peter has been studying various industrially-relevant systems including (together with ICI) the kinetics of chlorine evolution on titanium/ruthenium anodes. In this instance, the less familiar open-circuit potential decay method was used to elucidate important parameters such as the Tafel slope and exchange current density. Among the results that his group achieved were: the identification of an activity threshold effect dependent upon the ruthenium content (with the number of active sites being dependent upon how "hard" the electrode is driven) and the discovery that chlorine can evolve without charge transfer occurring.

A team from Newcastle University lead by Professor A. Hamnett and P. A. Christensen produced results on a number of aspects of electrocatalysis in fuel cells, including modelling the performance of a solid polymer direct methanol fuel cell, and the development of new oxygen reduction catalysts. The power output from a vapour-fed methanol single cell was reported to be around 200 mW/cm^2 at 113°C with 2 bar air, 5 M methanol and a catalyst loading of 2.5 mg Pt/cm^2. Methanol cross-over from the anode to the cathode remains a problem, and another restriction to cell performance may arise from proton conduction limitations at the membrane/catalyst interface. Improved platinum and platinum/ruthenium catalysts supported on carbon for methanol oxidation were obtained by deposition from aqueous sulphito complexes, using hydrogen peroxide as the reducing agent. In addition, the Newcastle group are studying ruthenium/molybdenum based metal chalcogenide catalysts, made by the reaction of the metal carbonyls in xylene; they continue to show promise as novel oxygen reduction catalysts with acid stability.

Another catalyst issue of practical importance, the dependency of intrinsic activity on particle-size for oxygen reduction, was described by R. J. Potter of Johnson Matthey during a presentation of technical issues in the hydrogen-air solid polymer fuel cell system. Work on dimensionally stable anode materials in which the service life of PdO/titanium electrodes for oxygen evolution in alkali solutions was significantly improved by the addition of zinc, was discussed by B. J. Hwang from the National Taiwan Institute of Technology.

In another presentation from Newcastle University, by K. Scott and W. M. Taama, palladium was again described as an effective anode catalyst, this time for the anodic oxidation of sulphur dioxide in sulphuric acid.

A number of groups are working on the development of conducting polymers containing redox active metal centres, which include ruthenium, osmium and platinum, where the main application is in sensor technology.

The next conference will be held at Bath University, and one hopes that this time there will be a greater presence from industry. R.J.P.

Ruthenium Effect on the Transformation in Equiatomic Titanium-Nickel Alloy

PHASE STABILISATION AND MARTENSITIC TRANSFORMATION

By E. L. Semenova, N. Yu. Rusetskaya, V. M. Petyukh and V. Ye. Listovnichiy

I. N. Frantsevich Institute for Problems of Materials Science, Kiev, Ukraine

Martensitic transformations in equiatomic titanium-nickel and titanium-nickel based alloys are of interest because they are associated with the shape memory effect. Equiatomic titanium-nickel, which possesses such superior mechanical properties as high strength, elevated ductility and corrosion resistance, is the most important of several shape memory alloys. Here, the character of the martensitic transformation in equiatomic titanium-nickel alloy with some of the nickel replaced by ruthenium is discussed. Data are presented on the temperature of the transformation upon heating and cooling, the transformation sequence and the stabilisation of the high temperature phase in TiNi-TiRu alloys, using electrical resistance, thermal expansivity and differential thermal analysis between ~300°C and liquid nitrogen temperatures. Alloys which contained 0.5 to 2 atomic per cent ruthenium were found to undergo a two stage transformation, while the high temperature phase in titanium-nickel-ruthenium, which has B2-type crystal structure, was stabilised by the addition of 2 atomic per cent ruthenium.

For the past twenty-five years we have been working on interactions occurring in binary and ternary systems containing platinum group metals. Among the systems we have studied are those of the binary alloys of zirconium and the platinum group metals. We have constructed phase diagrams for these systems and shape memory effects have been found for the equiatomic zirconium-rhodium compound, as well as for the equiatomic titanium-rhodium compound. Shape restoration is assumed to occur at about 1000°C for zirconium-iridium (1, 2). The crystal structures for the high- and low-temperature modifications to equiatomic zirconium-rhodium and zirconium-iridium compounds have been determined for the first time (2).

Later work has dealt with the ternary system: titanium-nickel-platinum group metal. The interactions in the systems of titanium-nickel-rhodium and titanium-nickel-iridium along the section with 50 atomic per cent titanium have been investigated and melting diagrams have been constructed. The effects of substituting rhodium and iridium for nickel in the equiatomic titanium-nickel compound and of nickel for rhodium in equiatomic titanium-rhodium systems, together with shape memory effects, have also been studied (3, 4).

We are now studying interactions in the titanium-cobalt-rhodium and titanium-nickel-ruthenium systems, and as a continuation of our work on the phase diagram of the latter system and on the effects to the martensitic transformation in equiatomic titanium-nickel compound caused by additions of the platinum group metals, we discuss here the effect caused by ruthenium. Alloys of the titanium-nickel-ruthenium system lying along the section through equiatomic phases of the titanium-nickel and titanium-ruthenium binary systems were investigated.

Rhodium and iridium additions are known to

TiNi-TiRu Transformation Temperature Data										
Composition, ruthenium, atomic per cent	Solid Transformation Temperature									
	Electrical resistance					Thermal expansion				
	M_s	M_f	A_s	A_f	T_R	M_s	M_f	A_s	A_f	T_R
0	76	40	78	109	-	-	-	-	-	-
0.5	37	17	-	-	49	22	17	-	-	37
1	9	–23	2	22	32	8	–28	17	32	32
2	–73	–113	– 65	– 43	20	–73	–113	– 68	– 43	22
5	—	-	-	-	–25	-	-	-	-	-

lower the martensitic transformation temperature of equiatomic titanium-nickel compound when 6 atomic per cent is added along the isopleth of 50 atomic per cent titanium; the B2 crystal structure phase being stabilised down to room temperature (3, 4). Taking other data into consideration, it can be concluded that the high temperature B2-phase stabilisation down to room temperature in TiNi-TiPt and TiNi-TiPd alloys does not occur (although a contrary interpretation has been given by others (5)).

In all the systems mentioned above the transformation in TiNi-based alloys with nickel partially substituted by rhodium, palladium or platinum occurs in two stages:

High temperature B2-phase → intermediate R-phase (rhombohedral structure) → low temperature monoclinic B19′-phase.

The latter phase is preserved down to liquid nitrogen temperatures. Such a two-stage transition in TiNi-based alloys is also typical of systems containing other Group VIII metals, such as cobalt and iron (7–9).

Experimental Method

The purities of the ruthenium powder and the nickel from which the alloys were prepared were 99.95 and 99.99 per cent, respectively; iodised titanium was also used. In order to avoid sputtering and losses during alloying, the ruthenium powder was sintered in vacuum at 1200°C and then melted in an arc furnace. Titanium-nickel-ruthenium alloys containing 0.5, 1, 2 and 5 atomic per cent ruthenium along the TiNi-TiRu section were prepared from melts of their component parts in an arc furnace under an argon gas atmosphere. In order to ensure a complete melt, the ingots were remelted four times. The weight losses which occurred on melting amounted to only 0.05 weight per cent, so the final compositions were considered to be identical to the initial ones. Investigations were carried out on both as-cast and annealed specimens.

Measurements of microhardness were carried out by a standard method at a load of 50 g. Other determinations of the temperature dependence of the electrical resistance and thermal expansivity were performed using custom designed equipment (6). A modified differential thermal analysis method was used to record the solid state transformations in the alloys, from liquid nitrogen temperatures up to room temperature.

Experimental Results and Discussion

The constitution of the TiNi-TiRu section of the titanium-nickel-ruthenium ternary system is important for the present work. It is necessary to know the state of the parent phase which then transforms upon cooling. During our investigations we found that the titanium-nickel equiatomic alloy formed a pseudo-binary continuous solid solution with the titanium-ruthenium equiatomic alloy, TiNi-TiRu.

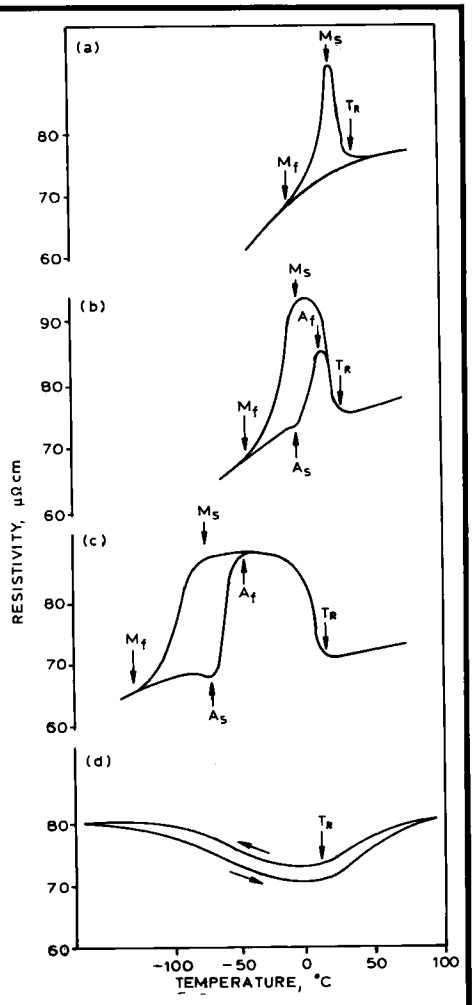


Fig. 1 Resistivity-temperature variations in:
(a) Ti50Ni49.5Ru0.5
(b) Ti50Ni49Ru1
(c) Ti50Ni48Ru2, and
(d) Ti50Ni45Ru5 alloys
Changes which occur at various temperatures are as follows:
At T_R the B2-phase begins to transform to the R-phase
At M_s the martensitic transformation starts
At M_f the martensitic transformation finishes
At A_s the B19′ transformation to R starts
At A_f the B19′ transformation to R finishes

Data showing the dependence of the electrical resistance upon temperature for alloys which contain 0.5, 1, 2 and 5 atomic per cent ruthenium, and measurements of thermal expansion with temperature for alloys containing 0.5, 1 and 2 atomic per cent ruthenium between room temperature and liquid nitrogen temperatures, are shown in Figures 1 and 2, and also in the Table.

Transformations in the TiNi-TiRu system occur in two stages, in a similar way to the transformations in titanium-nickel based alloys containing additives of iridium, rhodium and iron (1, 3, 4, 7). This can be clearly seen from the shapes of the electrical resistance curves for alloys containing 1 and 2 atomic per cent ruthenium. The sequence B2 → R → B19′ is the same as for the alloys mentioned above, see Figures 1(b) and 1(c). The stages are associated with rhombohedral (R) and monoclinic (B19′) lattice distortions. T_R is the temperature at which the parent B2-phase starts to transform into the intermediate R-phase and at which the electrical resistance sharply increases. At M_s the martensitic transformation from the R-phase starts, causing a decrease in the resistance. M_f is the temperature at which the martensitic transformation is complete. On heating the alloys from liquid nitrogen temperatures the reverse transitions take place. A_s and A_f are the temperatures at the start and finish of the B19′ → R transformation, respectively, for alloys containing 0.5 and 1, and 2 atomic per cent ruthenium.

One of the characteristics of the electrical resistance/temperature curves is that they reveal a pronounced hysteresis for R ↔ B19′ transformation, while the R-phase transformation, R → B2, does not. Thus the cooling and heating curves for alloys containing 1 and 2 atomic per cent ruthenium almost coincide at temperatures above A_f, see Figures 1(b) and 1(c).

The B2 → R transformation causes a decrease in the volume of the sample, that is, the alloy is observed to shrink, while the R → B19′ transformation results in an increase in the volume of the sample, that is, thermal expansion occurs, see Figures 2(b) and 2(c).

The observed variations in electrical resistance and thermal expansion with temperature show that the R → B19′ transformation appears to represent a first order transition. This correlates

well with the DTA data, which demonstrate the corresponding thermal effects on heating and cooling (the thermal curves in Figure 3 show only the effects caused by heating, because the data on cooling obtained in our experiments reveal the same transition temperature regardless of composition).

The B2 → R transformation is a reversible process, according to the electrical resistance data shown in Figure 1, and almost reversible, as shown by the thermal expansion data in Figure 2, and therefore can be considered as a transformation close to a second order transition. However the DTA data shown in Figure 3 illustrate that the B2 → R transformation is accompanied by thermal effects, as is the R → B19′ transformation.

It is worth noting that the intermediate phase formed during the B2 → R transformation in titanium-nickel based alloys with added iron (as well as in titanium-palladium based alloys with added nickel) is divided into ranges of incommensurate and commensurate phases with different crystal structures (10, 11). The first range (incommensurate phase) corresponds to the second order transition and the next range (commensurate phase) corresponds to the first order transition. This could explain the thermal effect which was observed in the B2 → R stage for the TiNi-TiRu alloys.

The solid state transformation in titanium-nickel-ruthenium alloy containing 5 atomic per

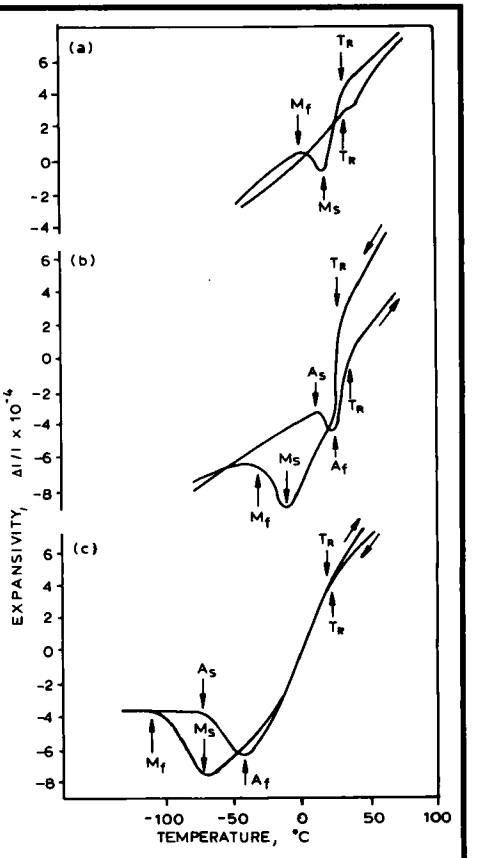


Fig. 2 Variation of thermal expansion with temperature for the alloys:
(a) Ti50Ni49.5Ru0.5
(b) Ti50Ni49Ru1
(c) Ti50Ni48Ru2

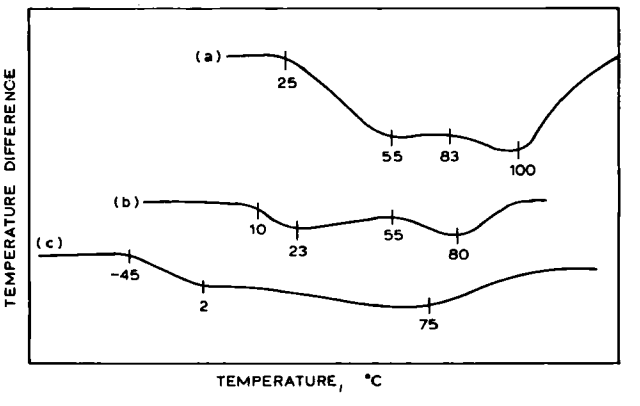


Fig. 3 Differential thermal analysis data on the solid state transformations on heating for the alloys:
(a) Ti50Ni49.5Ru0.5
(b) Ti50Ni49Ru1 and
(c) Ti50Ni48Ru2

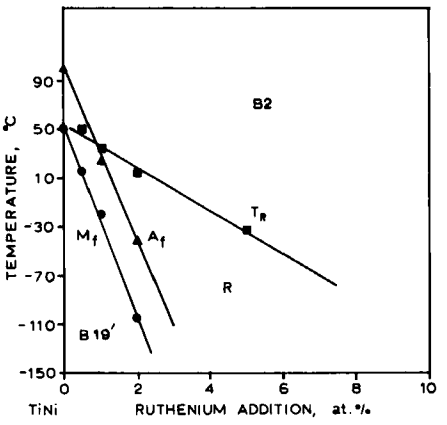


Fig. 4 Phase structure transformations with temperature in TiNi-TiRu alloys for ruthenium additions from 0 to about 8 per cent

cent ruthenium, see Figure 1(d), starts at –20°C. The R-phase exists over a wide temperature range, down to liquid nitrogen temperatures.

The martensitic transformation scheme, Figure 4, shows that the B2-phase is approximately stabilised at room temperature in alloy containing 2 atomic per cent ruthenium. The substitution of ruthenium for nickel results in a lowering of all critical transformation temperatures, but the decrease in the T_R temperature occurs less acutely than the decrease in the temperatures which indicate the transformation range

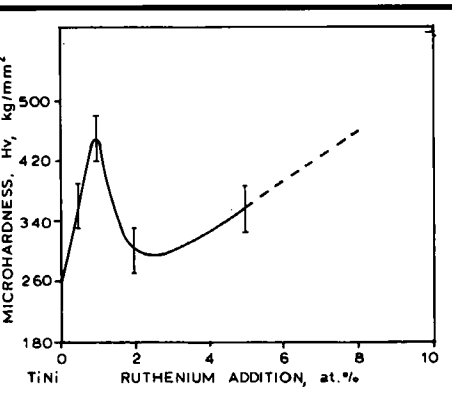


Fig. 5 Variation of the microhardness with composition for the TiNi-TiRu alloys, based on titanium-nickel alloy

of the phase having the B19′ crystal structure.

The microhardness of the titanium-nickel-ruthenium alloys varies with composition and is at a minimum for an alloy containing about 2 atomic per cent ruthenium, and at a maximum for an alloy containing about 1 atomic per cent ruthenium, see Figure 5. A comparison of these findings with those obtained from the electrical resistance and thermal expansion analyses indicates that the minimum is in accordance with the absence of a martensitic transformation in the alloys, and that the maximum is associated with accumulation of the R-phase.

Comparison of the results of the present investigation with data from the literature on the influence of platinum metals on the martensitic transformation in titanium-nickel based alloys enables the following observations to be made:

[a] Additions of ruthenium are very effective in reducing the martensitic transformation temperatures of titanium-nickel based ternary alloys. The B2-phase can be stabilised by the addition of approximately 2 atomic per cent ruthenium. (The same results can also be expected from additions of osmium.)

[b] Higher concentrations of rhodium and iridium (6 atomic per cent) are required to stabilise the B2-phase.

[c] Platinum and palladium do not appear to stabilise the B2-phase at room temperature.

Conclusions

The substitution of ruthenium for nickel in titanium-nickel-ruthenium ternary alloys along the TiNi-TiRu section, as examined by physical and chemical analyses, results in the stabilisation of the high temperature B2-type phase at room temperature for alloys containing at least 2 atomic per cent ruthenium. Alloys containing 0.5 to 2 atomic per cent ruthenium undergo a two stage transformation.

In continuation of our work with the platinum group metals, we intend to study phase equilibria in the titanium-nickel-ruthenium system both experimentally and by calculation, and following that calculate the effect of ruthenium on the martensitic transformation in equiatomic titanium-nickel compound. Data obtained from

the titanium-nickel-ruthenium alloys will make it possible to forecast the effect of osmium on martensitic transformations in TiNi-based alloys; we expect that it will sharply decrease the transformation temperatures in a way similar to that of ruthenium.

References

1 Yu. V. Kudryavtsev, E. L. Semenova, L. A. Tretyachenko, "The Stable and Metastable Phases in Materials", Kiev, IPM AS Ukr. SSR, 1987, 138

2 E. L. Semenova and Yu. V. Kudryavtsev, *J. Alloys Comp.*, 1993, **203**, 165

3 A. A. Klopotov, E. V. Kozlov, Yu. V. Kudryavtsev and E. L. Semenova, "Effects of Shape Memory and Superelasticity and their Application in Medicine", Tomsk University, Tomsk, 1989, 168 (Abstracts of I All-Union Conference) (in Russian)

4 E. L. Semenova, L. A. Tretyachenko, D. B. Chernov and Yu. V. Kudryavtsev, "Phase Equilibria, Structure and Properties of Alloys", Naukova Dumka, Kiev, 1990, 101 (in Russian)

5 N. M. Matveeva, I. E. Lyuboserdova, V. N. Khachin, V. P. Sivokha and D. B. Chernov, "The Rare Metals Alloys with Special Properties: Rare-Earth and Precious Metals", Nauka, 1983, 163 (in Russian)

6 V. E. Listovnichiy, V. P. Brodskiy and P. F. Fenyuk, "The Automated System of Measurements of the Electrical Resistance and Thermo-e.d.s. Temperature Dependence", *J. Zav. Lab.*, 1987, **53**, 47 (in Russian)

7 A. S. Savvinov, V. N. Khachin, and V. P. Sivokha, *Izv. Vys. Uch. Zav., Ser. Fiz.*, 1983, 7, 34 (in Russian)

8 S. G. Fedotov, N. N. Bashanova and N. F. Zhebeneva, *Izv. Acad. Nauk SSSR, Ser. Met.*, 1981, **4**, 147 (in Russian)

9 S. Miyazaki and K. Otsuka, *Philos. Mag. A*, 1984, **50**, 393

10 C. M. Hwang, H. B. Salamon and C. M. Wayman, *Philos. Mag. A*, 1983, **47**, 2, 177

11 K. Enami, T. Yoshida and S. Nenno, "Proc. of the International Conference on Martensitic Transformations", The Japan Institute of Metals, Osaka, Japan, 1986, 1032

Noble Metals Utilised in Drugs and Healthcare

Metal Compounds in Cancer Therapy, Metals in Health and Disease Series – Volume 1

EDITED BY SIMON P. FRICKER, Chapman & Hall, London, 1994, 256 pages, ISBN 0–412–54280–3, £55.00

There are about 92 elements in the Periodic Table to be understood and exploited for medical purposes, and this is the first volume in a new "Metals in Health and Disease Series". Metals in particular have an immense potential – as is shown by the function and diversity of trace metals in metalloproteins, and until recently many, if not most, have been overlooked.

