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Advances in Platinum Complex Cancer Chemotherapy

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It is over twenty years since cisplatin was first given to cancer patients, and a decade since the initiation of clinical trials of carboplatin. Nevertheless, platinum-based cancer therapy remains a topic of intensive laboratory and clinical research, as indicated by the presentation of over 300 papers at the Sixth International Symposium on Platinum and Other Metal Co-ordination Compounds in Cancer Chemotherapy, held last year (1). As the clinical trial data on cisplatin and carboplatin have matured their long-term efficacy and toxicities have become evident. The search for new platinum analogues continues and several of these initiatives, encompassing an assortment of chemical structures, have recently reached early Phase clinical trials. Resistance to cisplatin and carboplatin remains the major limitation. The current understanding of the mechanisms of tumour cell resistance and the cellular pharmacology of these agents could lead to new strategies to combat this frustrating problem.

Clinical Trials of Cisplatin and Carboplatin

The platinum derivatives are among the most active agents for the treatment of advanced cancer. Their most dramatic effect has been on the long-term survival of patients with advanced testicular cancer. This is an uncommon tumour-type but the average age of sufferers is only 30 years. Prior to the discovery of cisplatin the cure rate for this tumour was only 5 to 10 per cent. However, with current cisplatin-based chemotherapy protocols approximately 80 to 90 per cent of these patients can expect to survive long-term, free of disease (2). Long-term survival has also been demonstrated in advanced ovarian cancer patients following platinum chemotherapy. Approximately 30 per cent of patients with Stage III ovarian cancer (that is disease disseminated throughout, but confined to, the abdominal cavity) will live for at least 10 years following cisplatin-based therapy, whereas, without the use of cisplatin the survival rate is only about 10 per cent (3). Recent data, well reviewed by Smith and Talbot (4), has also suggested a possible role for cisplatin in the treatment of advanced breast cancer. This disease is responsible for approximately 12,000 deaths each year in the U.K. alone. Originally, interest in cisplatin was not great because studies in patients with refractory breast cancer had shown the drug to have little activity. Latterly, studies of cisplatin in previously untreated patients have shown activity comparable to some of the best available conventional regimens for this disease, for example, cyclophosphamide, methotrexate and 5-fluorouracil (CMF). Cisplatin has been combined, for the treatment of this tumour, with agents such as etoposide which show synergism with the platinum complex in other tumour types.

In spite of its impressive anti-tumour activity, treatment with cisplatin does result in severe toxicity. The most immediate and often the most disabling toxicities are nausea and vomiting (emesis). Use of corticosteroids, high dose metoclopramide, antihistamines and benzodiazepines can improve symptoms in some patients, but often at the expense of side-effects such as drowsiness and involuntary movements (referred to as dystonic movements). Emesis with cisplatin has been shown to be stimulated by the binding of 5-hydroxytryptamine (5-HT) to the 5-HT3 receptor. Inhibitors of this receptor, such as ondansetron, have resulted in the dramatic alleviation of nausea and vomiting without the side-effects induced by other antiemetic treatments (5). Furthermore, the
combination of a 5-HT3 inhibitor with dexamethasone has been shown to reduce significantly the number of vomiting episodes in the first 24 to 48 hours after cisplatin-containing combinations by 78 per cent, as compared with 30 per cent with ondansetron alone (6). Nerve damage is now the major dose-limiting factor for cisplatin since acute kidney damage has been substantially mitigated by the use of intravenous hydration. The predominant neurotoxic effect is the loss of sensory function in the limbs (peripheral neuropathy), but disturbances of hearing, balance and vision can also occur. Interestingly, workers from The Netherlands have identified a neuroprotective peptide (Org 2766) which, in randomised clinical trials, has been demonstrated to prevent the development of peripheral neuropathy in patients receiving cisplatin treatment for ovarian cancer (7). The long-term survival of patients following treatment has provided the opportunity to document the incidence of chronic side-effects from cisplatin. These are substantial and variously include: permanently impaired kidney function, peripheral neuropathy, impaired hearing, Raynaud’s phenomenon (a disorder causing symptoms like chilblains), psycho-sexual difficulties, impairment of sex hormone production, elevated blood pressure and elevations in blood cholesterol (8).

The severe toxicities of cisplatin are, to a large extent, circumvented by the use of carboplatin. This analogue causes little in the way of kidney or nerve damage, and the nausea and vomiting is less intense than with cisplatin. Randomised comparative trials of these two agents in both ovarian (9) and lung cancer (10) have confirmed their therapeutic equivalency, as well as substantiating the clinical advantages for carboplatin in terms of reductions in the severity and incidence of side-effects, and improved patient acceptability (11). Furthermore, it is now possible to give platinum chemotherapy in the course of a short visit to the outpatient’s department, since intravenous hydration and high-dose anti-emetics are generally not required.
with carboplatin. Bone marrow suppression is the major toxicity of carboplatin, with the predominant consequence being a transient reduction in the peripheral blood platelet count. The individualisation of carboplatin dosages according to kidney function using a formula first developed by Calvert (12) has made bone marrow suppression highly predictable and more manageable. Initiatives to circumvent bone marrow toxicity, such as autologous bone marrow transplantation and colony stimulating factors, are being studied in an attempt to increase both the dose and therapeutic activity of carboplatin (13). Such approaches rely on the existence of a steep relationship between the dose of drug and response of the tumour. A recent retrospective analysis of the dose-response relationship for carboplatin in ovarian cancer, however, suggests that this relationship is rather flat above conventional doses (14).

New Cisplatin Analogues

The chemical structures of ten cisplatin analogues currently undergoing early phase clinical testing are shown in Figure 1. These complexes include (i) diaminocyclohexane derivatives, (ii) platinum(II) complexes with dicarboxylate cyclobutane or related oxygenated leaving groups, analogous to carboplatin, and, (iii) an orally active mixed ammine/amine platinum(IV) complex. We have recently written a comprehensive review of the current status of these clinical trials to which the reader is referred for further details and references (15).

The rationale for the development of diaminocyclohexane (DACH) platinum complexes has been the property of non-cross resistance in cisplatin-resistant murine leukaemias. However, considerable doubt now exists as to the utility of the murine leukaemias as a model of cisplatin-refractory disease, since DACH compounds are frequently cross-resistant with cisplatin in alternative models of platinum resistance, for example, human ovarian carcinoma xenografts (16). A total of eleven DACH complexes have entered clinical trials over the last two decades, but most of these failed early in development because of either formulation difficulties or unacceptable clinical toxicity. Three DACH compounds remain in clinical trials.

Tetraplatin is a racemic mixture of the l-trans- and d-trans- isomers of tetrachloro(1,2-diaminocyclohexane)platinum(IV). This is the second platinum(IV) complex to enter clinical trials, the first being iproplatin. Phase I dose-finding studies are currently underway in the United States of America, and the toxicities encountered in these trials so far include nausea and vomiting, bone marrow suppression, mild liver damage and cumulative damage to the peripheral nervous system. Oxaliplatin, the trans-l-isomer of oxalato-1,2-diaminocyclohexane-platinum(II), is in clinical trials in France. In Phase I studies the dose-limiting toxicity was nerve damage, which was unusual in that it was characterised by the acute onset of paraesthesia (a sensation of pins and needles) during the drug infusion and the development of the cumulative loss of sensation in limbs (peripheral neuropathy) with repeated dosing. Phase II trials are ongoing and at this time oxaliplatin’s single agent activity and utility in platinum refractory disease are unknown. The third DACH complex in the clinic comprises of a racemic mixture of cis-bis-neodecanoato-trans-R, R-1,2-diaminocyclohexane-platinum(II) (L-NDDP) formulated within spherical lipid drug carriers (liposomes). Phase I studies of L-NDDP, given both intravenously and directly into the artery supplying the liver, have been conducted at the M.D. Anderson Cancer Centre (Houston, Texas). This preparation seems well tolerated, with blood count suppression being the major side-effect. Interestingly, little nerve damage has been seen. Laboratory studies are now focusing on the biological properties of the NDDP isomers and optimal constituents of the liposomal component.

As shown in Figure 1, several of the platinum complexes currently in early phase clinical trials have either dicarboxylate cyclobutane or closely related oxygenated leaving groups, conferring good water solubility and stability by comparison to cisplatin. In these respects these compounds are analogous to carboplatin. Both enloplatin, [1,1-cyclobutane-dicarb-
oxylato-(2−)-O2O [tetrahydro-4H-pyran-4,4-dimethanamine-N,N] platinum(II) (CL287, 110), and zeniplatin, [2,2-bis (aminomethyl)-1,3-propanediol-N,N']1,2-cyclobutane-dicarboxylato(2−)O,O’] platinum(II) (CL286, 558) are in development by the American Cyanamid Company. Both have identical leaving groups to carboplatin. However, unlike carboplatin, both zeniplatin and enloplatin caused kidney toxicity at maximally tolerable doses during Phase I trials. Interestingly, this finding appears contrary to the proposed relationship between leaving group stability and the nephrotoxicity of platinum complexes. Japanese efforts have focused on three analogues: (i) diammine (glycolato-O,O’)platinum(II) (254-S), (ii) (R)-2-aminomethyl-pyrrolidine(1,1-cyclobutane-dicarboxylato)platinum(II) monohydrate (DWA 2114R), and (iii) cis-1,1-cyclobutane-dicarboxylato(2R)-2-methyl-1,4-butanediamine platinum (II) (NK-121, CI-973). The clinical properties of these compounds are largely similar to carboplatin, with the exception of more pronounced gut toxicity with protracted administration schedules of DWA2114R, and white blood cell count depression rather than platelet count depression being dose-limiting for NK121. Finally, Phase I studies of a platinum(II) complex (1,2-diaminomethyl-cyclobutane-platinum(II)-lactate (Lobaplatin, D19466) under development by ASTA-Medica (Frankfurt, Germany) have recently been reported. In these studies thrombocytopenia, leucopenia, emesis and objective tumour responses were recorded.

Carboplatin is now clearly established as superior to cisplatin in terms of patient compliance, and the severity and incidence of side-effects (11). However, both cisplatin and carboplatin are given intravenously. The compliance and quality of life of cancer patients receiving platinum-based chemotherapy could, potentially at least, be further enhanced by the development of an oral platinum preparation. To this end, early phase clinical trials of an orally administrable platinum complex (ammine diacetato dichloro (cyclohexylamine) platinum(IV) (JM216), see Figure 1, have recently started at the Royal Marsden Hospital (Sutton, U.K.). This agent is the product of a collaboration between workers at the Institute of Cancer Research (Sutton, U.K.), The Johnson Matthey Technology Centres (Sonning Common, U.K.; West Chester, Pennsylvania, U.S.A) and Bristol-Myers Squibb Oncology Division (Wallingford, Connecticut, U.S.A).

Preclinical work has shown that after oral administration, JM216 has comparable activity to cisplatin and carboplatin given intravenously in a panel of four human ovarian carcinoma xenografts in vivo. Additionally, in rodents, oral JM216 has shown a lack of damage to the kidneys. The dose-limiting toxicity in mice was depression of peripheral blood white cell counts. Therefore, this platinum(IV) anti-tumour complex is well absorbed from the gastrointestinal tract and has toxic effects comparable to carboplatin.

In short, both neurotoxicity and lack of activity in human tumour models could be major limitations for the DACH complexes, while any clinical advantages for the "carboplatin analogues" over carboplatin itself are unclear at the present time. Finally, the successful development of an oral platinum drug could facilitate both the administration of out-patient chemotherapy and clinical studies on the schedule-dependency of platinum therapy.

How Do Tumour Cells Become Resistant to Platinum Drugs?

It is a well established clinical phenomenon that some patients whose tumours initially respond well to platinum-based chemotherapy become refractory to subsequent treatments. An understanding at the biochemical and molecular level of how such resistance develops might lead to the rational design of a new generation of more effective platinum-based anticancer drugs.

In a further collaborative venture between biologists at our Institute, chemists at the Johnson Matthey Technology Centres, and Bristol-Myers Squibb Oncology Division we are seeking to discover new platinum-containing anti-cancer agents with a broader spectrum
of activity than the currently available drugs. At the biochemical level, our efforts have concentrated on the development of appropriate laboratory models of cisplatin resistance and the elucidation of the mechanisms underlying their resistance. Using tissue culture methodology, we have grown tumour cells from patients presenting with advanced ovarian cancer representative of both responding tumours and those refractory to platinum-based chemotherapy (17). In addition, resistance to cisplatin has been generated in the laboratory by exposing tumour cells to cisplatin in vitro over several months (18).

A pictorial view of cisplatin being delivered to a tumour cell is shown in Figure 2. For the platinum to reach the DNA within the nucleus of the tumour cell, where it binds to produce its cell killing effects, it first has to traverse the cell membrane and then pass through the cytoplasm. There is experimental evidence indicating that resistance may occur at each of these three levels, as shown in Figure 2, that is, A = reduced influx or enhanced efflux at the plasma membrane, B = cytoplasmic inactivation, C = removal from DNA. Indeed, with some cisplatin-resistant tumours, resistance appears to have occurred at all three levels; for a review see (19).

Resistance mediated at the level of the plasma membrane is a common feature of cisplatin-resistant tumour cells. This occurs mainly through reduced drug influx rather than the increased pumping out of drug observed for some other commonly used anti-cancer drugs, for example, adriamycin, etoposide and vincristine. While it is still not entirely clear how cisplatin enters cells, whether by passive diffusion and/or active transport, in recent years changes in some membrane proteins have been associated with resistance to cisplatin (20, 21).

Cisplatin and carboplatin react avidly with sulphur ligands. Both the major cytoplasmic non-protein thiol, glutathione (GSH), and the major fraction of cytoplasmic protein thiols, metallothioneins (MTs), have been shown to be elevated in some cisplatin-resistant cells. Platinum binds to these increased levels of intracellular thiols to form inactive species, labelled B in Figure 2, thereby preventing the active aquated species from reaching the nucleus.

Once the platinum has successfully by-passed the resistance mechanisms occurring at the plasma membrane and in the cytoplasm, the tumour cell is still able to resist the potentially lethal effects of the drug at the level of DNA itself, labelled C in Figure 2. Platinum forms covalent adducts on guanine, and to a lesser extent adenine bases, on DNA. Approximately ninety-eight per cent of the adducts are formed on the same strand of DNA and are termed intrastrand crosslinks. Such a lesion is shown in Figure 2.
The remainder are formed between the two DNA strands and are termed interstrand crosslinks; for a review see (22). If these platinum-containing adducts on DNA are not removed the cell may not be able to divide successfully and such cells will ultimately die. Both normal and tumour cells, however, possess numerous enzymes which work together in specific pathways to remove such adducts from their DNA (22). It is clear that at least some cisplatin-resistant tumour cells possess an enhanced capacity to remove platinum-induced adducts from their DNA and thereby have the capacity to by-pass the potentially lethal effects of the drug.

Our collaborative programme is aimed at developing new platinum-containing complexes to tackle the above mechanisms of tumour cell resistance. As both cisplatin and carboplatin possess diammine ligands, which are retained as part of the DNA-platinum adduct, one strategy has been to synthesise complexes with asymmetric ammine/amine platinum(IV) dicarboxylates in which the axial chain differs from the cisplatin or carboplatin. Hence, they may at least partially overcome resistance which is due to enhanced removal of adducts from DNA. Furthermore, some of the ammine/amine platinum(IV) dicarboxylates in which the axial chain (R1) has been extended to greater than three carbons have been shown to be over 100-fold more potent than cisplatin against some cisplatin-resistant human ovarian tumour cells (23). Such agents, which are considerably more lipophilic than cisplatin, appear to be particularly effective at overcoming cisplatin resistance which is due to reduced uptake (18).

We are hopeful that these exciting laboratory-based in vitro findings will also eventually be achievable in cancer patients and lead to a new generation of even more effective platinum-based anti-cancer drugs.

Acknowledgement

We thank Swee Loh, Joan North and George Abel for their assistance during the preparation of this manuscript.

References

Ruthenium and Palladium in Hydrogen Detection

**DOPED LEAD PHTHALOCYANINE WITH HIGH SENSITIVITY**

In recent years metal phthalocyanines have been investigated for use as host materials in gas sensors. These organics are p-type semiconductors with very high resistivity, and sensors made from them are generally only suitable for detecting oxidising gases, including nitrogen dioxide and chlorine.

Now researchers at the College of Industrial Technology, Nihon University, Japan, have reported the results of a study made to overcome the difficulties that may be associated with the use of organic semiconductors as sensors for reducing gases such as hydrogen and carbon monoxide ("The Detection of H₂ Gas by Metal Phthalocyanine-Based Gas Sensors", S. Kanefusa and M. Nitta, Sens. Actuators B, 1992, 9, (2), 85-90).

Sensors were fabricated on high-purity alumina substrates printed with gold electrodes. Cobalt, lead, magnesium, nickel and zinc phthalocyanines were tested and sensors based on lead phthalocyanine were found to exhibit the highest sensitivity to hydrogen gas. Adding palladium black to the phthalocyanine increased its sensitivity and responsivity, by catalytic reaction. It also decreased the resistance, which was lowered still further by adding ruthenium oxide to the lead phthalocyanine and by building up the thickness of the sensor film to about 40μm.

The sensitivity of the sensors was found to be dependent on both the additions and the operating temperature, increasing with increasing sensor temperature and reaching a maximum at about 160°C. The highest sensitivity was exhibited by sensors doped with 10 weight per cent ruthenium oxide and one weight per cent palladium. For a sensor doped with 10 per cent ruthenium oxide and two per cent palladium the highest sensitivity and hydrogen response occurred at 120°C.

When the hydrogen concentration was 8000 ppm, the resistivity of lead phthalocyanine doped with ruthenium oxide and palladium was 10 times lower than it was in air, at 120°C.

Although pure lead phthalocyanine behaves as a p-type semiconductor, doping it with ruthenium oxide and palladium changes its semiconductor properties to that of an n-type semiconductor. This change in behaviour is considered.

The lead phthalocyanine sensors doped with ruthenium and palladium can be used at lower temperatures than ceramic sensors, but in practice they should be used above 100°C as atmospheric humidity can disturb the sensitivity at lower temperatures.

**Towards a Viable Fuel Cell**

Fuel cells to be used for traction purposes would advantageously be powered by a liquid fuel supplied from the existing oil distribution network; the properties of methanol make it attractive for this purpose. Interestingly, the only effective catalysts for the electro-oxidation of methanol are based upon platinum, although the mechanism of this reaction remains controversial.

Ways of increasing the effectiveness of platinum based catalysts for methanol oxidation are considered in a recent paper (A. Hamnett and G. L. Troughton, Chem. Ind. (London), 1992, (13), 480-483). Superior catalysts based on ternary alloys, better ways of using existing solid proton-conducting membranes and new membrane materials may all contribute to the development of a commercially viable fuel cell.
Controlling the Exhaust Emissions from Alternative Fuel Vehicles

NEW OPPORTUNITY FOR PLATINUM METALS CATALYSTS

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Johnson Matthey Catalytic Systems Division, Wayne, Pennsylvania, U.S.A.

To meet the increasingly exacting emission control standards that are emerging, alternative fuel vehicles will be needed. It appears that these will require optimised and dedicated systems utilising innovative control strategies to achieve the necessary standards. In this paper, the major emission control issues for engines fuelled with alcohol, natural gas, propane, or diesel fuels are identified. Control strategies employing dedicated emission control catalysts are discussed and performance results from laboratory, engine and vehicle tests are highlighted. Comparisons are made with gasoline fuelled engines, where significant experience has been accumulated over the past decade with the use of closed loop fuel control plus a catalytic converter to suppress the three main polluting emissions. The use of catalytic converters containing flow through catalysts is emphasised.

The development of vehicles using clean alternative fuels, such as methanol, ethanol, natural gas, propane, reformulated gasoline and clean diesel, has been hastened by tighter emission standards, such as the United States Federal Clean Air Act Amendments of 1990. As a result of legislative initiatives the regulatory agencies, the automotive industry and the manufacturers of emission control components are assessing the emission characteristics of these vehicles. At the same time, efforts are being made to develop effective and durable emission control systems suitable for vehicle fleets and prototype engines being developed for future automotive markets. Part of this development involves the catalytic converter technology already installed on over 150 million gasoline-powered vehicles to reduce hydrocarbons, carbon monoxide and oxides of nitrogen (1). This same technology offers considerable potential for responding to the emission control challenges associated with alternative fuelled vehicles. This paper discusses the emissions from such vehicles and how they differ from gasoline fuelled vehicles; it highlights the significant control issues and summarises recent developments in emission control catalysts.

Fuel Properties

The combustion properties of several fuels are summarised in Table I. The stoichiometric air:fuel ratio varies with the energy content of the fuel. The air:fuel ratio required for optimum combustion characteristics and thermal efficiency will affect both the engine operational parameters and the resulting exhaust gas composition, which determines the after-treatment strategy. This is highlighted below for natural gas and methanol fuelled vehicles.

For natural gas vehicles, the high stoichiometric air:fuel ratio implies that at an air flow rate comparable to that through gasoline engines a relatively low concentration of fuel will flow through the combustion chamber, thereby limiting the power generated by the engine. For lean burn engines where the air:fuel ratio is even higher, typically around 1.5 times the stoichiometric value, turbochargers are usually used to
increase fuel throughput. As a consequence, the potential for oil leaks increases. Such leaks have been known to poison the activity of emission control catalysts, necessitating limitations on the additives that can be used in lubricating oils. Methanol fuel presents an opposite scenario: to support fuel combustion the high fuel concentration requires special fuel pumps and fuel injection components, which must be compatible with the corrosive nature of methanol. Injector plugging can alter fuel calibration and affect the air/fuel control needed for maximising emission control catalyst performance.

The usual representation of the emissions from internal combustion engines is shown as Figure 1. The characteristics are generic for all

**Table 1**

Combustion Properties for Several Fuels

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Energy, MJ/kg</th>
<th>Energy relative to gasoline</th>
<th>Stoichiometric A/F ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gasoline</td>
<td>42.9</td>
<td>1.00</td>
<td>14.6</td>
</tr>
<tr>
<td>Diesel</td>
<td>42.5</td>
<td>0.99</td>
<td>14.5</td>
</tr>
<tr>
<td>Natural gas</td>
<td>50.1</td>
<td>1.17</td>
<td>17.2</td>
</tr>
<tr>
<td>Propane</td>
<td>46.1</td>
<td>1.08</td>
<td>15.6</td>
</tr>
<tr>
<td>Ethanol</td>
<td>26.9</td>
<td>0.63</td>
<td>9.0</td>
</tr>
<tr>
<td>Methanol</td>
<td>19.9</td>
<td>0.46</td>
<td>6.5</td>
</tr>
<tr>
<td>M85*</td>
<td>23.5</td>
<td>0.55</td>
<td>7.6</td>
</tr>
</tbody>
</table>

* 85% methanol + 15% gasoline

...
Three-way catalyst

Fig. 2 Performance characteristics for a three-way catalyst having the air:fuel window optimised for gasoline fuelled vehicles

Hydrocarbon emissions are high at low air:fuel ratios (fuel-rich), decrease to a minimum at lean-of-stoichiometry and increase again in the lean bum regime as the combustion temperature is lowered by dilution with excess air. Carbon monoxide emission parallels that for hydrocarbons in the fuel-rich regime as it drops at stoichiometry but remains low in the lean burn regime. However, the emission of nitrogen oxides is high on the lean side of stoichiometry and decreases as the air:fuel mixture becomes fuel-rich, and in the lean burn regime. Gasoline fuelled vehicles are generally calibrated to operate near stoichiometry, with a closed loop system utilising an oxygen sensor and a "three-way" emission control catalyst, which is optimised for the simultaneous oxidation of hydrocarbons and carbon monoxide, and the reduction of nitrogen oxides, see Figure 2.