The series sets out to explore the beneficial roles of metals in health and disease. Each volume of invited reviews will target a specific area, accumulating and evaluating published data. The series is aimed at graduates, post-graduates and researchers. It will also be of interest to a much wider readership.

Of course, Pt(II) is very much a success story, and not surprisingly features in the first two (S. P. Fricker and L. R. Kelland) of ten reviews. It is an interesting example of serendipity – Rosenberg's initial experiments in 1965 were to find if electrical fields applied across platinum electrodes effected the growth of *Escherichia coli*. In 1971 cisplatin entered clinical trials, and today the area is still extensively researched to achieve better understanding, and to identify better applications. Cisplatin and carboplatin are now top selling anti-cancer drugs. No doubt they will be bettered by other preparations, some already undergoing clinical trials, aimed at lessening unpleasant side effects, exploring other specificities, and introducing oral application.

The particular success of platinum in the treatment of testicular, ovarian and other soft tissue cancers is well documented. While platinum has many advantages there is no reason why other metals should not find similar application. Thus reviews on gold (C. F. Shaw), ruthenium compounds (G. Sava), rhodium, iridium and palladium (R. G. Buckley) are authoritative and provide a valuable update where the approach and general understanding is less well documented. The often unique properties of metals offer many opportunities. Metals can participate in biological redox reactions, undergo ligand substitution with biological molecules with a specific stereochemistry about the metal centre and with a controlled reactivity. Some metals have radioactive isotopes, with potential for tumour imaging or therapy. Further chapters cover other metals, adding diversity to the text.

This book is presented in an attractive, professional and readable manner. For those in the area it is an essential reading/reference work. For others it will provide an awareness of a growth area. It is an important series to launch at this time and is strongly recommended. A.G.S.

ABSTRACTS

of current literature on the platinum metals and their alloys

PROPERTIES

Formation of Thin Films of Platinum, Palladium, and Mixed Platinum:Palladium Nanocrystallites by the Langmuir Monolayer Technique

F. C. MELDRUM, N. A. KOTOV and J. H. FENDLER, *Chem. Mater.*, 1995, 7, (6), 1112–1116

Chloroform solutions of colloidal Pt, Pd and mixed Pt:Pd = 1:1 particles prepared by solvent extraction were dispersed on a H_2O subphase in a Langmuir trough to generate particulate films 30Å thick. A great amount of the stabiliser was incorporated in the films, thus preventing a completely close-packed arrangement of the metal particles.

Structural Investigation of Bimetallic Rh-Pt Nanoparticles through X-Ray Absorption Spectroscopy

L. E. ALEANDRI, H. BÖNNEMANN, D. J. JONES, J. RICHTER and J. ROZIÈRE, *J. Mater. Chem.*, 1995, 5, (5), 749–752

EXAFS studies of an isolated Rh-Pt colloid, $Rh_{0.44}Pt_{0.56}$, showed mixed-metal shells, with the environment around the Rh absorber consisting of 3.5 Rh atoms at a distance of 2.72 Å and 4.7 Pt atoms at 2.74 Å, and around the Pt absorber 3.6 Rh at 2.72 Å and 8.3 Pt atoms at 2.75 Å. The average co-ordination number was lower than the 12 expected for a f.c.c. structure. The system is best described as a nanoparticulate Rh-Pt alloy, surface rich in Rh.

Solid-State Reaction in Pd/ZnSe Thin Film Contacts

K. J. DUXSTAD, E. E. HALLER, K. M. YU, E. D. BOURRET, J. M. WALKER, X. W. LIN and J. WASHBURN, *Appl. Phys. Lett.*, 1995, **67**, (7), 947–949

Solid-state reactions in Pd thin film contacts on ZnSe initiated at the Pd/ZnSe interface by thermal annealing at 200°C, formed a tetragonal ternary phase $Pd_{5+x}ZnSe$ which had highly oriented grains and was stable up to an annealing temperature of 400°C. The Pd/ZnSe interface was thermally more stable than the corresponding Pd/GaAs and Pd/Si structures. Pd/semiconductor interfacial phenomena were studied.

Observation of Internal Structures of Martensites of Fe-Rh Alloys

N. TAKAHARA, M. TAKAHASHI and R. OSHIMA, *J. Jpn. Inst. Met.*, 1995, **59**, (6), 599–606

Internal structures of the martensites of Fe-5 at.% Rh and Fe-25 at.% Rh (1) were examined by XRD, optical microscopy and TEM. Both alloys showed surface reliefs, which result from martensite transformation. The martensites are of a dislocated lath type. In (1) alloy twinning shear is associated with the lattice invariant shear of the transformation.

Structure of Two-Dimensional Conductor of Sr_2RhO_4

M. ITOH, T. SHIMURA, Y. INAGUMA and Y. MORII, *J. Solid State Chem.*, 1995, **118**, (1), 206–209

The structure of the two-dimensional conductor Sr_2RhO_4 was refined by powder X-ray diffraction at room temperature. Sr_2RhO_4 crystallises with the symmetry of space group $I4_1/acd$, isostructural with Sr_2IrO_4, and the lattice parameter a = 0.54516(1) and c = 2.57539(4) nm. The structural data were similar to those for semiconducting and antiferromagnetic Sr_2IrO_4.

CHEMICAL COMPOUNDS

First Octahedral Platinum Cluster: Structure as a Function of Electron Count in Pt_6 Clusters

L HAO, G. J. SPIVAK, J. XIAO, J. J. VITTAL and R. J. PUDDEPHATT, *J. Am. Chem. Soc.*, 1995, **117**, (26), 7011–7012

Two new types of Pt_6 clusters, interconvertible by the gain or loss of two electrons, and one having octahedral stereochemistry, are reported. The dark red-purple, air-sensitive cluster $[Pt_6(\mu\text{-}CO)_6(\mu\text{-}dppm)_3]$ (dppm = $Ph_2PCH_2PPh_2$) (1) was prepared by reduction of $[PtCl_2(SMe_2)_2]$ and $[PtCl_2(dppm)]$ with $NaBH_4$ under CO, in high yield. (1) has two $Pt_3(\mu\text{-}CO)_3$ triangles bridged by 3 μ-dppm ligands, with D_{3h} symmetry and is easily oxidised to give the cluster cation $[Pt_6(CO)_6(\mu\text{-}dppm)_3]^{2+}$ with terminal carbonyl ligands.

Reductive Reactions in Synthesis of Low-Valence Platinum and Palladium Complexes

N. YU. KOZITSYNA and I. I. MOISEEV, *Usp. Khim.*, 1995, **64**, (1), 51–65

The use of reductive reactions of Pt(II) and Pd(II) complexes in the synthesis of complexes containing the metals in low-valence states ($0 \leq n \leq 2$) with π-acceptor ligands: phosphines, phosphides, phenanthroline and dipyridyl is discussed. Transformation of *tert*-phosphine ligands with a reductive agent and X-ray data for the mono- and polynuclear complexes of Pt and Pd in low oxidation states are reviewed. (138 Refs.)

Synthesis of Large Palladium Clusters. The Preparation of $Pd_{38}(CO)_{28}(PR_3)_{12}$ (R = Et, Bu^n) and $Pd_{34}(CO)_{24}(PEt_3)_{12}$

E. G. MEDNIKOV and N. I. KANTEEVA, *Izv. Akad. Nauk Rosii, Ser. Khim.*, 1995, (1), 167–170

The $Pd_{38}(CO)_{28}L_{12}$ cluster (L = PEt_3) was prepared by reacting $Pd_{10}(CO)_{12}L_6$ with CF_3COOH-Me_3NO, CF_3COOH-H_2O_2, and $Pd(OAc)_2$-Me_3NO and $Pd_2(dba)_3$ mixture (dba = dibenzylidenacetone). Tri-*n*-butylphosphine $Pd_{38}(CO)_{28}(PBu_3)_{12}$ was synthesised by the reaction of $Pd_{10}(CO)_{14}(PBu_3)_4$ with Me_3NO. The reaction of $Pd_4(CO)_5L_4$ with $Pd_2(dba)_3$ yielded clusters $Pd_{34}(CO)_{24}L_{12}$ and $Pd_{16}(CO)_{13}L_6$.

One-Pot Synthesis and X-Ray Studies on Cyclic Oligobipyridines and One of Their Dinuclear Ruthenium Complexes

C. KAES, M. W. HOSSEINI, R. RUPPERT, A. DE CIAN and J. FISCHER, *J. Chem. Soc., Chem. Commun.*, 1995, (14), 1445–1446

A one-pot synthesis of three new macrocycles containing two, three or four 2,2′-bipyridine units is described. A homodinuclear Ru^{II} complex was prepared in almost quantitative yield by reacting one of the macrocycles with 2 equiv. of $Ru(bipy)_2Cl_2$ in a butanol-H_2O solution. Precipitation of the PF_6 salt from an aqueous solution gave the pure complex as a mixture of diastereoisomers. The X-ray structure of one of the diastereoisomers of the dinuclear Ru complex shows two metal centres held in close proximity.

Chiral $[Ru(pp)_2(CO)_2]^{2+}$ Species (pp = Bidentate Polypyridyl Ligand) and Their Use in the Stereoselective Synthesis of Ligand-Bridged Dinuclear Complexes

T. J. RUTHERFORD, M. G. QUAGLIOTTO and F. R. KEENE, *Inorg. Chem.*, 1995, **34**, (15), 3857–3858

The decarbonylation of chiral $[Ru(pp)_2(CO)_2]^{2+}$ (pp= bidentate polypyridyl ligands) in the presence of excess pp showed stereoretention in the $[Ru(pp)_3]^{2+}$ product. Under the same conditions, its reaction with chiral $[Ru(pp')_2(BL)]^{2+}$ centres (pp and pp′ may or may not be identical; BL = bridging ligand) allows the synthesis of specific diastereoisomeric forms of the dinuclear species $[(pp)_2Ru(BL)Ru(pp')_2]^{4+}$.

ELECTROCHEMISTRY

Methanol Oxidation at Electrochemically Oriented Platinum Electrodes in Acidic Medium

A. A. EL-SHAFEI, *J. Phys. Chem. (München)*, 1995, **190**, (II), 231–239

Methanol oxidation was studied as a structure sensitive process on different Pt surfaces: polycrystalline Pt and reproducibly prepared electrochemically oriented Pt surfaces. The fabrication of Pt surfaces with preferred orientations or different surface concentrations of low index planes depends on the electrochemical treatment. Bulk MeOH oxidation depended both on the predomination of one low index plane and on the ratio of the surface planes.

Contribution to the Interpretation of the Multistep Cathodic Reduction of Oxygen at the Pt/Zirconia Base Electrolyte Interface at High Temperature

G. B. BARBI, *Ber. Bunsenges. Phys. Chem.*, 1995, **99**, (5), 741–748

The multistep cathodic reduction of O_2 molecules at high temperatures at the porous Pt/Y_2O_3 stabilised ZrO_2 solid electrolyte interface was analysed by steady state polarisation. For very thin and porous layers and O_2 mixtures of $\geq 1\%$ O_2, the rate of the overall process was controlled by the electrode/electrolyte interfacial diffusion of neutral and/or single ionised atoms.

Attempts to Modify an Electrode with a Conducting Platinum Cluster Compound

L. XU, F. LI and S. DONG, *Electroanalysis*, 1995, 7, (8), 734–737

A conducting Pt cluster compound $K_{1.64}Pt(C_2O_4)_2$ was electrochemically synthesised on a glassy C electrode through the electro-oxidation of $K_2Pt(C_2O_4)_2$ in an aqueous medium using single potential step and cyclic voltammetry methods. The excellent conductivity of the fibrous material that grew on the electrode was observed voltammetrically. Each conducting fibre in contact with the electrode could act as an ultramicroelectrode, and the electrode behaviour changed from a plain to an ultramicroelectrode array.

Absorption-Desorption of Deuterium at Pd95%-Rh5% Alloy. I: Environment and Temperature Effects

G. MENGOLI, M. FABRIZIO, C. MANDUCHI, E. MILLI and G. ZANNONI, *J. Electroanal. Chem.*, 1995, **390**, (1–2), 135–142

The gas phase and electrolytic loading of 5%Rh-Pd alloy with D_2 were studied. Gas loading was performed isochorically under 900 mbar D_2, by decreasing the temperature from 900 to 20°C. The absorption was measured at 20°C when the [D]:[Me] ratio exceeded the typical value for pure Pd. Electrolytic insertions of D_2 were carried out potentiostatically in alkaline D_2O electrolytes, giving maximum [D]:[Me] ratios at 25°C, while at 90°C alloy deuterides of large [D]:[Me] ratio were obtained.

A Novel Ru(VII)/Ru(IV) Mediatory System for Electrooxidation of Primary and Secondary Alcohols, Leading to Aldehydes and Ketones

S. TORII and A. YOSHIDA, *Chem. Lett.*, 1995, (5), 369–370

A soluble Ru(VII)/Ru(IV) redox system in MeCN/H_2O-Bu_4NOH-(Pt/Pt) was found to be a mild oxidising system for the electrochemical conversion of primary and secondary alcohols into their corresponding aldehydes and ketones under basic conditions. Direct evidence on the working of the Ru(VII)/Ru(IV) redox as a mediator system was obtained from UV spectroscopy.

PHOTOCONVERSION

Acid-Base Behavior of the Ground and Excited States of Platinum(II) Complexes of Quinoxaline-2,3-dithiolate

S. D. CUMMINGS and R. EISENBERG, *Inorg. Chem.*, 1995, **34**, (13), 3396–3403

Studies of the pH-dependent absorption and emission behaviour of $Pt(qdt)_2^{2-}$ (1) and Pt(phen)(qdt) (2) (qdt = quinoxaline-2,3-dithiolate and phen = 1,10-phenanthroline) showed pH-dependent changes in both their charge-transfer absorption and emission spectra, which were attributed to protonation of the qdt ligand at the imine N. For (1), single protonation leads to a large red shift (2582/cm), but for (2) the lowest-energy excited state involves charge transfer from an orbital of Pt(*d*)/S(*p*) to a phen π* orbital.

Electronic Spectra and Photochemistry of Trichlorostannyl Complexes of Ruthenium(II) and Osmium(II)

V. PAWLOWSKI, H. KUNKELY and A. VOGLER, *Inorg. Chim. Acta*, 1995, **234**, (1–2), 55–60

The absorption spectra and photochemistry of $[M(SnCl_3)_6]^{4-}$, $[M(SnCl_3)_5Cl]^{4-}$ and $[M(SnCl_3)_5AN]^{3-}$, where M = Ru, Os; AN = acetonitrile, in acetonitrile were studied. It is suggested that the lowest energy transitions are largely of the intraligand type. The photolysis in acetonitrile leads to substitutions of $SnCl_3^-$ or in the case of $[Ru(SnCl_3)_6]^{4-}$ to a ligand fragmentation as primary photoreactions. $[M(SnCl_3)_4(AN)_2]^{2-}$ was the terminal product of all the photoreactions.

Ruthenium(II) tris-(2,2′-bipyridine)-Specific Extrinsic Lyoluminescences of X-ray Irradiation Colored and Electrolytically Colored Alkali Halides

S. KULMALA, A. HAKANEN, P. RAERINNE, A. KULMALA and K. HAAPAKKA, *Anal. Chim. Acta*, 1995, **309**, (1–3), 197–210

Short-lived solid/solution interfaces, which are sufficiently energetic to initiate the radiative ^{3}MLCT-based transition lyoluminescence (LL) of Ru(II) tris-(2,2′-bipyridine)chelate can be produced on dissolving X-ray irradiation coloured or electrolytically coloured alkali halides in H_2O. Using $Ru(bpy)_3^{2+}$ as a model lyoluminophore, the basis of using LL as a new analytical tool is discussed. The extrinsic LL of F-coloured alkali halides allows detection of luminescent compounds at trace levels in aqueous solutions.

Control of Photosubstitution in Dinuclear Ruthenium Polypyridyl Complexes by Choice of Bridging Ligand

H. P. HUGHES and J. G. VOS, *Inorg. Chem.*, 1995, **34**, (15), 4001–4003

Photolysis of $[(Ru(bpy)_2)_2(bpzt)]^{3+}$ (Hbpzt is 3,5-bis(pyrazin-2-yl)-1,2,4-triazole) resulted in a unique labilisation of the metal moiety bound to the triazole N4 site. This is contrary to results obtained for the analogous compound based on the 3,5-bis(pyridin-2-yl)-1,2,4-triazole ligand for which both the N1 and N4 sites were subject to photochemical substitution. This is explained by changes in the rate of relaxation to the lowest excited state, due to the different natures of the luminescent properties in these complexes.

ELECTRODEPOSITION AND SURFACE COATINGS

Rhodium Plating

R. J. MORRISSEY, *Plat. Surf. Finish.*, 1995, **82**, (8), 69

Rh can be evaporated under vacuum, but is mostly electrodeposited. Electroplating solutions for Rh are highly acidic, and are usually based on the sulphate or phosphate. For decorative applications, Rh plating solutions contain ~ 2 g/l Rh and ~ 20 ml/l concentrated H_2SO_4, at 1–5 A/dm^2 and at 40–45°C. Rh can be plated from molten cyanide systems to a thickness of > 100 μm. Rh deposits are non-toxic and hypoallergenic.

APPARATUS AND TECHNIQUE

Calorimetric Measurement of the Energy Difference between Two Solid Surface Phases

Y. Y. YEO, C. E. WARTNABY and D. A. KING, *Science*, 1995, **268**, (5218), 1731–1732

The energy difference between two solid surface structures was measured using a single-crystal surface calorimeter which is a clean Pt{100} surface reconstructed to a stable phase where the surface layer of Pt atoms has a quasi-hexagonal structure. By comparing the heats of adsorption of CO and C_2H_4 on this stable Pt{100}-hex phase with those on a metastable Pt{100}-(1 × 1) surface, the energy difference between the two clean phases was measured as 20 ± 3 and 25 ± 3 kJ/mole of surface Pt atoms.

Platinum/Glassy Carbon Electrode as Detector for Liquid Chromatographic Determination of Hydroxyl-Containing Compounds

I. G. CASELLA, *Anal. Chim. Acta*, 1995, **331**, (1), 37–46

A Pt-modified glassy C electrode (CME) was studied as an amperometric detector for mono- and polyhydric compounds in flowing streams, including liquid chromatography. The Pt-CME showed good sensitivity and time stability. The electrode response was stable showing a signal loss of < 5% after 8 h trials.

Morphologic and Spectroscopic Characterization of Porous Pt/GaAs Schottky Diodes by Scanning Tunnelling Microscopy

J. MASÓ, N. BARNIOL, F. PÉREZ-MURANO and X. AYMERICH, *Thin Solid Films*, 1995, **261**, (1–2), 299–306

The porous character of the Pt film of Pt/GaAs Schottky diodes used as NH_3 gas sensors was studied using STM. Electrical measurements were also performed in very localised regions of the surface. The diameter of the Pt grains of the porous film was found to depend on its thickness.

Tunable, Long-Wavelength PtSi/SiGe/Si Schottky Diode Infrared Detectors

J. R. JIMENEZ, X. XIAO, J. C. STURM and P. W. PELLEGRINI, *Appl. Phys. Lett.*, 1995, **67**, (4), 506–508

The fabrication is reported of *p*-type PtSi/SiGe/Si Schottky diodes with barrier heights (from photoresponse) that are lowered (relative to PtSi/Si) and are highly dependent on the applied bias. Variability in barrier height was obtained by using the SiGe/Si valence band offset as an additional barrier close to the PtSi/SiGe Schottky barrier. The total effective barrier can then be altered by adjusting the applied reverse bias.

Study of the Adsorptive Voltammetric Behavior of the Rh^{III}-5-Br-PADAP Complex

C. WANG, C. HONG and H. LI, *Electroanalysis*, 1995, **7**, (8), 759–762

The adsorptive voltammetric behaviour of the Rh^{III}-2-(5-bromo-2-pyridylazo)-5-diethylaminophenol complex was studied by linear scan in a solution of NaOAc, HOAc and ethanol. This method provides sensitive selective adsorptive stripping voltammetry for the detection of $7.8 \times 10^{-9} - 9.7 \times 10^{-7}$ mol/l traces of Rh.

Novel Thick-Film pH Sensors Based on Ruthenium Dioxide-Glass Composites

H. N. MCMURRAY, P. DOUGLAS and D. ABBOT, *Sens. Actuators B*, 1995, **28**, (1), 9–15

Composite electrodes comprising thick films of 30 ± 10 μm RuO_2-glass composite on a Pyrex substrate were made and showed a near Nernstian dependence of potential on pH in aqueous buffer at pH 2–12 and at a RuO_2:Pb borosilicate glass ratio of 1:1. The electrodes displayed a maximum hysteresis of 30 mV and a response time of ~ 90 s. The electrodes are porous and the response time increased with the RuO_2:Pb borosilicate glass ratio in the composite.

HETEROGENEOUS CATALYSIS

A Novel Aminoalcohol Modifier for the Enantioselective Hydrogenation of Ethyl Pyruvate on Pt/Alumina

B. MINDER, T. MALLAT, A. BAIKER, G. WANG, T. HEINZ and A. PFALTZ, *J. Catal.*, 1995, **154**, (2), 371–378

A chiral modifier, (*R*)-2-(1-pyrrolidinyl)-1-(1-naphthyl)ethanol (PNE) was prepared and tested in the enantioselective hydrogenation of ethyl pyruvate over Pt/Al_2O_3. An enantiomeric excess in (*R*)-ethyl lactate of ≤ 75% was obtained. The optimum reaction conditions were 1–10 bar H_2 pressure, 0–25°C and a catalyst loading ≥ 15 g/l. The efficiency of PNE was shown by the very low modifier:reactant molar ratio, 1:30,000, to obtain maximum enantioselectivity.

Structural Characterization of a Model Catalyst: $Pt/Al_2O_3/NiAl(110)$

T. BERTRAMS, F. WINKELMANN, T. UTTICH, H.-J. FREUND and H. NEDDERMEYER, *Surf. Sci.*, 1995, **331–333**, (Part B), 1515–1519

The condensation of Pt was studied on clean NiAl(110) and on a thin ordered Al_2O_3 film grown on NiAl(110). On Al_2O_3/NiAl(110) and up to a coverage of one monolayer, Pt forms highly dispersed two-dimensional islands with an average diameter of 10–30 Å whose density increased with coverage. For higher Pt coverage the formation of three-dimensional Pt clusters was observed. Annealing of the Pt-covered surface led to Pt diffusion into the oxide film. On NiAl(110) and up to 1 monolayer, 2-dimensional growth of Pt with constant island density was observed.

The Positive Effect of Hydrogen on the Reaction of Nitric Oxide with Carbon Monoxide over Platinum and Rhodium Catalysts

R. DÜMPELMANN, N. W. CANT and D. L. TRIMM, *Catal. Lett.*, 1995, **32**, (3, 4), 357–369

The effect of adding 330–4930 ppm H_2 to a reaction mixture of NO and CO over Pt and Rh catalysts was studied at 200–250°C. The addition of H_2 results in a large increase in the conversion of both NO and CO. The equation for the reaction accounts for the 50–100% of CO_2 formed with Pt/Al_2O_3 and the 20–50% with Rh/Al_2O_3. The process arises by formation of isocyanic acid on the metal followed by hydrolysis to CO_2 and NH_3 on the support.

Naphthalene Hydrogenation over Pt/Al_2O_3 Catalyst in a Trickle Bed Reactor

T.-C. HUANG and B.-C. KANG, *Ind. Eng. Chem. Res.*, 1995, **34**, (7), 2349–2357

Naphthalene dissolved in different volatile solvents was hydrogenated over Pt/Al_2O_3 catalyst in a trickle bed reactor. The activity and selectivity were studied with various H_2 and feed flow rates at 513 K and 5.17 MPa. The activity of naphthalene hydrogenation increased with increasing wetting efficiency, and the selectivity of *cis*-decalin decreased with increasing solvent volatility.

Hydrogenation of Oxygen-Containing Acyclic Compounds Using Finely Dispersed Catalysts Based on Platinum Group Metals

T. N. ANTONOVA, A. A. KUNITSKII, E. M. CHABUTKINA, G. N. KOSHEL', A. L. SOKOLOV and S. P. KOROVINA, *Neftekhimiya*, 1995, **35**, (1), 49–55

Studies of the hydrogenation of the double bonds in 5,6-epoxy-*cis*-cyclooctene, 5-cyclooctene-1,2-diol and the reduction of aqueous cyclooctylhydroperoxide were performed using finely dispersed Pt group metal catalysts, such as 3–5%Pt/C, 1–5%Pd/C and 2–5%Rh/C. These finely dispersed catalysts were highly effective in producing cycloalkanol and cycloalkanone.

Vapour-Phase Hydrodehalogenation of Chlorobenzene over Platinum/H-BEA Zeolite

E. J. CREYGHTON, M. H. W. BURGERS, J. C. JANSEN and H. VAN BEKKUM, *Appl. Catal. A: Gen.*, 1995, **128**, (2), 275–288

Studies of Pt/H-BEA zeolite and Pt/Al_2O_3 catalysts during the vapour-phase hydrodehalogenation of chlorobenzene showed them to be highly active in the hydrogenolysis of the C-halogen bond. Deactivation of Pt/H-BEA is due to acid catalysed oligomerisation reactions and coke formation. Coke formation diminished and catalyst stability improved by replacement of Brønsted acid sites in the Pt catalyst by Na ions.

Skeletal Reactions on *n*-Hexane over Pt-NaY, Pt/SiO_2, HY, and Mixed Pt/SiO_2 + HY Catalysts

Z. PAÁL, Z. ZHAN, I. MANNINGER and W. M. H. SACHTLER, *J. Catal.*, 1995, **155**, (1), 43–51

The activity and selectivity of three 8%Pt/NaY catalysts calcined at 633, 723 and 823 K were studied with *n*-hexane as the model reactant at 603 K and subatmospheric pressure. The activity of all the Pt/NaY catalysts was superior to that of EUROPT-1 and they deactivated more slowly. The sample calcined at 633 K had the highest dispersion and the highest aromatisation selectivity.

First Heck Reactions of Aryldiazonium Salts Using Heterogeneous Catalysts

M. BELLER and K. KÜHLEIN, *Synlett*, 1995, (5), 441–442

A very simple and practical Heck reaction of diazonium salts and acrylic acid esters, based on heterogeneous Pd catalysts supported on C, Al_2O_3, SiO_2 and $BaSO_4$ has been developed. Cinnamic acid esters were obtained under very mild conditions in good to excellent yields. No addition of a base or of phosphane ligands was needed for good conversion.

High Activity of CO Oxidation over Nanocrystalline CuO-Pd/γ-Al_2O_3 Catalysts Prepared by the γ-Radiation Method

Y. ZHU, P. LIN, Y. QIAN, S. YU, Z. CHEN and M. ZHANG, *Chin. J. Chem. Phys.*, 1995, **8**, (3), 274–278

The nanocrystalline CuO (8 wt.%, 12 nm)-Pd (0.5 wt.%, 10 nm)/γ-Al_2O_3 catalyst prepared by the γ-radiation method was very active in CO oxidation reactions. It started operating at 110°C; its light-off temperature was 145°C and 100% CO conversion was obtained at 148°C. The catalyst showed thermal stability in its activity after thermal treatment at ≤ 750°C.

Structure and State of Surface of Aluminopalladium Catalysts from bis(π-Allyl Palladium Chloride)

N. V. PERKAS, G. D. ZAKUMBAEVA and T. D. LEVINTOVA, *Neftekhimiya*, 1995, **35**, (2), 141–147

Studies of the Pd/γ-Al_2O_3 catalyst prepared by reducing $(C_3H_5PdCl)_2$ with $N_2H_4.H_2O$ on γ-Al_2O_3 in aqueous ethanol solution, followed by drying in alcohol, showed the formation of highly dispersed Pd on the surface of the support. The active phase was of zero-valence order, containing low-valent ionic Pd forms, which were stabilised by organic ligands. The catalyst was highly reactive in liquid-phase hydrogenation.

Palladium-Ceria Catalysts: Reversibility of Hydrogen Chemisorption and Redox Phenomena

A. BENSALEM, F. BOZON-VERDURAZ and V. PERRICHON, *J. Chem. Soc., Faraday Trans.*, 1995, **91**, (14), 2185–2189

Studies of the H_2 interaction with Pd/CeO_2 catalysts showed that the ratio H_{irr} : Pd_{total}, H_{irr} = irreversibly adsorbed H, is 2.5–3.5. This is due to H spillover from Pd to CeO_2. The uptake of H by CeO_2 resulted in its complete surface reduction at room temperature, while bulk reduction started at 473 K. The reoxidation ratio depended on the outgassing temperature.

Catalytic Decomposition of N_2O over Rhodium-Loaded Metal Oxides

J. OI, A. OBUCHI, A. OGATA, H. YAGITA, G. R. BAMWENDA and K. MIZUNO, *Chem. Lett. Jpn.*, 1995, (6), 453–454

Studies of catalytic decomposition of N_2O to N_2 and O_2 on Rh-loaded metal oxide catalysts showed that Rh/ZnO had the highest activity. An air-pretreated 0.5 wt.% Rh/ZnO catalyst was the most active, giving a reaction rate of 4.0×10^4 μmol (N_2O)/gh under 950 ppm of N_2O and 5% of O_2 at 300°C.

Selective Hydrogenation over Ruthenium Catalysts

P. KLUSON and L. CERVENY, *Appl. Catal. A: Gen.*, 1995, **128**, (1), 13–31

A review is given of the preparation, characterisation and activities of Ru catalysts used in the selective hydrogenation of carbonyl groups in the vicinity of conjugated or isolated double bonds, for the production of α,β-unsaturated alcohols. The effects of promoters, particle size, inorganic and organic modifiers, and catalyst supports are discussed. (137 Refs.)

HOMOGENEOUS CATALYSIS

Palladium-Catalyzed Stereoselective Allylaminocyclization and 1,3-Butadien-2-ylaminocyclization of Allenyl Tosylcarbamates

M. KIMURA, S. TANAKA and Y. TAMARU, *J. Org. Chem.*, 1995, **60**, (12), 3764–3772

Pd catalysts, $PdCl_2(PhCN)_2$ or $Pd_2(dba)_3.CHCl_3$ (dba = dibenzylideneacetone) catalysed an allylaminocyclisation of 2,3-butadienyl tosylcarbamates (1) with allylic chlorides in the presence of Et_3N or K_2CO_3 base in THF at room temperature to give selectively *trans*-4,5-disubstituted 2-oxazolidinones in good yields. Under similar conditions, $Pd(PPh_3)_4$ catalysed an N-allylation of (1). In the absence of an allylic chloride, $Pd(PPh_3)_4$ and $PdCl_2(PhCN)_2$ catalyse a formal dimerisation of (1) to give C_4-triene-substituted 2-oxazolidinones in moderate to good yields.

Asymmetric Hydrosilylation of 1-Alkenes Catalyzed by Palladium-MOP

Y. UOZUMI, K. KITAYAMA, T. HAYASHI, K. YANAGI and E. FUKUYO, *Bull. Chem. Soc. Jpn.*, 1995, **68**, (3), 713–722

Asymmetric hydrosilylation of 1-alkenes with trichlorosilane at 40°C in the presence of 1×10^{-3} or 1×10^{-4} molar amounts of Pd-MOP catalyst proceeded with good regioselectivity and with high enantioselectivity to give high yields of 2-(trichlorosilyl)alkanes. The catalyst was prepared in situ from $[PdCl\text{-}(\eta^3\text{-}C_3H_5)]_2$ and (*S*)-2-diphenylphosphino-2′-methoxy-1,1′-binaphthyl ((*S*)-MeO-MOP). Oxidation of the C-Si bond gave optically active 2-alkanols (87–97% ee).

Stereoselective Addition of Carboxylic Acids to Electron Deficient Acetylenes Catalyzed by the $PdMo_3S_4$ Cubane-Type Cluster

T. WAKABAYASHI, Y. ISHII, T. MURATA, Y. MIZOBE and M. HIDAI, *Tetrahedron Lett.*, 1995, **36**, (31), 5585–5588

The mixed-metal sulphide cubane-type cluster complex $[PdMo_3S_4(tacn)_3Cl][PF_6]_3$ (tacn = 1,4,7-triazacyclononane) was found to be a highly efficient and selective catalyst for the addition of carboxylic acids to acetylenes with electron-withdrawing groups. The corresponding *trans* addition products were exclusively obtained in good yields under mild conditions in the presence of a catalytic amount of triethylamine.

Rhodium(I)- and Palladium(0)-Catalyzed Carbonylation of Triarylbismuthines with Carbon Monoxide via a Possible Oxidative Addition of a Carbon-Bismuth Bond to Rhodium(I) and Palladium(0)

C. S. CHO, Y. YOSHIMORI and S. UEMURA, *Bull. Chem. Soc. Jpn.*, 1995, **68**, (3), 950–957

Triarylbismuthines reacted with CO at atmospheric pressure in acetonitrile at 25°C in the presence of a catalytic amount of a Rh compound, such as $[RhCl(CO)_2]_2$, $RhCl_3.3H_2O$ and $[RhCl(COD)]_2$, where COD is cyclooctadiene, to give high yields of the corresponding diaryl ketones and methyl esters. With MeOH solvent, methyl benzoates are also produced. Oxidative addition of a C-Bi bond to Rh(I) and Pd(0) is the major step in the carbonylations.

Transformations of Formaldehyde and Glycolaldehyde during Rhodium-Catalysed Hydroformylation of Formaldehyde

N. N. EZHOVA, G. A. KORNEEVA, E. V. SLIVINSKII and R. A. ARONOVICH, *Izv. Akad. Nauk Rosii, Ser. Khim.*, 1995, (1), 75–78

The hydroformylation of formaldehyde to glycolaldehyde (GA) catalysed by $RhCl(PPh_3)_3$, $RhCl(CO)(PPh_3)_2$ and $RhCl_3$ + PPh_3 system in *N,N*-dimethylacetamide was studied. The hydroformylation was accompanied by the Kannizzaro-Tishchenko reaction, hydrogenation of CH_2O to MeOH, condensation of CH_2O with GA to polyoxyaldehydes C_3–C_{16} and dimerisation of GA. The formation of polyoxyaldehydes was the predominant side reaction, probably proceeded by GA co-ordination with a Rh atom. $RhCl_3$ + PPh_3 catalyst gave the best results for CH_2O hydroformylation. At the substrate conversion to 62–67%, the selectivity for GA formation was 96% and the yield was 60–65%.

Strong Electronic Effects on Enantioselectivity in Rhodium-Catalyzed Hydroborations with Novel Pyrazole-Containing Ferrocenyl Ligands

A. SCHNYDER, L. HINTERMANN and A. TOGNI, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, (8), 931–932

Studies of the Rh catalysed hydroboration of styrene with catecholborane using $[Rh(cod)_2]BF_4$ catalyst (cod=cyclooctadiene) showed the highest enantioselectivity yet for a hydroboration (98% ee) obtained with the pyrazolyl-containing ferrocenyl ligand containing Me, H and $4\text{-}CF_3C_6H_4$. The effect of the substituents on both the pyrazolyl and phosphano fragments was studied, and the results were interpreted in terms of the varying electronic asymmetry they produce at the metal centre.

Optically Active Bis(oxazolinyl)pyridine (Pybox) Rhodium Complexes: Asymmetric Hydrosilylation of Ketones

H. NISHIYAMA and K. ITOH, *J. Synth. Org. Chem. Jpn.*, 1995, **53**, (6), 500–508

Optically active bis(oxazolinyl)pyridine (Pybox) was developed as a chiral N ligand for asymmetric hydrosilylation of ketones. Pybox reacted with $RhCl_3$ in ethanol solution to give a stable $RhCl_3$(Pybox) complex, which showed powerful catalytic activity for the hydrosilylation of ketones with diphenylsilane in the presence of Ag tetrafluoroborate. Acetophenone was reduced to 1-phenylethanol in 91% yield and in 94% ee. Substituents on the oxazoline rings and on the pyridine ring were also examined.

Oxidative Regeneration of Phosphine-Modified Rhodium Hydroformylation Catalysts

E. V. SLIVINSKII, V. I. KURKIN, M. M. ALI, G. A. KORNEEVA, R. A. ARONOVICH, O. YU. PESIN, M. A. MORGULIS and YU. I. SOLOVETSKII, *Neftekhimiya*, 1995, **35**, (2), 159–163

Studies were made of oxidative regeneration of deactivated PPh_3/Rh catalyst during hydroformylation of olefins in atmospheric O_2. The results showed that the application of ozonisation, ultrasound and exposure to light of accelerated electrons noticeably intensified the regeneration of deactivated catalysts.

Chiral Ruthenium(II)-Bis(2-oxazolin-2-yl)-pyridine Complexes. Asymmetric Catalytic Cyclopropanation of Olefins and Diazoacetates

H. NISHIYAMA, Y. ITOH, Y. SUGAWARA, H. MATSUMOTO, K. AOKI and K. ITOH, *Bull. Chem. Soc. Jpn.*, 1995, **68**, (5), 1247–1262

The title chiral Ru(II) complex, which was prepared in situ from optically active bis(2-oxazolin-2-yl)pyridine (Pybox-*ip*) (1) and $[RuCl_2(p\text{-cymene})]_2$ (2), exhibited efficient activity for the asymmetric cyclopropanation (ACP) of styrene and a number of diazoacetates, to give the corresponding *trans*- and *cis*-2-phenylcyclopropane-1-carboxylates in good yields of 66–87%. A mixture of (1) and (2) in ethylene produced the *trans*-$RuCl_2$(Pybox-*ip*)(ethylene) complex which also proved to be a powerful catalyst for ACP.

ELECTRICAL AND ELECTRONIC ENGINEERING

Magneto-Optical Enhancement in Pt/($Ni_{1-x}Co_x$) Multilayers

R. KRISHNAN, M. NÝVLT, V. PROSSER, M. SEDDAT, Z. SMETANA, M. TESSIER and S. VISNOVSKÝ, *J. Magn. & Magn. Mater.*, 1995, **148**, (1–2), 283–284

Magneto-optical (MO) polar Kerr rotation (PKR) and ellipticity spectra of Pt/($Ni_{1-x}Co_x$) multilayers with $x = 0$, 0.3 and 1, prepared by evaporation under UHV, were studied. Layers formed at the Pt-magnetic layer interfaces resulted in a surface-induced perpendicular magnetic anisotropy and enhanced PKR in the near-UV spectral region. The possibility of optimising the MO characteristics, by changing x and the growth parameters, makes this Pt multilayer important for obtaining MO storage media able to work in blue light.

Improvement of Electrical Characteristics of Pt-Diffused Devices

B. DENG, C. SHU and H. KUWANO, *Jpn. J. Appl. Phys.*, 1995, **34**, (6A), 2969–2973

The electrical characteristics of Pt-diffused p^+n diodes were improved by reducing Pt-induced adverse effects. Pt diffusion induces mobile Pt ions to diffuse into the SiO_2 films and also changes the surface conditions near the Si-SiO_2 interface, thus increasing the leakage current. The Pt-diffused dipolar devices with a (100) substrate and a phosphosilicate glass film on SiO_2 film are effective in both the preservation of electrical stability and reduction of leakage current.

Spin-Valve Memory Elements Using [{Co-Pt/Cu/Ni-Fe-Co}/Cu] Multilayers

Y. IRIE, H. SAKAKIMA, M. SATOMI and Y. KAWAWAKE, *Jpn. J. Appl. Phys.*, 1995, **34**, Part 2, (4A), L415–L417

Development of a new type of magnetoresistive memory using magnetic spin-valve multilayers, where magnetisation switching of the semi-hard magnetic CoPt layer is used for data storage and that of the soft magnetic NiFeCo layer is used for data readout, is reported. The fabricated memory element was made of a word line of Au film and a magnetoresistive sense line of [{Co-Pt/Cu/Ni-Fe-Co}/Cu] multilayers.

NEW PATENTS

METALS AND ALLOYS

Manufacture of Finely Divided Particles of Silver-Palladium Alloys

E. I. DU PONT DE NEMOURS & CO.

U.S. Patent 5,429,657

Finely divided particles of Ag-Pd alloy are manufactured by aerosol decomposition of an aqueous solution containing Pd and Ag nitrates. The aerosol is heated to above the decomposition temperature of the Ag and Pd compounds, but below the melting point of the Ag-Pd alloy, to form a densified alloy, followed by separation of the Ag-Pd alloy particles. The powders are fully dense with high purity.

Ultrafine Palladium Alloy Particles

TANAKA KIKINZOKU KOGYO K.K.

Japanese Appl. 7/24,318

Ultrafine particles of Ag-Pd alloy are prepared by dissolving $Ag_2Pd(C_2O_4)_2$ in an aqueous solution containing polyvinylpyrrolidone (PVP) and irradiated by UV light in solution. The particles of the Ag-Pd alloy contain 50–80 at.% Ag, Ag-Pd alloy with an atomic ratio of Ag:Pt = 2:1, or Ag-Rh alloy with an atomic ratio of Ag:Rh = 2:1. In the production of ultrafine particles of Ag-Rh alloy, $AgRh(C_2O_4)_2$ is dissolved in an aqueous solution containing PVP and $NaBH_4$.

ELECTROCHEMISTRY

Palladium Surface Enriched Electrode

KOBE STEEL LTD. *Japanese Appl.* 7/26,390

Ti (alloy) electrode material comprises a layer enriched by a Pt group element, such as Pd, on its surface and an oxidised layer formed on the Pt group metal enriched layer. The electrode is used in sea water electrolysis and for the production of Cl_2. It has high corrosion resistance and high current efficiency.

Hydrogen Peroxide Production

MITSUBISHI GAS CHEM. CO. INC.

Japanese Appl. 7/33,410

Aqueous H_2O_2 is produced by reacting H_2 and O_2 in the presence of a Pt group metal catalyst, preferably Pd, which is chemically modified with at least one element selected from Pb, Zn, Ga or Bi, in a reaction medium containing a H_2O_2 stabiliser, such as aminotri-(methylphosphonic acid), 1-hydroxyethylidene-1,1-diphosphonic acid, ethylenediaminetetra(methylene phosphonic acid), or pyrophosphoric acid. No halogen ions are required in the reaction medium to promote the reaction of H_2 and O_2.

Ion Water Generation

BROTHER KOGYO K.K. *Japanese Appl.* 7/51,674

An ion H_2O generator is equipped with a pair of specific electrodes for H_2O electrolysis. The electrodes are made of Ti and are coated with a metal film, preferably Pt or Pt-containing alloy, containing a reduced amount of oxide impurities.

Electrode for Electrolysis

PERMELEC ELECTRODE LTD.

Japanese Appls. 7/62,583 and 7/62,585

An electrode assembly has contacting surfaces coated by Pt group metal or their oxides, thin film forming metal or a corrosion resistant conductive layer. The electrode consists of a base material, a coating layer of Pt group metal and at least one of Ti, Ta, Nb, etc., of thickness 10–200 μm. The electrodes can withstand alternating voltage and are assembled on a demountable fixture having little contact resistance, so are stable for long periods.