The primary means of removing gaseous hydrocarbons from exhaust emissions is via

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Engine-out</th>
<th>Tail pipe (1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gasoline</td>
<td>50 -100</td>
<td>3 -10</td>
</tr>
<tr>
<td>Ethanol (2)</td>
<td>350</td>
<td>70 -100</td>
</tr>
<tr>
<td>Methanol</td>
<td>300</td>
<td>15 -30</td>
</tr>
<tr>
<td>Methanol (3)</td>
<td>270</td>
<td>3 -10</td>
</tr>
</tbody>
</table>

(1) Tail pipe data shown for conventional three-way catalyst technology in underfloor position
(2) Ethanol data for open loop carburetted vehicles
(3) Fuel injected vehicles with close coupled catalysts

Table II

Typical Aldehyde Emissions for Light Duty Vehicles, mg/mile FTP Test
complete oxidation to carbon dioxide. The ease of oxidation increases in the order: methane < paraffins < aromatics < olefins < oxygenates. In general when operating near stoichiometry, palladium catalysts are superior to platinum catalysts for the oxidation of methane and unsaturated hydrocarbons, while platinum catalysts are better for the oxidation of paraffins. Rhodium is an excellent catalyst for steam reforming under rich conditions, and in addition it improves the durability of platinum and palladium catalysts and has high activity for the reduction of nitrogen oxides. Therefore, the catalyst formulation can greatly influence the hydrocarbon reactivity in automotive exhaust and allows emission control catalysts to be tailored for specific fuel-vehicle-catalyst systems. This approach has been successfully utilised for suppressing emissions from gasoline fuelled vehicles and appears to be required for the effective control of regulated, as well as unregulated (2), emissions from alternative fuelled vehicles.

**Emission Control for Alcohol Fuelled Vehicles**

Aldehyde and alcohol emissions are the primary concerns for emission control for vehicles fuelled with methanol and ethanol. Both emissions contribute to the formation of ozone. Also, aldehydes are considered to be toxic materials and the California Air Resources Board has adopted strict emission standards limiting aldehyde emission from light duty vehicles and heavy duty engines. Starting with the 1993 model year, the standard for passenger cars is to be 15 mg/mile and this figure falls to 8 mg/mile for 1997, and subsequent model years. These aldehyde emission levels are similar to tail-pipe emission levels measured on catalyst-equipped gasoline fuelled vehicles, Table II.

However, gasoline engines emit less aldehydes than alcohol engines and have higher exhaust gas temperatures which promote the catalytic destruction of emitted aldehydes. Existing three-way catalysts, as well as unoptimised catalysts coupled to methanol fuelled vehicles which have been converted from gasoline fuel, show aldehyde emission levels exceeding those required by the California Air Resources Board standard (3). Consequently, to reduce the levels of aldehydes from alcohol fuelled vehicles to levels similar to those from gasoline fuelled vehicles, and thus meet emission standards, the following are required:

(a) the catalyst moved closer to the engine to take advantage of a hotter exhaust
(b) dedicated catalyst technology, and
(c) optimised fuel control and engine calibration strategy.

The effect of catalyst positioning on aldehyde emission is illustrated in Figure 3 for platinum+rhodium catalysts. Significant reduction in aldehyde emission is achieved by moving the catalyst from an underfloor position to a close-coupled location where the exhaust temperature is higher (4). The addition of a starter catalyst in the manifold further improves the suppression of aldehyde emission.

To illustrate the importance of matching optimised catalyst technology and fuel calibration strategy to minimise aldehyde emission, a review of aldehyde emission and catalytic treatment is warranted. There are two sources of aldehyde emission from alcohol fuelled vehicles equipped with emission control catalysts.

1. Aldehydes are formed from the partial combustion of alcohol fuel post-flame, and in the quench layer and exhaust manifold of the engine combustion chamber. Platinum group metals catalysts are effective for the catalytic decom-
position of aldehydes and their subsequent oxidation to carbon dioxide. The oxidation is enhanced in the presence of excess oxygen in the exhaust (5, 6). This suggests that during a fuel-rich cold start situation, the addition of air to the exhaust gases upstream of the catalyst may be beneficial for the suppression of engine-out aldehydes (those leaving the engine).

2. Aldehydes are also formed over the emission control catalyst from the partial oxidation of unburned methanol exiting the engine. For catalysts containing platinum group metals this reaction occurs at relatively low temperatures (7). Maximum emission typically occurs over Hill 1 of the Federal Test Procedure (FTP) cycle following cold start, and prior to catalyst light-off which would give complete combustion to carbon dioxide. Figure 4 shows the oxidation characteristics for a platinum+rhodium catalyst in a simulated laboratory test; the conditions are shown in Table III. Peak aldehyde emission arising from partial oxidation of methanol precedes total combustion to carbon dioxide. The relationship is illustrated in Figure 5 for several platinum+rhodium and palladium+rhodium catalyst formulations. Aldehyde emission increases with the air:fuel ratio in the lean regime, is low in the fuel-rich regime, and is lowest near to stoichiometry, as shown in Figure 6. This suggests that stoichiometric air:fuel calibration during cold start would minimise this source of aldehyde emission.

For a particular engine, the need for air to be added to the exhaust is likely to be determined by the relative importance of the two aldehyde sources. The interplay between exhaust temperature (which may be lowered by the addition of air), and fuel and calibration control is a principal factor in this determination. Matching and optimising the air:fuel ratio control and the emission control catalyst appears necessary to effect a net suppression of

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**Table III**

Gas Composition for Synthetic Gas Test of Methanol and Aldehyde Conversions

Tests at 49,000/h gas hourly space velocity

<table>
<thead>
<tr>
<th>Gas component</th>
<th>0.33</th>
<th>1.00</th>
<th>3.03</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Lean</td>
<td>Stoichiometric</td>
<td>Rich</td>
</tr>
<tr>
<td>Methanol, ppmC₁</td>
<td>900</td>
<td>900</td>
<td>900</td>
</tr>
<tr>
<td>NOₓ, ppm</td>
<td>900</td>
<td>900</td>
<td>900</td>
</tr>
<tr>
<td>CO, %</td>
<td>0.34</td>
<td>0.34</td>
<td>1.90</td>
</tr>
<tr>
<td>H₂, %</td>
<td>0.16</td>
<td>0.16</td>
<td>0.16</td>
</tr>
<tr>
<td>O₂, %</td>
<td>1.12</td>
<td>0.34</td>
<td>0.34</td>
</tr>
<tr>
<td>CO₂</td>
<td>10.0</td>
<td>10.0</td>
<td>10.0</td>
</tr>
<tr>
<td>N₂</td>
<td>Balance</td>
<td>Balance</td>
<td>Balance</td>
</tr>
</tbody>
</table>
METHANOL LIGHT-OFF TEMPERATURE (for 50% conversion), °C

Fig. 5 The correlation between the peak aldehyde emission temperatures and the methanol light-off temperatures for 50% conversions is shown for platinum:rhodium and palladium:rhodium catalysts.

aldehyde and alcohol emissions. Such designs also need to be applied to "flexible fuelled" vehicles, these being vehicles which can operate on a variable mixture of alcohol and gasoline. Such vehicles can also operate on gasoline which contains sulphur, thus in addition to controlling hydrocarbons, carbon monoxide, nitrogen oxide, and aldehydes, it is necessary to control simultaneously the emission of hydrogen sulphide (8) by means of a "Five-Way" catalyst.

Emission Control for Natural Gas and Propane Vehicles

There is significant interest in the use of natural gas as a clean fuel for urban vehicles (9). Methane is the dominant hydrocarbon component in the exhaust of vehicles fuelled with natural gas; it is also the least reactive hydrocarbon (10) and contributes little to ozone formation, though it is a powerful greenhouse gas. While current and near term emission standards are generally based on non-methane hydrocarbon (NMHC), moves are underway to introduce legislation that will use a total hydrocarbon (THC) standard for all fuels, including natural gas. This will present a significant challenge for both emission control catalysts and engine calibration strategies for natural gas vehicles. The following is an assessment of the effect of engine calibration and catalyst performance characteristics on emission control strategies for both stoichiometric and lean burn engines fuelled with natural gas.

The performance characteristics for three-way emission control catalysts for gasoline fuelled vehicles were shown above in Figure 2. The catalysts are optimised to provide a wide air:fuel window which allows simultaneous oxidation of hydrocarbons and carbon monoxide, and reduction of nitrogen oxide. Fuel control is required to optimise the emission control system and is achieved by maintaining the air:fuel ratio at or near to stoichiometry, by the use of a feedback loop incorporating an oxygen sensor.

Platinum group metal catalysts possess high reactivities for methane (10, 11) and are the most effective catalysts for the treatment of natural gas exhaust, as they are for gasoline exhaust. The corresponding three-way characteristics for an aged platinum+rhodium catalyst developed for natural gas vehicles are shown in Figure 7 as a function of R, the redox value (defined as the molar ratio of reductants:oxidants). Gas compositions are shown in Table IV.

For natural gas, the observed air:fuel window is narrower than for gasoline, and the optimum is shifted toward the fuel-rich side of stoichiometry. This behaviour appears to be correlated with the reduced reactivity for methane conversion at, and on the lean side of stoichiometry. The high hydrocarbons conversion under fuel-rich conditions can be attributed to the catalytic steam reforming of methane (12). Figures 8 and 9 show the effect
of the reactivity of three particular hydrocarbons on the conversion of both hydrocarbons and nitrogen oxides; propane, being the most reactive in the series, exhibits the widest air:fuel window. The matched suppression in activity for hydrocarbons and nitrogen oxides at stoichiometry appears to highlight the role of hydrocarbon activity in the catalytic reduction of nitrogen oxides.

The reduced performance at the stoichiometric air:fuel ratio highlights the need for matching the fuel control strategy of the engine/vehicle with the three-way characteristics of the catalyst, and for maintaining calibration for optimum emission control. This matching can be aided by the use of a proportional (as opposed to a switching) oxygen sensor to fix the air:fuel control set-point, at a rich-of-stoichiometry value, and to minimise air:fuel swings outside the optimum air:fuel window of the catalyst. Such a strategy has been demonstrated to be effective in minimising emissions (13).

The data in Figures 8 and 9 suggest that the emission control characteristics for propane fuelled vehicles are similar to those for gasoline vehicles and that propane vehicles therefore can utilise conventional three-way catalyst technology for emission control. However, nitrogen oxides emissions may be higher for propane fuelled engines (as is the case with natural gas) and may require exhaust gas recycling and also high activity catalysts for effective control (14).

Lean burn engines fuelled with natural gas require an oxidation catalyst for reducing the emissions of hydrocarbons and carbon monoxide. Nitrogen oxides emissions are inherently low for this calibration and are not affected significantly by the oxidation catalyst. Since methane is the dominant hydrocarbon in the exhaust, and the least reactive, its catalytic oxidation is characterised by high light-off temperatures. Oxidation catalysts containing platinum metals are the most effective for the oxidation of methane (10, 11) and have been optimised to suppress hydrocarbons and carbon monoxide in the exhaust of lean burn engines. Efforts are underway to develop catalysts to suppress nitrogen oxides emissions under
the lean burn environment. Such catalysts appear necessary to meet future, more stringent emission standards for nitrogen oxides.

The combustion of methane in engines produces a significant concentration of CH radicals, which are precursors to aldehydes. Additionally, the exhaust contains some particulates—though substantially less than from diesel engines—arising from uncombusted lubricating oil. With the exception of two-stroke engines, exhaust gas temperatures for most natural gas vehicles are generally higher than for gasoline fuelled vehicles. This provides favourable conditions for platinum metals catalysts to suppress both aldehyde and particulate emissions.

**Emission Control for Diesel Engines**

The development of emission control technologies for diesel engines has been the subject of numerous publications, see for example (15), and is not reviewed in this paper. The emerging emission control requirements, however, are reviewed from technical perspectives and are classified as follows:

1. **Meet particulate emission standards.** The most stringent of these standards are those adopted in the U.S.A. for heavy duty engines, namely 0.1 g/bhp-hour for 1994 trucks and 1993 urban buses, with the possibility of the adoption of 0.07 g/bhp-hour standard for 1994 urban buses. Several strict standards are also being adopted for light duty passenger cars, particularly in Europe where a significant and growing number of vehicles are fuelled with diesel. Engine manufacturers usually set an engineering target of about 75 per cent of the levels dictated by the standards in order to provide a safety margin for engine manufacturing variability and durability.

2. **Reduce exhaust odour and gaseous hydrocarbons.** Aldehydes and ketones characterise the odorous emissions from diesel engines but oxidation catalysts are usually effective in suppressing both these odours and the hydrocarbons emissions from diesel exhaust. While gaseous hydrocarbons emission from diesel engines is low, the requirement for meeting a combined hydrocarbons+nitrogen oxide emissions standard for Europe presents a need to limit hydrocarbons emissions, since currently it is difficult to reduce nitrogen oxides emissions under lean conditions from mobile sources via catalytic means, and without sacrificing the

<table>
<thead>
<tr>
<th>Gas Component</th>
<th align="right">0.400</th>
<th align="right">0.612</th>
<th align="right">0.787</th>
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<tr>
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<td align="right">1450</td>
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<td align="right">Balance</td>
<td align="right">Balance</td>
</tr>
</tbody>
</table>
control of particulate emissions via nitrogen oxide-particulate emissions trade-off.

To meet control requirements for particulate emission, an after-treatment device such as a flow-through catalyst appears necessary. Platinum group metals catalysts are known to be effective oxidation catalysts and are used to suppress gaseous emissions from various vehicle engines. The catalysts can also produce significant reductions in particulate-bound hydrocarbons, known as the soluble organic fraction (SOF), originating from uncombusted lubricating oil and fuel (16). The combustion of the soluble organic fraction must occur at temperatures below 300°C since diesel exhaust is generally characterised by low temperatures, particularly for direct injection engines. Particulate condensation and trapping by the catalyst must be minimised to prevent device plugging, which can lead to an increase in back pressure and reduced engine performance. This problem has plagued the use of particulate traps and has brought into focus the potential use of a flow-through catalyst as the after-treatment device of choice (17), particularly since prototype engines are being developed with low particulate emission. For these engines to meet emission targets safely, the catalyst is needed to “trim” the particulate emissions sufficiently to overcome production variability and engine wear.

Sulphate emission from diesel engines is produced during the combustion process in the engine cylinder. Approximately 2 per cent of fuel-bound sulphur is converted to sulphur trioxide and is emitted as sulphuric acid or metal sulphate. Their contribution to particulate emission is further increased by their hygroscopic properties which lead to the absorption of water to approximately 130 per cent of their weight. The emission of sulphate from diesel engines equipped with oxidation catalysts can be significantly higher than that in uncatalysed baseline engine-out emissions (17, 18). The catalyst must therefore exhibit minimum activity in converting exhaust sulphur dioxide to sulphur trioxide, which leads to the emission of sulphuric acid and increases particulate emissions.

As the conversion of sulphur dioxide to sulphur trioxide increases with temperature below the thermodynamic limit, at about 600°C, the catalyst is required to limit the reaction in a temperature range of about 300 to 600°C.

The previous discussion suggests that when coupling a catalyst to a diesel engine, significant reductions in the soluble organic fraction can occur at the expense of substantial increases in both sulphuric acid and particulate sulphate emissions, particularly for active catalysts and under high temperature exhaust conditions. This trade-off between the reduction in the
soluble organic fraction and the increase in sulphate is controlled by engine speed and engine load conditions, as depicted in the generic representation of Figure 10 for operational regimes characterised by the engine exhaust temperatures, which are shown increasing from $T_1$ to $T_3$. Catalysts with high selectivity are required to possess high activity for reducing the soluble organic fraction content at low exhaust temperatures, and also to have low activity for the conversion of sulphur dioxide to sulphur trioxide.

In general, the emission control system of which the catalyst is a component can be engineered for maximum effectiveness using the known exhaust characteristics of the engine and the catalytic properties of the device. Figure 11 illustrates the characteristics for an active platinum-based oxidation catalyst, where performance is plotted as a function of a generalised reaction parameter such as exhaust temperature or catalyst volume. For such a catalyst less sulphate is produced in operational regime A as compared with regime B. This is achieved at the expense of some reduction in catalyst capability for the soluble organic fraction conversion. Such a trade-off in activity may be acceptable in controlling emissions for some engines. In general however, the device must be effective for the combustion of the soluble organic fraction-rich particulate at low temperatures, and may be required simultaneously to have low activity for converting sulphur dioxide to sulphur trioxide at high temperatures. This will minimise the resulting sulphuric acid emission and the sulphate contribution to particulate emissions (19).

Total (net) particulate conversion over a range of steady-state modes represented by exhaust temperatures measured at the catalyst inlet, and given in Table V, is shown in Figure 12. The region of negative conversion is attributed to the tail-pipe particulate emission being dominated by sulphate particulates generated by the catalyst. The new Eurocycle for certification of future passenger cars in Europe requires, simultaneously, high soluble organic fraction and

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**Table V**

<table>
<thead>
<tr>
<th>Conditions for a Diesel Bench Engine Test</th>
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</thead>
<tbody>
<tr>
<td>1.8l Naturally Aspirated Engine, 0.20 wt.% Sulphur Fuel, 0.47 Catalyst Volume/Engine Swept Volume</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Speed, rpm</th>
<th>Torque, Nm</th>
<th>Exhaust temperature, °C</th>
<th>Particulates, g/h</th>
<th>HC, ppm</th>
<th>NOx, ppm</th>
<th>CO₂, per cent</th>
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</thead>
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<td>250</td>
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<td>91</td>
<td>181</td>
<td>0.2</td>
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<tr>
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<td>300</td>
<td>7.1</td>
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<td>221</td>
<td>0.2</td>
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<tr>
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<td>85</td>
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<td>100</td>
<td>500</td>
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<td>69</td>
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</tr>
</tbody>
</table>
gaseous hydrocarbons conversions at low temperatures (characteristic of the ECE component of the cycle), and low sulphur dioxide conversion at high temperatures (characteristic of the EUDE component of the cycle). The results for catalyst C in Figure 12 suggest that it has performance characteristics which can meet these requirements.

Catalyst development could be aided significantly if the amount of sulphur in the fuel was to be dropped below 0.05 weight per cent, the level currently being adopted by several countries. The use of low sulphur fuel would circumvent the soluble organic fraction-sulphate trade-off, and very active catalysts could then be developed to suppress both the soluble organic fraction and the hydrocarbons emissions (20).

Summary

Emission characteristics, fuel control strategies, and emission control systems for alternative fuelled vehicles have been considered; some of the most notable features are:

* Control of aldehyde emission from alcohol fuelled vehicles is needed to meet emission control requirements. “Five-Way” catalysts placed close to the engine manifold to make use of higher exhaust gas temperatures are effective for suppressing aldehyde and alcohol emissions from flexible fuelled vehicles.

* Emission control for “stoichiometrically” calibrated natural gas vehicles has been shown to be optimum at a rich-of-stoichiometric air:fuel calibration, to match the air:fuel window for dedicated three-way catalysts. Oxidation catalysts with improved light-off for methane combustion can be utilised to control hydrocarbons and carbon monoxide emissions from lean burn engines.

* The principle emission control issues for diesel engines are the reduction of the soluble organic fraction of diesel particulates and the gaseous hydrocarbons emissions at low temperatures, coupled with the simultaneous suppression of sulphate generation at high temperatures by means of emission control catalysts. Lowering the level of sulphur in fuel will aid further the development of more effective catalysts.

Acknowledgements

This paper is based largely upon a presentation made to the Society of Automotive Engineers at their meeting on “Alternative Automotive Fuels and the Environment”, Melbourne, Australia, 1991. The author wishes to acknowledge Southwest Research Institute and the California Air Resources Board for the flexible fuel vehicle tests, and Ricardo Engineers Ltd., for the diesel engine tests.

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*Platinum Metals Rev.*, 1992, 36, (4)
Continuing interest in metal-hydrogen systems and in the advancement of the so-called hydrogen economy, has been demonstrated by two recent meetings, each attended by participants from some thirty countries. The first was at Uppsala University, Sweden during June, and the second was held in Paris later that month. At both it was evident that considerable research work involving the platinum group metals is taking place throughout the world.

The 1992 biennial International Symposium on Metal-Hydrogen Systems, fundamentals and applications, was held under the chairmanship of Professor S. Rundqvist of Uppsala University from June 8th to 12th, with some 300 participants. Many papers concerned hydrogen interactions with the platinum metals, the majority dealing with palladium.

Hysteresis Effects
A still incompletely resolved issue concerning the palladium-hydrogen system is that of “hysteretic” effects associated with regions of phase transition. These correspond to differences between values of the hydrogen content and steady state hydrogen pressures (and other experimental parameters) that are derived during sequences of increases and decreases of hydrogen content, respectively. This topic was discussed by B. Baranowski, Polish Academy of Sciences, Warsaw, who concluded that hysteresis was an inherent stress gradient dependent factor, with both absorption and desorption relationships representing effective equilibrium conditions.

Palladium Alloys
The influence of the relative sizes of alloying elements on the form of changes in the pressure-composition (p-n) and electrical resistance-composition relationships were reported by R-A. McNicholl and F. A. Lewis of Queen’s University, Belfast. Electrical resistance measurements of β-phase hydride composition ranges for a wide variety of palladium alloys at low temperatures were discussed by A. W. Szafrański, Polish Academy of Sciences, Warsaw. Derivations of p-n relationships for palladium-indium and palladium-aluminium alloys, together with associated thermodynamic correlations, were reported by Y. Sakamoto, N. Ishimaru, M. Hasebe, E. Kakihi, and Y. Kinari from the University of Nagasaki. This group also reported studies on series of alloys: palladium-rhodium, palladium-nickel and palladium-lithium, acting as hydride electrodes in nickel-hydrogen (hydride) batteries. Studies of the effect of hydrogen on electrotransport and thermoelectric power in palladium-copper alloys were reported by J. Toth, K. Tompa and T. Tarnoczi, Central Research Institute for Physics, Budapest, while studies of the stability of β-phases in a series of palladium-zirconium, palladium-indium and palladium-iron alloys formed by electrolytic charging were reported by V. M. Christov, B. S. Sidzimov, St. D. Neov and L. Bozucov, Institute for Nuclear Research and Nuclear Energy, University of Sofia. An investigation of hydrogen site occupation in palladium-gold alloys by Mössbauer spectroscopy was reported by M. Baier, M. Karger, R. Ostermayer and F. E. Wagner, Technical University of Munich, H. J. Bauer and I. Dugandžić, University of Munich, V. E. Antonov, T. E. Antonova and V. I. Rashupkin, Russian Academy of Sciences, Chernogolovka, and S. M. Filipek, Polish Academy of Sciences, Warsaw. Some positron annihilation studies of

hydrogen in palladium-silver alloys were reported by E. Debowska, from the University of Wroclaw, Poland.

**Structural Information**

With regard to structurally related measurements of the effects of hydrogen in palladium, M. Tkacz and B. Baranowski, Polish Academy of Sciences, Warsaw, reported X-ray evidence of a phase transition region appearing over certain ranges of high pressure for particular β-phase palladium:hydrogen ratios. Also in studies at high pressures V. A. Somenkov and I. N. Goncharenko, Kurchatov Institute, Moscow, reported results of neutron diffraction measurements of palladium:deuterium composition ratios. Considerations of structural alterations related to changes in electrical resistivity were discussed by J. P. Burger, University of Paris Sud. Studies by the small angle neutron diffraction technique, of trapped electrons in palladium were reported by D. K. Ross and K. L. Stefanopoulos, University of Salford, U.K., S. Forcey, Research Centre, Ispra, Italy and I. Iordanova, University of Sofia.

**Films and Surfaces**

Ways of utilising both the absorptive capacity and the relatively high catalytic activity of palladium were illustrated by studies of the electrical resistivity and Hall coefficients of palladium films coated on vanadium and niobium, by D. E. Azofeifa and N. Clark, University of Costa Rica; such surface films facilitated measurements of hydrogen diffusion coefficients in the aluminium substrate (H.-J. Schlüter and H. Züchner, University of Münster; R. Braun and H. Buhl, DLR, Köln). On the other hand the use of palladium as a substrate provided a means of determining hydrogen diffusion coefficients in MgH₂ (P. Spatz, H. A. Aebischer, A. Krozer and L. Schlapbach, University of Fribourg) and acted as a control on hydrogen adsorption levels, studied by colour changes of tungsten trioxide (J. Kleperis and A. Lusis, Solid State Physics Institute, University of Latvia, Riga). Hall coefficient and also the magnetoresistance of hydrided palladium films were measured by E. Flouda and C. Papastaikoudis, Institute of Materials Science, Athens.

Observations by LEED measurements of initial structures developed by hydrogen on palladium surfaces were reported by L. Stauffer, H. Ezzehar and H. Dreysses, Physics Laboratories, Mulhouse and Vandoeuvre-Les-Nancy, France. Activation of MgH₂ storage material by ruthenium and platinum co-deposited on charcoal was reported by H. Imamura and M. Nakamura, Yamaguchi University, Ube, Japan. Evidence of the production of hydrogen in atomic form during desorption from palladium films was indicated by its adsorption on gold (E. Nowicka, Z. Wolfram, W. Lisowski and R. Dús, Polish Academy of Sciences, Warsaw).

**Diffusion: Lattice Expansion**

Studies by NMR of hydrogen diffusion in Ti₄Ir were reported by D. Guthardt, D. Beisenherz and H. Wipf, Technische Hochschule (TH), Darmstadt, and of deuterium in Zr₄PdD₄ by L. P. Ferreira, University of Coimbra, Portugal and A. Baudry and P. Boyer, CEN, Grenoble. Nuclear resonance reaction measurements were used by B. Hjörvarsson, University of Uppsala, to estimate hydrogen profiles in a platinum-nickel single crystal. Gorsky Effect measurements of deuterium coefficients in β-phase palladium-deuterium at low temperatures were recorded by B. Coluzzi, C. Costa, A. Biscarini, B. Sobha and F. M. Mazzolai, University of Perugia and R.-A. McNicholl, Belfast. Hydrogen diffusion coefficients in palladium-yttrium alloys were studied by P. R. Stonadge, M. J. Benham and D. K. Ross, University of Salford, and measured in both cast and annealed palladium by Y. Q. Lei, D. L. Sun, Y. L. Chen, J. Wu and Q. D. Wang, Zhejiang University, Hangzhou, China.

The consequences of expansion and strain gradients produced by hydrogen on estimates of hydrogen diffusion coefficients in α-phase palladium hydride were treated in papers by J. Čermák and A. Kufudakis, Institute of Physics, Prague and F. A. Lewis, Belfast, and in α and α + β palladium hydride by Y. Sakamoto,
H. Tanaka, Nagasaki University, and F. A. Lewis and X. Q. Tong, Belfast. Allied studies with Pd, Ag, and H were reported by X. Q. Tong, K. Kandasamy, F. A. Lewis, Belfast and R. V. Bucur, University of Uppsala. The strain effects of hydrogen in dislocation networks on hydrogen solubilities in palladium were considered by R. V. Bucur, University of Uppsala and F. A. Lewis, Belfast. Studies of volume changes produced by hydrogen absorbed in CeRu, were reported by L. Severin and B. Johansson, University of Uppsala.

Hydrogen Isotopes in Palladium Electrodes

A review of recent information on the possibility of fusion of electrolytically discharged deuterium in palladium was reported by D. Lewis, Royal Institute of Technology, Stockholm. Consolidation measurements of hydrogen contents in palladium electrodes corresponding to effective pressures of hydrogen generated electrolytically were provided by F. A. Lewis, S. G. McKee and R.-A. McNicholl, Belfast. Similarly, for studies partly initiated by the possibility of cold fusion, R. N. Kuz‘min, A. P. Kuprin and P. O. Revokatov, M. V. Lomonosov Moscow State University, reported on accumulations of electrolytically discharged tritium in palladium cathodes. A model for determining the concentration profiles during electrolytic charging and discharging of hydrogen by palladium was presented by Y. Sakamoto and N. Ishimaru, Nagasaki University. A discussion of electrochemical hydrogen discharge processes was presented by G. Jerkiewicz, Sherbrooke University, Canada. The effects of current density and of prior cold working of palladium cathodes on radioactive emissions were reported by H. Uchida, Y. Hamada, Y. Matsumura and T. Hayashi, Tokai University, Kanagawa, Japan.

Hydride Complexes of Platinum Group Metals

Considerable research activity was reported in regard to complexes of the platinum metals. X-ray structural analyses of alkali metal complexes such as NaPd,H, were reported in three papers by the group of D. Noréus, University of Stockholm. Results of examining structurally related hydrides, such as Na,(K,)PtH, were presented by G. Auffermann and W. Bronger and by W. Bronger, K. Jansen, G. Ridder, G. Auffermann and P. Müller, Institute of Inorganic Chemistry, TH Aachen, and included a description of a method of high pressure preparation; and by F. Bonhomme and K. Yvon, University of Geneva and P. Fischer, ETH Zürich, for the deuterated complex Mg,RuD,.

Structures of analogous compounds of cerium and gadolinium together with measurements by SEM and DSC were reported by Y.-G. Kim and J.-Y. Lee, Korea Advanced Institute of Science and Technology, Taejon; while structures of mixed Group II and Group III compounds [SrEuRuH, and their magnetic behaviours were studied by R. Lindsay, R. O. Mayer, W. Strange, D. F. Storey, W. H. Clapp and J. R. Knapp, Trinity College, Hartford, Connecticut. Generalised problems of hydrides, including those of the platinum metals, were dealt with in contributions by M. M. Jakšić, University of Belgrade, J. K. Nerskov, Technical University, Lyngby, Denmark, and W. A. Oates, Institut für Festkörperforschung, KFA Jülich, Germany.

The papers presented at the Uppsala Symposium will be published in the Zeitschrift für Physikalische Chemie and subsequently gathered into a volume of proceedings under joint editorship with Professor E. Wicke.

The next meeting in this series is planned to be organised in Japan by Professor S. Suda, Department of Chemical Engineering, Kogakuin University, Tokyo.

The Ninth World Hydrogen Energy Conference was held in Paris from 22th to 25th June, 1992, under the co-chairmanship of Dr. C. Dérive and Dr. J. Pottier. As for previous conferences, a central objective has been to effect advancement of hydrogen as an environmentally acceptable source of energy. Primary conference topics have included the
means of hydrogen production, methods of purification and ways of increasing the utilisation of hydrogen.

Membranes of Palladium Alloys

In addition to the main established means of hydrogen production – such as the various processes of interaction of water (steam) with methane or other carbonaceous materials – significant volumes of hydrogen can also be abstracted from residues of other processes and purified by passage through palladium alloys membranes, such as those reported as developed by N. I. Timofeev, F. N. Berseneva and V. M. Makarov, Russian Academy of Sciences, Ekaterinburg, and recently reviewed here by V. Z. Mordkovich, Yu. K. Baichtock and M. H. Sosna (*Platinum Metals Rev.*, 1992, 36, (2), 90–97).

Such palladium membranes were also reported as being incorporated into a regenerative fuel cell using alkali metal hydride technology by P. Roy and S. A. Salamah, General Electric Company, San José, California, and were also suggested for encapsulation of hydrogen storage electrodes by F. A. Lewis, R.-A. McNicholl and K. Kandasamy, Belfast, and R. V. Bucur, University of Uppsala and Y. Sakamoto, University of Nagasaki. Impedance techniques for studying diffusion coefficients at the surfaces of palladium alloy membranes were discussed by C. G. Chen, R. Durand, R. Faure, ENSEEG, St Martin d'Hères, France and G. Jorge, School of Chemistry, UCV, Caracas.

Hydrogen Storage: Hydrides

In a measure of correlation with the Uppsala Symposium, one section of the Paris programme concerned developments of metal hydrides for hydrogen storage and paid attention to increasing utilisation in nickel-hydrogen batteries.

Granular composites of palladium and palladium-aluminium alloys were employed as reference materials in considerations of mass and heat transfer in storage compounds by A. Perevezentsev, A. Kroglov and B. Andreev, Mendeleev Institute, Moscow. Kinetic improvements by additions of catalytically assisting palladium to the hydrogen storage compound MgH₂ were reported by D. K. Slattery and R. Zidan, Solar Research Centre, Cape Canaveral, Florida. Thermodynamic aspects of hydride heat pump operation in platinum catalysed cycles of hydrogenation and dehydrogenation were discussed for acetone/2-propanol (Y. Yamashita, E. Ito and Y. Souto, University of Tokyo) and for cyclohexane/benzene (R. G. Sarmurzina, of the Kazakhstan Academy, Alma-Ata). Developments of polyhydride complexes containing rhodium and iridium as storage materials were outlined by K. R. McKinley, R. E. Rocheleau, P. K. Takahashi, Hawaii Natural Energy Institute; E. J. Bylina, Pacific Biomedical Research Center and C. M. Jensen, University of Hawaii. Problems concerning site energies in regard to hydrogen occupation by metals including palladium-platinum alloys were examined by Z. A. Matysina, B. Yu. Zaginaichenko and O. S. Pogoralova, University of Dnepropetrovsk, Ukraine.

Hydrogen from Solar Energy

Methods of solar energy conversion for hydrogen production have become increasingly investigated. Platinum group metal, or compound, assisted photochemical dissociation of water, or other hydrides produced by irradiation of semiconductor materials such as silicon, (N. Getoff, G. Li, H. Stockenhuber, University of Vienna and K. Koteev, Bulgarian Academy of Sciences, Sofia); or cadmium sulphide (C. A. Linkaus, T. E. Mingo and N. Z. Muradov, Solar Energy Center, Cape Canaveral) or Bi₂O₃ (P. Maruthamuthu, K. Gurunathan, E. Subramanian and M. V. S. Sasri, University of Madras) have been exemplified by platinum in cases of cathodic reactions (hydrogen evolution) and by oxides, such as RuO₂, in cases of anodic reactions (oxygen evolution). Additionally or alternatively, initial photochemical activations of ruthenium complexes that have been utilised to effect electron transfer oxidation state changes may be either heterogeneously or homogeneously catalysed by suggested rhodium compounds (R. Bauer and C. Konigstein, Technical University, Vienna;
Electrolysers

Modern forms of electrolysers represent important sources of hydrogen generation powered by various physical sources, including water, wind and solar energy. Platinum group metals and compounds have been utilised as catalyst materials for both cathodic and anodic processes, for various forms of electrolysers which are incorporated into generalised hydrogen energy programmes, such as in Saudi Arabia (H. Steeb, H. Aba-Oud and W. Seeger, D.L.R. (German Aerospace Research Establishment), Stuttgart and K.A.C.S.T, Riyadh, Saudi Arabia); in China (D. Z. Chen and J. Y. Huang, Jiaotang University, Xian) and in Brazil (L. G. de Lima, University of Uberlandia and T. N. Veziroglu, Clean Energy Research, Coral Gables, Florida). An electrolyser with an RuO₂ activated anode has been proposed for preparation of methanol from carbon dioxide and hydrogen (M. Specht, A. Bandi and C. U. Maier, Solar and Hydrogen Energy Research Center, Stuttgart and University of Stuttgart). Platinum silicide has been suggested for electrodes (A. K. Vrij, Institut de Recherche d’Hydro-Quebec).

In principle the currently interesting nickel/hydrogen batteries can be regarded as a class of electrolysers in which the discharged hydrogen is temporarily stored rather than evolved as gas. One proposed form of hydride electrode (G. Crepy and Y. Borthomieu, Alcatel and Saft Research Groups, Marcoussis and Romainville, France) is that of platinum dispersed within a charcoal matrix.

Fuel Cells

The discharge stage of nickel/hydrogen batteries could be regarded as a special case of hydrogen fuel cell operation. In the more usual operating circumstances of gaseous hydrogen fuel, platinum metals and compounds have been employed as electrode catalysts, somewhat analogously to their uses in electrolysers, both in general (A. J. Appleby, Texas A and M University; P. Hoogeveen, Air Products, Netherlands, B. G. Marcenaro, Ansaldo Research, Italy; L. Vermeeren, Elenco, Belgium and J. P. Cornu, Saft, France; M. Ghouse, H. Aba-Oud, M. Ba-Junaid, M. Al-Garni and M. I. Quadri, Solar Products, Riyadh, Saudi Arabia) and in the particular cases of phosphoric acid fuel cells (L. E. van Bibber, W. A. Summers and J. P. Cornu, Saft, France; M. Ghouse, H. Aba-Oud, M. Ba-Junaid, M. Al-Garni and M. I. Quadri, Solar Products, Riyadh, Saudi Arabia) and alkali fuel cells (A. N. Arshinov, Ural's Electrochemical Plant, Ekaterinburg, Russia) polymer electrolyte fuel cells (N. V. Korovin, Moscow Power Engineering Institute, Moscow, P. Staiti, Z.
Hydrogen Isotope Separation and General Information

Platinum metal activated electrode surfaces were among those examined by D. L. Stojic, S. S. Miljanic, T. D. Grozdic and M. M. Jakšić, University of Belgrade, within a study of electrolytic separation of protium and deuterium, and information available for palladium concerning hydrogen isotope exchange processes has been utilised for the development of a method to abstract tritium from tritium polluted water (B. Andreev, Y. Sakharovskij, A. Perevezentsev and M. Rosenkovich, Mendeleev Institute of Chemical Technology, Moscow).

Articles which concerned the availability of information within general areas of study were presented by R. Fromageau, E.N.S.C., Paris and by V. A. Goltsov, C. Droniou and M. Rubinstein, L. F. Goltsova and V. A. Garkusheva, Polytechnic Institute, Donetsk.

Presented papers have been collected into a proceedings volume, "Hydrogen Energy Progress IX", edited by T. N. Veziroglu, C. Derive and J. Pottier and printed by M.C.I, Paris on behalf of the International Association for Hydrogen Energy. The next World Hydrogen Energy Conference will be held in Orlando, Florida during 1994 under the chairmanship of Dr David L. Block of the Florida Solar Energy Center, Cape Canaveral.

Platinum and Iridium Intermetallic Films

Carbon-carbon composites have high strength but their structural use is restricted by their rapid degradation in oxidising environments at temperatures as low as 500°C. For demanding aerospace applications such as for rocket nozzles and jet engine combustion chambers, where temperatures in excess of 200°C may be encountered, a coating that would provide oxidation-resistance for even a short time would be advantageous.

As part of a programme to develop high-temperature, oxidation-resistant coatings for carbon-carbon composites researchers at GenCorp Aerojet Electronic Systems Division, in Azusa, California, investigated a closed-shell molecule, the Engel-Brewer compound zirconium triplatinide, ZrPt, (1). This material was selected because its melting point is in excess of 2190°C and it can be formed by heating a mixture of the two elements at temperatures above 2500°C.

An electron-beam evaporation procedure was used to build up a multilayered structure of zirconium and platinum on both pyrolytic graphite and phenolic resin/graphite samples. Three layers of each metal were deposited to give a total thickness of either 0.5 or 2.0 μm, the relative thicknesses of the individual layers being determined by the amounts calculated to yield stoichiometric ZrPt₃, when homogenised. Preliminary results demonstrated that the zirconium/platinum multilayers were adherent and provided oxidation-resistance to the underlying substrate. The metallic layers react together at high temperatures, either during a preparatory annealing stage or in high temperature operation, to form the stable oxidation-resistant ZrPt₃ compound. Also, the highly reflective nature of the coating reduced the heat load on the substrates for short-time and high-temperature applications.

A more recent paper from the same laboratory reports the results of an investigation of the reaction mechanisms of oxygen, hydrogen and water vapour with ZrPt₃ and also HfIr₃ as a function of temperature and under ultra high vacuum conditions (2). The effect of hydrogen on the oxidation reaction is considered to be particularly relevant as hydrogen is present in rocket exhaust emissions.

The results indicate that these compounds only partially react with oxygen and water vapour, forming a surface oxide layer with a maximum thickness of 35Å. Vacuum annealing and hydrogen dosing prior to oxidation inhibit any subsequent oxidation of ZrPt₃, while exposure to hydrogen after oxidation reduces the surface oxide.

These materials show promise as oxidation-resistant coatings, providing they completely cover the carbon substrate.

References
1 M. D. Alvey and P. M. George, Carbon, 1991, 29, (4/5), 523–530
Electrogenerative Systems

POTENTIAL USES INCLUDE CLEAN-UP OF FLUE GASES FROM COAL FIRED STATIONARY POWER PLANTS

By Stanley H. Langer
Chemical Engineering Department, University of Wisconsin, Madison, U.S.A.

The concept of utilising favourable exothermic heats of overall reaction to produce chemicals while at the same time generating electrical energy in an electrochemical cell arrangement is appealing from an aesthetic viewpoint, and also responds to present day concerns about conservation and the environment. Some possibilities were noted by such eminent figures as Grove, the inventor of fuel cells in 1842 (1), and Nernst and others at the end of the nineteenth century (2). Yet, despite significant advances in electrochemical syntheses (3–6) and electrocatalysis since that time, the application of this electrogenerative approach to chemical processing has not progressed beyond research efforts in a few laboratories. Thus, many possibilities are not appreciated or have been overlooked. In this introductory discussion, which is intended for stimulation of further consideration, electrogenerative processing is explained and some means for its implementation are given, as are its limitations. Several types of systems also are described, as are some selectivity features, and possible ways for applying this approach to controlling nitrogen oxide and sulphur dioxide emissions.

More extensive discussion and pertinent references can be found in several reviews and recent articles (2, 6–12).

"Electrogenerative systems" or processes combine the favourable thermodynamics of overall reaction (ΔG<0) where the change in Gibbs' free energy should be negative, with mechanistic and kinetic factors to produce or remove a desired chemical, and to generate DC current between matched electrodes in an electrochemical cell arrangement. Fuel cell operations, which are related, generally emphasise energy production aspects in the cell and complete oxidation (13, 14, 15). Electrogenerative systems share the use of catalytic electrodes and possibly even fuel cell components, but they differ significantly in that their main function is chemical processing with attendant considerations, and the electrical power is a by-product. The "electrogenerative" designation emphasises the chemical processing goals (6, 7, 9, 12). A consequence of this is that catalytic requirements at both electrodes may differ considerably from those of fuel cells.

With the long term view influenced by an interest in catalysis and the considerations above, a number of systems have been devised for performing selected electrochemical syntheses in a galvanic or "electrogenerative" mode (6, 7, 9, 12). Some electrogenerative systems of interest to this discussion are listed in the Table. While a variety of conventional and modified electrochemical methods can be used to study the pertinent half-cell electrode reactions (for example 17–19), in our laboratories overall electrogenerative systems generally have been investigated without any external power source and with simple controls. They incorporate two coupled electrode reactions, an appropriate barrier electrolyte, a provision for product recovery, and a circuit with a load for using the electrical energy, or possibly only to dissipate it, as illustrated by the system for studying electrogenerative hydrogenation in Figure 1. This approach insures feasibility and has stimulated continued improvement in current densities, components and cell configurations. Generally we have worked with aqueous solutions or aqueous compatible barrier electrolytes, such as some ion exchange membranes. Some other work on electrogenerative processes using solid electrolytes has been summarised recently by Vayenas (20),
and Stoukides (21), while Winnick and co-workers (22) have also discussed important related applications using solid electrolytes.

**Some Electrogenerative Systems and Their Characteristics**

The hydrogenation of simple alkenes, conventionally a heterogeneous catalytic reduction, was utilised as an initial model system for investigating organic electrogenerative system operation (23, 24) and has been among the most extensively studied to-date. While the electrogenerative production of alkanes from alkenes is not a system of ordinary commercial interest, it is related to a number which are, and it has been useful for demonstration studies. Many approaches used in analysing electrogenerative alkene hydrogenation (for example the determination of rate expressions and mechanism) are applicable to other electrogenerative systems of the type described later. In this hydrogenation, hydrogen reacts across a barrier electrolyte phase bounded by porous, electrolyte-impermeable, catalytic electrodes. Figure 1 illustrates a cell design, together with associated circuitry, chosen from a number which have been used.

During operation, hydrogen ions which formed at the anode are transferred through the electrolyte, while electrons are conducted through the external circuit. Hydrogenation occurs at the counter, catalytic cathode (reducing electrode) at a controlled rate. With aqueous acid electrolyte, overall processes are:

- **Anode:** \( \text{H}_2 \rightarrow 2\text{H}^+ + 2e^- \) (i)
- **Various Solution Transport Processes:** \( \text{H}^+(\text{anode}) \rightarrow \text{H}^+(\text{cathode}) \) (ii)
- **Cathode:** \( \text{RCH}=\text{CHR}'+2\text{H}^++2e^- \rightarrow \text{RCH}_2-\text{CH}_2\text{R}' \) (iii)
- **Overall:** \( \text{RCH}=\text{CHR}'+\text{H}_2 \rightarrow \text{RCH}_2-\text{CH}_2\text{R}' \) (iv)

The open circuit cell potential is given by \( E_{\text{cathode}} - E_{\text{anode}} \). For the hydrogenation of olefins, a characteristic reproducible open circuit voltage close to that calculated on the basis of free energy change (see the Table) is observed, although the olefinic electrode is not considered reversible. By varying the simple external load the rate (current) of reaction can be controlled. Electrode potential also varies because of polarisation. In this example, the low solubility of reactants and products in the barrier electrolyte limits any direct chemical reaction between hydrogen and the olefin reactants or "chemical shorting", so that the thermodynamic driving force is maintained. Reactions (i) and (iii) led to an overall reaction with an invariant electrolyte composition at significant current densities (> 70 mA/cm²) using high surface area, gas diffusion electrodes (23–25).