ELECTRODEPOSITION AND SURFACE COATINGS

Iridium-Coated Products

NIPPON ELECTROPLATING ENGINEERS K.K.

Japanese Appl. 7/34,289

Ir-coated products, for crucibles or electric contacts, comprise a base of W, Mo, Ta or their alloy, coated by an Ir layer. In an example, a W crucible was first coated with Pt which was then coated with Ir in a bath containing 10 g metal/l Na hexabromoiridium(III), 40g/l boric acid and 0.02 mol/l disodium maloate, at pH 5 and 85°C, and at 0.15 A/dm^2. The Ir layer was 8μm thick and was highly adhesive.

Palladium Electroless Plating Solution

KOJIMA KAGAKU YAKUHIN K.K.

Japanese Appl. 7/62,549

A Pd electroless plating solution contains 0.0001–0.5 mol/l of Pd compounds, 0.0005–8 mol/l NH_3 and/or amine compounds, 0.0005–5 mol/l aliphatic mono-, di- and/or polycarboxylic acids. High purity, stable and cracking free Pd plating is obtained with good coating and bonding abilities.

Polyimide-Metal Foil Composite Film

OKUNO PHARM. IND. K.K. *Japanese Appl.* 7/70,762

A Pd layer 3–400Å thick is formed by vapour deposition on one or both sides of an aromatic polyimide film, electroless plated and electroplated, with Cu for example, to yield a polyimide-metal foil composite film. The method is used for printed circuit boards. The polyimide-metal foil has excellent heat resistance, so high temperature treatment is possible.

Spherical Electroless Plating Powder

NIPPON CHEM. IND. CO. LTD.

Japanese Appl. 7/118,866

Spherical core material, such as resin, is coated with a 0.05–0.3μm thick layer of 7–15 wt.% Ni-P alloy. Pd ions are electroless plated on the surface of the core material by dispersing complexing agent in the core material slurry and in a plating bath, followed by ball mill grinding. A well dispersed spherical electroless plating powder, and a conductive material are obtained.

APPARATUS AND TECHNIQUE

Treatment of Acid Water

KURITA WATER IND. LTD. *Japanese Appl.* 7/80,473

The treatment of acid H_2O (1) containing H_2O_2 and surfactant comprises keeping (1) in contact with a Pt catalyst and with activated C. The method particularly treats rinsed drainage released from a semiconductor manufacturing plant. The Pt catalyst is applied to the acid region of pH 3 and almost completely decomposes and removes H_2O_2. The activated C efficiently absorbs and removes the surface active agent. The method is used to prepare ultrapure H_2O from waste H_2O semiconductor rinses.

Oxygen Recovery from Life Support System

DORNIER G.m.b.H. *German Appl.* 4,333,504

O_2 recovery from life support systems uses a low temperature catalyst, especially RuO_x/TiO_2, to convert CO_2 to CH_4 and to electrolyse H_2O. The electrolytic cell may have a KOH electrolyte, one containing H_3PO_4 or solid electrolyte; a proton-exchange membrane; or may be a molten carbonate cell. The recovery occurs at 20–200°C. Gas permeation to concentrate CO_2 uses a liquid membrane, or activated charcoal, adsorption/desorption with solid amine, etc., as adsorbent. The process is especially useful for space travel.

Gas Cleaning Apparatus

FUJITSU LTD. *German Appl.* 4,426,081

Gas cleaning apparatus incorporates rotating catalytic metal blades of Pt, Pd, Ru or Rh metal catalyst, within a housing where the housing wall incorporates a magnet which generates high density plasma. The apparatus treats industrial effluent and vehicle exhaust. Incoming gas impinges on the blades in the O_2-free environment. The combination of catalytic treatment and high density plasma generates synergy between the cleaning processes; and O_2-rich gases are cleaned.

JOINING

Platinum Material for Brazed Ornaments

TANAKA KIKINZOKU KOGYO K.K. *Japanese Appls.* 7/41,885–86

Pt brazing material comprises 0.01–1 wt.% of at least one of Ti, Zr, Hf and rare earth elements, and balance Pt. It may also contain elements, such as Y, Sm, Eu and Er. The materials are used for ornaments having high hardness.

HETEROGENEOUS CATALYSIS

But-2-ene-1,4-diol Production

BASF A.G. *European Appl.* 646,562A

But-2-ene-1,4-diol is produced by selective hydrogenation of but-2-yne-1,4-diol in aqueous solution on a Pd-containing solid-bed catalyst, which is doped with Pb or Cd. The catalyst is obtained by successive vapour-phase deposition or sputtering of Pd, and Pb or Cd, onto a metal wire mesh or metal foil support, then formed in air at high temperature. There is minimal by-product formation.

Preparation of Unsaturated Glycol Diester

MITSUBISHI CHEM. CORP. *European Appl.* 647,611A

Unsaturated glycol diesters are prepared by reacting a conjugated diene with a carboxylic acid and O_2 over a Pd and Te catalyst supported on solid SiO_2, where 80% of the pore volume has a radius of 5–50 nm, relative to the total volume of pores of radius 1.8–10,000 nm. The process can be performed industrially and deactivation rates for > 3900 h of 0.42 can be obtained.

Dehydrogenation of Gas Streams

HALDOR TOPSØE A.S. *European Appl.* 655,431A

H_2 is removed from a HC-dehydrogenation reaction effluent by mixing with an O_2-containing gas and reacting over a catalyst containing a noble metal or its alloy in massive form. In an example, Pd and 70%Pd-Ag alloy catalysts were used as flakes with a size of 16 cm^2/g metal, and 0.5 g of this catalyst was loaded in a quartz tubular reactor. The process gives complete removal of H_2.

Catalyst for Purification of Engine Gases

CATALER IND. CO. LTD. *European Appl.* 657,204A

A catalyst for purification of engine exhaust gases comprises a support of TiO_2-Al_2O_3, ZrO_2-Al_2O_3 or SiO_2-Al_2O_3 carrying a N oxide adsorbent which may be alkali metal(s), alkaline earth metal(s), etc., and a Pt group metal catalyst, selected from Pt, Pd and Rh. The catalyst inhibits poisoning from S oxides, and N oxides can be purified even during engine operation in the fuel-lean mode.

Exhaust Gas Purification Catalyst

TOYOTA JIDOSHA K.K. *European Appl.* 658,370A

A catalyst is produced by loading an N oxide adsorbent on a porous support, carbonating the support with the adsorbent, which is an alkali metal compound, etc., to convert it to carbonate, and loading a Pt, Pd or Rh metal catalyst onto the support. NOx can be effectively purified in exhaust gases that contain O_2 concentrations at stoichiometry, or higher concentrations than needed for oxidising CO and HC.

Catalyst for Exhaust Emission Control

HONDA MOTOR CO. LTD. *World Appl.* 95/9,048A

An exhaust emission control catalyst has θ- and α-phases, and is made of modified Al_2O_3 with an α ratio of 0.5–95% and a catalytic metal, such as Pt, carried on the modified Al_2O_3. In addition, a catalyst with improved NOx cleaning capability is constituted by using the above catalyst as a catalytic element and aluminosilicate or CeO_2.

Three-Way Catalyst

ALLIED-SIGNAL INC. *World Appl.* 95/9,687A

CO, HC and NOx are removed from the exhaust gases of lean burn diesel and other engines, containing O_2 in excess of the stoichiometric amount needed for complete combustion, by contact with a Pt and/or Pd catalyst, preferably Pt, supported on Al_2O_3, CeO_2 and Ba sulphate, SiC, ZrO_2, SiO_2, TiO_2, etc. The catalyst has been treated in an O_2-inert gas mixture, optionally including steam at ≥ 400°C, to give NOx reduction at a predetermined temperature window.

Purification Catalyst for Lean Mixture Exhausts

KEMIRA OY. *World Appl.* 95/10,356A

A catalyst comprises a body with flow through conduits for exhaust gas, a high surface area support of an Al_2O_3 plus La oxide mixture on the surface of the body, with active catalytic Pt and Pd substances on the support. The catalyst purifies exhaust gases from lean mixture engines, particularly diesel engines, containing SO_2. Hydrocarbons and CO in the exhaust gases are converted to CO_2 and H_2O. Light-off temperatures are lower and the catalyst has a long life.

Pentafluoropropane Production

DAIKIN KOGYO K.K. *World Appl.* 95/13,256A

1,1,1,3,3-Pentafluoropropane (1) is prepared in high yield and selectivity by reducing 3-chloro-1,1,1,3,3-pentafluoropropane with H_2 in the vapour phase in the presence of 0.05–10 wt.% of Pd, Pt and/or Rh catalyst, supported on C, Al_2O_3, SiO_2 gel, TiO_2 and/or ZrO_2. The product is a substitute for CFCs and HCFCs for use as a coolant, foaming agent, etc.

Reduction of Nitric Oxide

W. R. GRACE & CO. *World Appl.* 95/15,208A

NO is reduced by organics in the presence of O_2 by passage over a catalyst comprising 0.2–10 wt.% of a Pt group metal catalyst, such as Rh and/or especially Pt, on a stable dealuminated Y zeolite, from which non-framework Al_2O_3 was removed. The zeolite framework has molar ratio SiO_2: Al_2O_3 > 10. The catalyst has improved NO reduction ability and more resistance to any reduction in activity caused by H_2O or SO_2.

Preparation of Hydroxylamine Derivatives

DSM N.V. *World Appl.* 95/16,667A

N-Alkyl-N,O-diacetyl hydroxylamine is prepared in a simple one-step reaction by catalytic reduction of the corresponding nitroalkane, preferably nitromethane, in the presence of acetic anhydride over Pt/Al_2O_3 catalyst. The reduction is carried out at 20–100°C and 1–9 MPa. The acylating agent, acetic anhydride, separates the products.

High Purity Benzene Production

CHEVRON RES. & TECHN. CO. *U.S. Patent* 5,401,365

Benzene is produced in high purity from olefin-containing aromatic feed by distillation to remove high boilers (1), followed by extractive distillation (2). Also claimed is a process for contacting a HC feedstream with a non-acidic Pt/L-type zeolite catalyst. The predistillation step (1) prevents detrimental dimerisation reactions in (2), thus removing the need for hydrogenation before or after (2), or clay after-treatment.

Tertiary Butyl Alcohol Preparation

TEXACO CHEM. INC. *U.S. Patent* 5,401,889

Tertiary butyl alcohol (1) is prepared from a charge stock solution containing 5–30 wt.% tertiary butyl hydroperoxide by continuous contact with a pelleted hydroperoxide decomposition catalyst $Pd\text{-}Au/Al_2O_3$ in liquid phase agitation, at 25–250°C, space velocity of 0.5–2 vol. of charge stock/vol. catalyst/h and 0–1,000 psig pressure. The process gives improved conversion rate and selectivity to (1).

Catalyst for Purification of Exhaust Gases

NISSAN MOTOR CO. LTD. *Japanese Appl.* 7/16,466

A purification catalyst is composed of 0.1–10 g/l Pt or Pd, 1–30 g/l K, Cs, Sr or Ba oxides, 1–50 g/l Co or Mn oxides, Ce oxide and activated Al_2O_3. HC, CO and NOx in exhaust gases are removed efficiently even under O_2-deficient and HC-rich atmospheres.

Purification Catalyst Production

MATSUDA K.K. *Japanese Appl.* 7/16,469

A metal containing silicate and aqueous Rh solution, such as Rh nitrate, is added to a Pt solution, such as a Pt amine, and to an Ir solution, such as $IrCl_3$, to form a slurry which is filtered to become the NOx purification catalyst. A metal containing silicate, supporting highly dispersed Pt, Ir and Rh, is obtained.

Preparation of High Purity Terephthalic Acid

MITSUBISHI KASEI CORP. *Japanese Appl.* 7/17,903

The preparation of high purity terephthalic acid (1) comprises dissolving crude (1), made by a liquid phase oxidation of *p*-xylene in H_2O at 220–320°C, and then contacting with a Pt group metal catalyst, such as Pd/C. This is followed by cooling to crystallise a first crop of (1), and separation from the mother liquor, with further cooling to recover a second crop. The recovery yield is improved by the second crop. About 90–99.5% of (1) is crystallised in high purity.

Diesel Engine Exhaust Purification Catalyst

ICT K.K. *Japanese Appl.* 7/24,260

A catalyst consists of a three dimensional structure coated with a catalyst composite of Pt and/or Pd loaded inorganic oxide powder (1) and another inorganic oxide powder (2). Powder (2) forms 0.25–25 g/l of the structure. Powder (1) is loaded with 5–50 wt.% Pt and/or Pd, and a metal oxide selected from W, Sb, Mo, Ni, B, Mn, Fe, Bi, Co, Zn or alkaline earth metal. The catalyst is used to remove C and S-containing particulates from diesel engine exhaust. The formation of sulphate is suppressed.

Exhaust Gas Purification Catalyst

NE. CHEMCAT K.K. *Japanese Appl.* 7/31,884

Ir and an alkaline earth metal, such as Ca, Sr and Ba, are supported by metal carbide, such as SiC, or a metal nitride, which is moulded or coated on a refractory substrate, and contacted with an exhaust gas containing HC, NOx and excess O_2 to reduce HC and purify it. NOx is removed efficiently in the presence of O_2 and under a high space velocity using the catalyst.

Hydrosilylation Catalyst

DOW CORNING TORAY SILICONE *Japanese Appl.* 7/41,678

A hydrosilylation catalyst with average particle size 0.1–10 μm comprises a Pt catalyst, containing 0.01–5 wt.% Pt metal, and a polycarbonate resin with a glass transition point of 50–200°C. The catalyst is useful as a curing catalyst for organopolysiloxane compositions. It does not show catalytic activity at ordinary temperature, so this composition has good storage stability, and the composition is easily cured by heating, even after a long period of storage.

Removal of Organic Chlorine Compounds

SUMITOMO METAL MINING CO. *Japanese Appl.* 7/47,270

A catalyst carrier, for removing organic chlorine compounds in air, is prepared by dropping an alkali solution into an aqueous solution of 10–20 wt.% of a Zr mineral acid salt to react them, ageing to give Zr hydrate and calcining at 500–600°C. The carrier is impregnated with Pt containing solution to give 0.3–5 wt.% of Pt, followed by further calcining.

Metal Support for Catalysts

TANAKA KIKINZOKU KOGYO K.K. *Japanese Appl.* 7/80,327

A metal support for a catalyst used for high temperature gas purification, such as in gas turbine engines, has a coating of Pt, Pd or Pt-Pd alloy film. The support has good resistance to heating and oxidation at > 1000°C. In an example, plates of stainless steel and Pt were immersed in an electrolytic cell of aqueous chloroplatinate solution to form a Pt layer on the steel. A porous Al_2O_3 layer and a further Pt layer were added.

Hydrocarbon Absorbing Catalyst

NISSAN MOTOR CO. LTD. *Japanese Appl.* 7/124,468

Hydrocarbon absorbent comprises a monolithic carrier, coated with an aqueous slurry containing zeolite, such as mordenite, USY, β-zeolite, etc., and further coated with active CeO_2 and/or Al_2O_3 slurry containing at least one of Pt, Pd and Rh. The zeolite has micropores to assist diffusion of gas to the absorption sites. 51.7% HC was absorbed in 125 s of cold start.

Reactor for Removing Carbon Monoxide

DAIMLER-BENZ A.G. *German Appl.* 4,334,981

A reactor for catalytic removal of CO in H_2-rich gas is coated with a selective CO-oxidation catalyst containing Pt group metal catalysts, such as Pt/Al_2O_3, Ru/Al_2O_3 or Pt/zeolite. The structure of the reactor creates turbulent flow and heat transport. The reactor can be used in conjunction with a fuel cell and prevents steep temperature gradients.

Exhaust Gas Purification Catalyst

MAZDA MOTOR CORP. *German Appl.* 4,435,074

A catalyst component for exhaust gas purification comprises a mixture of a metallosilicate having at least one active Pt group metal, such as tetra valent Pt and Ir, mixed with Al_2O_3 and/or CeO_2. Also claimed is the production of a honeycomb catalyst comprising the component, which is wash-coated or aged, or vice versa. The addition of Al_2O_3 and/or CeO_2, and the use of Pt and/or Ir in the +4 oxidation state shifts the peak temperature of NOx reduction to higher values.

A Palladium Catalyst

AS. SIBE. CATALYSIS INST. *Russian Patent* 1,420,714

A catalyst for the production of dimethylvinylcarbinol is prepared by dissolving Pd chloride in a boiling Na molybdate solution in molar ratio Mo:Pd of 1–1.5:1, before reducing with H_2 to form Pd metal, and mixing with an inorganic carrier. The catalyst gives improved activity and productivity without significant reduction in selectivity.

A Noble Metal Catalyst

KUNMING INST. NOBLE METALS CHINESE NON. *Chinese Appl.* 1,087,031

A Pt group metal catalyst for purifying waste gas from I.C.E. contains one of Pt, Pd, Rh or Ru (0.06–0.3 wt.%) as the active component. The carrier is in the form of a ball or honeycomb made of China clay and industrial Al oxide. A quick dipping method is used to add the active component to the carrier. The catalyst gives high purification and a long service life.

HOMOGENEOUS CATALYSIS

Preparation of *N*-Vinyl Compounds

BASF A.G. *European Appl.* 646,571A

The preparation of an *N*-vinyl compound from NH compounds uses acetylene at 50–250°C and 1–30 bar in the presence of a Pt group metal compound catalyst, such as $PdCl_2$, $OsCl_3$, $Ru(acac)_3$, $RuCl_3$, etc. The process gives an improved space-time yield and better control of the conversion of the acetylene. The *N*-vinyl compounds can be used as monomers, giving polymers for clarifying liquids, detergents, etc.

Hydroxy-Carbonylation of Butadiene

RHONE POULENC CHIM. *European Appl.* 648,731A

The hydroxy-carbonylation of butadiene and/or derivatives was produced by reaction with CO and H_2O in the presence of a Pd catalyst, such as $PdCl_2$, Pd acetate, etc., which is soluble in the reaction medium. The reaction is performed in the presence of crotyl chloride (≥ 2 mole/mole of Pd) as the promoter.

Production of Higher Vinyl Esters

UNION CARBIDE CHEM. & PLAST. TECHNOL. *European Appl.* 648,734A

Homogeneous liquid phase vinyl carboxylates are produced by reacting ethylene and carboxylic acid, preferably butyric, crotonic, benzoic, etc., using a Pd(II) catalyst formed in situ, Cu oxidant and Li promoter. Higher yields, ~ 69%, of vinyl esters are obtained.

Low Temperature Carbonylation

IMPERIAL CHEM. IND. P.L.C. *World Appl.* 95/15,938A

Low temperature carbonylation of acetylenically unsaturated compounds with CO in the presence of an allenically unsaturated compound, uses a catalyst system formed from a Pd compound, such as Pd acetate, etc., a protonic acid and an organic phosphine. The catalyst tolerates allenically unsaturated compounds and carbonylates them, e.g. butyne, pentyne, cyclohexylethyne from feedstocks obtained from cracking oil fractions.

Stereoselective Synthesis of Carbohydrates

SCRIPPS RES. INST. *World Appl.* 95/16,049

Carbohydrate is prepared by stereoselectively converting an alkene to an aldol intermediate by an Os-catalysed asymmetric dihydroxylation reaction, then stereoselectively elongating the aldol intermediate with a nucleophilic donor using an aldolase-catalysed aldol addition reaction. A rapid synthesis of ketose sugars is achieved by a minimal numbers of steps.

Method for Producing Allylic Alcohols

UNIV. IOWA STATE RES. FOUND. INC. *U.S. Patent* 5,401,888

Preparation of allylic alcohols in good yields comprises a Pd catalysed cross-coupling of vinylic epoxides and aryl halide, vinylic halide or vinylic triflates. Pd (II) catalysts, such as $PdCl_2$, $Pd(OAc)_2$, $PdBr_2$, $Pd(CN)_2$, etc., are used. The Pd(0) catalyst is $Pd(dba)_2$ or $Pd(PPh_3)_4$. The organic base is a 6–20C trialkylamine or dicycloalkyl(alkyl)amine. The reaction is performed at 60–120°C for 5–50h.

Hydrodehalogenation of Halogenated Benzenes

BAYER A.G. *German Appl.* 4,334,792

Hydrodehalogenation of halogenated benzenes comprises reacting with H_2 at 100–250°C in the presence of a catalyst prepared by depositing Pd and/or Pt salts, and optionally Cu salts, on an Al_2O_3 or TiO_2 support. The process produces useful lower halo-benzenes, such as *o*-dichlorobenzene, monochlorobenzene and/or benzene, from higher chlorobenzenes and *p*-dichlorobenzene. Good yields and selectivity, without forming cyclohexane derivatives, are achieved.

FUEL CELLS

Fuel Battery Electric System

NGK INSULATORS LTD. *Japanese Appl.* 7/57,758

A fuel battery power generation system incorporates a gas isolated membrane made up of Pd alloy, containing dissolved H_2 gas, which covers the support body. The fuel gas is refined using the H_2 gas isolator.The support body carries a negative electrode. The system increases the density of the fuel gas. It has improved electric power efficiency and removes CO_2 which poisons the electrode.

CHEMICAL TECHNOLOGY

Hexahydroxoplatinic Acid Preparation

TANAKA KIKINZOKU KOGYO K.K. *Japanese Appl.* 7/97,221

Preparation of $H_2Pt(OH)_6$ comprises neutralising Na hexahydroxoplatinate by ion exchange through contact with an inorganic acid via a cation exchange membrane.The $H_2Pt(OH)_6$ obtained can be used as a raw material for catalysts and as an intermediate for Pt compounds. The waste liquor contains no organic compounds, and can be treated easily at low costs.

ELECTRICAL AND ELECTRONIC ENGINEERING

A Hard Disc Recording Medium

HEWLETT-PACKARD CO. *European Appl.* 651,380A

A hard disc with textured surface having reduced static and dynamic friction is formed by applying a Ni-Pt layer on a metal substrate, than polishing to surface roughness of < 2 nm RMS, then sputtering on a metal layer having RMS surface roughness 1.0–8.0 nm. Low flying height between the recording head and the spinning recording media is obtained.

Structure for Mounting Electronic Parts

KYOCERA CORP. *Japanese Appl.* 7/40,569

Electronic parts are mounted on a ceramic baseplate by soldering the electrodes of the electronic parts onto the wiring layer on the ceramic baseplate. The wiring layer comprises a lower layer of Pd and an upper layer of Ni or Cu. The Pd metallic layer is laminated. The connection is reliable against thermal changes and parts can be mounted to a high density.

Overwritable Recording Medium

TOSOH CORP. *Japanese Appl.* 7/44,915

A photomagnetic recording medium for high density recording or overwriting comprises a substrate, recording film of artificial lattice film made of laminations of a layer comprised of at least one element selected from Fe, Co or Ni and a layer based on Pt and/or Pd, and at least one layer of a rare earth transition metal alloy layer (1). The artificial lattice film is reverse sputtered, and (1) is formed on it.

Multilayer Interconnection Board

IBIDEN CO. LTD. *Japanese Appl.* 7/106,758

An additive process for manufacturing multilayer interconnection board maintains the density of Pd ions in the liquid that is used during the Pd catalyst nucleus activation process at ≤ 1.2 ppm. An insulated adhesive layer is formed on a substrate; followed by a conductive layer, and then through hole formation.

Bump Electrode Formation Method

TANAKA DENSHI KOGYO K.K. *Japanese Appl.* 7/122,563

The method uses Pd wire, ≥ 99.9% pure, which is elongated by 2–6%. The wire is shaped as a thin line and is inserted into a capillary tube. A ball is produced under Ar, and adheres to the top surface of an Al wiring of a semiconductor chip. If the capillary is removed, the wire gets disconnected at a predetermined location, and a bump electrode is formed.

MEDICAL USES

Dental Alloy

JENERIC/PENTRON INC. *U.S. Patent* 5,423,680

The dental alloy, free of Pd, Ga and Cu, comprises (by wt. %): (a) 40–80 Au; (b) 5–50 thermal-expansion adjuster, selected from Pt, Ag, Nb and Ta; (c) 2–10 strengthener and oxide-former; (d) ≤ 1.5 grain refiner selected from Ir, Ru, Rh, Re and Co; and (e) 0.25 deoxidiser. The alloy is compatible with high-TCE dental porcelains and composites.

Yellow Dental Alloy

HERAEUS KULZER G.m.b.H. *German Appl.* 4,429,728

A yellow dental alloy contains mainly Au plus Pt group metals and base metals, and has the following composition (in wt.%): 80–95 Au, 5–20 Pt, 0.01–0.3 Rh, 0–0.1 Ir, 0.5–2.5 Zn and 0.01–0.5 Mn. The alloy is used to manufacture multi-section bridgework.

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

AUTHOR INDEX TO VOLUME 39

	Page
Abbot, D.	183
Abrams, M. J.	14
Abys, J. A.	138
Achiba, Y.	81
Adachi, H.	32
Adams, J. B.	37
Agbossou, F.	87
Ahmed, Z.	43
Aika, K.-I.	139
Aitani, A. M.	27
Aleandri, L. E.	180
Ali, M. M.	185
Alonso-Vante, N.	39
Alper, H.	86, 140
Al-Shareef, H. N.	64
Amado, M. M.	38
Amano, M.	87
Amezawa, K.	83
An, L. D.	139
Anpo, M.	84
Antonelli, E.	140
Antonova, T. N.	183
Antos, G. J.	27
Aoki, K.	185
Arata, K.	85, 138
Arblaster, J. W.	164
Arenshtam, A.	137
Arimitsu, S.	87
Armor, J. N.	133
Aronovich, R. A.	185
Asayama, E.	81
Ashokkumar, M.	40
Ashton, S. V.	13, 32, 132, 159
Auciello, O.	64
Auffermann, G.	39
Aye, K. T.	136
Aymerich, X.	182
Baak, M.	136
Baiker, A.	138, 183
Baker, M. J.	87
Balzani, V.	136
Bamwenda, G. R.	184
Barbi, G. B.	181
Barbier, J.	85
Bardin, M.	84
Barnard, C. F. J.	63
Barniol, N.	182
Barton, J. K.	84
Bashilov, V. V.	38
Battle, P. D.	38
Bat'ko, I.	88
Becker, E. R.	171
Bednorz, J. G.	32
Beller, M.	183
Bellina, F.	139
Bellur, K. R.	64
Belser, P.	136
Belyaev, V. D.	88
Belykh, L. B.	79
Bennett, S.	87
Bensalem, A.	184
Ben-Jacob, E.	137
Bergamini, F.	140
Bertani, R.	134
Bertin, V.	85
Bertolini, J. C.	42
Bertrams, T.	183
Besson, M.	159
Bhanaga, B. M.	62
Bilitewski, U.	41
Blake, A. J.	82
Block, J. H.	80
Boelrijk, A. E. M.	44
Bönnemann, H.	42, 180
Boonekamp, E. P.	80
Bosch, P.	85
Boukamp, B. A.	133
Bourdelande, J. L.	83
Bourret, E. D.	180
Bouwmeester, H. J. M.	133
Bozon-Verduraz, F.	184
Bradley, J.	41
Braga, M. E.	38
Brinkmann, R.	42
Bronger, W.	39
Brook, R. J.	134
Brookes, H. C.	107
Brown, J. M.	62
Brown, S. M.	87
Bruce, R.	45
Bruk, L. G.	139
Buckley, T.	39
Buffle, J.	132
Buisman, G. J. H.	140
Burch, R.	84, 138
Burgers, M. H. W.	183
Burggraaf, A. J.	133
Burgstaller, A.	38
Bustin, D.	137
Cabrera, A. L.	80, 133
Cabrera, C. R.	82
Cacucci, A.	84
Cade, N. A.	141
Cai, H.	42
Candela, G. A.	137
Cant, N. W.	183
Cao, G. Z.	133
Carley, A. F.	41
Carpita, A.	139
Carvill, B. T.	41
Casella, I. G.	182
Castaño, A.	41
Castillón, S.	87
Cavinato, G.	86
Cazorla-Amorós, D.	84
Cerveny, L.	184
Chabutkina, E. M.	183
Chan, T. H.	88
Chatani, N.	141
Chaudhari, R. V.	62
Chen, C. S.	133
Chen, C.-H.	39
Chen, J. F.	80
Chen, L.	41
Chen, L. J.	80
Chen, Q.	41, 137
Chen, Z.	136, 184
Chernov, S. F.	41
Chevalier, B.	38
Chikahisa, T.	85
Cho, C. S.	184
Cho, J.-J.	82
Choy, J. H.	134
Chu, V.	86
Claver, C.	87
Coia, G. M.	135
Colell, H.	39
Conole, G.	87
Coote, S. J.	86
Cottington, I. E.	67, 78
Coupland, D. R.	98
Couzens, G.	112
Cowley, A. J.	116
Crangle, J.	37
Creyghton, E. J.	183
Crozet, M.	136
Csöregi, E.	137
Cummings, S. D.	181
Da Silva, M. de F. C. G.	134
Das, M. L.	40
Date, M.	37
Davidson, J. L.	41
Davies, S. G.	62
Davis, M. E.	62
Dawson, G. J.	86
De Boer, F. R.	38
De Cian, A.	181
De Cola, L.	136
De Peuter, G.	42
Deganello, G.	139
Del Angel, G.	85
Delarue, E.	133
Delcourt, M. O.	133
Delmas, H.	62
Demazeau, G.	134, 135
Deng, B.	185
Deng, F.	139
Deshpande, R. M.	62
Desu, S. B.	45, 141
Di Monte, R.	85
Diesner, K.	39
Dimitrov, D. A.	129
Do, Y.	134
Dobreva, E. D.	137
Doherty, A. M.	85
Doherty, A. P.	39
Dong, S.	81, 181
Donò, A.	135
Douglas, P.	183
Doyle, M. P.	44
Dube, S.	83
Duca, D.	139
Dümpelmann, R.	183
Duff, R. R.	140
Duncan, P. N.	112
Durussel, P.	37
Dux, R.	136
Duxstad, K. J.	180
D'Agostino, R.	84
Ebert, H.	38
Echigoya, J.	83
Efremenko, I. G.	42
Eisenberg, R.	181
Elefant, D.	38
El-Shafei, A. A.	181
Enoki, H.	83
Espeel, P. H.	42
Essalik, A.	44
Esteruelas, M. A.	140
Étourneau, J.	38
Evens, J. M.	98
Eyert, V.	134
Ezhova, N. N.	185
Fabrizio, M.	181
Fendler, J. H.	180
Feng, Q.	135
Feschotte, P.	37
Fiechter, S.	39
Fierro, J. L. G.	84
Fischer, J.	181
Flachbart, K.	88
Flanagan, T. B.	133
Fokkink, L. G. J.	80
Font, J.	83
Fornasiero, P.	85
Fowler, J. B.	72
Fox, M. A.	42
Fracassi, F.	84
Freund, H.-J.	183
Fricker, S. P.	150, 179
Frost, J. C.	126, 171
Fu, H. G.	88
Fujita, T.	32
Fukuda, M.	83
Fukushima, K.	87
Fukuyo, E.	184
Funatsu, K.	135
Gallezot, P.	159
Gal'vita, V. V.	88
Gam, K. S.	45
Gandhi, H. S.	84, 85
Gao, C.	37
Gao, Y.	40
Garcia, R.	159
Garnett, J. L.	140
Gasteiger, H. A.	82
Gas'kov, A. M.	37
Gautheron, B.	37
Gehlen, M.	39
Ghosh, K.	81
Giger, T.	138
Giles, M. F.	87
Giordano, G.	44

	Page
Gladii, S. L.	43
Gladun, C.	38
Gleiter, H.	80
Golberg, D.	126
Gomez, R.	85
Gontazh, R.	88
Gonzalez, R. D.	138
González-Marcos, M. P.	41
González-Velasco, J. R.	41
Gorelov, V. P.	88
Gori, R.	139
Goto, S.	139
Gotoh, K.	43
Gould, R. D.	45
Grandberg, K. I.	39
Grandjean, B. P. A.	45
Graziani, M.	85
Griffiths, S. P.	41
Grigoryan, E. A.	40
Grimmeiss, H. G.	134
Grivas, S.	140
Grötzschel, R.	38
Gruzdkov, Y. A.	40
Gudavičiūtė, L.	68
Guerrero-Ruiz, A.	84
Guez, D.	82
Guo, J.	85
Gurbuz, Y.	41
Gurunathan, K.	83
Gutiérrez-Ortiz, J. I.	41
Gutiérrez-Ortiz, M. A.	41
Haapakka, K.	182
Hagen, W. R.	45
Hahn, P.	139
Hakanen, A.	182
Haller, E. E.	180
Hanaoka, T.	43
Hao, L.	180
Hapiot, F.	87
Hara, K.	135
Hards, G. A.	9, 160
Hartley, J. P.	98
Harvey, P. D.	136
Hasen, J.	80
Hashimoto, H.	32
Hassan, A. K.	45
Havela, L.	38
Hawker, P. N.	2
Hayashi, T.	184
Haynes, A.	134
He, C.	18
Heinrich, A.	38
Heinz, T.	138, 183
Heller, A.	137
Henrion, W.	38, 39
Hetrick, R. E.	40
Hibino, T.	137
Hidai, M.	139, 184
Hightower, T. R.	139
Hino, M.	85, 138
Hintermann, L.	185
Hirai, T.	83
Hodgson, D. R.	137
Hoffman, M. Z.	40
Holmlin, R. E.	84
Holtz, R. L.	137
Hong, C.	182
Hongo, S.	141
Horikawa, H.	126
Hosseini, M. W.	181
Hsu, C.-M.	138
Huang, T. S.	88
Huang, T.-C.	183
Hubbard, C. P.	84
Hughes, H. P.	182
Hutchison, J. E.	39
Ibata, T.	87
Ibbotson, A.	41
Ichikawa, M.	139
Igarashi, M.	83
Iglesia, E.	43
Iizuka, N.	141
Ikemoto, I.	81
Ikonen, M.	82
Imamura, H.	81
Imamura, T.	135
Inaguma, Y.	180
Indolese, A. F.	87
Inoue, T.	85
Irie, Y.	185
Ishida, S.	37
Ishii, Y.	139, 184
Ishikawa, M.	133
Ito, M.	82
Ito, S.	83
Ito, Y.	83, 140
Itoh, K.	185
Itoh, M.	180
Itoh, Y.	185
Ivanov, E.	38
Ivey, D. G.	45
Iwamoto, M.	85
Iwasawa, Y.	85
Iyoda, M.	81
Izumi, Y.	139
Jacobs, P. A.	42
Jacquet, L.	136
Jansen, J. C.	183
Jayaraman, V.	136
Jia, Shichong,	167
Jian, P.	45
Jiang, X.	82
Jimenez, J. R.	182
Jin, Z.	136
Johnson, B. F. G.	82
Johnson, D. R.	85
Johnston, P.	41
Jones, D. J.	180
Jung, D.-Y.	135
Juzikis, P.	40, 68
Kadija, I. V.	138
Kaes, C.	181
Kaga, H.	43
Kakiuchi, F.	141
Kaliaguine, S.	45
Kamatani, A.	141
Kamegaya, Y.	135
Kamer, P. C. J.	86, 140
Kameyama, K.	39
Kandasamy, K.	133
Kang, B.-C.	183
Kang, K. H.	45
Kang, W. P.	41
Kanoh, H.	135
Kanteeva, N. I.	180
Karasik, A. A.	43
Karsanov, I. V.	79
Kašpar, J.	85
Kato, H.	45
Kato, K.	141
Kawataka, F.	134
Kawawake, Y.	185
Keeling, A. G.	45
Keene, F. R.	181
Kelly, D. M.	39
Kelly, J. J.	80
Kelly, J. M.	136
Keppler, B. K.	45
Kerns, D. V.	41
Kessler, M.	87
Khairullina, R. Z.	43
Khannanov, N. K.	40
Kharitonov, V. G.	43
Khil Shin, H.	85
Kibel, M. H.	45
Kido, H.	135
Kikuchi, K.	81
Kim, G.-H.	133
Kim, H.-J.	134
Kim, S. H.	38
Kim, Y.-G.	45
Kimura, A.	135
Kimura, M.	184
Kincaid, J. R.	136
King, D. A.	182
King, R. A.	141
Kingon, A. I.	64
Kirsch-de Mesmaeker, A.	136
Kitagawa, J.	133
Kitakami, O.	141
Kitani, A.	83
Kitayama, K.	184
Kittel, M. U.	40
Klootwijk, A.	140
Kluson, P.	184
Knecht, A.	134
Knight, G.	45
Kobayashi, H.	83, 135
Kobayashi, T.	138
Kokkinidis, G.	82
Kolyadko, E. A.	39
Komatsubara, T.	37
Konno, M.	85
Kornberg, B. E.	85
Korneeva, G. A.	185
Korovina, S. P.	183
Koshel', G. N.	183
Kotov, N. A.	180
Kozitsyna, N. Yu.	180
Kramer, H.	85
Kraus, G. A.	139
Krausz, E.	40
Krishnan, R.	185
Królas, K.	81
Kruidhof, H.	133
Kubasheva, A. Zh.	42
Kudo, A.	40, 135
Kudrak, E. J.	138
Kudryavtsev, Yu. V.	88
Kübler, J.	134
Kühlein, K.	183
Kulmala, A.	182
Kulmala, S.	182
Kumada, T.	37
Kumobayashi, H.	87
Kunitskii, A. A.	183
Kunkely, H.	182
Kuriyama, Y.	141
Kurkin, V. I.	185
Kurochkin, I. N.	41
Kuwano, H.	185
Kuwano, R.	140
Kuz'mina, L. G.	39
Labeau, M.	37
Laine, R. M.	86
Landsman, D. A.	165
Lange, H.	38
Langer, S. H.	135
Larock, R. C.	139
Lastovyak, Ya. V.	43
LeCorre-Frisch, A.	134
Lee, C. W.	140
Lee, J.	135
Lee, J.-H.	134
Lee, P.-Y.	138
Lee, S.-J.	88
Lee, S.-M.	133
Leech, P. W.	45
Lees, A. J.	136
Lerner, B. A.	41
Levintova, T. D.	184
Levy, M.	85
Lewis, F. A.	29, 75, 127, 133
Li, F.	181
Li, G.-F.	18
Li, H.	138, 182
Li, Q.	136
Li, T. K.	141
Lichtenberg, F.	32
Lihn, C. J.	80
Lin, H.-M.	138
Lin, L.	42
Lin, P.	184
Lin, R. Y.	136
Lin, X. W.	180
Lin, Y. S.	136
Linares-Solano, A.	84
Lindström, S.	140
Liotta, L. F.	139
Lipponer, K.-G.	45
Lirkov, A. L.	137
Listovnichiy, V. Ye.	174
Liu, A.-M.	139

	Page
Liu, C.-L.	37
Liu, G.-B.	86
Liu, J.	41
Liu, W.	37, 81
Liu, Y.	81
Loader, P. K.	84, 138
Loboda-Cackovic, J.	80
Loginova, I. V.	79
Loheac, P.	84
Long, M. A.	140
Lopez-Agudo, A.	84
Lorkovic, I. M.	140
Lu, F.	41
Lu, S.	39
Lukey, C. A.	140
Mackenzie, R. A. D.	141
Macková, S.	133
Madon, R. J.	43
Maeno, Y.	32
Maggini, M.	135
Maier, J.	134
Maisano, J. J.	138
Maitlis, P. M.	134
Makhlouf, S. A.	38
Makhmotov, E. S.	43
Malashkevich, A. V.	139
Malik, S. K.	81
Mallat, T.	138, 183
Mamedyarova, I. A.	39
Manduchi, C.	181
Manivannan, A.	82
Manninger, I.	183
Marécot, P.	85
Marković, N. M.	82
Markovitsi, D.	82
Marqués, G.	83
Martin, M. E.	140
Martinez, J.	141
Maruszewski, K.	136
Maruthamuthu, P.	83
Marvaud, V.	82
Masdeu, A. M.	87
Masó, J.	182
Massara, R.	37
Massardier, J.	42
Mataka, S.	86
Matar, S. F.	134
Matsubara, T.	44
Matsuda, I.	140
Matsumoto, H.	185
Matsumoto, M.	87
Matsumoto, Y.	40
Matsushima, T.	37
Matsuyama, H.	81
Matsuzaki, T.	43
Matulionis, E.	68
McCabe, R. W.	85
McGrath, R. B.	98
McIntyre, B. J.	13
McMurray, H. N.	183
McNicholl, R.-A.	133
Mednikov, E. G.	180
Meheux, P. A.	41
Meldrum, F. C.	180
Menchikova, G. N.	40
Mengoli, G.	181
Menon, L.	81
Meriani, S.	85
Mešároš, Š.	137
Meyer, T. J.	135
Michelin, R. A.	134
Miegge, P.	42
Mikul'shina, V. V.	43
Milli, E.	181
Mills, A.	44
Minder, B.	183
Minowa, T.	83
Misumi, Y.	139
Mitamura, T.	135
Miyai, Y.	135
Miyake, T.	87
Mizobe, Y.	184
Mizukami, T.	44
Mizuno, F.	83
Mizuno, K.	184
Moiseev, A. I.	79
Moiseev, I. I.	43, 180
Monteil, F.	140
Morales, E.	133
Morales-Leal, E.	80
Morgulis, M. A.	185
Morii, Y.	180
Morinaga, K.	81
Morneau, A.	82
Morris, G. E.	134
Morris, R. H.	135
Morrissey, R. J.	182
Mortreux, A.	87
Moss, J. R.	33
Mostafavi, M.	133
Mousa, M. S.	80
Mozzon, M.	134
Müller, T. J. J.	87, 141
Mumtaz, K.	83
Murai, S.	141
Murakami, Y.	39, 82
Murakami, Y.	126
Murase, K.	37
Murata, T.	184
Murayama, T.	85
Murray, R. W.	39
Musakova, E. Yu.	43
Mutoh, H.	87
Naidoo, M. N.	137
Nakabayashi, M.	82, 136
Nakagomi, S.	88
Nakamura, T.	44
Nakane, H.	32
Nakato, Y.	83
Nakotte, H.	38
Nara, K.	45
Natarajan, M. P.	83
Neddermeyer, H.	183
Neely, D.	80
Nefedova, M. N.	39
Neiteler, P.	42
Neumann, K.-U.	37
Ng, K. Y. S.	84
Ni Dhubhghaill, O. M.	45
Nicoloso, N.	134
Nikam, S. S.	85
Ning, Y.	19
Nishimura, J.	83
Nishiyama, H.	185
Nishizaki, S.	32
Nohira, T.	83
Noskov, Yu. G.	86
Novikov, Yu. N.	82
Nývlt, M.	185
Obara, M.	141
Ober, K.	85
Obuchi, A.	184
Oda, K.	37
Ogata, A.	184
Ogawa, Y.	81
Ohara, T. J.	54
Ohkawauchi, H.	82
Ohshima, K.-I.	133
Ohta, T.	87
Oi, J.	184
Okada, Y.	83
Okaji, M.	45
Okino, F.	134
Oliván, M.	140
Ollivier, J.	86
Onoue, S.	39
Ooi, K.	135
Orejón, A.	87
Orij, E. N.	86
Orito, K.	43
Oro, L. A.	140
Orpen, A. G.	87
Oshima, R.	180
Oto, K.	37
Otsuka, K.	126
Otto, K.	84
Ovchinnikov, A. N.	41
Paál, Z.	183
Pässler, R.	134
Pakala, M.	136
Pakkanen, T. A.	39
Pakkanen, T. T.	39
Pan, W.	45
Panella, F.	140
Papenmeier, D. M.	84
Papkovsky, D. B.	41
Papoutsis, A.	82
Parera, J. M.	27
Park, J. T.	82
Park, S. B.	88
Parsons, S.	82
Parthasarathy, N.	132
Pasichnyk, P. I.	43
Pawlowski, V.	182
Pazderskii, Yu. A.	43
Pearson, J. M.	134
Pedrero, M.	137
Pellegrini, P. W.	182
Pentin, A. Yu.	79
Pereira, C. J.	171
Pérez-Murano, F.	182
Perkas, N. V.	184
Perng, T. P.	80
Perrichon, V.	184
Perry, R. J.	43
Perutz, R. N.	111
Pesin, O. Yu.	185
Petit, M.	84
Petrov, E. S.	86
Petrovskii, P. V.	38
Pettersson, H.	134
Petyukh, V. M.	174
Pfaltz, A.	138, 183
Pindeva, L. I.	137
Pinto, R. P.	38
Pitschke, W.	38
Plichon, V.	84
Podlovchenko, B. I.	39
Pombeiro, A. J. L.	134
Ponomarev, G. V.	41
Poon, S. J.	38
Postlethwaite, T. A.	39
Potgieter, J. H.	107
Potter, R. J.	173
Poulios, I.	82
Power, D. C.	117
Prato, M.	135
Pratt, A. S.	32
Prokes, K.	38
Prosser, V.	185
Provenzano, V.	137
Prunier, M. L.	65
Puddephatt, R. J.	180
Purwanto, A.	38
Purwoko, A. A.	136
Qian, Y.	184
Qin, Z.-C.	81
Qiu, J.-Q.	139
Quagliotto, M. G.	181
Raerinne, P.	182
Rajendran, S.	88
Rajumon, M. K.	41
Ralph, T. R.	9
Ramakrishnan, S.	81
Ranga Rao, G.	85
Rao, N. N.	83
Rar, A.	37
Rasinkangas, M.	39
Raub, Ch. J.	40
Rebizant, J.	38
Reedijk, J.	44
Reeves, G. K.	45
Regnault, D.	133
Richard, N.	84
Richardson, J. N.	39
Richter, J.	180
Riesen, H.	40
Rievaj, M.	137
Roberts, M. W.	41
Robinson, R. A.	38
Rodriguez-Ramos, I.	84
Román-Martínez, M. C.	84
Ronchin, L.	86
Roobeek, K. F.	134
Ross, P. N.	82
Rossi, R.	139
Rossin, J. A.	84