With constant ionic strength perchlorate electrolyte, the kinetics of ethylene electrogenerative hydrogenation at the cathode could be studied at liquid-impermeable, Teflon-bonded, platinum black American Cyanamid LAA-2 electrodes (9 mg Pt/cm²) (25). Either the ethylene partial pressure or the concentration of the...
Some Electrogenerative Systems of Interest (6, 7)

<table>
<thead>
<tr>
<th>Overall reaction</th>
<th>*n</th>
<th>$\Delta H^o_R$ kcal/mol</th>
<th>$\Delta G^o_R$ kcal/mol</th>
<th>$E^o,V$ (calculated)</th>
<th>$E,V$ (observed)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Reductions:</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$C_2H_2 + H_2 \rightarrow C_2H_4$</td>
<td>2</td>
<td>-32.7</td>
<td>-24.1</td>
<td>0.52</td>
<td>0.51</td>
</tr>
<tr>
<td>$C_2H_4 + 3H_2 \rightarrow C_2H_6$</td>
<td>6</td>
<td>-49.3</td>
<td>-23.4</td>
<td>0.17</td>
<td>0.14</td>
</tr>
<tr>
<td>$2NO_2 + H_2 \rightarrow N_2O_4 + 2H_2O$</td>
<td>2</td>
<td>-70.4</td>
<td>-36.7</td>
<td>1.59</td>
<td>0.90</td>
</tr>
<tr>
<td>$NO + 1.5H_2 + H_2O \rightarrow NH_2OH + H^+ + HCl(\text{aq})$</td>
<td>3</td>
<td>-52.3</td>
<td>-34.3</td>
<td>0.50</td>
<td>b</td>
</tr>
<tr>
<td>$NO + 2.5H_2 + H_2O \rightarrow NH_3 + H_2O$</td>
<td>5</td>
<td>-121.7</td>
<td>-96.4</td>
<td>0.84</td>
<td>b</td>
</tr>
<tr>
<td><strong>Halogena tions:</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$C_2H_4 + Cl_2 \rightarrow CHClCH_2Cl$</td>
<td>2</td>
<td>-52.2</td>
<td>-35.5</td>
<td>0.769</td>
<td>0.81</td>
</tr>
<tr>
<td>$C_2H_4 + Cl_2 + H_2O \rightarrow CH_2ClCH_2OH + HCl(\text{aq})$</td>
<td>2</td>
<td>-46.7</td>
<td>-35.6</td>
<td>0.742</td>
<td>0.81</td>
</tr>
<tr>
<td>$C_2H_4 + Br_2 \rightarrow CH_2BrCH_2Br$</td>
<td>2</td>
<td>-23.3</td>
<td>-21.2</td>
<td>0.460</td>
<td>0.61</td>
</tr>
<tr>
<td><strong>Oxidations:</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$C_2H_2OH + 0.5O_2 \rightarrow CH_3CHO + H_2O$</td>
<td>2</td>
<td>-51.8</td>
<td>-48.4</td>
<td>1.05</td>
<td>0.64</td>
</tr>
<tr>
<td>$C_2H_4OH + 0.5O_2 \rightarrow CH_2COOH + H_2O$</td>
<td>4</td>
<td>-128.5</td>
<td>-110.2</td>
<td>1.20</td>
<td>0.64</td>
</tr>
<tr>
<td>$C_2H_2OH + 0.5O_2 \rightarrow C_2H_4O_2$</td>
<td>12</td>
<td>-396.8</td>
<td>-318.3</td>
<td>1.15</td>
<td>0.64</td>
</tr>
<tr>
<td>$C_2H_4 + 0.5O_2 \rightarrow C_2H_2O$</td>
<td>2</td>
<td>-65.3</td>
<td>-53.3</td>
<td>1.16</td>
<td>b</td>
</tr>
<tr>
<td>$SO_2 + 0.5O_2 + H_2O \rightarrow H_2SO_4(\text{aq})$</td>
<td>2</td>
<td>-77.6</td>
<td>-48.8</td>
<td>1.06</td>
<td>0.65</td>
</tr>
</tbody>
</table>

| Hydrogen ions was kept constant, at steady state positive potentials, while the other was varied under conditions where transport was not limiting. Thus, an order in each reactant at the cathode could be determined from: |

$$
\left( \frac{\delta \log \text{i}}{\delta \log \text{C}_i} \right)_{T,[\text{Cl}]} = Z_i \quad (v)
$$

with the assumption of a simple exponential rate expression for the rate of reaction. Here, i is current density, T is temperature, E is potential, and C_i represents the concentration of a specific reactant at the electrode, C_1 is the concentration of other reactants, and Z_i is the order of reaction with respect to any reactant. In recent years, more elaborate studies have been conducted on this hydrogenation reaction (26-28) for both platinum and palladium catalysts.

A variety of electrogenerative halogenation systems can also be operated to give dihaloalkanes and haloalcohols (6, 7, 16, 29) with olefins introduced at the anode. With electrogenerative bromination, for example, the overall electrode reactions with aqueous bromide electrolyte are:

**Cathode:**  $Br_3 + 2e \rightarrow 2Br^-$  (vi)

**Anode:**  $RCH=CHR' + 2Br^- + 2e + RCH-CHR' \rightarrow Br + OH$  (vii)

When Reaction (viii) occurs the electrolyte is no longer invariant. One challenge is to control the system so that either Reaction (vii) or (viii) occurs selectively, since either bromohydrin or dibromoalkane can be the desired product. Control of selectivity, through potential or electrocatalysts at the anode, in order to favour either dihaloalkanes or haloalcohols has been described elsewhere for electrogenerative halogenations (16, 29). With a mixed reaction route available at the anode, as well as irreversibility, it is not surprising that the open circuit voltages for this system vary somewhat from those...
calculated, as are shown in the Table.

The "potential windows" for the operation of cells for electrogenerative hydrogenation and bromination of ethylene are shown in Figure 2, together with the standard potentials of the reversible hydrogen and bromine electrodes, respectively. Potential regions on this scale where corresponding, energy consuming, electrolytic processes generally are operated are also indicated. It can be seen that the potential regions tend to be different. Electrogenerative hydrogenation occurs above the standard hydrogen reversible potential (~0 V) at positive voltages, while electrogenerative bromination occurs below the standard bromine/bromide reversible potential (~1.06 V) where bromide ion ordinarily would be discharged; see the caption discussion in Figure 2. Thus, for both types of reactions, the driving force for product formation in the electrogenerative mode contributes to ion discharge and the overall reaction at the electrode.

Nitric oxide, a gas of special interest from both basic and environmental considerations can also be reduced in the electrogenerative mode as a consequence of favourable thermodynamics (ΔG < 0, see Table), in a cell similar to that shown as Figure 1. A polarisation or performance curve, A, corrected for ohmic loss in the electrolyte (IR correction), for the nitrogen oxide/hydrogen system at a moderate nitric oxide flow rate is shown in Figure 3; reaction conditions are indicated in the caption (30).

For comparison, the curve without IR correction is also presented in this Figure. The correction or voltage loss varies with current. Substantial currents of the order of 100 mA/cm² or higher are seen to be generated in the nitric oxide/hydrogen system with high surface area LAA-2 gas diffusion electrodes, which are gas permeable as well as electrolyte impermeable (31).

With the porous, catalytic electrodes, the following nitric oxide reactions can take place and have been observed under varying conditions:

\[
\begin{align*}
\text{Cathode:} & \\
2\text{NO} + 2\text{H}^+ + 2\text{e}^- & \rightarrow \text{N}_2\text{O} + \text{H}_2\text{O} \quad E^\circ = 1.59 \quad \text{(ix)} \\
2\text{NO} + 4\text{H}^+ + 4\text{e}^- & \rightarrow \text{N}_2 + 2\text{H}_2\text{O} \quad E^\circ = 1.6 \quad \text{(x)} \\
2\text{NO} + 6\text{H}^+ + 6\text{e}^- & \rightarrow 2\text{NH}_3 + 2\text{H}_2\text{O} \quad E^\circ = 0.38 \quad \text{(xi)} \\
2\text{NO} + 10\text{H}^+ + 10\text{e}^- & \rightarrow 2\text{NH}_3 + 2\text{H}_2\text{O} \quad E^\circ = 0.73 \quad \text{(xii)}
\end{align*}
\]

where \(E^\circ\) is the standard potential for these reactions. The hydrogen oxidation reaction at the platinum anode (Equation (i)) occurs fairly reversibly and readily, close to 0 V. Similar nitric oxide reduction products have been reported in a variety of heterogeneous catalytic studies. At the electrogenerative nitric oxide electrode, product selectivity is determined by kinetics and mechanism under the indicated cell conditions as well as by thermodynamics (17, 32, 33). Standard potential alone does not determine the course of the reaction.

The polarisation behaviour shown in Figure 3 can be interpreted in terms of two potential regions (30). From open circuit, 0.9, to 0.4 V...
nitrous oxide (laughing gas) is the major product. The sharp potential drop with virtually no current increase corresponds to complete depletion of the entering nitric oxide stream (100 per cent conversion). Such limiting current behaviour can be observed with platinum electrocatalysts with relatively low nitric oxide flows, and corresponds to Reaction (ix).

For further selectivity analyses, current efficiencies (CE) can be considered. These are based on the calculated current for any product using the production rate and the number of electrons indicated in Equations (ix) to (xii) for the calculation, and dividing by the total measured current at a given potential (30, 34). The current efficiencies found in our laboratories (30) with perchlorate electrolyte are represented in Figure 4 as a function of the cathode potential referred to the reversible hydrogen electrode (RHE). Below 0.4 V the nitrous oxide current efficiency decreases sharply, while significant nitrogen formation begins; see Figure 4 and refer to Figure 3, (Curve A). The current efficiency for nitrogen formation, Reaction (x), goes through a maximum around 0.25 V. Ammonia formation also begins as nitrous oxide production drops off, at about 0.3 V. It is the major product at potentials below 0.15 V. While some hydroxylamine is formed at potentials below 0.3 V, the current efficiency for its formation is not important (< 5 per cent) relative to other products under these conditions. However palladium, rhodium and ruthenium electrocatalysts all tend to promote more hydroxylamine formation (17). Both ammonia and hydroxylamine accumulate in the acid electrolyte while nitrogen and nitrous oxide exit in the cathode effluent.

Hydroxylamine is of special interest because it is relatively valuable, being used in the manufacture of caprolactam and aldoximes. Selectivity to hydroxylamine, Equation (xi), can be favoured by altering the conditions in a variety of ways (electrolyte, catalyst, etc.) (17, 34). By depositing sulphur in a controlled manner on the platinum catalyst, current efficiencies for hydroxylamine formation of ninety per cent or higher can be achieved (18, 33). These and other results suggest that there is the possibility of utilising an electrogenerative operation to produce hydroxylamine, as an alternative to the heterogeneous catalytic process (35). One special advantage of the electrogenerative option

---

**Fig. 3** NO/H₂ cell polarisation curves for nitric oxide reduction show: Curve A: IR corrected; dashed line, A', uncorrected for ohmic drop (IR loss). Platinum LAA-2 cathode at 25°C with 3M HClO₄ electrolyte; nitric oxide flow rate 5.4 cm³/min (30). Curve B, 2M HClO₄ electrolyte, nitric oxide flow rate 20 cm³/min (34). Both cells incorporate LAA-2 anodes

**Fig. 4.** Selectivity during nitric oxide reduction showing current efficiency versus cathode potential referred to hydrogen electrode (RHE). This is for cell of curve A in Figure 3. Ammonia current efficiency at 0.1 V was obtained with nitric oxide flow of 0.6 cm³/min (30)
is that both anode and cathode gaseous effluents can be recycled without any need for a separation stage.

The selectivity features of the nitric oxide/hydrogen system are illustrative of significant factors which can arise in electrogenerative processing, as compared with fuel cell operation. Besides selectivity, special problems include controlled catalysis and catalytic activity, as well as reactant and product recovery from processed streams. As can be seen from Figure 4, if attempts are made merely to maximise power or DC current generation without regard to desired chemical selectivity, cell operation might be shifted to unfavourable voltage ranges. The optimal conditions of operation also illustrate an important advantage for electrogenerative processing as compared with heterogeneous catalysis, in that the former offers the special possibility of controlling selectivity and rate through electrode potential, as well as through altering catalyst, surface structure and concentrations.

Currents in the nitric oxide/hydrogen cell can also be increased considerably through increased nitric oxide flow rate at the anode, in order to produce selectively nitrous oxide which is also of value. A polarisation curve for such a situation is shown as curve B in Figure 3. Of special interest is the fact that electrogenerative cells can be operated so that nitric oxide, in dilute gas mixtures, is reduced to a very low level (32-34, 36) suggesting a possible electrogenerative application to waste gas treatments.

**Electrogenerative Processing of Potential Polluting Streams**

Flue gas treatments or aspects of these treatments are among the most interesting potential applications for electrogenerative processes. Sulphur dioxide and nitrogen oxides present in the flue gas emitted from fossil fuel-fired power generators are recognised as the largest source of acid rain in the United States of America, and are very significant factors elsewhere. These atmospheric pollutants are also associated with other types of processing, such as nitric oxide and sulphuric acid manufacture, as well as with waste incineration and ore processing. Awareness of these problems continues to grow throughout the world. Electric utilities and industrial boilers were projected to emit 21 million tons of sulphur dioxide and 11 million tons of nitrogen oxides, accounting for 85 and 52 per cent, respectively, of these pollutant emissions during 1990 in the U.S.A. alone (37). A major portion of the sulphur dioxide emissions comes from older operations of modest capacity. With more coal-fired capacity coming online during the next decade, these types of operations may well be under pressure to achieve further emission reductions. In a comparison with conventional technology, electrochemical stages might well be more viable for modular, small-scale installation and so could emerge as better suited for these retrofit applications, as well as for some new uses. There was interest in electrochemical flue gas clean-up processes earlier (38, 39), but the high costs generally associated with them tended to discourage any

![Fig. 5. Polarisation curves are shown for sulphur dioxide oxidation with an oxygen cathode in an ion exchange membrane divided electrogenerative cell for sulphuric acid production. Electrolyte flows through cathode compartment into anode compartment. LAA-25 American Cyanamid electrodes are 5.1 cm², 25 mg Pt black/cm². Each electrolyte chamber is 4.8 mm thick. Cell resistance at 30°C (△) 0.38 ohms; at 60°C (●) about 0.31 ohms; the dashed line indicates cell voltage at 60°C corrected for IR, loss. RAI Research R4010 cation exchange membrane separator. E, is measured at terminals. Reproduced with permission (7), copyright (1985), ACS]
significant efforts. With electrogenerative processing, however, costs might be directed toward useful chemical production as well as to the elimination of pollutants. Earlier studies in our laboratories in connection with sulphuric acid production have shown that sulphur dioxide can be processed in electrogenerative cells at ambient temperature, and at 60–70°C, to give sulphuric acid and high currents (7,9) although both the sulphur dioxide and the oxygen electrodes operate about two-tenths of a volt away from standard potentials, even at open circuit. Cell performances with current densities approaching 200 mA/cm² are illustrated in Figure 5. The electrode reactions for sulphur dioxide oxidation can be represented as shown below (40).

Anode:

\[ 2\text{SO}_2 + 4\text{H}_2\text{O} \rightarrow 2\text{H}_2\text{SO}_4 + 4\text{H}^+ + 4e^- \quad \text{E}^0 = +0.17 \ (\text{xiii}) \]

Cathode:

\[ \text{O}_2 + 4\text{H}^+ + 4e^- \rightarrow 2\text{H}_2\text{O} \quad \text{E}^0 = 1.229 \ (\text{xiv}) \]

Overall:

\[ 2\text{SO}_2 + \text{O}_2 + 2\text{H}_2\text{O} \rightarrow 2\text{H}_2\text{SO}_4 \quad \text{E}^0 = 1.06 \ (\text{xv}) \]

A general electrochemical approach to the flue gas clean-up not involving an external power source can then be proposed (41, 42). One possibility, a modification of a standard approach, is shown in Figure 6. Particulates, sulphur dioxide and nitric oxide are all removed in separate stages. As we have seen, the pertinent electrogenerative reactions for flue gas clean-up have been demonstrated to be feasible separately at high currents in preliminary reactor studies. These are sulphur dioxide oxidation to sulphuric acid, Equation (xv), and nitric oxide reduction to ammonia or hydroxylamine. Efforts for implementing these processes in clean-up would be in the direction of modifying them to meet performance criteria (including costs) for each stage, so that one or both types of reactors could be applied for low sulphur dioxide or nitric oxide concentrations. While platinum group catalysts in bulk form have been satisfactory for feasibility testing, catalysts supported on conductors such as carbon and in other configurations will be required for the future, because of economic considerations.

Dilute gaseous streams containing sulphur dioxide might be treated directly, or concentrating procedures such as the Bergbau-Forschung and Wellman-Lord or related processes might be applied to provide more concentrated gas streams or solutions for liquid phase processing (41, 42). Both commercial gas diffusion type anodes and packed bed electrodes have been studied for processing and removing low sulphur dioxide concentrations from gaseous and from liquid streams (42, 43, 44). The gaseous concentrations have approached those of common flue gases (43). These cited studies also can be reviewed as models for investigating other dilute gas streams for clean-up through electrogenerative processing. In connection with the investigation on electrogenerative processing of dilute sulphur dioxide in our laboratories, additional work

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**Figure 6** A general electrochemical approach to flue gas clean-up which incorporates electrogenerative stages

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was done on a pretreatment for anodic current enhancement through sulphur deposition onto an electrocatalyst via sulphur dioxide reduction. While some related treatments were used by other investigators earlier, little had been done on high surface area porous electrode treatments for reproducible, steady state use.

For dilute sulphur dioxide studies with gas diffusion electrodes (43), the design of the cell of Figure 1 was altered to provide a rectangular working anode configuration of 13 x 51 mm (6.45 cm² in area). Results for electrogenerative processing of 1 per cent sulphur dioxide in nitrogen are shown in Figure 7, for an LAA-2 electrode. Currents, of course, are well below those observed earlier with concentrated sulphur dioxide gas streams. However, relatively high conversions of 89 per cent and 55 per cent, depending on flow rate, could be achieved even with this small working area. Other data, more comparable to scaled-up cells, were obtained at higher flow rates. For scale-up, higher conversion could be achieved from longer flow paths and even several separate stages in series with anodes operating at different potentials, depending on clean-up and power generating strategy. Further investigation of commercial type gas diffusion electrodes obtained through Johnson Matthey showed that a gas diffusion electrode (NSX88/4/E1) incorporating carbon support, platinum (1.5 mg/cm²) promoted with manganese, and a Teflon backing, would give an anode performance comparable to that of the more heavily loaded LAA-2 electrode which was used initially (43).

The effect on cell performance from lowering sulphur dioxide concentrations to levels close to those of effluent gas flow levels from power plants is illustrated in Figure 8. Differing high gas flow rates were used for various reasons but all were in substantial excess, so that the gas phase concentration was the critical factor in controlling the generated current. The important result is that electrogenerative operation is quite feasible at low concentrations and that these concentrations of sulphur dioxide can be reduced to still lower levels. Additional work has shown that even a three per cent oxygen concentration in a simulated 0.3 per cent sulphur dioxide effluent stream was not very deleterious to sulphur dioxide/oxygen cell performance when using a platinum-manganese/carbon anode and a high performance cathode with 3 molar sulphuric acid electrolyte (43).

An alternative strategy for processing sulphur dioxide from effluent gas streams is to anodically remove it from scrubbing liquors or solu-
tions resulting from concentrating procedures, such as those implied in the arrangement shown as Figure 6. With this in mind, oxidation of dissolved sulphur dioxide in liquid phase electrogenerative reactors with packed bed anodes also has been studied. In this feasibility investigation, platinum loadings in the range of 0.5 to 6 mg/cm² on porous graphite supports were emphasised (44). The hybrid type cell combined a gas diffusion cathode with the packed bed anode. Earlier work was done on both heavily loaded platinum anodes and graphite supported platinum (42), but the effects of a pretreatment protocol together with electrode preparation details were not quantified in many instances. Currents of 80 mA/cm² were generated though at room temperature with 0.5 M sulphur dioxide in 3 M sulphuric acid using a porous graphite anode sheet containing 18 mg/cm² of platinum and an efficient gas diffusion counter electrode in the hybrid cell and pretreatment. Further work showed that a loading decrease to 6 mg platinum/cm² could be attained with little sacrifice in performance.

Moving to lower loadings, it was found that with 1.5 mg platinum/cm² on the rectangular graphite sheet, packed bed anode (3 mm thick) in the hybrid cell, 55 per cent of entering 0.35 M sulphur dioxide in 3 M sulphuric acid electrolyte flowing at 0.63 cm³/min, could be converted (44). A polarisation curve for a faster flow rate is shown in Figure 9. Significant currents of the order of 3 mA/cm² could be generated even at 0.003 M sulphur dioxide concentrations. For the future we must determine the extent to which increased platinum dispersion can be achieved with improved preparation methods to lower catalyst loading.

As already indicated, earlier work showed that nitric oxide reduction is very feasible in electrogenerative cells (34, 41, 45) and currents of 100 mA/cm² or higher are readily achieved. With more than 10 million tons of nitrogen oxides – originally mostly nitric oxide – produced in stationary power plants in the United States of America each year there are attractive possibilities for the recovery of this effluent component in chemical form; see Reactions (xi) and (xii). Furthermore, if nitric oxide can be removed economically through electrogenerative processing, power plant protocol, which is formulated so as to minimise its formation, might even be altered. Little work has been done with supported catalysts and dilute nitric oxide streams. However with LAA-2 type electrodes and some sulphur pretreatment it has been shown that electrogenerative nitric oxide conversions are particularly effective (33, 46).

In studies with two to three per cent nitric oxide in various gaseous diluents, ninety to ninety five per cent conversions take place readily even in small scale laboratory cells with circular electrodes of the type in Figure 1.

Some questions regarding nitric oxide material balances remain for future consideration. The extent to which nitric oxide can be reduced to nitrogen (30, 47) has not been evaluated for dilute nitric oxide streams, and the maximum achievable concentrations of electrolyte soluble products must be determined. For flue gas clean-up applications, studies of operations with gas diffusion electrodes at low nitric oxide feed concentrations, for example 0.05 per cent, still must be undertaken. To process feed for cost effective current densities, that is, adequate nitric oxide removal rates, cells with special cathode gas channels may be required. Flow
across the face of the electrode should be controlled so as to assure lateral dispersion, while pressure drop must not be excessive. This type of problem, and others not discussed, are part of the challenge in future electrogenerative reactor design (48).

Additional Electrogenerative Possibilities

With growing interest in facets of biomass processing, alcohol oxidations to aldehydes or ketones become another area worthy of attention. Ethanol oxidation is of special interest particularly in the presence of water or water vapour. This is because the acetaldehyde product has a low boiling point (20.8°C) which facilitates subsequent separation where desired. In Figure 10, the rates of production of acetaldehyde and carbon dioxide from aqueous ethanolic vapour at a platinum anode, in a cell with an oxygen cathode, are compared (6). Their formation can be represented by Equations (xvi) and (xvii):

\[
\text{CH}_3\text{CH}_2\text{OH} \rightarrow \text{CH}_3\text{CHO} + 2\text{H}^+ + 2\text{e} \quad \text{(xvi)}
\]

\[
\text{CH}_3\text{CH}_2\text{OH} + 3\text{H}_2\text{O} \rightarrow 2\text{CO}_2 + 12\text{H}^+ + 12\text{e} \quad \text{(xvii)}
\]

while at the cathode

\[
\text{O}_2 + 4\text{H}^+ + 4\text{e} \rightarrow 2\text{H}_2\text{O} \quad \text{(xviii)}
\]

Reaction (xvi) would be the desired one. In Figure 10, it can be seen that as the anode potential increases, acetaldehyde production also increases, reaching a maximum at about 0.68 V (versus RHE). At a higher voltage, the production of acetaldehyde then diminishes while undesired carbon dioxide formation, a desired fuel cell reaction, increases. Above about 0.73 V, catalyst activity deteriorates with time reflecting platinum oxide formation and catalyst deactivation (6). Thus, even though there is a pronounced increase in cell current with increasing potential, acetaldehyde selectivity considerations dictate the range and potential region of operation for this cell. It can be further noted that while an open circuit cell voltage of 1.05 can be calculated for standard conditions, as shown in the Table, the observed value is 0.64 V. Neither the ethanol anode nor the oxygen cathode ordinarily operate close to reversible potentials. Nevertheless, controlled electrogenerative conversion of ethanolic vapour to acetaldehyde seems feasible.

Stafford adapted fuel cell type components for a study of the electrogenerative oxidation of propylene at a palladium catalysed anode, using 25 per cent phosphoric acid electrolyte in the temperature range of ambient to 80°C (12). The interesting and special catalytic properties of palladium for allylic oxidation were demonstrated through the formation of acrolein and acrylic acid. Although selectivity was poor and currents were low in this pioneering effort, future improvements can be anticipated. Experiments with similar results to those of Stafford but with the catalysts deposited on solid polymer electrolytes have been reported more recently by Japanese workers (49). A number of related studies with solid polymer electrolytes have also been described (50).

Prospects for the Future

Electrogenerative systems differ from conventional electrolytic processing systems in that the need for an external power source can be
eliminated in many instances, thus providing advantages with respect to ease and scale of operation as well as capital investment. Even at the present stage of development, there is the promise that with minor refinements these cells can be developed advantageously to become standard laboratory devices since electrogenerative processing can be convenient while retaining many advantages of conventional electrolytic processing relative to heterogeneous catalysis. Among these are simple reaction rate control and special selectivity, as well as the capacity for operation under mild, controlled conditions. Views on costs and related factors in conventional electrochemical processing have been clouded by the uncertainty about future electric power costs and capital investment needs for equipment. However, when nine proposed electrochemical processes were thoroughly reviewed and analysed (3), the electrogenerative based preparation of methyl ethyl ketone from butene was one of two selected for potential future energy savings relative to corresponding chemical processes (51).

Limited work with electrogenerative and related systems to-date has also limited the recognition of their potential applications and their special features despite some recent activity in this direction (9, 10, 12, 49). While the types of processes studied in our laboratories have been emphasised here, other investigators, already cited, have emphasised solid electrolytes (20, 21) or catalytic electrodes supported on solid polymer electrolytes (49, 50). Interested readers may wish to consult the references provided here to work beyond the scope and breadth of this introductory discussion and identify additional candidate electrogenerative systems. Platinum and palladium have been the catalysts emphasised in work to-date but many possibilities exist for controlling selectivity with other metals and different approaches (17, 30, 46, 48). Electrogenerative type operations would seem to hold special promise for the future, even with modest electrochemical energy recovery. They might alleviate future energy needs while providing special advantages. With external electrochemical energy recovery, process cooling costs for highly exothermic reactions might be reduced (9). Basic research in this area also offers the promise of providing a link between heterogeneous gas phase catalytic systems and electrochemical syntheses (26, 27, 52). Further advances expected in the near future, should stimulate other workers and planners to give serious consideration to electrogenerative or related electrochemical routes in the processing industries.

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Platinum Metals in Catalysis

A REVIEW OF SOME OF THE PAPERS PRESENTED AT THE TENTH INTERNATIONAL CONGRESS ON CATALYSIS

The 10th International Congress on Catalysis, arranged by an Organising Committee chaired by Professor L. Guzci (and sponsored by the International Union of Pure and Applied Chemistry, the Chemistry Section of the Hungarian Academy of Sciences, the Federation of European Chemical Societies and the Hungarian Chemical Society), took place in Budapest from 19th to 24th July, 1992. It was attended by about 1000 persons; more than 100 papers were presented and over 350 posters were available for inspection. With such rich fare, it is impossible to do justice to all the contributions relating to catalysis by the platinum group metals. Reluctantly, therefore, attention is confined to the orally presented papers, and within this group almost one-third referred to platinum group metals.

Catalysis on Single Crystal Surfaces

Many powerful techniques are now available for the study of molecules chemisorbed on single-crystal metal surfaces, and important extensions now permit catalytic interactions between adsorbed molecules to be examined. It is however necessary to remember that there will be differences as well as similarities between these systems and the small supported metal particles found in practical catalysts. These factors are well illustrated by a group of papers discussed at the Congress.

It is now firmly established that some catalysed oxidation reactions, particularly the carbon monoxide-oxygen reaction, can under certain conditions exhibit oscillation. Use of photoemission electron microscopy, which senses the work function variation over the surface, showed that on Pd(110) various travelling waves and spatial patterns were formed in consequence of “gas-phase communication” (M. Ehsasi, M. Berdau, A. Karpowicz, K. Christmann and J. H. Bloch, Fritz-Haber Institut and Freie Universität, Berlin). Clearly such waves and patterns cannot exist on very small metal particles, but supported metals also show oscillatory phenomena, presumably because gas-phase communication is also possible there.

The trimerisation of ethyne to benzene is another reaction which has been well studied on palladium catalysts. C. J. Baddeley, R. M. Ormerod and R. M. Lambert (Cambridge University) reported that simultaneous adsorption of nitric oxide on Pd(111) caused compression of the adsorbed ethyne phase, with a consequent increase in rate. Palladium on alumina catalysts are also active in this reaction, and the use of bimetallic palladium-gold catalysts, formed by evaporating palladium onto Au(111), showed the extreme structure-sensitivity of the reaction.

The way in which the inert partner in a bimetallic catalyst affects the behaviour of the active one has been debated for many years, the consensus now being that it merely serves to reduce the mean ensemble size of the active element. However when palladium is deposited by evaporation onto tantalum, tungsten, rhenium and ruthenium surfaces, there are distinct differences in the palladium 3d binding energy observed in XPS, and in the temperatures at which adsorbed carbon monoxide desorbs (R. A. Campbell, J. A. Rodriguez and D. W. Goodman, Texas A and M University). This betokens some electronic modification, but, as the subsequent discussion showed, the interpretation is still controversial.

Noble Metals in Zeolites

Turning now to metals in a highly dispersed form, several papers presented results on small noble metal particles in zeolite cavities. The discovery, reported in 1980, that platinum particles in the non-acidic L-zeolite were highly selective in dehydrocyclisation of n-hexane to
benzene has generated a number of further studies of this system, some of which were reported at this Congress. E. Iglesia and J. E. Baumgartner (Exxon Research and Engineering Co.) discussed the reaction mechanism in terms of inhibited deactivation of platinum sites within zeolite channels, while the effects of sulphur on platinum/KL-zeolite (J. L. Kao, G. B. McVicker, M. M. J. Treacy, S. B. Rice, J. L. Robbins, W. E. Gates, J. J. Ziemik, V. R. Cross and T. H. Vanderspurt from the same organisation) and of the type of cation on n-heptane aromatisation (R. F. Hicks, W.-J. Han and A. B. Kooh, University of California) were also described. G. Larsen and G. L. Haller (Yale University) prepared and studied palladium/L-zeolite catalysts made both by impregnation and ion exchange, and M. Vaarkamp, J. T. Miller, F. S. Modica; G. S. Lane and D. C. Koningsberger (Eindhoven University) used the intensities of the white lines at the $L_{2}$ and $L_{3}$ X-ray absorption edges to determine the local density of states. They concluded that platinum particles on acidic supports were more electron-deficient than those on neutral supports.

Two studies were reported of bimetallic particles in the cavities of Y zeolite. W. M. H. Sachtler, Z. Zhang, A. Yu. Stakheev and J. S. Feeley (Northwestern University, Evanston) examined palladium-nickel/Y-zeolite catalysts using XRD and EXAFS, and found that during carbon monoxide hydrogenation there was a pronounced metal redistribution at the macroscopic level. O Bong Yang and Seong Ihl Woo (Korea Advanced Institute of Science and Technology) prepared platinum-iridium particles in NaY-zeolite and found that they were more active and stable in n-heptane reforming than the monometallic platinum analogue.

**Supported Metal Catalysts**

Zeolites represent a somewhat special class of supports for metals, with their regular pore structure and facility for acid/base control. Interest continues at a high level in dispersed metals on more usual supports such as silica and alumina; the applicability of catalysts of this type in petroleum reforming clearly influences the kind of work performed. However, the interpretation of the behaviour of bimetallic catalysts continues to be the subject of debate, but in the cases of platinum-rhenium and platinum-tin reforming catalysts there are questions concerning the interaction of the second element with the support. G. Munuera, P. Malet and A. Caballero (Seville Institute of Science of Materials) explored the effect of Cl in stabilising the interaction of Re$^{+}$ with the alumina support, while G. C. Bond, R. H. Cunningham and E. L. Short (Brunel University, U.K.) determined the kinetics of hydrogenolysis of the lower alkanes on typical reforming catalysts which were either clean or partially coked. Disagreement still continues concerning the role of tin in platinum-tin reforming catalysts; J. Schwank, K. Balakrishnan and A. Sachdev (University of Michigan) concluded that most of the platinum was in a monometallic form, but that the particles were in contact with ionic tin (2+ or 4+) associated with the alumina support. B. H. Davis (University of Kentucky) on the other hand detected platinum-tin alloys, with the role of the tin depending on the acidity of the support. Clearly more research is needed to resolve these conflicting findings.

Other techniques of great potential usefulness in the characterisation of catalysts and their precursors were described. Scanning tunnelling microscopy (STM) permits the creation of images of surfaces with a resolution approaching the atomic scale, and M. Komiyama and M. Kirino (Yamanashi University, Japan) reported topographic and barrier-height images of platinum particles vacuum-deposited on thick silica films. The resolution is however not yet sufficient to afford information of great value. Laser Raman spectroscopy (LRS) on the other hand can sensitively detect oxides of the platinum group metals (rhodium, iridium and platinum) attached to ceria microphases in ceria-alumina mixed oxide supports (L. L. Murrell, S. J. Tauster and D. R. Anderson, Engelhard Corporation).

The use of a neutral zeolitic support, as described above, is not essential for the effective
conversion of linear alkanes to aromatics. E. G. Derouane, V. Jullien-Lardot, R. J. Davis, N. Blom and P. E. Højlund-Nielsen (Facultés Universitaires, Namur) have demonstrated that palladium on alumina-stabilised magnesia affords high selectivities in conversion of n-hexane to benzene. They used $^{27}$Al magic-angle spinning NMR to show that $\text{Al}^{3+}$ ions occupied both tetrahedral and octahedral holes in the magnetic structure.

**Syngas Reactions**

The popularity of syngas reactions as a subject for research is now much diminished, and only three contributions to the Congress dealt with the role of the platinum metals as catalysts for these reactions. Rhodium is well-known for its ability to give higher oxygenates, especially ethanol, and A. L. Borer and R. Prins (Federal Institute of Technology, Zurich) confirmed previous findings on the promoting effect of lanthanum on rhodium on silica catalysts. They showed moreover that the order in which the components are introduced to the support is important, higher dispersions of rhodium being obtained when lanthanum is applied first to the silica. Higher oxygenates can also be produced when carbon monoxide reacts on rhodium catalysts with adsorbed species formed from chlorinated molecules and alkenes (M. W. Balakos, S. C. Chuang, R. Krishnamurthy and G. Srinivas, University of Akron). K. R. Krishna and A. T. Bell (University of California, Lawrence Berkeley Laboratory) applied transient-response isotopic tracer methods to follow chain-growth during Fischer-Tropsch synthesis on ruthenium upon titania catalysts. The chain-growth probability, $\alpha$, decreases with temperature because the activation energy for termination exceeds that for propagation.

**Conclusion**

The 10th International Congress on Catalysis proved a most stimulating and enjoyable occasion, and the organisation was faultless. The posters, as well as the papers presented orally, confirmed the pre-eminent role of the metals of the platinum group in the field of heterogeneous catalysis. The proceedings will be published in the first half of 1993. The 11th Congress will take place in Baltimore, Maryland, U.S.A, in 1996. G.C.B.

**Progress in Palladium Membrane Catalysis**

In the April 1992 issue of this journal two papers from Russia were concerned with palladium alloy membrane technology (1, 2). Now this topic has again been featured, in a useful review of high temperature membrane catalysis by John N. Armor of Air Products & Chemicals, Inc., Allentown, Pennsylvania (3).

High temperature membranes are those that can be used at temperatures above 200°C, and suitable materials include: inorganic oxides, carbon, palladium and its alloys, and composites. While the use of palladium-based membranes is limited to reactions that involve hydrogen, the high solubility of hydrogen in palladium and the fact that it is currently being fabricated into thin foils makes it particularly suitable for these reactions. To avoid problems associated with the $\alpha/\beta$ phase transformation, the operating temperature should be above 310°C.

The benefits that are encountered when palladium is alloyed with silver, ruthenium, rhodium and rare earths, are considered, as are the limitations of such membranes. For the future, the potential for commercial exploitation is seen to be with catalytic materials deposited on monomodal sub–8 Å inorganic membranes, and with thin metal alloy coatings on mesoporous supports. Already studies have been made of composite membranes consisting of palladium and silver-palladium deposited on the outer surface of porous glass tubes and porous alumina cylinders by electroless plating techniques.

While many problems have still to be overcome, it is concluded that the progress made to-date in membrane catalysis encourages further fundamental research on the topic.

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It is as Alfred Werner's primary scientific adversary and the chemist whose work on co-ordination compounds provided the experimental basis for Werner's revolutionary co-ordination theory that Jørgensen is usually remembered. Yet in his work on what were then called "molecular compounds" he made valuable contributions to our basic knowledge of rhodium and platinum complexes.

Although unjustly neglected today, Sophus Mads Jørgensen was an important chemist during his lifetime, and his work aroused great interest among his contemporaries. In 1906 the French Académie des Sciences presented him with its Lavoisier Medal. Early in 1907, the first year in which Alfred Werner was nominated for the prize, Jørgensen received two nominations for the prize — by 1906 Nobel chemistry laureate Henri Moissan (1852–1907) and Jean-Gaston Darboux (1842–1917) of the Institut de France, Académie des Sciences (1). In his nomination Darboux cited "parmi les travaux de M. Jørgensen l'ensemble de ses recherches sur les bases ammoniées métalliques et plus particulièrement sur les bases du platine" (2). Moissan died later that year, and Jørgensen was never renominated.

The Werner-Jørgensen Controversy

Today most chemists, regardless of their fields of specialisation, are acquainted with the nature and importance of the work of Alfred Werner (1866–1919) (3–5). Indeed, almost every chemistry student is now introduced to at least the essentials of his co-ordination theory. Yet, except

Sophus Mads Jørgensen
1837–1914

While his fame rests upon his investigation of the co-ordination compounds of platinum, rhodium, cobalt and chromium, he also had an illustrious career as a teacher. During his forty-one years of teaching, he exerted a profound influence on an entire generation of Danish chemists. Through his textbooks he was able to extend his teaching influence far beyond his own country. Probably his most famous text is "Fundamentals of Chemistry", published in 1902. In it he gave a summary of the basic concepts of chemistry and also a survey of its historical development. This was translated into several languages, including German, Italian, Greek and English. Jørgensen undertook a wide variety of activities, for example being President of the Kemisk Forening from its foundation in 1879 until 1902 and from 1903 to 1906. From 1871 he was a member of the Board of Directors of the Rosenborg Brandanstalt.
for those who have had occasion to delve into the study of complex compounds, Jørgensen's name remains entirely unknown.

Few realise that Werner's new and revolutionary theory was based upon experimental data carefully and painstakingly accumulated over a number of years by Sophus Mads Jørgensen, Professor of Chemistry at the University of Copenhagen. It is perhaps not an exaggeration to say that Werner's theory might never have been proposed had not Jørgensen's work provided the observations requiring explanation.

Except for some early isolated organic and inorganic research, Jørgensen devoted himself exclusively to investigating the co-ordination compounds of cobalt, chromium, rhodium and platinum; this important work was carried out between 1878 and 1906. Jørgensen created no new structural theory of his own. His interpretations of the luteo (hexaammines), purpureo (halopentaammines), roseo (aquapentaammines), praseo (trans-dihalotetraammines), violo (cis-dihalotetraammines), croceo (trans-dinitrotetraammines), flavo (cis-dinitrotetraammines) and other series of co-ordination compounds were made in the light of his logical extensions to and modifications of the famous chain theory of the Swedish chemist Christian Wilhelm Blomstrand.

For fifteen years Jørgensen's views remained the most acceptable of the numerous theories advanced to explain the properties and reactions of the so-called molecular compounds, which were not explicable in terms of the contemporary valence theory.

In 1893 Alfred Werner, an unknown twenty-six-year-old Privat-Dozent at the Eidgenössisches Polytechnikum in Zürich, challenged the old system with his radically new co-ordination theory (4b). The ensuing controversy between Jørgensen and Werner constitutes an excellent example of the synergism so often encountered in the history of science (6). Jørgensen's strong sense of history caused him to view Werner's new theory as an unwarranted break in the development of the theories of chemical structure. He regarded it as an ad hoc explanation insuff-
continued his studies with the encouragement of Professor Edward Augustus Scharling. In 1863 he received his Master of Science degree in chemistry. He then worked at the university until 1864 becoming Scharling's assistant.

Three years later he became a manager of the chemical laboratories and an instructor at the Polytekniske Laereanstalt (Polytechnic School). In 1869 he received his doctorate with the dissertation, “Polyiodides of Alkaloids”. In 1871 he married Louise Wellmann, and in the same year he became a lecturer at the university. In 1887 he became Professor of Chemistry, a position which he held until his retirement in 1908. Jørgensen died on April 1, 1914 and is buried in the Holmen Cemetery in Copenhagen (6-10).

As a research worker, Jørgensen was methodical, deliberate and careful. Although he could have delegated much routine work to assistants, he insisted on personally performing all his analyses. He reserved one day per week specifically for this task (11). In spite of his passion for perfection, his output was tremendous, and we are indebted to him for many of the basic experimental facts of co-ordination chemistry.

Like many famous chemists, Jørgensen was not content merely to make original contributions in the laboratory but was also keenly interested in the historical development of chemistry, especially in Denmark. His studies in this field are characterised by the same enthusiasm and thorough workmanship shown in his laboratory investigations. Unfortunately, few of these studies have been published.

Considering the volume and quality of Jørgensen’s work, it is difficult to see how he found time to participate in the scientific and administrative activities that he undertook. He also served as an associate editor of the Zeitschrift für Anorganische Chemie from its founding in 1892 until his death.

Jørgensen also held many administrative positions. From 1871 until his death he was a member of the Board of Directors of the Rosenborg Bændanstalt. From 1872 to 1908 he was technical consultant for the Customs Administration and Harbour Administration. In 1885 he was elected a member of the Board of Directors of the Carlsberg Foundation, and in 1909 he became chairman, a post which he held until 1913 when illness forced him to resign. From 1886 until his death he was a member of the Direktion of the Selskabet for Naturlærens Udbredelse. In 1889 he was elected chairman of the Carlsberg Laboratories. He was also a member of commissions for sugar (1870), pharmacopoeia (1889) and gypsum (1893).

Jørgensen’s Research

Jørgensen’s research, which resulted in 76 articles and 19 books (8b) can be divided into seven groups. The first (1866–1878) includes a few isolated papers and his work on alkaloid polyiodides (the subject of his doctoral dissertation), while the other six (1878–1906) constitute the work for which he was famous – his investigations of metal-ammine complexes. These studies appeared in various publications of the Videnskaberens Selskab, then in the Journal für Praktische Chemie, and after 1892 in the newly founded Zeitschrift für Anorganische Chemie. Indeed, the fortunate subscriber had an opportunity to follow the scientific controversy between Jørgensen and Werner.

Platinum Compounds

Jørgensen’s first work on inorganic co-ordination compounds involved platinum rather than the cobalt-ammines which figured so prominently in the Werner-Jørgensen controversy. In the first article Jørgensen described platinosoplatinic oxide, PtO₄, prepared by fusing Na₂[PtCl₄] with Na₂CO₃ and washing the black residue with water, dilute HNO₃, and aqua regia (12). The “compound”, which is reduced to platinum black by formic acid, hydrogen, or coal gas, was later shown to be a mixture of PtO and PtO₂ (13). In the second article Jørgensen described yellow Ag₂[PtCl₆] (formulated as 2AgCl.PtCl₄), prepared by metathesis of AgNO₃ and H₂[PtCl₆]; the compound reacted with water:

Ag₂[PtCl₆] + 2H₂O → H₂[PtCl₄(OH)₂] + 2AgCl↓

He also prepared PtCl₆(OH)₂ (the anhydride
of \( \text{H}_2[\text{PtCl}_3(\text{OH})_2] \) and \( \text{H}_2[\text{PtCl}(\text{OH})_3] \) (prepared only in solution and formulated as a solution of \( \text{PtCl}(\text{OH})_3 \) (14). In his research on various complex cations of different metals Jørgensen routinely prepared \( \text{[PtCl}_6]^{2-} \) and \( \text{[PtCl}_5]^{3-} \) salts, but these works need not be considered here.

In his first article on the platinum(II)-ammines Jørgensen attempted to elucidate the constitution and isomerism of compounds (15). In this classic work he prepared the cis and trans isomers of \( \text{[PtCl}_4(\text{NH}_3)_2] \) (16), which he formulated in terms of the Blomstrand chain theory as:

\[
\begin{align*}
\text{Pt} & \hspace{1cm} \text{Cl} & \hspace{1cm} \text{NH}_3 & \hspace{1cm} \text{NH}_3 & \hspace{1cm} \text{Cl} \\
\text{Cl} & \hspace{1cm} \text{Pt} & \hspace{1cm} \text{Cl}
\end{align*}
\]

He used the reactions of these isomers with pyridine to decide which formula belongs to the one and which to the other series, preparing in the course of this proof the following compounds (modern formulae in parentheses):

- \( \text{platosemidipyridine chloride} \) (cis-\( \text{[PtCl}_2\text{py},] \)) (where py is pyridine) (17);
- \( \text{platosopyridine chloride} \) (trans-\( \text{[PtCl}_2\text{py},] \)) (17);
- \( \text{platodipyridine platinous chloride} \) (\( \text{[Pten}_2\text{Cl}] \));
- \( \text{platodesamminedamine chloride} \) (sic) chloride (\( \text{[Pten(NH}_3)_2\text{Cl}] \)).

In a subsequent paper, taking into account Petersen's later published evidence (19) for monomolecular molecular weights by freezing-point and conductance measurements, Jørgensen halved his formulae of the first and second compounds, formulating them as \( \text{Cl.Pt.en.Cl} \) and \( \text{Pt.en}_2\text{.Cl} \), respectively (20).

Jørgensen prepared the acid corresponding to Zeise's salt, \( \text{K[PtCl}_3(\text{C}_2\text{H}_4)\text{.H}_2\text{O]} \), by heating sodium hexachloroplatinate(IV) with ethanol (21):

\[
\text{Na}_2[\text{PtCl}_6] + 2\text{C}_2\text{H}_4\text{OH} \rightarrow \text{H[PtCl}_3(\text{C}_2\text{H}_4)\text{]} + 2\text{NaCl} + \text{HCl} + \text{CH}_3\text{CHO} + \text{H}_2\text{O}
\]

By metathesis with KCl and \( \text{NH}_4\text{Cl} \) he used it to prepare Zeise's salt, an improvement over Zeise's original method (22), and the corresponding ammonium salt, respectively. In the same article he also reported the preparation of \( \text{[PtCl}_4(\text{C}_2\text{H}_4)\text{]} \), \( \text{[Pt(NH}_3)_2\text{Cl}] \), and the compound \( \text{[Pt(NH}_3)_2\text{][PtCl}_2(\text{NH}_3)_2\text{]} \), first prepared by Alfonso Cossa (23).

Jørgensen described several methods for the preparation of platopyridinamminediamine chloride, \( \text{Ptpy}(\text{NH}_3)_2\text{Cl}_2\text{.H}_2\text{O} \), which on heating yielded cis-\( \text{[PtCl}_2\text{py}(\text{NH}_3)_2\text{]} \), trans-\( \text{[PtCl}_2\text{py},] \) and trans-\( \text{[PtCl}_2\text{py},] \) (24). He also prepared \( \text{[Ptpy(\text{NH}_3)_2][PtCl}_2\text{.H}_2\text{O},} \text{[Pten(\text{NH}_3)_2][PtCl}_4\text{]} \), and by various reactions he claimed that, contrary to Blomstrand's and Cleve's view, Peyrone's chloride (cis-\( \text{[PtCl}_2(\text{NH}_3)_2\text{]} \)) is the symmetrical compound \( \text{Cl.NH}_3\text{.Pt.NH}_3\text{.Cl} \), while Reiset's (second) chloride (trans-\( \text{[PtCl}_2(\text{NH}_3)_2\text{]} \)) is the unsymmetrical compound \( \text{Cl.NH}_3\text{.NH}_3\text{.Pt.Cl} \).

In the first of seven papers in the series "Über Metalldiaminverbindungen" Jørgensen was the first to prepare ethylenediamine complexes of platinum(II) and cobalt(III) and the first to recognise the bidentate nature of this organic ligand (18). He prepared platosemiediamine chloride, (PtCl=en)] where en is ethylenediamine); platodiethylenediamine chloride (\( \text{[Pten}_2\text{Cl}] \)); platodiethylenediamine platinous chloride (\( \text{[Pten}_3\text{[PtCl}_4\text{]} \)); and platoethylenediamineamine chloride (sic) chloride (\( \text{[Pten(NH}_3)_2\text{Cl}] \)).
prepared trans-$[\text{Pt} \text{py}_2(N\text{H}_3)_2]\text{Cl}_2 \cdot \text{H}_2\text{O}$ (15) and the platinum(IV) compounds, cis- and trans- $[\text{PtCl}_2\text{py}_2]$ (15, 24).