	Page
Rotondo, E.	44
Rousset, J. L.	42
Rowling, S.	87
Rozenberg, V. I.	43
Rozière, J.	180
Ruckenstein, E.	138
Ruiz, A.	87
Ruppert, R.	181
Rusetskaya, N. Yu.	174
Russell, M. J. H.	65, 172
Rutherford, T. J.	181
Ryan, M. E.	128
Sachtler, W. M. H.	41, 183
Sadler, P. J.	45
Saha, D. K.	133
Saito, N.	40
Saito, Y.	44
Sakakima, H.	185
Sakata, T.	40, 135
Sakauchi, J.	138
Salanov, A. N.	81
Salaün, J.	86
Salinas-Martínez de Lecea, C.	84
Salmeron, M.	13
Salvatierra, D.	83
Sanchez, J. P.	134
Santi, R.	140
Sasahara, A.	42
Sasaki, K.	83
Sasaki, Y.	135
Sato, N.	37
Satomi, M.	185
Satyanarayana, N.	86
Savadogo, O.	44
Savchenko, V. I.	81
Sawabe, K.	40
Sawamura, M.	140
Scaros, M. G.	65
Schamp, A. L.	40
Schieck, R.	39
Schlaf, M.	135
Schmalz, K.	134
Schmid, R. D.	41
Schmidtke, D. W.	137
Schnyder, A.	185
Schötz, E.	141
Schuller, I. K.	80
Schumann, J.	38
Scorrano, G.	135
Searles, R. A.	112
Sechovský, V.	38
Seddat, M.	185
Seido, N.	87
Sekine, S.	141
Sellinger, A.	86
Semenova, E. L.	174
Senateur, J. P.	37
Sepulveda-Escribano, A.	84
Seraglia, R.	134
Seret, A.	38
Sergeeva, E. V.	43
Shanklin, M. S.	44
Shapovalova, L. B.	43
Shen, J. Y.	43
Shephard, D. S.	82
Shido, T.	139
Shimada, S.	138
Shimada, Y.	141
Shimizu, I.	134
Shimizu, Y.	83
Shimura, T.	180
Shindo, Y.	83
Shiono, T.	87
Shirai, J.	140
Shong, W.	167
Shu, C.	185
Shu, J.	45
Siegel, R. W.	37
Simons, K. E.	41, 138
Sinn, E.	87
Slivinskii, E. V.	185
Slutzky, M.	137
Smetana, Z.	185
Smirniotis, P. G.	138
Smith, G. D. W.	141
Smith, J. G.	37
Smyslova, E. I.	39
Sobyanin, V. A.	88
Sokolov, A. L.	183
Sokolov, V. I.	38, 39
Solovetskii, Yu. I.	185
Somora, M.	88
Somorjai, G. A.	13
Song, H.	82
Sonoda, M.	141
Sousa, J. B.	38
Spirlet, J. C.	38
Spivak, G. J.	180
Starchevskii, M. K.	43
Sternik, M.	81
Stonehart, P.	44
Stuhr, U.	80
Sturm, J. C.	182
Su, H.	141
Sugawara, Y.	185
Sugg, B.	81
Sugi, Y.	43
Sugiyama, K.	37
Sugiyama, T.	141
Suh, I.-H.	134
Sumiyama, K.	38
Sun, H.	40
Sunley, G. J.	134
Sutherland, I. M.	41
Suzuki, K.	38
Svoboda, P.	38
Swain, M.	80
Sweetman, M. J.	42
Sykes, A. G.	179
Tago, T.	83
Takahara, N.	180
Takahashi, M.	180
Takahashi, N.	138
Takano, N.	82, 136
Takaoka, S.	37
Takasu, Y.	39, 82
Takaya, H.	87
Takebe, H.	81
Takeda, N.	133
Takeno, N.	82, 136
Takeuchi, K.	43
Taki, M.	83
Tamaru, Y.	139, 184
Tamura, H.	42
Tanaka, A.	139
Tanaka, K.-I.	42
Tanaka, S.	139, 184
Tanaka, Y.	141
Tao, W.	141
Tardy, B.	42
Tashiro, M.	86
Taylor, M. J.	87
Temkin, O. N.	139
Teraoka, T.	32
Tercier, M.-L.	132
Tessier, M.	185
Thompsett, D.	165
Thompson, D. T.	27, 62, 108, 172
Thompson, M.	141
Thomson, J.	42
Tielen, M. C.	42
Togni, A.	185
Toktabaeva, N. F.	42
Tokura, H.	80
Tolosa, J. I.	140
Tomčík, P.	137
Tomishige, K.	85
Tong, X. Q.	133
Toniolo, L.	86
Torii, S.	181
Traldi, P.	134
Trandafilov, A. T.	137
Treptow, B.	87
Tributsch, H.	39
Trimm, D. L.	183
Trivedi, D. C.	88
Trost, B. M.	87, 141
Trovarelli, A.	85
Trzeciak, A. M.	44
Tsurumi, K.	44
Tumanskii, B. L.	38
Tung, C.-Y.	138
Turner, A. P. F.	41
Tvarožek, V.	137
Udovic, T. J.	80
Ueki, T.	126
Uemura, S.	184
Ueno, H.	81
Uozumi, Y.	184
Usatov, A. V.	82
Usmen, R. K.	85
Uttich, T.	183
Van Bekkum, H.	183
Van Leeuwen, P. W. N. M.	86, 134, 140
Van Rooy, A.	86
Vanicky, D.	88
Vargaftik, M. N.	43
Vermaak, C. F.	116
Vijay, D. P.	45
Villegas, I.	82
Vincent, H.	81
Viney, C.	86
Vinogradova, L. E.	82
Višňovský, Š.	185
Vittal, J. J.	180
Vogler, A.	182
Voitländer, J.	38
Volkening, F. A.	137
Volkov, P.	38
Vorontsov, E. V.	43, 82
Vorontsova, N. V.	43
Vos, E. J.	140
Vos, J. G.	39, 182
Wakabayashi, T.	184
Wakoh, K.	38
Walker, J. M.	180
Wan, C. C.	80
Wan, K. T.	62
Wang, B.	37
Wang, C.	182
Wang, G.	138, 183
Wang, H.-L.	139
Wang, J.	41, 137
Wang, L.	42
Wang, P.-W.	42
Wang, W.	18
Wang, W.-K.	81
Warshawsky, A.	85
Wartnaby, C. E.	182
Washburn, J.	180
Watanabe, K.	40
Watanabe, M.	44, 85, 135
Watt, R. J.	87
Weaver, M. J.	82
Webster, D. E.	73
Weinstein, V.	137
Weissmüller, J.	80
Wells, P. B.	41
White, P.	107, 126
White, S. F.	41
Williams, D. S.	135
Williams, E. W.	45
Williams, J. M. J.	86
Williams, P.	141
Wilson, B. D.	43
Winand, J. M.	38
Window, B.	80
Winkelmann, F.	183
Winnubst, A. J. A.	133
Wipf, H.	80
Woodward, S.	87
Worsley, D.	44
Wrighton, M. S.	140
Wu, L.	37
Wu, Z.	37
Xi, C.	136
Xiao, J.	180
Xiao, T.-C.	139
Xiao, X.	182
Xu, L.	81, 181
Xu, Y.	38, 126
Yagita, H.	184

	Page		Page		Page		Page
Yahikozawa, K.	39, 82	**Yeo, Y. Y.**	182	**Zang, T.**	42	**Zheng, G. Z.**	88
Yahiro, H.	85	**Yoo, I. K.**	45	**Zannoni, G.**	181	**Zhou, L.**	37
Yamamoto, A.	134	**Yoshida, A.**	181	**Zayer, N. K.**	37	**Zhou, Y.**	18
Yamamoto, T.	88	**Yoshida, K.**	32	**Zhan, Z.**	183	**Zhu, Y.**	184
Yamashita, H.	84	**Yoshimori, Y.**	184	**Zhang, D.**	167	**Ziebeck, K. R. A.**	37
Yanagi, K.	184	**Yu, K. M.**	180	**Zhang, M.**	184	**Zikrina, Z. A.**	79
Yang, N.-H.	139	**Yu, S.**	184	**Zhang, Q.**	167	**Ziółkowski, J. J.**	44
Yang, S.-M.	88			**Zhang, Y.**	81	**Zlokazov, M. V.**	44
Yang, Z.	19	**Zakumbaeva, G. D.**	42, 43, 184	**Zhao, H.**	19	**Zou, W.**	138
Yasui, K.	139			**Zheng, D.**	139	**Zung, T. T.**	139

SUBJECT INDEX TO VOLUME 39

a = abstract — Page

Acetylenes, reactions, *a* 42, 136, 140, 184
ACT™, pgm coating technology 98
Acyclic Compounds, hydrogenation, on Pt, *a* 183
Advanced Coating Technology, ACT™ 98
Alcohols, 2-alkanols, synthesis, on Pd catalysts, *a* 184
electro-oxidation on Ru(VII)/Ru(IV), *a* 181
methyl, electro-oxidation, at Pt, Ru, Pt-Ru, *a* 82, 181
oxidation, by $Pd_{561}Phen_{60}(OAc)_{180}$, *a* 43
Rh carbonylation catalyst, *a* 87
optically active, production, *a* 140
primary, aromatic, oxidation, by RuO_4, *a* 88
Aldehydes, benzaldehyde, allylation, *a* 139
branched, from Rh chiral catalysts, *a* 140
formaldehyde, hydroformylation, on Rh, *a* 185
oxidation, by RuO_4, *a* 88
from primary/secondary alcohol electro-oxidation, *a* 181
yield, from pentane carbonylation, *a* 40
Alkenes, addition reactions, via Ru complexes, *a* 87, 141
1-alkenes, asymmetric hydrosilylation, *a* 184
hydroformylation, by Rh(I) complexes, *a* 44
isomerisation, by Rh complex, *a* 140
Wacker oxidation, *a* 42
Alkenyl Halides, coupled to aryl-alkynyl Zn chlorides, *a* 139
2-Alkylaminooxazoles, high yield synthesis, *a* 87
α-Alkylation, hydroxyalkynoates, via CpRu(COD)Cl, *a* 141
Alkynes, addition to alkenes, by Ru complexes, *a* 87
Alkynylcarboxylic Acid Esters, production, *a* 139
1-Alkynylzinc Chlorides, coupled to alkenyl halides, *a* 139
Allenyl Tosylcarbamates, cyclisation on Pd, *a* 184
Allyl Acetates, reaction with sodiodimethylmalonate, *a* 86
Allylaminocyclization, allenyl tosylcarbamates, *a* 184
Allylation, benzaldehyde, *a* 139
Allyloxyaromatic Esters, reactions, *a* 86
Allylsilanes, synthesis, *a* 86
Ammonia, oxidation, Pd alloy catchment gauzes 19
sensor, *a* 182
synthesis, from N_2, *a* 83
$[Ru_6N]$ clusters for, *a* 139
Aromatisation, alkane mixtures, on Pt/zeolite composites, *a* 138
Aryl Halides, reactions, *a* 139
Arylation, Heck, on benzene-Pd(II)/polymer, *a* 42
2-Arylbenzothiazoles, new synthesis, *a* 43
Aryldiazonium Salts, Heck reaction, *a* 183

Ballard Bus, 4th Grove Fuel Cell Symposium 160
Biofuels, glycerol oxidation 159
Book Reviews, "Catalysis of Organic Reactions" 65
"Catalytic Naphtha Reforming, Science & Technology" 27
"Computer-Aided Design of Catalysts" 171
"Insights into Speciality Inorganic Chemicals" 172
"Metal Compounds in Cancer Therapy" 179
"Phase Diagrams of Precious Metal Alloys, First Suppl." 18
"Rhodium Express" 78
"The Platinum Group Metals: A Global Perspective" 116
Butadienes, reactions *a* 42, 140
Butane, reactions, *a* 42, 85
Butenolides, synthesis, CpRu(COD)Cl catalysed, *a* 141

C-H Bonds, addition to olefins, *a* 141
Cancer, anti, *trans*-$[RuCl_4(Him)_2]^-$ complex, *a* 45
chemotherapy, conference 63
Pt drugs, binding to DNA, *a* 141
Ru compounds in NO mediated disease 150
Ru phthalocyanines, for photodynamic therapy 14
Capacitors, $RuO_2/Pb(ZrTi)O_3/RuO_2$ with Pt interlayers 64
Carbon Oxides, CO_2, electroreduction, on Pd, Pt, *a* 39
at Pt gas diffusion electrode, CH_4 production, *a* 135
CO, adsorption at Pt, Ru, Pt-Ru electrodes, *a* 82
hydrogenation, on **Rh/Mo/SiO_2**, *a* 43
interdiffusion in Ru pellets, for Fischer-Tropsch, *a* 43
oxidation, over CuO-Pd/γ-Al_2O_3, *a* 184
reaction with NO and H over Pt, Rh catalysts, *a* 183
for triarylbismuthines carbonylation, *a* 184
Carbonyl Compounds, α,β-unsaturated, hydrosilation, *a* 88
Carbonylation, aryl iodides, by $PdCl_2(PPh_3)_2$-$Co_2(CO)_8$, *a* 139
by $PdCl_2(PPh_3)_2$-$Ru(CO)_{12}$, *a* 139
halogenoalkynes to alkynylcarboxylic acid esters, *a* 139
MeOH, by Rh complex, *a* 87
photo-, pentane, in $Rh_2Cl_2(CO)_4$ + PMe_3, *a* 40
triarylbismuthines, with CO, *a* 184
Carboxylates, production using Ru chiral complexes, *a* 185
Carboxylic Acids, acetylene addition, by Pd cluster, *a* 184
Catalysis, biphasic 107
heterogeneous, *a* 41-43, 84-85, 138-139, 183-184
homogeneous, *a* 43-44, 86-88, 139-141, 184-185
modelling techniques 171
review of the 14th N. Am. Catalysis Soc. meeting 126
Catalysts, automotive, new Mexican plant opens 72
review of 2nd European Precious Metals Conf. 112
SAE conf., 1995 73
biphasic Rh systems 62
electro-, Pt-Al/C, for SO_2 oxidation, *a* 135
industrial, book review 65
phase transfer, *a* 88
Iridium Complexes, Ir chloro complexes, H isotope exchange in aromatics, *a* 140
$[Ir(COD)(\eta^3\text{-}^iPr_2PCH_2CH_2OMe)][BF_4]$, phenylacetylene hydrosilylation, *a* 140
Palladium, 5%Pd/$BaSO_4$ for O-benzyl hydroxamates, *a* 85
Pd(II) complex/polymer, for Heck arylation, *a* 42
CuO-Pd/γ-Al_2O_3, for CO oxidation, *a* 184
glycerol from rapeseed oil, oxidation 159
Pd colloids/NR_4^+, preparation, stabilisation, *a* 42
Pd-Cu/zeolite, for Wacker oxidation of alkenes, *a* 42
Pd/Al_2O_3, methane combustion, *a* 84
Pd/γ-Al_2O_3, Pd/ZrO_2, SO_2 propane oxidation effect, *a* 84
preparation, liquid-phase hydrogenation activity, *a* 184
selective acetylene hydrogenation, *a* 42
Pd/C + $AsPh_3$, for cross-coupling reactions, *a* 139
Pd/C, Al_2O_3, SiO_2, $BaSO_4$, for Heck reaction, *a* 183
Pd/CeO_2, interaction with H_2, *a* 184

Page

Catalysts, Palladium *(contd.)*
Pd/polymer microdispersions, H_2 generation, *a* 85
Pd/SiO_2, Rh modified, ethene hydroformylation, *a* 138
Pd/WO_{3-x}, nanocrystalline, catalytic properties, *a* 138
Pd/ZnO/γ-Al_2O_3, CCl_3F_3, hydrogenolysis, *a* 42
$PdCl_2(PPh_3)_2$-$Co_2(CO)_8$, aryl iodide carbonylation, *a* 139
$PdCl_2(PPh_3)_2$-$Ru(CO)_{12}$, aryl iodide carbonylation, *a* 139
$Pd(OAc)_2$ + $AsPh_3$, for cross-coupling reactions, *a* 139
PdSAPO-5, one-step synthesis, *a* 139
$Ph_3P[Pd(dba)_2/Ph_3P]$, oxysilylation reactions, *a* 86
Palladium Alloys, Pd-Ni, butadiene hydrogenation, *a* 42
Palladium Complexes, $[PdMo_3S_4(tacn)_3Cl][PF_6]_3$, *a* 184
$Pd_2(dba)_3CHCl_3$, cyclised, butadienyl tosylcarbamates, *a* 184
$Pd_{561}Phen_{60}(OAc)_{180}$, for MeOH oxidation, *a* 43
Pd-HCl, for H transfer from H_2O-CO, *a* 86
Pd-MOP, 1-alkenes asymmetric hydrosilylation, *a* 184
$[Pd(allyl)Cl]_2$ for allyl acetate reactions, *a* 86
$PdCl_2$.dppf, for [2.2]paracyclophanes synthesis, *a* 43
$PdCl_2(dppf)/K_2CO_3$, one-pot method for enamides, *a* 43
$PdCl_2(Ph_3P)_2$, for styrene hydrocarboxylation, *a* 86
$PdCl_2(PhCN)_2$, cyclised butadienyl tosylcarbamates, *a* 184
$PdCl_2(PPh_3)_2$, for 2-arylbenzothiazoles, *a* 43
Pd(II) + cyclic aminomethyl phosphines, *a* 43
$Pd(OAc)_2$:PPh_3, for allylsilane synthesis, *a* 86
$Pd(OAc)_2$, for enones, enals synthesis, *a* 139
for olefin hydroesterification, *a* 140
$Pd(OAc)_2/PPh_3/Na_2CO_3$, enamide synthesis, *a* 43
Pd(O)L, for cyclodimerisation of butadiene, *a* 140
$Pd(PPh_3)_4$, for benzaldehyde allylation, *a* 139
for imidazo[4,5-b]pyridines phenylation, *a* 140
for tribromomethylbenzene to diarylacetylenes, *a* 86
PdX_2-LiX, for carbonylations, *a* 139
Pd/pumice, phenylacetylene liquid-phase hydrogenation, *a* 139
Pd/WO_{3-x}, nanocrystalline, catalytic properties, *a* 138
Platinum, for diesel filter trap 2, 114
EUROPT-1, compared with Pt catalysts, *a* 183
glycerol from rapeseed oil, oxidation 159
Pt(100), activity for NO+H_2 reaction, *a* 42
Pt, cinchona-modified, pyruvate hydrogenation, *a* 41
Pt-Au/SiO_2, preparation, characterisation, *a* 85
Pt-MFI zeolite, NO reduction, *a* 85
Pt-NaY, Pt/SiO_2, HY, *n*-hexane reactions, *a* 183
Pt-Sn/Al_2O_3, modified by Sm, Li, *a* 42
Pt-Sn/SiO_2, for unsaturated nitrile synthesis, *a* 85
Pt/Al_2O_3, for chlorobenzene hydrodehalogenation, *a* 183
enantioselective ethyl pyruvate hydrogenation, *a* 183
ethyl peruvate hydrogenation, *a* 138
methane reactions, *a* 84, 138
slurry-phase hydrogenation of phenol, *a* 41
in trickle bed reactor, naphthalene hydrogenation, *a* 183
Pt/Al_2O_3, Rh/Al_2O_3, adding H_2 to NO+CO, *a* 183
Pt/Al_2O_3/NiAl(110), model, characterisation, *a* 183
Pt/BaKL composite, to reform alkane mixtures, *a* 138
Pt/C, metal-support interaction, *a* 84
Pd/C, Rh/C, acyclic compounds hydrogenation, *a* 183
Pt/γ-Al_2O_3, Pt/ZrO_2, SO_2, propane oxidation, *a* 84
Pt/H-BEA, chlorobenzene hydrodehalogenation, *a* 183
Pt/H-mordenite, methylcyclopentane conversion, *a* 41
Pt/κ-δ Al_2O_3, for $CHCl_3$, CH_2H_2 oxidation, *a* 84
Pt/SiO_2, high surface area, preparation, *a* 138
Pt/ZrO_2, superacid, butane isomerisation, *a* 138
Pt/WO_{3-x}, nanocrystalline, properties, *a* 138
Platinum Complexes,
Pt-1,3-divinyltetramethyldisiloxane, *a* 86
Pt/BaKL zeolites, reforming alkane mixtures, *a* 138
Rhodium, Rh/Al_2O_3, preparation, *a* 85
Rh/CeO_2-ZrO_2, O exchangers, *a* 85
Rh/Pt(100), NO + H_2 reaction, *a* 42
Rh/SiO_2, promoted by Mo, CO hydrogenation, *a* 43
Rh/ZnO, for N_2O decomposition, *a* 184
Rhodium Complexes, in biphasic catalysis 108
cis-[RhI(CO)($Ph_2PCH_2P(S)Ph_2$)], activity for MeOH carbonylation, *a* 87
(η^6-$C_6H_6BPh_3$)-Rh(COD), acetylene silylformylation, *a* 140
$HRhPP(CO)_2$, for asymmetric hydroformylation, *a* 140