Six years later Jørgensen (25) treated the ethylenediamine salt of Zeise’s acid with cold water to yield yellow s-platoethylenediamine ethylene chloride:

$$\text{C}_2\text{H}_4(N\text{H}_3)_2(\text{Cl}_2\text{PtC}_2\text{H}_4\text{Cl}_2)\rightarrow \text{C}_2\text{H}_4(\text{ClNH}_2\text{PtC}_2\text{H}_4\text{Cl}_2) + 2\text{HCl}$$

The new compound has the structure:

$$\begin{array}{c}
\text{Cl} \quad \text{Pt} \quad \text{Cl} \\
\text{C}_2\text{H}_4 \quad \text{NHCH}_2\text{CH}_2\text{NH}_2 \quad \text{Cl} \\
\text{C}_2\text{H}_4
\end{array}$$

Jørgensen also reiterated his contention about the structures of Peyrone’s chloride and Reiset’s second chloride based on the reaction of Peyrone’s chloride with dimethylamine to yield cis-$[\text{PtCl}_2((\text{CH}_2)_2\text{NH})_2]$. He also prepared the salts $[\text{Pt}(\text{CH}_2)_2\text{NH}(\text{NH}_3)_2]X_2$, where $X = \text{Cl}$, Br or $[\text{PtCl}_4]$.

In his last published experimental article (26) and the only paper to bear the name of a co-author, Jørgensen described a red isomer of one of the earliest, most famous, and most important co-ordination compounds to be named after its discoverer, Magnus’ green salt, tetrakis(dimethylglyoximato)platinum(II) tetrachloroplatinate(II), discovered in 1828 (27) by Heinrich Gustav Magnus (28). The compound was obtained by the metathetical reaction used to prepare the green salt:

$$[\text{Pt}(\text{NH}_3)_4]\text{Cl}_2 + K_2[\text{PtCl}_4] \rightarrow [\text{Pt}(\text{NH}_3)_2][\text{PtCl}_4] \downarrow + 2\text{KCl}$$

Conditions favourable for the production of the red isomer are the absence of $K_2[\text{PtCl}_4]$ (traces of which are often present in $K_2[\text{PtCl}_4]$) and a very dilute neutral or slightly ammoniacal solution. The same isomer was also obtained by reaction of s-platoethylenediamine ethylene chloride (25) with $[\text{Pt}(\text{NH}_3)_4]\text{Cl}_2$ in the presence of a large excess of water. The red isomer is very stable when dry, but on boiling with water it is converted quantitatively into the green form. Jørgensen explained the isomerism, which has still not been satisfactorily explained (29), by the formulæ:

$$\begin{array}{c}
\text{Pt} \quad (\text{NH}_3)_2\text{Cl}_2 \\
\text{Pt} \quad (\text{red})
\end{array}$$

$$\begin{array}{c}
\text{Pt} \quad (\text{NH}_3)_2\text{Cl}_2 \\
\text{Pt} \quad (\text{green})
\end{array}$$

**Rhodium Compounds**

Jørgensen’s first article on rhodium compounds is a 2-page preliminary communication (30) in which he thanked the Carlsberg Foundation for providing him with costly rhodium so that he could extend his studies of metal-ammines ($\text{Metallammoniokomplexe}$). He announced that the rhodium complexes are completely analogous to the corresponding cobalt and chromium complexes, and he summarised the results of his experiments to be published in the future. The following year (1883), in his first detailed article, he reported the preparation of three new series of pentaaammines and one new series of tetraammines (31). The pentaaammines included $\text{Cl}_2(\text{Rh}_{10}\text{NH}_2)\text{X}_4$ (the doubled formulæ were still in use for cobalt, chromium and rhodium complexes), chloropurpureorhodium salts ($[\text{RhCl}(\text{NH}_3)_2]\text{X}_2$, where $X = \text{Cl}$, Br, I, OH, NO$_2$, CO$_2$, CO$_2$-$[\text{SiF}_4]$ or $[\text{PtCl}_4]$); $\text{Br}_2(\text{Rh}_{10}\text{NH}_2)\text{X}_4$ bromopurpureorhodium salts ($[\text{RhBr}(\text{NH}_3)_2]\text{X}_2$, where $X = \text{Br}$, I, NO$_2$, OH, CO$_2$, CO$_2$-$[\text{SiF}_4]$ or $[\text{PtBr}_4]$); and $\text{I}_2(\text{Rh}_{10}\text{NH}_2)\text{X}_4$ iodopurpureorhodium salts ($[\text{Rhl}(\text{NH}_3)_2]\text{X}_2$, where $X = \text{I}$, Cl, Br, OH, NO$_2$, CO$_2$, CO$_2$-$[\text{SiF}_4]$ or $[\text{PtI}_4]$). To the tetraammine series he assigned the formula $\text{Cl}_2(\text{Rh}_{10}\text{py})\text{X}_4$, and the name dichlorotetrapyridinerhodium salts ($[\text{RhCl}(\text{py})]\text{X}_2$, where $X = \text{Cl}$, Cl, HCl, Br, NO$_2$, OH, CO$_2$, CO$_2$-$[\text{SiF}_4]$ or $[\text{PtCl}_4]$).

Because $[\text{RhCl}(\text{NH}_3)_2]\text{Cl}_2$ and $[\text{RhBr}(\text{NH}_3)_2]\text{Br}_2$ can be prepared readily in a state of high purity and because the elements, other than rhodium, that they contain have had their atomic weights accurately ascertained, Jørgensen

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*Platinum Metals Rev., 1992, 36, (4)*
suggested that they could be used to determine the atomic weight of rhodium (31). By heating the chloride in air and afterwards in hydrogen and oxygen-free carbon dioxide, he obtained the atomic weight of 103.06 as the average of four determinations. Similar treatment of the bromide yielded a value of 103.03 as the average of two determinations. The currently accepted value is 102.91.

In his next article, "On the Relationship between Luteo and Roseo Salts" (32), Jørgensen cited dozens of examples to demonstrate that the luteo (hexaammine) and roseo (aquapentaammine) salts of cobalt, chromium and rhodium are analogous not only in composition (the luteo salts contain 2NH₃ in place of the 2H₂O of the roseo salts) but also in solubility, crystalline properties, appearance, formation and reactions. The structural formulae he proposed are given below, where R = cobalt, chromium, or rhodium:

**Roseo salts**

- \[ \text{H}_2\text{O}, \text{X} \]
- \[ \text{H}_3\text{N}, \text{H}_3\text{N}, \text{X} \]
- \[ \text{R}_2 \]
- \[ \text{H}_3\text{N}, \text{H}_3\text{N}, \text{H}_3\text{N}, \text{X} \]
- \[ \text{H}_3\text{N}, \text{H}_3\text{N}, \text{H}_3\text{N}, \text{H}_3\text{N}, \text{X} \]
- \[ \text{H}_3\text{N}, \text{H}_3\text{N}, \text{H}_3\text{N}, \text{X} \]
- \[ \text{H}_2\text{O}, \text{X} \]

(modern, aquapentaammines, \([\text{H}_2\text{O} (\text{NH}_3)_6]X_3\))

**Luteo salts**

- \[ \text{H}_3\text{N}, \text{X} \]
- \[ \text{H}_3\text{N}, \text{H}_3\text{N}, \text{X} \]
- \[ \text{R}_2 \]
- \[ \text{H}_3\text{N}, \text{H}_3\text{N}, \text{H}_3\text{N}, \text{X} \]
- \[ \text{H}_3\text{N}, \text{H}_3\text{N}, \text{H}_3\text{N}, \text{H}_3\text{N}, \text{X} \]
- \[ \text{H}_3\text{N}, \text{H}_3\text{N}, \text{H}_3\text{N}, \text{X} \]
- \[ \text{H}_3\text{N}, \text{X} \]

(modern, hexaammines, \([\text{R(NH}_3)_6]X_3\))

In fact, in the case of the luteorhodium (hexaamminerhodium(III)) salts, Jørgensen's proposal was a sheer prediction, for he did not succeed in preparing these compounds until the year 1891.

Jørgensen next described, in a 3-part article, the detailed preparation, properties and reactions of \([\text{Rh}_{23}10\text{NH}_32\text{H}_2\text{O}]X_3\), roseorhodium salts (\([\text{Rh}_2\text{H}_2\text{O}(\text{NH}_3)_6]X_3\)), where X = OH, NO₃, NO₃, HNO₃, Cl, Br, SO₄, I, SI₄O₆, HPO₄, (NaP₂O₇), \([\text{Co(CN)}_6]_3\), \([\text{Fe(CN)}_6]_3\), \([\text{SO}_4]\text{AuBr}_3, \text{NO}_3]\text{PtCl}_4\text{ or }\text{SO}_4]\text{PtCl}_4\\text{)} (33); \((\text{NO}_2)_2[\text{Rh}_{23}10\text{NH}_32\text{H}_2\text{O}]X_3\), nitratopentaurorhodium salts (nitratopentaammines, \([\text{RhNO}_2(\text{NH}_3)_6]X_3\)), where X = NO₂, Cl or \([\text{S}_2\text{O}_5]_2\) (34); and \((\text{NO}_2)_2[\text{Rh}_{10}\text{NH}_3]X_3\), xantherhorodium salts (nitratopentaammines, \([\text{RhNO}_2(\text{NH}_3)_6]X_3\)), where X = OH, NO₃, Cl, Br, \([\text{SO}_4]\text{, }\text{SO}_3\text{H}_2\text{SO}_4\), \([\text{SiF}_6]\text{Cl}_2, [\text{SiF}_6]\text{Cl}_2\text{ or }\text{[PtCl}_6]\) (35).

In 1891 Jørgensen finally succeeded in preparing the parent series of the rhodium-ammines - the long-sought luteorhodium (hexaamminerhodium(III)) salts (36), from sodium roseorhodium pyrophosphate \((\text{Rh}_2\text{H}_2\text{O}(\text{NH}_3)_6)\text{-} \text{NaP}_2\text{O}_7\text{-} \text{H}_2\text{O}) (31, 33) by a tedious process. A simpler process involved heating chloropurpureorhodium chloride with concentrated ammonia for four days (36):

\[
[\text{RhCl}(\text{NH}_3)_6]\text{Cl}_2 + \text{NH}_3 \rightarrow [\text{Rh}(\text{NH}_3)_6]\text{Cl}_3
\]

Jørgensen (36) prepared the compounds \([\text{Rh}(\text{NH}_3)_6]X_3\), where X = NO₃, NO₃, HNO₃, (37), Cl, Br, I, \([\text{SO}_4]_2\text{, }\text{I}_{\text{SO}_4}\text{, }\text{Br}_{\text{SO}_4, \text{I}_{\text{PO}_4, \text{I}_{\text{NaP}_2\text{O}_7, \text{I}_{\text{P}_2\text{Cl}_6, \text{I}_{\text{Cl}[\text{P}_2\text{Cl}_6, \text{I}_{\text{SO}_4]_2 \text{[P}_2\text{Cl}_6]}\text{ and }\text{I}_{\text{SO}_4]_2 \text{[P}_2\text{Cl}_6]}\text{. He also prepared }\text{[Rh}_2\text{H}_2\text{O}(\text{NH}_3)_6]_2(\text{NO}_3)_2\text{HNO}_3\text{ (37 and later, in his first article attacking Werner's views (38), }\text{[Rh}(\text{NH}_3)_6]_2(\text{RhCl}_3)_3\text{ and }\text{[RhCl}(\text{NH}_3)_6]\text{ [RhCl}_3)_2\text{. The hexaamminerhodium(III) salts, to which he assigned the monomolecular formula }\text{[Rh}_6\text{NH}_3]_2X_3\text{, are very stable; after the passage of more than four decades the composition of Jørgensen's samples was found to be unchanged (39).}

In his last article on rhodium, published in 1903 (40), Jørgensen returned to his work of two decades earlier (31). Because of the analogous behaviour of rhodium and iridium he decided that the chloropentaamminerhodium(III) chloride used in his determination of the atomic weight of rhodium (31) might have contained iridium. Using \([\text{RhCl}(\text{NH}_3)_6]\text{Cl}_2\text{ purified by two different methods, he repeated his atomic weight determination and obtained the previous value.}

**Conclusion**

Like Alfred Werner, Jørgensen was primarily interested in one of the most fundamental problems of chemistry, the nature of the chemical
bond and the constitution and configuration of chemical compounds. Co-ordination compounds, known in his time as Molekülverbindungen (molecular compounds), provided him with an ideal means to this end. Although he interpreted their structure in terms of the now defunct Blomstrand-Jørgensen chain theory, his pioneering experimental research on new series of platinum and rhodium compounds (as well as those of cobalt and chromium) has provided us with some of the most fundamental data of inorganic chemistry that are still valid today.

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**ABSTRACTS**

of current literature on the platinum metals and their alloys

**PROPERTIES**

**On the Atomic Interdiffusion in Co/Pt Superlattices**


XRD was performed on molecular beam epitaxially grown <111> and <001> oriented Co(3 Å)/Pt(18 Å) superlattices, with the scattering vector Q covering a plane which included a major component perpendicular to, and a minor component parallel to the sample plane. The diffraction peaks of the superlattice had a large width parallel to the plane of the film, indicating strong in-plane disorder.

**Properties of PTC Ceramics/Metal Sintered Compact**


Mixtures of powders (Ba, Sr)(Ti, Sb)O₃ PTC ceramics and 0.5–11 vol.% Pt, Au or Ag powders were sintered at 1600 K for 3.6 ks in air and their properties were investigated. The specific resistivity increased up to 10 vol.% for Pt, although the PTC characteristics remained for a small amount of metal. The thermal conductivity and fracture toughness were improved by ~1.6 and 1.9 times, respectively, by the addition of 10 vol.% Pt.

**Dealloying Properties of Pt-NiCr Thin Films on Glass**


A dealloying reaction between sputter-deposited Pt and NiCr thin films on Pyrex glass was studied after annealing. Cubic Pt, Cr and Ni,Pt intermetallic phases emerged after annealing at 450°C, although no stability was observed at room temperature. The phases were no longer present at an anneal temperature of 700°C. There was complete dealloying of the NiCr film by the Pt, forming a tertiary alloy of Pt, Ni and Cr with an ordered f.c.t. structure.

**Scaling of the Electrical Conductivity of Ultrathin Amorphous Palladium Films**


The temperature dependent electrical conductances of sets of ultrathin amorphous Pd films prepared by successive deposition in situ at low temperatures were found to scale over a range of conductances covering both the strongly and weakly localised regimes. The scaling parameter, which collapses the data onto a single curve, falls to zero as thickness or conductance increase. The scaling suggests a unified picture of the insulator-to-metal transition in two dimensions.

**Diffusion of Pd Adatoms and Stability of Pd Overlayers on the (011) Surface of Pt**


Field ion microscopy was used to examine the migration of Pd atoms and the stability of Pd overlayers on the (011) surface of Pt. Pd atoms migrated within the (011) surface channels at 207–235 K with an activation energy of 0.58±0.05 eV. Cross-channel displacements are not seen. Clusters of Pd atoms on Pt(011) form stable (1x1) structures at < 300 K and do not reconstruct to the “missing-row” structure. Pd adatoms deposited on top of (1x1) overlayers diffused in channels at 167 K. Pt atom migration on a Pd overlayer occurs at much lower temperatures, near the centre of the plane.

**Magnetic Properties of Multi-Layer Co/Pd Films**


Studies were performed of the magnetic properties of multilayer Co/Pd films of layer thickness ~8-0.25 nm. There were intrinsic deposits with perpendicular magnetic anisotropy at the crystallographic surface and magnetostrictive anisotropic states. The occurrence of an induced magnetic moment on the magnetic Co/Pd layer was examined.

**Permeability and Diffusivity of Hydrogen in Palladium-Rich Pd-Y(Gd)-Ag Ternary Alloys**


The permeabilities and diffusivities of H in Pd₁₀₀₋ₓ(Y(Gd))ₓAg alloys, where x = 5, 10, 15, 20 and 24 at.%, and x in at.% is the Y(Gd) content, fitting the condition y + 3x = 24, were measured as possible diffusion membranes for H purification at 523–673 K and input H pressures of 267–667 kPa. The Pd₁₀₀₋ₓ(Y(Gd))ₓAg alloys with x = 6.3 were the most permeable to H, with permeability values a factor of 2–2.5 higher than those in Pd-24 at.% Ag alloy.

**Schemes of the Phase Equilibria in the Quaternary System Palladium-Titanium-Cobalt-Nickel at 800°C**


Studies of the system Pd-Ti-Co-Ni were performed at 800°C in the concentration range 0–25 at.% Ti. Physico-chemical interactions and structural diagrams of the phase equilibria at 6, 10 and 25 at.% Ti were characterised.
Coherence of the Superconducting Wavefunction between the Heavy-Fermion Superconductor UPd₂Al₃ and Niobium
Quantum coherence of the superconducting wavefunction between superconductor Nb and heavy-fermion superconductor UPd₂Al₃ was demonstrated using a pointed rod of UPd₂Al₃ to bridge the gap in an almost closed Nb ring. Persistent currents in the composite ring and trapped flux, which was in discrete quantum states separated by the flux quantum h/2e, were observed.

Electrical and Magnetic Properties of U-X (X = Ru, Rh and Ir) Intermetallic Compounds
Magnetic and electrical properties of U-X intermetallic compounds, where X = Ru, Rh and Ir, were found from measuring electrical resistivity, Hall coefficient, thermoelectric power, specific heat, etc. Most U-Ru compounds, except U₃Ru₄, are Pauli-paramagnetic. U₁Ru₄ orders antiferromagnetically below 13 K. U₁Rh₄ and U₁Rh₃ are Curie-Weiss type paramagnetic compounds. URh orders ferromagnetically below 57 K, similar to UIr.

Photorefractive Properties of SBN:60 Systematically Doped with Rhodium
Crystals of strontium barium niobate were grown and doped with 6 Rh concentrations from 0.015 to 0.2 wt.%. The results were analysed by net coupling, optimal gain conditions, etc. An effective coupling coefficient of almost 14/cm was observed in the 0.2 wt.% Rh doped sample for polarisation independent directional coupling. Two-beam coupling was enhanced by Rh doping throughout the visible spectrum.

CHEMICAL COMPOUNDS
Reversible Carbon Monoxide Addition to Sol-Gel Derived Composite Films Containing a Cationic Rhodium(1) Complex: Toward the Development of a New Class of Molecular-Based CO Sensors
Synthesis and CO binding properties of Zr₂O₅ and TiO₂ glasses impregnated with a Rh ether-phosphate compound are reported. The complex [Rh(TMPP)₂(CO)]⁺ (TMPP = tris(2,4,6-trimethoxyphenyl)phosphine) reversibly binds CO within a glassy polymer matrix to form the dicarbonyl species [Rh(TMPP)₂(CO)₂]⁺.

Cs₄[IrO₄]₁, a New Iridate with Planar Anion [IrO₄]₁⁻
Structure studies of black single crystals of Cs₄[IrO₄] obtained by heating mixtures of Cs₂O₂ and IrO₂ at a molar ratio Cs:Ir = 4.30:1.00 at 740°C showed them to be monoclinic with a K₃[IrO₄]-type structure. The structure was determined by four circle diffractometer data.

Preparation and Crystal Structure of the Actinoid Ruthenium Phosphides ThRu₂P₂ and URu₂P₂
New compounds ThRu₂P₂ and URu₂P₂ were prepared by the reaction between the powders of elemental Th with RuP and a U-Ru alloy with elemental P, respectively, in a Sn flux. The compounds crystallised in the orthorhombic space group Pnma with the structure of both showing a tendency for higher co-ordination typical of intermetallic phases. The structures of ThRu₂P₂ and URu₂P₂ are discussed with other related compositions.

ELECTROCHEMISTRY
Oxidation of Formic Acid at Pt Bonded SPE Membrane Electrode
K. FUKIYAMA and K. TAKEYA, Denki Kagaku, 1992, 60, (6), 557–559
A solid polymer electrolyte (SPE) membrane electrode carrying Pt was studied for HCOOH vapour oxidation in a gas diffusion type cell. Reactant HCOOH vapour + Ar carrier gas was supplied to the Pt side of the electrode, while the SPE side was in contact with H₂ saturated 1M HClO₄ solution. Potential sweeps of 20 mV/s at 20°C were performed, and compared to those of CO oxidation on the same electrode. Current density at 0.9 V is larger by one or two orders at the Pt-SPE than at a Pt plate electrode, giving a current < a few mA/cm². A wide hysteresis loop is observed over the 0.25–1 V potential range, which is a broader range than for the Pt plate.

Study of Methanol Electrooxidation on Rh-Sn Oxide, Pt-Sn Oxide, and Ir-Sn Oxide in Comparison with that on the Pt Metals
The catalytic activities of oxides of Rh-Sn, Ir-Sn and Pt-Sn were studied for the Sn oxide effect in comparison to those of the Pt metals and to each other. Sn oxide enhanced the catalytic activity of Pt-Sn oxide for MeOH electrooxidation with respect to Pt in acidic, but not alkaline solutions. Sn oxide had negative activity effect in Rh-Sn oxide and no effect in Ir-Sn oxide, with respect to Rh and Ir, respectively. This was linked to the presence or absence of redox coupling of the respective Pt group metal species.
Methanol Oxidation on Platinum-Tin Catalysts Dispersed on Poly(3-methyl)thiophene Conducting Polymer


Studies of the effect of catalyst support and Pt loading on the electrochemical oxidation of MeOH were performed on Pt-Sn catalysts prepared by electrodeposition on poly(3-methyl)thiophene. Pt-Sn catalyst deposited in the H adsorption potential region showed an order of magnitude increase in surface area. The thickness and distribution of the catalyst layer in the conducting polymer support were estimated by Rutherford backscattering spectrometry. H oxidation was observed at Pt loadings as low as 20 µg/cm².

Diffusion Rate of Deuterium in Pd during Cathodic Charging


The absorption and release rates of D into or from Pd were measured during electrolysis in a closed cell. The difference in diffusion constants of the two states of D in Pd which were deduced from the diffusion behaviour, was two orders of magnitude — 10⁻⁶ and 10⁻⁸ cm²/s, respectively, at room temperature.

Anodic Oxidation of Formic Acid at Nafion-Modified Palladium Electrocatalsysts

M. MORITA, H. KIJIMA and Y. MATSUDA, Denki Kagaku, 1992, 60, (6), 554–556

Results on the improved activities of Pd electrocatalysts deposited by RF sputtering on a Nafion-coated glassy C surface are reported for the anodic oxidation of HCOOH. Maximum electrode activity occurred for a 20 s sputtering time, which should give island-like Pd deposition. Larger amounts of Pd decreased the activity. The acidic properties of the thin Nafion film could contribute to the high activity of Pd/Nafion/GC. The Nafion coating was effective for both improved activity at ≤ 0.15 V and suppressing the degradation of activity at > 0.15 V.

Hydrogen and Oxygen Evolutions on Ru-Ir Binary Oxides


The electrocatalytic activities of Ir/Ru mol% containing solutions on mixed Ru-Ir oxide electrodes, were compared for H₂ and O₂ evolution from 1N H₂SO₄ and 1N NaOH solutions. Maximum activity resulted from a coating solution with 60–80 mol% Ir. Pure RuO₂ coated electrode had a polycrystalline structure; its activity was worst for O₂ evolution in alkaline solutions, while its electrochemical behaviour for H₂ evolution was the same for acidic and basic solutions. The redox transition Ir(IV)/Ir(V) of the pure IrO₂ coated electrode strongly depended on pH; the rate determining step depended on current density (cd); at low cd H₂ desorption predominated, while at high cd H₂ adsorption predominated.

Water Oxidation at Polycrystalline OsX₂ Electrodes


Polycrystalline OsX₂ powders, where X = S, Se or Te, have been synthesised, made into pressed electrode disks and electrochemically investigated for the oxidation of H₂O. Os₂S₄ was identified as O₂ evolution catalyst, whereas OsTe₂ was completely decomposed. The difference in catalytic behaviour is related to differences in the X-ray photoelectron valence band spectra and is discussed in terms of electronic states involved in charge transfer.