Page

Catalysts, Rhodium Complexes *(contd.)*
$(Ph_3)_4RhH$, hydrosilation of α,β-unsaturated carbonyls, *a* 88
$Rh_2Cl_2(CO)_4$ + PMe_3, pentane photocarbonylation, *a* 40
$[Rh_2(\mu$-(-)-DIOS)$(cod)_2]_n$, styrene hydroformylation, *a* 87
$Rh_2(OAc)_4$, for 2-alkylaminooxazoles synthesis, *a* 87
for cycloheptatrienes, norcaradiene synthesis, *a* 87
$Rh_4(CO)_{12}$, acetylene silylformylation, *a* 140
Rh-PPh_3, catalyst regeneration, *a* 185
Rh(acac)$(P(OPh)_3)_2$/$P(OPh)_3$, for hydroformylation, *a* 44
$RhCl_3$(Pybox), ketone asymmetric hydrosilylation, *a* 185
$[RhCl(CO)_2]_2$, triarylbismuthines carbonylation, *a* 184
$[RhCl(CO)_2Cl]_2$, for poly(methylhydrosiloxane), *a* 86
$RhCl(CO)(PPh_3)_2$, formaldehyde hydroformylation, *a* 185
$RhCl(PPh_3)_2$, for 2-propanol dehydrogenation, *a* 44
$RhCl(PPh_3)_3$, formaldehyde hydroformylation, *a* 185
for poly(methylhydrosiloxane), modification, *a* 86
$Rh(CO)_2$acac, for hydroformylations, *a* 86
$[Rh(cod)_2]BF_4$, for hydroborations, *a* 185
for keto esters hydrosilylation, *a* 140
$[Rh(COD)Cl)]_2$/TPPTS, biphasic 62
$[Rh(cod)(OOCR)]_2$, alkene hydroformylation, *a* 44
$[Rh(CO)(PPh_3)(\mu$-$Cl)]_2$, isomerisation, *a* 44
[Rh(dppc)-(acetone)], hydrosilation, hydrogenation, *a* 140
for ketones, alkenes reduction, isomerisation, *a* 140
[Rh(dppc)NED](PF_6), precursor, isomerisation, *a* 140
Ruthenium, hydrogenation, review, *a* 184
$[Ru_6N]$ clusters, for NH_3 synthesis, *a* 139
Ru, FeRu, Pt, FePt/C, pyridine hydrodenitrogenation, *a* 84
Ru pellets, Fischer-Tropsch, H_2/CO diffusion effect, *a* 43
Ru-Cr-Mn/Al_2O_3, for CO hydrogenation, *a* 43
$RuO_2.xH_2O$, O catalytic activity, *a* 44
Ruthenium Complexes,
for addition of C-H bonds to olefins, *a* 141
BINAP-Ru(II), olefin asymmetric hydrogenation, *a* 87
chiral, with glass microbeads, in biphasic catalysis 108
CpRu(COD)Cl, for alkynes addition to alkenes, *a* 87
$[Ru(azpy)_2(H_2O)(py)]^{2+}$, glucopyranoside oxidation, *a* 44
$[RuCl_2(cod)(R_2C(C{=}NCHRCR_2O)_2)]$, for aerobic alkene epoxidation, *a* 87
trans-$RuCl_2$(Pybox-ip)(ethylene), for asymmetric cyclopropanation, *a* 185
Ru(II)-bis(2-oxazolin-2-yl)pyridine, chiral, for asymmetric cyclopropanation of styrene, *a* 185
Ru(II)(AMPP), α-ketoesters hydrogenation, *a* 87
RuO_4, phase catalyst transfer, oxidation reactions, *a* 88
Catchment Gauzes, Pd alloy 19
Chemical Compounds, *a* 38-39, 81-82, 134-135, 180-181
Chemical Technology, CH_4 steam reforming, in Pd membrane reactor, *a* 45
Chlorobenzene, hydrodehalogenation, *a* 183
Chloroform, catalytic oxidation, *a* 84
Cinnamic Acid Esters, production, *a* 183
Clusters, $K_{1.64}Pt(C_2O_4)_2$, on glassy C electrode, *a* 181
$Pd_{38}(CO)_{28}L_{12}$, synthesis, *a* 180
$[Ru_6(CO)_{18}]^{2-}$, in NaX zeolite, O sensitive, *a* 139
$[Ru_6N]$ for NH_3 synthesis, *a* 139
Coatings, Ir, on isotropic graphite, thermal cycling, *a* 83
Pd, for semiconductor packages, *a* 138
pgms, ACT™ technology for glass manufacturing 98
Ru-Sn, on Ti, *a* 137
see also **Electrodeposition**
Cobalt, in alloys, *a* 68, 88
see also **Thin Films**
Colloids, palladium, catalysts, preparation, *a* 42
Ru_2S, preparation, luminescence, *a* 40
Composites, *a* 133,134
Conferences, 14th Fuel Cell Seminar, San Diego, CA, Nov.-Dec. 1994 9
14th N. Am. Catalysis Soc, meeting, Snowbird, Utah, June 1995 126
1st Int. Workshop on Diffusion and Stresses, Kossuth Univ., Hungary, May 1995 127
1st Int. Symp. Fuel Cell Systems, Montreal, 9-13 July, 1995 165
2nd European Precious Metals, Lisbon, May 1995 112

Page

Conferences *(contd.)*
4th Biennial Int. Symp. on Metal-Hydrogen Systems, Fujiyoshida, 6-11 Nov. 1994 75
4th Grove Fuel Cell Symp., London, Sept. 1995 67, 160
6th Int. Conf. on Platinum Group Metals, York Univ., July 1996, announcement 111
7th Int. Symp. on Metal Co-ordination Compounds in Cancer Chemotherpy, Amsterdam, March, 1995 63
Electrochem '95, Bangor, 10-14 Sept. 1995 173
"Noble and Rare Metals", Donetsk, Ukraine, Sept. 1994 29
SAE, Feb.-March 1995, Detroit 73
Corrosion Protection, Ru *in stainless steel* 107
in $RuO_2.xH_2O$, *a* 44
Crystals, $Ir_xRu_{1-x}S_2$, *a* 39
nano, Pd, in H_2 sensor, *a* 137
Pt/WO_{3-x}, Pd/WO_{3-x}, catalytic properties, *a* 138
Cyclisations, 2,3-butadienyl tosylcarbamates, by Pd, *a* 184
Cycloaddition, reactions, *a* 87
Cycloalkanol, Cycloalkanone, production, *a* 183
Cyclodimerisation, butadiene, by Pd complex, *a* 140
Cycloheptatrienes, synthesis, *a* 87
Cyclohexene, hydroformylation, by Rh catalysts, *a* 86
Cyclopentene, hydroformylation, *a* 44
Cyclopropanation, asymmetric, styrene, diazoacetates, *a* 185

Debrominative Coupling, reactions with Pd catalysts, *a* 86
Dehydrogenation, reactions, *a* 42, 44
Dehydropipernonalines, synthesis, *a* 43
Deposition, Pd-Fe alloys, electrolytically, *a* 40
Rh on brass, *a* 40
Desorption, H_2, from Pd, Ru-Pd foils, *a* 133
Detectors, air humidity, *a* 41
air-fuel ratio for automotive exhaust, with Pt, *a* 40
biosensor for Pt anticancer drugs, *a* 141
DNA, *a* 84
glucose, *a* 41, 54, 137
H_2, *a* 41, 137
IR, *a* 182
lactate biosensor, *a* 137
monohydrics, polyhydrics in flowing streams, *a* 182
NH_3, by Pt/GaAs porous Schottky diode, *a* 182
pH, *a* 183
Rh, *a* 182
Deuterium, *absorption/desorption, diffusion, a* 80, 181
Diarylacetylenes, catalytic production, *a* 86
1,2-Diarylethenes, catalytic production, *a* 86
Diazoacetates, asymmetric cyclopropanation, *a* 185
Dichloromethane, catalytic oxidation, *a* 84
Dienamides, conjugated, one-pot synthesis, *a* 43
Diesel, reduction of NO in exhaust, *a* 85
trap, review of 2nd European Precious Metals Conf. 112
Diesel Engines, particulate emission control 2
Diffusion, H, D, in Pd, Pd alloys, *a* 80, 127
Diodes, *p*⁺*n*, Pt diffused, in SiO_2 films, *a* 185
Diphenylimidazo[4,5-b]pyridines, synthesis, *a* 140
Dispersion, Pd in Pd/Al_2O_3, *a* 42
DNA, *a* 84, 136, 141
Doctoral Theses, CIS 79
Doping, *see also* **Modifiers**
Drugs, metal based, book review 179

Electrical Contacts, ohmic, Au/Ge/Pd to *n*-type InP, *a* 45
Pd/Ge to *n*-type InP, *a* 45
Pd/In/Pd, Pd-In/Pd, Pd-In/*n*-GaAs, comparisons, *a* 88
Pd/Zn/Pd/Au to *p*-type InGaAs/InP, *a* 45
Pd/ZnSe, thin film, solid state reactions, *a* 180
Electrical Engineering, *a* 5, 88, 141, 185
Electrochemical Cell, Pd/YSZ/Pd, NO, CH_4 removal, *a* 137
Electrochemistry, *a* 39, 82, 135-136, 173, 181
Electrodeposition, *a* 40, 83, 136-137, 182
Pd-Fe alloys, *a* 40
Ru-Co alloy 68
Ru-Sn on Ti, *a* 37
see also **Electroless Deposition**

Page

Electrodes, anodes, platinised Ti, *a* 88
cathodes, Pt/Y_2O_3 stabilised ZrO_2, *a* 181
chlorosilylated Pt oxide surfaces, *a* 39
interdigit array, Pt/insulation/Pt-IDA, trace Fe analysis, *a* 137
microelectrodes, Ir, for water quality testing 132
$K_{1.64}Pt(C_2O_4)_2$, *a* 81
Pd, for Pd-Li alloy formation from eutectic melts, *a* 83
Pd microparticles/poly-[N-(5-hydroxypentyl)-pyrrole] film, for C_2H_2 hydrogengation, *a* 136
Pd poly(N-pyrrole)film-coated, *a* 82
Pd/Pt, for CO_2 reduction, at + potentials, *a* 39
Pt, surfaces, for MeOH electro-oxidation, *a* 181
gas diffusion, for CO_2 reduction, a 135
$K_{1.64}Pt(C_2O_4)_2$/glassy C fibres, ultramicroelectrodes, *a* 181
Ru, Pt-Ru, CO adsorption, *a* 82
Pt/C, highly dispersed, fabrication, *a* 135
Pt/γ-MnO_2, for Li ion insertion, *a* 135
Pt/modified glassy C, for monohydrics, polyhydrics, *a* 182
Pt/pHAPh, rotating disc, *a* 82
Pt/Ti/Pt/Au base, for bipolar transistors, *a* 141
Rh-dispersed C paste, for lactate biosensing, *a* 137
with $[Rh(bpy)_3]^{3+}$, for nicotinamide reduction, *a* 83
$[Rh(bpy)_3]^{3+}$/hydrogel, for nicotinamide reduction, *a* 83
Ru_2S colloids/TiO_2, sensitisation, *a* 40
RuO_2, reactive ion etching, *a* 45
RuO_2-glass, composite, for pH sensing, *a* 183
wire, with Os complex for glucose detection, *a* 137
Electroless Deposition, Ni, aided by Pd/Si(110), *a* 80
Emission Control, in diesel engines 2, 114
technology 113
SAE conf. 73
Emitters, Pd silicide coated Si, *a* 141
Enals, production from enol silanes, *a* 139
Enamides, conjugated, one-pot synthesis, *a* 43
Enol Silanes, conversion to enones, *a* 139
Enones, from enol silanes, *a* 139
Epoxidation, aerobic alkene, Ru complex promoted, *a* 87
Esters, keto, hydrosilylation, *a* 140
Etching, dry, Pd thin films, by F sputtering, *a* 84
Ethene, hydroformylation, on Rh-modified Pd/SiO_2, *a* 138
Ethyl Peruvate, hydrogenation, over Pt/Al_2O_3, *a* 138
Ethyl Pyruvate, enantioselective hydrogenation, *a* 183

Feeder Tubes, coated by Johnson Matthey ACT™ 98
Pt, for hollow glassware, *a* 141
Fibre Optics, in air humidity sensor, *a* 41
Films, PLZT on (111)Pt/Ti/SiO_2/Si, for memories, *a* 141
Pt, sputtered, properties, *a* 80
Filters, for diesel engine emissions 2
Foils, Pd, Pd alloys, H absorption/desorption, *a* 80, 133
Formic Acid, electro-oxidation, *a* 82
Fuel Cells, 14th Fuel Cell Seminar, conf. report 9
4th Grove Fuel Cell Symp. 67, 160
a 44, 88
new materials, conference 165
SPE, a 88
Fullerenes, [60]-derivative with Ru tris(bpy), synthesis, *a* 135
C_{60}-Pt-MV, photoreduction of H_2O to H_2, *a* 83
$(\eta^2\text{-}C_{60})Pt(PPh_3)_2$, *a* 38
$(\eta^2\text{-}C_{60})Ru(CO)_4$, *a* 39
Ir-C_{60}, Ir-C_{70} complexes, *a* 82
Os_3-C_{60} complexes, *a* 82
Pt-C_{60}, Pt-C_{70} complexes, *a* 81

Gas Turbines, pinning wires for blades 117
Glass, ACT™, pgm coating technology 98
RuO_2 composite, conduction mechanism, *a* 134
Glass Technology, *a* 141
Glucose, sensors 41, 54, 137
Glycerol, rapeseed oil by-product, oxidation 159
Glycolaldehyde, from formaldehyde, *a* 185

Halogenoalkynes, carbonylation, *a* 139
Heck, reactions, *a* 42, 183
Heptine-1, hydrogenation, + aminomethyl phosphines, *a* 43

Page

n-Hexane, reactions, *a* 138, 183
Humidity, sensor, *a* 41
Hydridosilanes, reactions with allyloxyaromatic esters, *a* 86
Hydridosiloxanes, reactions with allyloxyaromatic esters, *a* 86
Hydroboration, styrene, *a* 185
Hydrocarbons, synthesis, Fischer-Tropsch, on Ru, *a* 43
Hydrocarboxylation, styrene, *a* 86
Hydrodehalogenation, chlorobenzene, *a* 183
Hydrodenitrogenation, pyridine, catalytic, *a* 84
Hydroesterification, olefins, by Pd catalyst, *a* 140
Hydroformylation, alkenes, by Rh(I) complexes, *a* 44
asymmetric, styrene, by Rh catalysts, *a* 87
using $HRhPP(CO)_2$, *a* 140
ethene, on Rh-modified Pd/SiO_2, *a* 138
1-octene, by Rh biphasic catalyst 62
olefins, on Rh, catalyst regeneration, *a* 185
reactions, on $Rh(acac)(P(OPh)_3)_2/P(OPh)_3$, *a* 44
Hydrogen, desorption from Pd, Ru-Pd foils, *a* 133
diffusion in Pd, Pd alloys, *a* 80, 127
effects in metals, conference 29
effects in Pd, Pd alloy-H, p-c(n)-T, *a* 133
induced ordering in Pd-Au, *a* 133
interaction with Pd/CeO_2, *a* 184
interdiffusion in Ru pellets, for Fischer-Tropsch, *a* 43
isotope exchange reactions, Ir catalysed, *a* 140
in Pd-H, Pd alloy-H systems, conf. 75
photoevolution, *a* 83
reaction with NO, over RhPt(100), *a* 42
reaction with NO and CO over Pt, Rh catalysts, *a* 183
sensitive Pd-Si MIS, *a* 88
sensors, *a* 41, 137
separation by Pd impregnated Al_2O_3 membrane, *a* 88
solubility, vibrational modes in nanocrystalline Pd, *a* 80
sorption, in thin Pd, Pd alloy foils, *a* 80
storage by bicarbonate/formate reaction, *a* 85
transfer to β-benzoylacrylic acid, Pd catalysed, *a* 86
Hydrogenation, 1,3-butadiene, on Pd-Ni alloys, *a* 42
acetylene, on Pd, *a* 42, 136
asymmetric, α-ketoesters, by Ru(II)(AMPP), *a* 87
olefins, by BINAP-Ru(II) complexes, *a* 87
CO, on $Rh/Mo/SiO_2$, $Ru-Cr-Mn/Al_2O_3$, *a* 43
enantioselective, of ethyl pyruvate, *a* 183
ethyl peruvate, over Pt/Al_2O_3, *a* 138
heptine-1, by Pd(II) + cyclic aminomethyl phosphines, *a* 43
liquid-phase, on $Pd/\gamma\text{-}Al_2O_3$, *a* 184
naphthalene, *a* 183
O-containing acyclic compounds, *a* 183
phenol, slurry-phase, *a* 41
phenylacetylene, on Pd/pumice, *a* 139
pyruvate, enantioselective,
by cinchona-modified Pt, *a* 41
on Ru catalysts, review, *a* 184
Hydrogenolysis, 1,1,2-trichlorotrifluoroethane, *a* 42
Hydrosilation, α,β-unsaturated carbonyl compounds, *a* 88
Hydrosilylation, reactions, *a* 140, 184, 185
Hydroxyalkynoates, α-alkylation, *a* 141
Hydroxyls, detector, *a* 182

Imidazo[4,5-b]pyridines, phenylation, *a* 140
Indium, in electrical contacts, *see* **Electrical Contacts**
Infrared, detector, *a* 182
Iridium, coatings on graphite, thermal cycling, *a* 83
compounds, BaFeIrCoO, *a* 81
CrIrO, ferromagnetism in, a 134
$IrH(CO)(PPh_3)_3$, reaction with C_{60} & C_{70} fullerenes, *a* 82
$Ir_xRu_{1-x}S_2$, crystals, *a* 39
in microelectrodes, for testing water quality 132
Iridium Alloys, Ir-Pt, tips for SEM, *a* 137
Iridium Chlorides, for highly acidic catalysts, *a* 85
Iridium Complexes, $[MeCOIr(CO)_2I_3]^-$, synthesis, *a* 134
Iridium Oxides, films, sputtered, *a* 84
$IrO_2\text{-}RuO_2\text{-}TiO_2$, *powders, preparation, a* 39
$IrO_2\text{-}SnO_2$ ultrafine binary oxides, sol-gel production, *a* 82
Sr_2MIrO_6, perovskite structure, *a* 135
Iridium Silicides, Ir_xSi_{1-x}, thin films, properties, *a* 38

Page

Iron, trace analysis, in ultrapure spectral C, *a* 137
Isomerisation, butane, to isobutane, *a* 85
$[Os(tpy)(Cl)_2(N)]^+$, *a* 135
$[Rh(CO)(PPh_3)(\mu\text{-}Cl)]_2$, *a* 44
Isotope Exchange Reactions, H, catalysed by Ir, *a* 140

JM1226, new Ru drug 150
Johnson Matthey, filter for diesel engines 2
JM1226, new Ru drug 150
Mexican autocatalyst plant opening 72
"Platinum 1995" 128
Joining, Pd, Pd alloy electrodeposits, solderability, *a* 138

α-Ketoesters, hydrogenations, *a* 87, 138
Ketones, asymmetric hydrosilylation, *a* 185
diaryl, from triarylbismuthines, *a* 184
from electro-oxidation of alcohols, *a* 181
isomerisation, by Rh complex, *a* 140

Lactate, detector, *a* 137
Lasers, trimming Pt thin films 129
Legislation, automotive, reviewed at conf. 112
Liquid Crystal Polymers, formation, *a* 86
Lithium, *a* 42, 135
Lithography, using Pd as proton source 32
Luminescence, in air humidity sensor, *a* 41
lyoluminescence, in Ru(II)tris(bpy)chelates, *a* 182
in Ru compounds, complexes, *a* 40, 82, 83
Lyoluminescence, in Ru(II)tris(bpy)chelates, *a* 182