Electrochemical Reduction of Carbon Dioxide in Water: Analysis of Reaction Mechanism on Ruthenium-Titanium-Oxide


The kinetics of H₂ formation and CO₂ reduction were studied on mixed TiO₂/RuO₂ rotating disk electrodes prepared by thermal decomposition of the halides on Ti sheets. Current-voltage curves at pH = 4–7 showed a current-limiting behaviour at small overpotentials for H₂ evolution. The current efficiency for CO₂ reduction reaches a maximum under current-limiting conditions for H ion reduction, before a steep onset for H₂ evolution takes place, due to water reduction.

PHOTOCONVERSION

Solid State Photochemistry of (C₇H₁₂)Pt(N₃)₂ as Thin Films on Si(111) Surfaces


The solid state photochemistry of (COD)Pt(N₃)₂ (1), where COD is 1,5-cyclooctadiene, has been investigated after deposition as a film on a Si(111) surface. Photolysis of a thin film of (1) initially lead to loss of a single azide radical and the formation of (COD)Pt(N₃), further photolysis lead to the loss of the remaining ligands. The final films were identified as 115 nm thick Pt films, with good adherence to the SiO₂ substrate.

Photocatalysis of Metal Clusters in Cages: Effective Photoactivation of the Water Gas Shift Reaction Catalysed on NaY Zeolite-Entrapped Pt₁₂ and Pt₄ Carbonyl Clusters


Pt carbonyl clusters [Pt₄(CO)₆]⁻ (n = 3, 4) in NaY zeolite pores were catalytically active for the H₂O gas shift reaction at low temperatures, and were effective photocatalysts for this reaction with a large enhancement (~38 times) at 293 K, under Xe lamp illumination, compared to the dark reaction. The photoexcited Pt₁₂ carbonyl anions may enhance H₂O oxidation to form an active intermediate "COOH" by nucleophilic attack of OH on the cluster carbonyls.
Palladium Catalysis of O Reduction by 
Electrons Accumulated on TiO₂ Particles 
during Photoassisted Oxidation of Organic 
Compounds
C.-M. WANG, A. HELLER and H. GERSCHER, J. Am. 
Electrons accumulated on slurried TiO₂ particles 
during photoassisted oxidation of 1.6 M aqueous MeOH, 
and persisted there, for at least 1 min, even in O₂-
saturated solutions. Incorporating Pd in the TiO₂ 
particles surface increased the quantum efficiency of 
and persisted there, for at least 
the photoassisted oxidation of 
saturated solutions. Incorporating Pd in the TiO₂,
C.-M.
Compounds
Photophysical Properties of Rhodium(Ill) 
Ligand Macrocycle Effects on the 
dichloropropionate 
Complexes. A Detailed Investigation of 
macrocycle Rh(III) complexes trans- and 
trans-Rh([14]aneN₄)(CN)₂⁺ (I, IV and 
1,4,8,12-tetraazacyclotetradecane, [1
had an order of magnitude longer life.
96, (16), 6640–6650
Rh([15]aneN₄)²⁺ and trans-Rh([16]aneN₄) 
(CN)₂⁺ (I, IV and II, respectively, [1
= 1,4,8,11-tetraazacyclotetradecane, [5
aneN₄ = 1,4,8,12-tetraazacyclotetradecane) and related 
compounds are described. I and II luminesced strongly 
in ambient temperature aqueous solutions, but (I) 
with an order of magnitude longer life.

Photochemical Behavior of Chlorocarbonyl 
(triphenylphosphine)rhodium(I), CIRh(CO) 
P₃(P = PPh₃). Laser Flash Photolysis with 
Infrared Detection
S. OISHI and T. KAWASHIMA, Chem. Lett. Jpn., 1992, 
(5), 747–750
Laser flash photolysis of CIrh(CO)P₃ with IR detection 
showed that CO was photoeliminated, rather 
than P. The generated CIrhP reacted with the 
remaining CIrh(CO)P₃ to give a transient binuclear 
Rh carbonyl, which regenerated CIrh(CO)P₃ via 
the reaction with CO.

A Novel Photo-Induced Patterned Film 
Formation of Organic Pigments Using 
Tris(2,2′-bipyridine)ruthenium(II) 
and Surfactant with Ferroenyl Moiety
H. Mizuno, K. Hoshino, J.-I. Hanha and H. Korado, 
When an acidic aqueous dispersion of an organic 
pigment containing a ferrocene attached surfactant, a 
Ru(bpy)₃²⁺ photocatalyst and a sacrificial agent, was 
illuminated at 450 nm through a masked In-Ti oxide-
coated glass plate pigment layers were deposited onto 
unilluminated, but not illuminated, areas of the 
substrate. By this method, H₂Pc pigments (Pc = phthalal-
cyanine) and other pigments: Cu phthalocyanines, 
halogenated Cu phthalocyanine (Pc Green) and peryl-
ene derivatives, were used for clear-cut patterns.

ELECTRODEPOSITION AND 
SURFACE COATINGS
Deposition and Characterization of Thin 
Electroless Palladium Films from Newly 
Developed Baths
M. L. CHOU, N. MANNING and H. CHEN, Thin Solid Films, 
213, (1), 64–71
Pd films ~100 nm thick were deposited on activated 
hydrogenated amorphous Si by electroless deposition 
from hypophosphite based Pd-ammine baths. The 
baths were stable at 35–50°C operating temperatures. 
Active Pd aggregates have small irregularly shaped 
grains whose density and distribution depended on 
immersion time and substrate type. Higher coverage 
uniform, crack-free Pd films were obtained from NH₄-
NH₄Cl, EDTA and TEA baths than from citrate 
baths.

Laser-Assisted Organometallic Chemical 
Vapor Deposition of Films of Rhodium and 
Iridium
J. S. COHAN, H. YUAN, R. S. WILLIAMS and J. I. ZINK, Appl. 
High purity Rh and Ir thin films with no C contam-
ination detectable by XPS were deposited by UV irradiation 
of (η-C₅H₁₂)M(C₅H₁₀)₂ (M is Rh or Ir) 
organic precursor in the presence of H₂. Wavelength 
dependence studies of the Rh compound precursor 
showed that only irradiation into the charge transfer 
bond of the compound caused deposition.

APPARATUS AND TECHNIQUE
Amperometric Needle-Type Glucose Sensor 
Based on a Modified Platinum Electrode with 
Diminished Response to Interfering Materials
C.-Y. CHEN, M. GOTOH, H. MAKINO, Y.-C. SU, E. TAMIA 
A needle type glucose sensor for determining glucose 
in serum and whole blood samples, using Pt wire as 
the working electrode and a disposable hypodermic 
stainless-steel needle electroplated with Pt as the 
counter and reference electrode, was developed. The 
enzyme was immobilised by cross-linking with glu-
ceraldehyde and photocross-linking of PVA-SbQ₃ (a 
poly(viny1 alcohol)), and the sensor showed good 
response, stability and reproducibility.

Development of SnO₂-Based Ethanol Gas 
Sensor
T. MAEKAWA, J. TAMAKI, N. MIURA, N. TAMAZOE and S. 
The sensitivity and selectivity of SnO₂-based elements 
to EtOH vapour of 1000 ppm in air at 300°C were sig-
nificantly improved by adding several basic oxides 
and then by loading the elements with Pt or Pd met-
als. The doubly promoted elements Pd(0.5 wt. %)- 
La₂O₃(5 wt. %)-SnO₂ and Pt(0.5 wt. %)-La₂O₃-SnO₂ 
showed excellent sensing properties to EtOH vapour 
in the range 100–1000 ppm at 300°C.

Applicability of Discontinuous Palladium Films as Strain Gauges
Discontinuous Pd films were prepared by evaporation and sublimation on glass substrates. The variation in DC resistance of the films with time was investigated in air at room temperature. Sublimed films had better stability than evaporated films. The piezoresistance of the discontinuous Pd films was measured at different strains and the gauge factor, $\nu$, was deduced. Sublimed films had higher $\nu$ than evaporated films.

**HETEROGENEOUS CATALYSIS**

**Catalytic Synthesis of C-Alkylimidazoles in the Presence of Pt/Al$_2$O$_3$ Catalysts**
Studies of the synthesis of C-alkylimidazoles from 1,2-diamines and carboxylic acids in the presence of bifunctional Pt/Al$_2$O$_3$ showed a good yield of 2-alkyl- and 2,4-dialkylimidazoles, including those with long chain alkyls. The effect of the reaction temperature, space velocity of feed and H dilution on the yield of 2-methylimidazole was studied. The stability of Pt/Al$_2$O$_3$ in the reaction cycles with intermediate oxidative regeneration was studied.

**The Influence of Pretreatment at Different Temperatures on the Surface Structure and Performance of Pt/Al$_2$O$_3$**
The effects on activity and selectivity of pretreatments at different temperatures in H$_2$ and N$_2$ and of thiophene poisoning, were examined on Pt/Al$_2$O$_3$ catalysts for reactions of C$_n$ alkanes with H$_2$. For high temperature treatment in H$_2$ the Pt particle sizes were unchanged, the surface atom ratios: Pt:Al, O:Al and C:Al were only slightly changed but hydrodenylation of $n$-C$_n$ was drastically decreased. This decrease in activity also occurred after treatment at high temperature in N$_2$. For prepoisoning with thiophene the activity for $n$-C$_n$ was rapidly reduced.

**Study of New Reforming Catalyst. Aromatization of C$_{6}$-C$_{5}$ Alkanes over Pt/BaKL Zeolite**
The aromatisation performance of Pt/BaKL zeolite was studied in a continuous flow microreactor using C$_{6}$-C$_{5}$ alkanes as reactants. Pt particle size distribution on zeolite and the role of Pt were studied. Selectivity to aromatics of 90–95% was achieved at 95% conversion of $n$-C$_n$ over Pt/BaKL. Small amounts of cracking and isomerisation products were formed. Pt zeolite also acted as a mono-functional catalyst.

**Kinetics of Reduction of Np(V) to Np(IV) by Platinum Black as Reduction Catalyst**
The kinetics and mechanism of the reduction of Np(V) to Np(IV) by Pt black catalyst were studied to see if extraction of Np from high level radioactive liquid waste from spent fuel reprocessing was possible. Tests using HNO$_3$ solution containing hydroxyammonium (HA) nitrate with added Pt black and Np solution found that reduction of Np(V) did not occur without HA. Reduction of Np(V) by Pt group metals catalysts occurred without heat. The insoluble residue of spent fuel could act as catalyst since its main components are Pt group metals.

**IR-Spectra of Catalysts and Adsorbed Molecules. Part 39. Acidic and Catalytic Properties of Pentasil Modified with Pt, Cr and Zn**
Incorporating Pt into pentasil catalysts increased the concentration of L-centres by twice without changing the number of B-centres. There was a maximum in B-centre concentration at 0.72 wt.% Cr in Pt-Cr catalysts. The B-centre concentration decreased in catalysts simultaneously promoted with Pt, Cr and Zn, while the L-centre concentration increased.

**Regioselective Hydrogenation of Unsaturated Compounds Using Platinum-Zeolite Coupled with Organosilicon Alkoxide by CVD Method**
Regioselective hydrogenation of unsaturated compounds was performed by a Pt/zeolite catalyst coupled to an organosilicon alkoxide prepared by a CVD method. When a mixture of 1-nonene (1) and tran-4-nonene (2) was hydrogenated by this catalyst, the reaction rate of (1) was much greater than that of (2). Excellent selectivity was obtained when diphenyldiethoxysilane was the coupling reagent on the Pt/zeolite.

**Catalytic Oxidation of Methane over Palladium Supported on Alumina. Influence of the Oxygen-to-Methane Ratio**
The oxidation of CH$_4$ over a Pd/Al$_2$O$_3$ catalyst was studied for O$_2$:CH$_4$ ratios of 4–0.66. After ageing under a mixture of the reactants at 600°C, an increase in catalytic activity was observed, independent of the O$_2$:CH$_4$ ratio, while the reaction selectivity depended on it. In O$_2$-deficient mixtures, the formation of CO was observed at conversion levels corresponding to the total O$_2$ consumed. Pd/Al$_2$O$_3$ was active in CH$_4$ steam reforming at moderate temperature.
Characteristics of Carbon-Supported Palladium Catalysts for Liquid-Phase Hydrogenation of Nitroaromatics


The support and preparation of Pd/C catalysts were examined for dispersion, metal distribution and activity effects during liquid-phase hydrogenation of dimethyl sulfoxide. Oxidation of the C support increased the number of surface O groups and enhanced Pd dispersion, but catalytic activity did not improve in proportion. In C-metal salt slurry, nuclei formation and growth by ion exchange and/or reduction were most important in determining the final state of catalysts prepared by alkali hydrolysis. Catalyst activity depended on metal location.


A study of the effect of temperature of reduction by H$_2$ on Pd/CeO$_2$ catalysts on the accessibility of the Pd to CO adsorption showed that no adsorption occurred when the reduction temperature was $>$ 673 K. The behaviour of catalysts with crystallites of the same morphology, was independent of Pd loading. The CO adsorbed could be completely recovered after oxidising the catalysts at 723 K followed by H$_2$ reduction at 423 K.

Catalytic Hydrodechlorination of 1,2-Dichloroethane and Trichloroethylene over Rh/SiO$_2$ Catalysts


Reactions of H$_2$ with 1,2-dichloroethane (1) and trichloroethylene (2) over Rh/SiO$_2$ catalysts at 365–553 K and 0.1 MPa produced HCl and C$_2$H$_4$. Selectivity for C$_2$H$_4$ increases with increasing temperature. Minor products are: C$_2$H$_4$Cl for (1) and partially dechlorinated hydrocarbons for (2).

Novel Catalysts on Carbon Support Exhibiting Activity in Gas-Phase Ammonia Synthesis in the Absence of Specially Added Promoter


Deposition of K$_2$[Ru$_3$(CO)$_{11}$] on the graphite-like “Sibunit” produced a system which catalysed gas-phase NH$_3$ synthesis at $\geq$ 250°C and atmospheric pressure without a promoter. The fastest synthesis was obtained at 350°C when the stationary NH$_3$ concentration in the gas stream reached $\approx$ 77% relative to equilibrium value at 350°C and 90% at 400°C.

HOMOGENEOUS CATALYSIS

C-H Activation in Aqueous Medium. The Diverse Roles of Platinum(II) and Metallic Platinum in the Catalytic and Stoichiometric Oxidative Functionalization of Organic Substrates Including Alkanes


Studies of the oxidation of ethers, alcohols, esters and light alkanes by K$_2$PtCl$_4$ and PtO$_2$ in aqueous medium showed that unactivated C-H bonds were attacked and oxidised by Pt(II), whereas C-H bonds $\alpha$ to an O were activated and catalytically oxidised by metallic Pt in the presence of O$_2$. For example, Pt(II) oxidised ethane selectively to EtOH and ethylene glycol. In the presence of metallic Pt and O$_2$, further oxidation of the alcohol functionality occurred to generate the corresponding carboxylic acids.

Novel Synthesis of Indoles via Palladium-Catalyzed Reductive N-Heterocyclization of $\alpha$-Nitrostyrene Derivatives


Indole derivatives were prepared from the reductive N-heterocyclisation of $\alpha$-nitrostyrene derivatives in the presence of a catalytic amount of PdCl$_2$(PPh$_3$)$_2$-SnCl$_2$ under a CO pressure of 20 kg/cm$^2$ at 100°C for 16 h. P ligands, such as triphenylphosphine and tributylphosphine, were also necessary for high catalytic activity. When $\alpha$-nitrostilbene was used in the reaction, 2-phenylindole was formed in 75% yield.

Palladium-Catalyzed Formate-Nitrobenzene-Carbon Monoxide Reaction: Formation of Carbamate Ester


The catalyst PdCl$_2$(PPh$_3$)$_2$ together with OP(n-Bu)$_2$ and KBr, promoted the reaction of formate ester with nitrobenzene under CO pressure to produce good yields of N-phenylcarbamate. This new reaction did not involve the formation of aniline before the carbamate ester formation.

A New Synthesis of Trimethyl Acenitrate by Palladium-Catalysed Triple Carbonylation of Propynyl Alcohol


Studies of a two-step Pd catalysed carbonylation consisting of an oxidative carbonylation of propynyl alcohol, followed by a substitutive carbonylation showed high yields of E and Z aconitic trimethyl esters. The first step occurred in MeOH at 20°C, 1.5 MPa of CO and 0.5 MPa of air under the catalytic action of Pd$_2$+K(I) or Pd/C+K(I) systems. The second step was catalysed by the ionic [Pd(thiourea)$_3$]I$_2$ complex at 40°C and 6.00 MPa of CO.
Palladium-Catalyzed Vinylation of Aryl Chlorides. Chelate Effect in Catalysis
A synthetically useful direct vinylation of aryl chloride, using Pd(OAc)₂ catalyst, was performed with the dippb ligand (dippb = 1,4-bis-(diisopropylphosphino)butane), which is specific for vinylation. This gives a reaction which tolerates various substituents and generally gives high yields.

Hydroformylation and Isomerization of Hex-1-ene Catalyzed by [Rh(acac)(CO)(PPh₃)]: Effect of Modifying Ligands
Hex-1-ene hydroformylation performed in the presence of [Rh(acac)(CO)(PPh₃)] catalyst at 1 MPa and 353 K yielded 68% hex-2-ene and 20% aldehydes. IR studies showed the presence of [Rh(acac)(CO)]₃ and [Rh₂(CO)₁₄] carbonyls in the post-reaction mixture which, when used as catalysts, yielded 70–90% hex-2-ene. Free triphenylphosphine increased the aldehyde yield to 80%.

Molecular Size Control of Rhodium Carbonyl Clusters Using Polystyrenes and Their Catalyst Function
The reaction of Ru₄(CO)₁₆ with aminated polymers, (prepared from chloromethylated PS with hydroxyl and ether functions), at 40°C under 6 atm of CO gave Rh₄ cluster anions, while a Rh₁₄ species was formed in the polymers at 100°C under 1 atm of CO. Treating the Rh₄ species with KOH gave Rh₃ species. Polymer-bound Rh₄ complexes were catalytically active for olefin hydroxymethylation. The Rh₁₄ species catalysed the deoxygenation of nitrobenzene to aniline by the water gas shift reaction.

Ruthenium-Catalysed Transfer Hydrogenation of Imines by Propan-2-ol
Imines were readily transfer hydrogenated by propan-2-ol under mild reaction conditions in the presence of a catalytic amount of RuCl₂(PPh₃)₂ and base. The reactions were carried out in 15 ml propan-2-ol with a substrate:catalyst ratio of 200:1, using 13.8 mg of K₂CO₃ as base.

Ruthenium Catalysts of Liquid-Phase Hydrocracking of n-Alkanes
Ru catalysts of higher activity than Ru powder were prepared by decomposition at 180–200°C of Ru₂(CO)₁₂, Ru₃(CO)₁₄ and Ru₄AlH at 5 MPa H₂ pressure and of (benzene/cyclohexadiene:1,5)Ru at 20°C and 0.1 MPa H₂ pressure in the presence of alkanes.

Highly Active Coal Liquefaction Catalyst: Soluble Ruthenium Complexes as Catalyst Precursors
Ru complexes: Ru₄(CO)₁₂, Ru(cyclooctadiene)(cyclooctatriene) and Ru(acetylacetonate) were examined as catalyst precursors for coal hydro-liquefaction in non-H donor solvent 1-methylnaphthalene. For Australian Yallourn brown coal, adding 0.02 wt.% Ru catalyst, gave 89.3% coal conversion and 45.9% oil yield, but with 0.07 wt.% Ru coal conversion was 96.5% and oil yield 57.8% at 673 K, under initial H pressure of 5.0 MPa. At 623 K the oil fraction dropped to 19.2% with 85.6% coal conversion.

Homogeneous Catalysis: A Ruthenium-Based Lewis-Acid Catalyst for the Diels-Alder Reaction
A Ru based catalyst trans-[Ru(salen)(NO)(H₂O)]SbF₆ where salen is the N,N'-bis(salicylidene)ethylenediamine dianion ligand was used for the Diels-Alder reaction. At 1 mol.% loading, the catalyst accelerated the reaction by many orders of magnitude, often >10⁵ over the corresponding thermal reaction. The binding of the Diels-Alder adduct of methacrolein and isoprene with the catalyst was also examined. Binding of the dienophile was stronger than that of the adduct.

FUEL CELLS
The Role of Hydrous Oxide Species on Platinum Electrocatalysts in the Methanol/Air Fuel Cell
Thick deposits of incipient hydrous oxide species can be readily produced on Pt electrodes, in 3.0 M H₂SO₄ at 60°C, typical MeOH/air fuel cell conditions, by multicycling the electrode potential between suitable limits.

Influence of Electrodid Properties on Water Management in a Solid Polymer Electrolyte Fuel Cell
Water transport in a SPEFC having dual-layer electrodes with 0.5 mg/cm² Pt and 40% w/w PTFE as the catalyst layer, was regulated by varying the amount of hydrophobic polyfluoroethylene propylene in the gas diffusion layer of the anode or by using C paper or C cloth substrates. C paper electrodes had low water transport giving higher ionic resistance, but C cloth electrodes performed better, due to greater H₂O penetration, not hindering the gas flow.
CHEMICAL TECHNOLOGY

Measurement of Diffusive and Surface Transport Resistances for Deuterium in Palladium-Coated Zirconium Membranes


A Zr membrane with 2 μm Pd coating electrolessly plated on both sides, was tested for D transport at 600–700 K and upstream D pressures of 2.7 $10^{-2}$–6.7 $10^{-4}$ Pa. At very low pressures, transport is limited by molecular adsorption on the Pd surface, whereas at higher upstream pressures Zr permeability limits transport.

A Membrane Reactor with Two Dispersion-Free Interfaces for Homogeneous Catalytic Reactions


A two-bundle polypropylene hollow fibre membrane reactor, operating as a single-bundle and as a two-bundle membrane reactor, was used to study the use of multiple-membrane-bundle reactors for homogeneous catalysis, for example, in direct oxidation of ethylene to acetaldehyde in aqueous PdCl$_2$–CuCl$_2$ solution. The two-bundle membrane reactor achieved higher conversions than a comparable single-bundle membrane reactor.

GLASS TECHNOLOGY

Processing of Bi-Sr-Ca-Cu-O Glasses Using Platinum and Alumina Crucibles


Reactions with Pt and Al$_2$O$_3$ crucibles were studied during preparation of Bi$_2$Sr$_2$Ca$_2$Cu$_2$O$_9$ glasses. With Al$_2$O$_3$, the glasses were completely homogeneous, free of secondary phases, but contained 2.26% Al in solution. After heat treatment, SrCaAlO$_3$ particles formed mostly along grain boundaries of the 2212 superconducting phase. Contamination with Pt was < 0.02 at.%, and no Pt-containing secondary phases were found in samples.

ELECTRICAL AND ELECTRONIC ENGINEERING

Influence of the Electron Beam Evaporation Rate of Pt and the Semiconductor Carrier Density on the Characteristics of Pt/n-GaAs Schottky Contacts


Schottky barrier diodes (SBDs) were prepared on epitaxially grown n-GaAs substrates with different free carrier densities by e-beam evaporation of Pt. LV measurements on Pt SBDs deposits with and without shielding the substrate from stray electrons during metallisation showed that shielding was essential for high quality devices.

Infrared Photoemission of Holes from Ultrathin (3–20 nm) Pt/Ir-Compound Silicide Films into Silicon


The photoemissions of Schottky barrier IR detectors fabricated on PtSi, IrSi and compound silicide films were characterised at low temperatures, and compared to a Monte Carlo modelling of the emission process. The films are 3–20 nm thick and act as an electrode on p-type Si. The total yield for internal hole photoemission is 1% per incident photon for PtSi and 0.1% for IrSi at a wavelength of 4 μm. The cut-off wavelengths are 5.4 and 8.2 μm for PtSi and IrSi, respectively. The thinnest PtSi film (3.0 nm) had the greatest responsivity observed.

Investigation of Ruthenium Schottky Contacts to n-GaAs


Ru evaporated onto n-GaAs to form Schottky contacts produced near ideal behaviour, with low current leakage and good stability on thermal ageing at ≤ 300°C. However, on ageing at > 400°C the diode rapidly deteriorates. A room temperature operating life of the order of 10$^5$ h was estimated.

TEMPERATURE MEASUREMENT

Thick Platinum Films as Low Temperature Thermometers


Resistance measurements of thick Pt films between 4.2 and 300 K are reported. The thick films were prepared by standard screen printing methods. Experimental data at 77–300 K were fitted to mathematical expressions, with an error in temperature < 0.2%. Their properties and the ability to prepare even small thermometers on substrates ≤ 0.2 mm suggests a use as very low heat capacity sensors. This will enable production of small calorimeters or thermometers with short relaxation times for > 77 K.

MEDICAL USES

DNA Binding Properties of cis-[Pt(NH$_3$)$_2$(C$_6$H$_5$NH$_2$)Cl$_2$], a Metabolite of an Orally Active Platinum Anticancer Drug


The cyclohexyl substituent on the amine ligand in cis-[Pt(NH$_3$)$_2$(C$_6$H$_5$NH$_2$)Cl$_2$] was found to have a profound effect on the selectivity for DNA binding sites and the ability of the resulting lesions to alter the processing of the damaged DNA. The results showed that the DNA adduct profile, and also the mechanism of activity, of the new class of orally active Pt complexes was similar to that of cisplatin.
NEW PATENTS

METALS AND ALLOYS

Production of a Sintered Palladium-Silver Alloy Membrane
NISSHIN STEEL K.K. Japanese Appl. 3/267,327
A Pd-Ag sintered alloy membrane is produced by mixing a metallic Pd powder with an Ag-Pd composite powder containing 50-95 wt.% Ag and 10-70 wt.% Pd, (both powders having an average particle diameter of 0.01-5 μm), compacting the mixture into the desired shape, and sintering at 500-700°C. The porous sintered alloy membrane produced is useful for separation of hydrogen isotopes and has a higher separation factor and permeability than a non-porous Pd alloy membrane.

Permanent Magnet Composition Containing Platinum
SEIKO EPSON CORP. Japanese Appl. 4/26,103
A rare earth-Fe permanent magnet is obtained by melting an alloy containing a rare earth metal, Fe, B and Cu as the base composition, and one or more of Pt, Au and Ag, casting the melt, hot working the ingot to refine the crystal grains, orienting the crystal axis in a specified direction and making the cast alloy magnetically anisotropic. The method is used to make rare earth-Fe permanent magnets having improved corrosion resistance without reducing the magnetic characteristics.

CHEMICAL COMPOUNDS

Organic Palladium Compound Used for Laminated Ceramic Capacitors
DOWA MINING CO. LTD Japanese Appl. 4/19,906
A Pd tertiary alkyl(phenyl) mercaptide is synthesised by reacting an alkyl sulphide complex compound of Pd chloride with a tertiary alkyl(phenyl) mercaptan (4-20C alkyl). The organic Pd compound produced is used as an electrode material for a laminated ceramic capacitor, or as a material for a resinate paste. A uniform, thin Pd film can be obtained.

ELECTROCHEMISTRY

Platinum Coated Anode for Ozone Manufacture
JOHNSON MATTHEY P.L.C. European Appl. 470,761A
An electrode used in the manufacture of ozone consists of one or more of W, Ti, Ta and Nb in contact with at least one area, up to 30 mm², of Pt or a Pt containing material, which is itself in contact with the electrolyte. The Pt coating prevents oxide formation which would otherwise render the surface inactive. The electrode is preferably used as the anode in an electrolytic cell to manufacture ozone.

Bipyridyl Ruthenium Complex for Electrochemiluminescent Electrode
CAPE COD RES. U.S. Patent 5,075,172
An electrochemiluminescent (ECL) electrode has an ECL layer consisting of a homogeneous mixture of a tris (2,2'-bipyridyl) Ru complex and a polytetrafluoroethylene polymer backbone, deposited on an etched glass substrate layered with a light transparent, conducting, fine grained substance for supporting and activating the ECL layer. The electrodes are used in apparatus for monitoring the concentration of organic material in H₂O, and the improved ECL layers are especially useful for monitoring petroleum contaminated ground waters.

Palladium-Tin Coated Anodes for Electrolysis of Chloride Solutions
M.F. REZNIK Russian Patent 1,638,208
Anodes for electrolysis of chloride solutions to produce chlorine, hypochlorites and chlorates are prepared by depositing a catalytically active coating of SnO₂ and PdO on a Ti substrate. The coating is applied in layers by electrolytic deposition from a solution containing 100-150 g/l Sn(BF₄), and 0.1-0.5 g/l PdCl₂ at the current density of 50-100 mA/cm², and each layer is heat treated to give a uniform, adherent and active coating. Stable anode operation is achieved, with a high level of electrocatalytic activity.

ELECTRODEPOSITION AND SURFACE COATINGS

Platinum Plating Bath for Jewellery Manufacture
ELECTROPLATING ENG. European Appl. 465,073A
A plating bath for electroplating or electroforming consists of 2-100 g/l Pt as a Pt compound, 2-100 g/l of an alkali metal hydroxide, a compound selected from soluble carboxylates, phosphates and sulphates, and an alloying metal salt of Pd, Ir, Ru, Ag or Au. Materials with high hardness, thickness and improved corrosion and scratch resistance are produced.

Chemical Vapour Deposition of Superior Quality Metal Films
IBM CORP. U.S. Patent 5,096,737
Chemical vapour deposition of Rh, Ir, Ag or Cu from a ligand stabilised (+1) β-diketone co-ordination complex of the metal is effected by heating the substrate, producing a vapour from the metal-containing precursor, and decomposing the vapour to deposit metal on the substrate in the (0) oxidation state. The method deposits metal films of superior conformity, surface smoothness and vertical hole-filling, allowing the fabrication of multilayer structures.
Catalyst Solution Used in Electroless Plating
Hitachi Chemical K.K. Japanese Appl. 4/26,774
A catalyst used for electroless plating is obtained by mixing a divalent Pd compound and at least two lower alkylamines into a buffer solution consisting of 0.001-0.5 mol/l Na citrate and 0.001-0.5 mol/l NaOH, where the Pd:alkylamine molar ratio is 1:1 to 1:10. The catalyst is used for electroless plating high density multilayer printed circuit boards, by dipping insulating materials in the catalyst solution, then dipping in reducing agent and electroless plating.

Composite Plating by Laser Irradiation
Mitsubishi Heavy Ind. K.K. Japanese Appl. 4/26,791
Composite plating of layers of one or more kinds of ion is effected by immersing a Pt anode and the workpiece into a plating solution containing one kind or different kinds of ion, and irradiating with a variable wavelength laser beam. The plating procedure is simple and gives a desirable composite electroplating.

Platinum-Tungsten Alloy Electroplating Bath
Tanaka Kikinzoku Kogyo Japanese Appl. 4/32,595
An electroplating bath used for electroplating Pt-W alloy objects contains a Pt compound and tungstic acid and/or a tungstate, and has a pH of at least 3. A novel Pt alloy plated film is obtained which is preferably amorphous, and has high corrosion resistance even to aqua regia. The Pt-W alloy plated film is useful for electrodes, sensors and ornamental goods for which high corrosion resistance is required.

Humidity Sensor with Platinum-Silica Sensitive Film
Seiko Epson Corp. Japanese Appl. 3/295,457
The humidity sensitive film of a humidity sensor consists of Pt particles dispersed in a silica film. In an example an Al substrate having screen printed Pt-Pd comb-type electrodes was coated with a silica sol containing dispersed Pt particles, then dried and sintered to form a silica film. Humidity sensors of low resistance, low cost and high accuracy can be obtained.

Oxygen Sensors
Japanese Appl. 3/295,461 and 4/19,555
O2 sensors have a zirconia tube or other ceramic tube having oxygen ion conductivity, a pair of Pt electrodes formed on the inner and outer surfaces of the tube, and an optional Pt catalyst layer formed on the outside surface so that it contacts the engine exhaust. After the Pt electrodes are adhered, the tube may be given a high temperature and pressure treatment at 1000°C (or more) and 10-100 atm in Ar, in which case a sensor having high heat resistance is obtained.

Gas Sensor with Excellent Reliability
Fuji Kasui Eng. K.K. Japanese Appl. 4/55,747
A gas sensor consists of two separate electrodes formed directly on a base plate, a gas sensitive layer of Sn oxide carrying 0.5-2.0 wt.% Pd formed over the base plate and in contact with the electrodes, and covering this layer a coating layer which is formed by a reaction of Sn oxide and Al2O3 carrying 1.5-3.0 wt.% Pt. The coating layer removes the interfering alcohol gas and eliminates the temperature dependency for gases containing CH4 and H2. Thus the sensor has excellent reliability and does not require a stabilised voltage source.

Palladium Alloy Membrane for Hydrogen Purification
Topchiev Petrochem. Synth. Russian Patent 1,643,450
H2 purification is effected by diffusion through a Pd alloy membrane at 400-900°C, where the alloy contains 6-8 wt.% In and 0.5-1.0 wt.% Ru, with a surface Ru concentration of (0.01-0.6) × 10^-4 g/cm². The membrane has an extended working life of at least 2000 h, and the process has twice the throughput of the previous method at 600°C.
Production of a Moisture Indicator Using Ruthenium or Osmium Complexes

MOSCOW LOMONOSOV UNIV. Russian Patent 1,644,024

A moisture indicator is produced by treating silica with a solution of Ru(II) or Os(II) tris-(1,10-phenanthroline) chloride, bromide or iodide, or complexes of Ru(II) or Os(II) tris-(2,2'-dipyridyl) chloride, bromide or iodide, then removing the water and drying. An increased rate of colour change is achieved using this indicator, to determine the moisture in gases.

JOINING

Palladium Solder for Improved Bonding of Carbon and Metal Materials

NISSAN MOTOR K.K. Japanese Appl. 4/6,178

A method for bonding C and metal materials involves applying an active metal (such as Ti, Zr) or active metal hydride on one or both surfaces, and then soldering at 1100°C in a vacuum with a Pd solder containing 4.0–7.0 wt.% Si. A stress-relaxing layer is preferably formed between the materials. The method enables strong chemical bonding instead of mechanical joints and improves high bonding strength.

HETEROGENEOUS CATALYSIS

Catalytic Converter for Alcohol Fuelled Engines

GENERAL MOTORS CORP. European Appl. 470,653A

A monolithic catalytic converter for use with automobile exhaust gas from engines using alcohol-containing fuels has a first, upstream region with Pd deposited on the surface, and a second, downstream region having a uniform loading of one or more of Pt, Pd or Rh on the surface. The catalytic converter minimises the formation of aldehydes, and is characterised by a rapid heat-up period and a correspondingly lower light-off time.

Diesel or Petrol Engine Combustion Catalyst

STTS SPECIALITES World Appl. 92/1,505A

A perovskite based catalyst suitable for treatment of diesel or petrol engine exhaust preferably consists of La, Y, Nd or Pr; Sr, Mn or Co; Pt, Pd, Rh or Ru; cationic vacancies; and oxygen, and can be extruded or deposited on a honeycomb support. One of the compounds particularly claimed for treatment of diesel exhaust containing soot is La,0.9Sr,0.2Mn,0.9Pd,0.001O,3.

Supported Palladium Catalyst for Butene Isomerisation

CHEMICAL RES. & LICENSING U.S. Patent 5,087,780

2-Butene is isomerised to 1-butene by contacting a feed containing 2-butene, 1-butene and H2 with a fixed bed of a PdO/Al2O3 catalyst in a distillation column, at 150–180°C and 100–150 psig. An overhead stream rich in 1-butene and a bottoms stream rich in 2-butene are obtained, and any butadiene present is simultaneously hydrogenated to butenes.

Catalyst for Removal of Nitrogen Oxides

OSAKA GAS K.K. Japanese Appl. 3/293,035

A catalyst for NOx removal consists of at least one of Pt, Rh or Ir on a porous carrier which is at least one of Al2O3, ZrO2 or Ti oxide; with the carrier having a pore diameter distribution maximum at 50–1000 Å. The catalyst is used for decomposing and removing NOx in combustion exhaust gas from fuel gas such as LNG or LPG, and can be used in combustion tools such as burners, engines or generators. NOx can be removed stably, over a long period, at low temperature, without a reducing agent even in the presence of O2.

Palladium-Antimony-Vanadium Catalyst for Preparation of Unsaturated Diesters

TOSOH CORP. Japanese Appl. 3/294,244

An unsaturated diester is prepared by the gas phase reaction of a conjugated diene with a carboxylic acid and O2 in the presence of a catalyst and a 4–5C unsaturated halogenated hydrocarbon. The catalyst consists of a carrier having 0.1–10 wt.% Pd, Sb and V, and also supporting 0.1–40 mmol/g (total) of an alkali metal carboxylate and alkali metal halide as promoter.

Metal Catalyst with Well-Adhered Noble Metal

N. ECHEM CAT. K.K. Japanese Appl. 4/4,042

A noble metal catalyst is prepared by treating a metal material such as honeycomb, net or wire with a solution containing 0.5–20 wt.% of a noble metal as a Pt, Pd, Rh, Ir, Ru, Au, Ag or Re salt containing no halogen, 0.05–10 wt.% of a refractory metal oxide as a compound containing no halogen (such as alumina sol), and 1–50 wt.% of an alkyl alcohol such as CH3OH, and then heating. A metal catalyst with supported noble metal is easily produced at low cost, with the noble metal well adhered to the support.

Exhaust Purification Catalyst with High Oxygen Storage Capacity

NISSAN MOTOR K.K. Japanese Appl. 4/4,043

A heat resistant catalyst for purifying exhaust gas consists of at least one of Pt, Pd and Rh on a supporting layer obtained by co-precipitation and containing Al2O3, Ce oxide and Zr oxide. The support has high O2 storage capacity and a large specific surface area, and the catalyst maintains high activity after using for a long period at high temperature.

Palladium-Iron Catalyst for Dealkylation Process

JGC CORP. Japanese Appl. 4/18,039

Dealkylation of alkyl aromatic compounds to produce dealkylated aromatic compounds and synthesis gas is effected by contacting with CO2 in the presence of a Pd-Fe catalyst. The catalyst is prepared by impregnating 0.01–50 wt.% Pd and Fe on a carrier such as Al2O3, SiO2, zeolite, and so on, with a Pd:Fe wt. ratio of 10:1–1:10, sintering and reducing.
Catalytic Converters for Lean Burn Engines
MITSUBISHI MOTOR CORP. Japanese Appls. 4/22,706-07

Catalytic converters for use with a lean burn engine consist of (a) at least one of Pt, Pd and Rh directly supported on a metal support, with a Cu/zeolite washcoat layer formed on at least the front side of the metal support; or (b) Pt, Pd and/or Rh supported on a Cu/zeolite washcoat layer formed on a support. NOx from a lean burn engine is decomposed at the active sites of the Cu/zeolite structure, and the hydrocarbons, CO and NOx released during transient operation are reduced at the active sites. The catalytic converters give improved purification efficiency for NOx.

Durable High Temperature Combustion Catalyst
BABCOCK-HITACHI K.K. Japanese Appl. 4/27,433
An high temperature combustion catalyst consists of a refractory inorganic support loaded with Pd oxide and a double oxide of Pd and La, with La:Pd atomic ratio 0.01-0.4:1. In an example the catalyst was prepared by loading La/Al2O3 on a honeycomb support and firing at 900°C, then impregnating with an aqueous solution of La and Pd nitrates and firing at 800°C. The catalyst has an extended operating life.

Multipurpose Palladium-Magnesium Carbonate Catalyst
JENAPHARM VEB. East German Patent 294,430
A supported Pd catalyst is produced by precipitation of Pd metal or oxide onto basic Mg carbonate from Pd salt solutions or suspensions, at room temperature. The catalyst has higher activity and selectivity, reproducible properties, low toxicity, and easy recovery of Pd. The catalyst is useful for selective and quantitative reduction of a substituted nitroketone.

HOMOGENEOUS CATALYSIS

Rhodium Hydroformylation Catalysts with Phosphite Ligands
BASF A.G. European Appl. 472,071A
Rh catalysts used for hydroformylation of 2-20C olefins contain bis-phosphite ligands, and show higher activity and greater hydrolysis resistance than previous Rh complexes. The catalysts show low volatility and allow easy separation of the catalyst and products.

Pollution Reduction
B.J. ROBINSON U.S. Patent 5,085,841
A method for reducing the pollution emitted from a combustion chamber involves introducing a mixture of precious metals homogeneously to the flame zone of the combustion chamber for simultaneously enhancing oxidation of C in the fuel and inhibiting oxidation of N2 in the air. The mixture contains 1-9 mg Pt, 0.2-3 mg Rh and 0.3-3 mg Re, with no more than 15 mg metal per 24 kg fuel. The method is used for diesel and gasoline motor vehicle engines.

Production of Alkylarylcarbinols
MITSUBISHI KASEI CORP. Japanese Appl. 4/21,644
Alkylarylcarbinols are produced by hydrogenating aromatic ketones at 50-250°C under 0.1-200 kg/cm2 pressure, for 1-20 h, in a homogeneous liquid medium, in the presence of 0.0001-100 mol/l of a Ru compound, an organophosphine and a P compound. The products are produced in high yield, under milder conditions and are useful as starting compounds for drugs and agrochemicals.

FUEL CELLS

Fuel Cell for Electricity Generation with Noble Metal Anode
PHYSICAL SCI. INC. World Appl. 92/2,965A
A fuel cell anode has a first fluid-permeable face and a second face in contact with the electrolyte which has as electrocatalyst a crystalline particulate alloy consisting of Au as the main component and a Group VIII noble metal. Electricity is generated in the compact fuel cell by oxidising a lower primary alkanol to CO2 and H2O at the anode and reducing a reducible gas at the cathode. Using this method, poisoning by adsorbed reaction intermediates is avoided or minimised.

Catalyst Powder for Hydrogen Fuel Cell Electrode
DAIKI GUM KOGYO K.K. Japanese Appl. 4/18,933
A highly active electrode is prepared by mixing highly active catalyst powder with C powder and hydrophobic fluoride resin, coating on a conductive base, and heating. The catalyst powder is prepared by soaking an alloy containing at least one of Ti, Zr, Nb or Ta, at least one of Pt, Pd, Rh, Ir or Ru, and at least one of Ni or Co, in hydrofluoric acid. The catalyst powder and electrode have excellent activity for H2 oxidation, can be made without a complicated or expensive process and can be used for a H2 fuel cell electrode.

ELECTRICAL AND ELECTRONIC ENGINEERING

Ceramic Coatings Suitable for Electronic Devices
DOW CORNING CORP. U.S. Patent 5,091,162
A perhydrosiloxane copolymer is dissolved in a solvent to give a 0.1-50 wt.% solution which optionally includes 5-500 ppm of a Pt or Rh catalyst (based on the weight of copolymer), and a modifying ceramic oxide precursor. The copolymers are converted to ceramic coatings having low defect density by coating the solution on a substrate, evaporating and heating at 20-1000°C for up to 6 h in an atmosphere of NH3 or amines. The coatings are used on electronic devices for protection, as dielectric layers and as diffusion barriers against ionic impurities.
Conductor Containing Ruthenium
TANAKA MASSEI K.K. *Japanese Appl. 4/39,812*
A conductor composition consists of a metal powder containing at least Ag and an inorganic binder powder dispersed in a vehicle, where the inorganic binder contains 0.1-12 wt.% glass frit, a Bi compound and a Ru compound (0.05-3 wt.% as oxide) as an additive. The conductor composition has improved adhesion and wettablility of solder.

Manufacture of Low Resistance Platinum Heating Elements
TANAKA KIKINZOKU KOGYO *Japanese Appl. 4/43,586*
A Pt resistance heating element is made by forming heating element circuits on a heat resisting matrix using a photoresist; by electroless Pt plating and heat treatment at 450-600°C. The method is used for making Pt resistance heating elements having low electrical resistance, and uses less Pt.

Ultra High Density Photomagnetic Recording Medium
HITACHI K.K. *Japanese Appl. 4/53,045*
The recording film of a magneto-optical recording medium is up to 500 Å thick and is made of two magnetically bound layers, one of which is an alloy of Tb, Dy or Ho and Fe or Co, while the other is a reciprocal laminate of a Pt group element and an Fe group element, for example Pt and Co. The medium has a larger Kerr rotating angle at the short wavelength domain, and is used for ultra high density recording.

TEMPERATURE MEASUREMENT
High Temperature Thermocouple with Noble Metal Sheath
JGC CORP. *Japanese Appl. 4/38,429*
The outer surface of the temperature measuring part of a thermocouple body is covered with a first sheath tube of at least one of Pt, Rh and Ir; which is itself covered with a second sheath tube of heat resisting ceramics including 50 wt.% or more of Cr oxide. The thermocouple can withstand continuous use for temperature measurement in high temperature furnaces including molten material, for one year (8000 h) or more.

Measuring Resistor for Resistance Thermometer
HERAEUS SENSOR G.m.b.H. *German Appl. 4,026,061*
An electrical resistor for resistance thermometer is prepared by depositing a Pt thin film on a substrate by vapour deposition or sputtering, applying a layer of Pt resistate and Rh sulpho-resinate by screen printing, drying, firing and heat treating at 1000-1400°C. This method gives a uniform distribution of 0.01-10 wt.% Rh in the resistor layer. The temperature coefficient is obtained in the range 1600-3860 ppm/K.

MEDICAL USES
Diagnosis of Cells Resistant to Platinum Anti-Neoplastic Agents
ONTARIO CANCER INST. *European Appl. 467,366A*
A plasma membrane antigen is correlated with resistance to Pt-containing anti-neoplastic agents such as cis-diaminedichloro Pt(II), carboplatin, tetraplatin or iroplatin. The plasma membrane antigen is used to obtain antibodies and nucleotide sequences for detection and diagnosis of cells resistant to Pt-containing anti-neoplastic agents.

New Platinum Complexes for Diagnosing Infections
STICHT KLINISCHE RE. *World Appl. 92/1,699A*
New square planar Pt(2+) complexes and octahedral Pt(4+) complexes have optionally interconnected ligands, where at least one is a labile ligand such as Me2SO, Cl or H2O, and at least one is a detectable marker ligand, such as a fluorescent ligand derived from tetramethyl rhodamine. The new Pt complexes are useful for labelling nucleic acids, especially for production of labelled hybridisation probes for detection of viruses, bacteria, parasites, genetic deviations or gene expression.

Palladium Alloy for Use as a Medical Implant
TOYAMA KIKINZOKU K.K. *Japanese Appl. 4/342*
An alloy consisting of 45-60 mol% Ti and 40-55 mol% Pd+Co, with up to 30 mol% Co, is held at 500-1000°C, and then quenched to prepare an alloy used as an implant, artificial coxae, bone setting plate, and as artificial bones. The alloy has high mechanical strength, excellent corrosion resistance and bio-compatibility.

Titanium-Palladium Alloy for Corrective Dentistry
TOKIN CORP. *Japanese Appl. 4/38,948*
A TiPd alloy containing 45.0-51.0 at.% Pd, and Ti, has at least one of Fe, Cu and W substituted for at least 50 at.% of the TiPd alloy. The alloy is not biotoxic and is used for corrective dentistry.

Platinum Co-ordination Compound
ZENT INST. KREBSFORSCH EAST GERMAN PATENT 295,987
An agent used for treating retroviral infections, especially HIV infections contains, as the active ingredient, a Pt co-ordination compound including, as ligands, an amine, disopropylamine or diaminocyclohexane, an acid anion, and optionally an OH group. The Pt compound is highly effective, has good bio-availability, tolerable specific toxicity, and has a good long term effect even with low doses. It reduces the virus content in the blood and limits the denaturing of normal tissue.

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

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