Magnetism, in annealed Co-Pd-Si amorphous alloys, *a* 133
in BaFeIrCoO, *a* 81
Co-Pt/Cu/permalloy sandwiches, magnetoresistance, *a* 141
ferromagnetism, in CrIrO, *a* 134
in Pd_2TiAl, *a* 37
high field magnetisation of UPd_2Al_3, *a* 37
in SrLaZnRuO, *a* 38
in U_2Pd_2In, U_2Pd_2Sn, *a* 38
Magneto-Optics, *a* 185
Co/Pd multilayer films, a 88
spin valve memory, Co-Pt/Cu/Ni-Fe-Co/Cu, *a* 185
Medical, *a* 45, 141
Membranes, Pd, impregnated Al_2O_3, H_2 separation, *a* 88
Pd, Pd/Ag/stainless steel, steam reforming CH_4, *a* 45
ultrathin on porous ceramic, sputter deposited, *a* 136
Memory, PLZT films on $(111)Pt/Ti/SiO_2/Si$, *a* 141
Methane, adsorbed & photoirradiated, on Pt(111), *a* 40
catalytic combustion, *a* 84
oxidation, over Pt, in SPE fuel cell, *a* 88
on Pt/Al_2O_3 catalysts, *a* 138
removal by Pd/YSZ/Pd electrochemical cell, *a* 137
steam reforming, in Pd membrane reactor, *a* 45
Methyl Esters, from triarylbismuthines, *a* 184
Methylcyclohexane, reforming, on Pt/BaKL composite, *a* 138
Methylcyclopentane, conversion, *a* 41
reforming, over Pt/BaKL zeolite composite, a 138
Mexico, Johnson Matthey autocatalyst plant 72
Microelectronics, Pd source of protons for lithography 32
Mineralogy, in CIS, conference 29
Modifiers, Sm, Li, on $Pt\text{-}Sn/Al_2O_3$, *a* 42
Molybdenum, promoter for $Rh/Mo/SiO_2$, *a* 43
Multilayers, Co-Pt/Cu/Ni-Fe-Co/Cu, memory elements, *a* 185
Pt/(NiCo), for magneto-optics, *a* 185

Nanocatalysis, by Pt-Rh tip 13
Nanocrystallites, Pt-Pd, in a Langmuir trough, *a* 180
Nanoparticles, Rh-Pt colloids, structure, *a* 180
Nanotechnology, by Pt-Rh tip, for nanocatalysis 13
fabrication of nanophase Pd, *a* 37
see also **Thin Films**
Naphtha, reforming, book review 27
Naphthalene, hydrogenation, *a* 183
Nickel, electroless deposition, aided by Pd/Si(100), *a* 80
Nitriles, unsaturated, synthesis, from NO-alkane/alkene, *a* 85
Nitrogen, reduction, on irradiated (Ru, Os/TiO_2), *a* 83

Page

Nitrogen Oxides, N_2O, decomposition on Rh/ZnO, *a* 184
NO, in the body, Ru compounds for 150
in diesel exhausts, reduction on Pt-MFI zeolite, *a* 85
reaction with CO and H over Pt, Rh catalysts, *a* 183
reaction with H_2, over RhPt(100), *a* 42
removal by Pd/YSZ/Pd cell from gas flow, *a* 137
NMR, of ^{99}Ru, ^{101}Ru in h.c.p. Ru, *a* 38
Norcaradiene, synthesis, *a* 87

O-Benzyl Hydroxamates, deprotection by Pd/$BaSO_4$, *a* 85
Octenes, hydroformylations, on Rh catalysts, *a* 62, 86
Octyl-D-Glucuronic Acid, synthesis, *a* 44
Octyl-α-*D*-Glucopyranoside, oxidation, by Ru, *a* 44
Olefins, reactions, *a* 87, 140, 141, 185
Osmium, the densest metal 164
redox polymer, $[Os(bipy)_2(PVP)_{10}Cl]Cl$, stabilisation, *a* 39
Osmium Chlorides, for highly acidic catalysts, *a* 85
Osmium Complexes, Os_3-C_{60} fullerenes, clusters, *a* 82
$Os_3(CO)_{11}(NCCH_3)$, cluster growth on surfaces, *a* 82
Os bi(phenanthroline)dipyrido phenazine, DNA probe, *a* 84
Os bipyridyl redox polymers, for glucose electrodes 54
$[Os(bpy)_3]^{2+}$, fast efficient energy transfer, *a* 136
$[Os(\eta^2\text{-}H_2)(CO)(quS)(PPh_3)_2]^+$, synthesis, *a* 135
$[Os(tpy)(Cl)_2(N)]^+$, *a* 135
trichlorostannyls, electronic, photo properties, *a* 182
in wired sensor, for glucose detection, *a* 137
2-Oxazolidinones, synthesis, by Pd, *a* 184
Oxidation, chloroform, dichloromethane, *a* 84
CO, over CuO-Pd/γ-Al_2O_3, *a* 184
electro-, MeOH & H_2CO_2 at Pt, Ru, Pt-Ru, *a* 82
electrochemical, SO_2, with Pt-Al/C black, *a* 135
MeOH, catalysed by $Pd_{561}Phen_{60}(OAc)_{180}$, *a* 43
methane, on Pt/Al_2O_3 catalysts, *a* 138
in SPE fuel cell, *a* 88
octyl-α-*D*-glucopyranoside, by Ru catalyst, *a* 44
propane, *a* 84
Rh, *a* 81
Wacker, of alkenes, *a* 42
Oxygen, reactions, *a* 37, 85, 181

Palladium, in Au/Pd thermocouples, *a* 45
bonding ability, *a* 138
clusters, giant, $Pd_{561}Phen_{60}(OAc)_{180}$, MeOH oxidation, *a* 43
large, $Pd_{34}(CO)_{24}(PEt_3)_{12}$, preparation, *a* 180
$Pd_{38}(CO)_{28}(PR_3)_{12}$, preparation, *a* 180
colloids, in catalysts, *a* 42
complexes, Pd phosphine-phosphinite, *a* 134
composites, ZrO_2(YSZ)-Pd, O permeation, properties, *a* 133
compounds, Pd_2TiAl, ferromagnetism, *a* 37
U_2Pd_2In, U_2Pd_2Sn, magnetic ordering, *a* 38
UPd_2Al_3, magnetisation of, *a* 37
diffusivities of H, D, *a* 80
foils, H absorption, H desorption studies, *a* 80, 133
H effects in, p-c(n)-T, *a* 133
impregnated Al_2O_3 membrane, for H_2 separation, *a* 88
in magneto-optic multilayer films with Co, *a* 88
membranes, *a* 45, 136
microparticles, in poly(N-pyrrole)film electrodes, *a* 82
nanocrystalline, H solubility, vibrational modes, *a* 80
for solid state gas sensor, *a* 137
nanophase technology, *a* 37
nanosize particles/Si(100), Ni electroless deposition, *a* 80
nuclei, activated on plastic, *a* 137
in Pd_2Si layer in field emitters, *a* 141
Pd-Ag powders, morphology, thermal properties, *a* 133
Pd-H, Pd alloy-H systems, conf. 75
PdCu(110) single crystal, surface analysis, *a* 80
pinning wires for gas turbine blades 117
as proton source for lithography 32
with Si in tunnel insulator, H_2 sensitive, *a* 88
systems, $Ce_3Pd_{20}Si_6$, heavy electron system, *a* 133
dry etching, by F sputtering, *a* 84
see also **Conferences**; **Thin Films**
Palladium Alloys, Pd alloy-H, H effects in, *a* 133
bonding ability, *a* 138

Page

Palladium Alloys *(contd.)*
Pd-Ag, foils, H absorption studies, *a* 80
porous stainless steel, in membrane reactors, *a* 45
Pd-Au, H induced ordering, *a* 133
Pd-Co-Si, amorphous, annealing, magnetisation, *a* 133
Pd-Fe, electrolytic deposition, *a* 40
Pd-Li, eutectic formation on Pd electrodes, *a* 83
Pd-5%Ni, ammonia catchment gauzes 19
Pd-rare earths, formation from eutectic melts, *a* 83
Pd-5%Rh, D_2 loadings, *a* 181
Pd-Ru, foils, H absorption studies, *a* 80
H desorption, *a* 133
for pinning wire in gas turbine blades 117
shape memory effect 126
Palladium Chlorides, for highly acidic catalysts, *a* 85
Palladium Complexes, $Pd_3(dppm)_3CO^{2+}$, photoaddition, *a* 136
low valence complex, with π-acceptor ligands, *a* 180
trans-$[PdPh(py)(PMe_3)_2]BF_4$, synthesis, *a* 134
trans-$[PdPh(solvent)(PMe_3)_2]BF_4$, synthesis, *a* 134
Palladium Silicides, formation studies, *a* 37
$Pd_{82}Si_{18}$, amorphous, heat of crystallisation, *a* 81
bulk nanophase, prepared by quench melting, *a* 81
PdSi, Pd_2Si, phases in Pd thin films/(111)Si, *a* 80
Paracyclophanes, synthesis, by $PdCl_2$.dppf, *a* 43
Particulates, from diesels, filter emission control 2
Pentane, photocarbonylation, by $Rh_2Cl_2(CO)_4$, *a* 40
Pentenolides, synthesis, CpRu(COD)Cl catalysed, *a* 141
pH, detection, *a* 183
Phase Diagrams, book review 18
Pt-Sn, *a* 37
Phenol, slurry-phase hydrogenation, on Pt/Al_2O_3, *a* 41
Phenylacetylene, reactions, *a* 139, 140
Phenylation, of imidazo[4,5-b]pyridines, *a* 140
Photoconversion, *a* 40, 83, 136, 181-182
Photodynamic Therapy, with Ru phthalocyanines 14
Photoelectrochemical Cells, *a* 83
Photolysis, in $[(Ru(bpy)_2)_2(bpzt)]^{3+}$, *a* 182
Pipernonalines, synthesis, *a* 43
Plating, Rh, *a* 182
"Platinum 1995" 128
Platinum, cancer drugs 63, 141
clusters, $K_{1.64}Pt(C_2O_4)_2$/glassy C, ultramicroelectrodes, *a* 181
clusters, $[Pt_6(\mu\text{-}CO)_6(\mu\text{-}dppm)_3]$, first octahedral, *a* 180
compounds, $(\eta^2\text{-}C_{60})Pt(PPh_3)_2$, *a* 38
doping in SnO_2 thin films, electronic conduction, *a* 45
feeder tubes for glass production, *a* 141
in photoreduction of H_2O to H_2, *a* 83
Pt(111), CH_4 adsorption, photoirradiated, *a* 40
Pt(533), O desorption, dissociation, *a* 37
Pt100-hex and Pt100-(1× 1), surface energy, *a* 182
Pt/*p*-InP(100) photoelectrochemical cells, *a* 83
sputtered films, properties, *a* 80
in thermometry 45, 129
Platinum Alloys, Pt-Co catalysts, in PAFC, *a* 44
Pt-H_2WO_4 electrocatalyst, for PAFC, *a* 44
Pt-Ir, tips for SEM, *a* 137
Pt-Ni, short range order, *a* 133
Pt-Rh tip, for nanocatalysis 13
Pt-Zr, Pt-Zr-Y, structure, dispersion strengthened 167
Platinum Chlorides, for highly acidic catalysts, *a* 85
Platinum Complexes, cluster, $K_{1.64}Pt(C_2O_4)_2$/C, synthesis, *a* 81
Pt-C_{60}, Pt-C_{70} fullerenes, *a* 81
$PtCl_6^{2-}$, photoconversion in aqueous TiO_2, H, Cl, *a* 136
$[Pt(N_2C(H)CO_2)(PPh_3)_2]$, fumarate derivatives, *a* 134
$Pt(NO_2)_2(NH_3)_2$ for Pt/C electrodes, *a* 135
$Pt(qdt)_2^{2-}$, Pt(phen)(qdt), absorption/emission, *a* 181
low valence complex synthesis, π-acceptor ligands, *a* 180
Platinum Silicides, PtSi, thin film superconductivity, *a* 37
PLZT films, on (111)Pt/Ti/SiO_2/Si, for memories, *a* 141
Pollution Control, filter to remove diesel soot 2, 112
in water, Ir microelectrode, to test Pb and Cd 132
Polymerisation, electro-, 2-hydroxy-3-aminophenazine, *a* 82
Polymers, liquid crystals, formation, *a* 86
redox, $[Os(bipy)_2(PVP)_{10}Cl]Cl$, *a* 39
to support Ru, Pd catalysts 109

Page

Poly(methylhydrosiloxane), modified by Rh, *a* 86
Powders, Ag-Pd, morphology, thermal properties, *a* 133
IrO_2-RuO_2-TiO_2, preparation, *a* 39
Ru and $Ru_{40}Al_{60}$, *a* 38
Promoters, *a* 42, 43, 139
Propane, catalytic oxidation, *a* 84
2-Propanol, dehydrogenation, *a* 44
Pyridine, hydrodenitrogenation, catalytic, *a* 84
Pyruvate, hydrogenation, by cinchona-modified Pt, *a* 41

Rapeseed Oil, glycerol oxidation 159
Reactors, membrane, Pd, Pd/Ag stainless steel, *a* 45
Reduction, cathodic, of nicotinamide by Rh(bpy), *a* 83
electro-, CO_2, on Pd/Pt wire net and plate, *a* 39
on Pt gas diffusion electrode, *a* 135
N_2, over Ru, Os/TiO_2, to NH_3, *a* 83
photo, of H_2O, *a* 83
Reforming, alkane mixtures, on Pt/zeolite composites, *a* 138
n-hexane, over Pt/BaKL zeolites, *a* 138
naphtha, book review 27
steam, methane, in Pd membrane reactor, *a* 45
Resistance Thermometers, *a* 45
Resistivity, in $LaRh_2Si_2$, $Ce(Rh_{1-x}Ru_x)_2Si_2$, *a* 38
Rhodium, compounds, CeLaRhSb, superconductivity, *a* 81
$LaRh_2Si_2$, resistivity, thermopower, *a* 38
Sr_2RhO_4, 2D conductor, structure, *a* 180
crack-free deposition on brass, *a* 40
detection, *a* 182
modifier, for Pd/SiO_2, ethene hydroformylation, *a* 138
plating, *a* 182
Rh(100) & polycrystalline Rh, interactions with O_2, *a* 81
Rh(III)/Cu(II), on Fe_2O_3, for H_2 photoproduction, *a* 83
"Rhodium Express" 78
segregation in dilute Ag-Rh alloys, *a* 81
Rhodium Alloys, Rh segregation in, *a* 81
Rh-Fe, martensites, structure, *a* 180
Rhodium Chlorides, for highly acidic catalysts, *a* 85
Rhodium Complexes, $[(9S3)Rh(\mu\text{-}SPh)_3MCp^*]^{2+}$, *a* 134
$(HBPz^*_3)Rh(CO)_2$, photochemistry, *a* 136
Li_3RhH_6, preparation, structure, *a* 39
$[Rh(bpy)_3]^{3+}$/hydrogel, nicotinamide electroreduction, *a* 83
$Rh^{(III)}$, voltammetry, for trace Rh detection, *a* 182
Ruthenium, additions to stainless steel 107
clusters, $[Ru_6(CO)_{18}]^{2-}$, in NaX zeolite, O sensitive, *a* 139
compounds, Al_2Ru, semiconducting properties, *a* 38
$Ce(Rh_{1-x}Ru_x)_2Si_2$, resistivity, thermopower, *a* 38
$Ir_xRu_{1-x}S_2$, crystals, *a* 39
NO-mediated disease, anti-cancer activity 150
Ru porphyrins, photophysical properties, *a* 82
SrLaZnRuO, solid solution, structure, properties, *a* 38
SrRuO, superconductor 32
effect on transformations in Ti-Ni alloys 174
implanted in Si, electrical, optical properties, *a* 134
nanocrystalline, production from RuAl powder, *a* 38
NMR of ^{99}Ru, ^{101}Ru, *a* 38
Ru(VII)/Ru(IV) system, alcohols electro-oxidation, *a* 181
Ruthenium Alloys, $Ru_{40}Al_{60}$, production & leaching, *a* 38
Ru-Co, electrodeposition 68
Ru-Pd foils, H desorption, *a* 133
Ru-Sn, coatings on Ti, *a* 137
Ruthenium Chlorides, for highly acidic catalysts, *a* 85
Ruthenium Complexes, [60]-fullerene derivative, *a* 135
anticancer, *a* 45
$CpRuC_5H_4(AuPPh_3)_2^+BF_4^-$, *a* 39
dinuclear, macrocycles, with bpy units, *a* 181
$(\eta^2\text{-}C_{60})Ru(CO)_4$, *a* 39
$[(pp)_2Ru(BL)Ru(pp')_2]^{4+}$, synthesis, *a* 181
$Ru_6C(CO)_{14}(\eta^5\text{-}C_5H_4PPh_3)$, cluster, *a* 82
Ru phthalocyanines, photodynamic cancer therapy 14
Ru polyaminocarboxylate, new drug 150
$[(Ru(bpy)_2)_2(bpzt)]^{3+}$, photolysis, *a* 182
$Ru(bpy)_2(daf)^{2+}$, in zeolite Y supercages, *a* 136
$[Ru(bpy)_3]^{2+}$, fast efficient energy transfer, *a* 136
$Ru(bpy)_3^{2+}$, *a* 40, 83
Ru(bpy)(bpm)(bpz), quenchers of luminescence, *a* 40

Page

Ruthenium Complexes *(contd.)*
Ru(II)tris(bpy)chelates, lyoluminescence, *a* 182
$Ru(OEP)(H_2PyP_3P)_2$, synthesis, *a* 135
$[Ru(pp)_2(CO)_2]^{2+}$, chiral, decarbonylation, *a* 181
$Ru(TAP)_2(2\text{-}TAP\text{-}G)^{2+}$, for metal-DNA binding, *a* 136
ruthenocene auration, *a* 39
trichlorostannyls, spectra, photochemistry, *a* 182
very large molecules 33
Ruthenium Oxides, RuO_2/Fe_2O_3, H_2 photoproduction, *a* 83
RuO_2-glass composite, conduction mechanism, *a* 134
for pH sensing, *a* 183
RuO_2-IrO_2-TiO_2, powders, preparation, *a* 39
RuO_2-thermometers for mK range, *a* 88
$RuO_2.xH_2O$, corrodability, O catalytic activity, *a* 44
Ruthenium Sulphides, Ru_2S colloids/TiO_2, luminescence, *a* 40

Scanning Tunnelling Microscope, Pt-Ir tips, *a* 137
Schottky Diodes, in sensors, *a* 41, 182
Sensors, *see* **Detectors**
Shape Memory Alloys, Pd 126
Silicon, Ru implanted, electrical, optical properties, *a* 134
Silylformylation, acetylenes, *a* 140
SIROFS, *a* 84
Sodiodimethylmalonate, reactions, Pd catalysed, *a* 86
Sol-Gel Process, for powder production, *a* 39, 82
Sputter Deposition, pgm metals, *a* 80, 84, 136
Steel, stainless, Ru additions 107
Stilbenes, epoxidation by Ru complexes, *a* 87
Styrene, reactions, *a* 86, 87, 185
Sulphur Dioxide, oxidation, with Pt-Al/C black, *a* 135
Superacids, *a* 85, 138
Superconductivity, in CeLaRhSb system, *a* 81
Superconductors, PtSi, ultrathin films, *a* 37
$Sr_{n+1}Ru_nO_{3n+1}$, perovskite 32

Temperature Detection, by thin film sensors 129
Thermocouples, Au/Pd, stability, properties, *a* 45
Thermometers, Pt resistance, *a* 45
RuO_2, for mK range, *a* 88
Thermopower, in $LaRh_2Si_2$, $Ce(Rh_{1-x}Ru_x)_2Si_2$, *a* 38
Theses, CIS doctoral 79
Thick Films, RuO_2-glass composite, pH sensing, *a* 183
RuO_2-thermometers for mK range, *a* 88
Thin Films, Co-Pt/Cu/permalloy sandwiches, *a* 141
Co/Pd magneto-optic, *a* 88
Ir_xSi_{1-x}, electrical, optical properties, *a* 38
PbZrTiO, reactive ion etching, *a* 45
Pd, dry etching, by F sputtering, *a* 84
Pd on (111)Si, silicides formation, *a* 80
Pd on ceramic, ultrathin, by sputter deposition, *a* 136
Pd doped SnO_2, synthesis, *a* 37
Pd/Si, nanothin, multilayers, formation, *a* 37
Pd/ZnSe contacts, structure, *a* 180
Pt, laser trimming, for temperature sensors 129
Pt, Pd, Pt-Pd, in a Langmuir trough, *a* 180
Pt in Pt/NiCo multilayers for magneto-optics, *a* 185
Pt-doped Sn oxide, electronic conduction, *a* 45
PtSi, superconductivity, *a* 37
Titanium Alloys, Ru in martensitic transformations 174
Transistors, AlGaAs/GaAs, Pt/Ti/Pt/Au electrodes, *a* 141
Triarylbismuthines, carbonylation, *a* 184
Trichlorosilyl Alkanes, synthesis, *a* 184
Trichlorotrifluoroethanes, hydrogenolysis, *a* 42
Turbine Blades, pinning wire 117

Vinyl, compounds reactions, *a* 44, 140

Wacker, oxidation, alkenes, *a* 42
Water, photoreduction, by C_{60}-Pt-MV, *a* 83
testing its quality, by Ir microelectrode 132
Wires, pinning, for gas turbine blades 117

Yttrium, added to Pt alloys 167

Zirconium, added to Pt alloys 167