ABSTRACTS
of current literature on the platinum metals and their alloys

PROPERTIES
Reduction of Pt(II) by H2: Effects of Citrate and NaOH and Reaction Mechanism

Aged aqueous PtCl2+ solutions are reduced by H2 in the absence of a stabiliser and in the presence of stabilising Na citrate or/and NaOH. The slowly formed colloidal Pt nanoparticles were studied by high-resolution electron microscopy. In dilute solutions, the rate of reduction was proportional to the square of the Pt(II) concentration. In the presence of citrate and NaOH, the reduction occurs more slowly.

CuAlPd Alloys for Sensor and Actuator Applications
Z. C. LIN, W. YU, R. H. ZEE and B. A. CHIN, Intermetallics, 2000, 8, (5–6), 605–611

CuAlPd alloys were found to have an austenite transformation temperature range of 115–370°C, and hysteresis range from 17–85°C, depending on composition, heat treatment and working process. Optimal shape memory properties were found for Cu-13.1 wt.% Al-2.4 wt.% Pd.

The Effect of Alloying of Palladium with Silver and Rhodium on the Hydrogen Solubility, Miscibility Gap and Hysteresis

The variation of H solubilities in Pd-5.0 and 10.0 at.% Ag and Pd-5.0 and 10.0 at.% Rh alloys was studied by a gas phase method. An increase of low pressure H solubility with increasing Ag content and a decrease of it with increasing Rh content occurs. The plateau pressure ($p_{\text{h}}$) of Pd-Rh-H had a remarkably higher value than that of Pd-Ag-H. The $p_{\text{h}}$ value decreased with increasing Ag content, whereas it increased with increasing Rh content. Pd-10.0 at.% Ag-H showed the lowest loss of energy for hysteresis.

Chemical Compounds
The Reactions of [M(dppe)$_2$] (M = Pd, Pt) with Elemental Selenium or Tellurium: Preparation and Structure of the Platinum Polyselenide [PtSe$_4$(dppe)]

Reaction of [Pt(dppe)$_2$] (1) (dppe = 1,2-bis(di-phenylphosphino)ethane) with Se or of [PtCl$_2$(dppe)] with Li polyselenide, gave [PtSe$_4$(dppe)]. Reaction of (1) with Te, followed by treatment with CH$_3$Cl, gave [Pt($\mu$-Te)$_2$(dppe)$_2$]Cl$_2$. [Pd(dppe)$_2$] reacts with Se to give [Pd($\mu$-Se)$_2$(dppe)$_2$] or [Pd($\mu$-Se)$_3$(dppe)$_2$]Cl$_2$, depending upon the conditions.

Synthesis and Utility of Novel C-meso-Glycosylated Metalloporphyrins

C-meso-glycosylated porphyrins were prepared by using either a dipyrrylmethane/aldehyde [2+2] cyclocondensation protocol, or a direct pyrrole/aldehyde macrocyclisation. When complexed with Pd(II), and fully liberated from the protecting groups, bis-uridinyl porphyrin and tetra-glycosylated porphyrin gave H$_2$O-soluble metallated species (1). (1) are efficient DNA cleavers with visible light at room temperature.

γ-Halogenated Iridium(III) Acetylacetonates

Ir(acac)$_2(\text{acac})_2$ (acac = CH$_3$COCHCOCH$_3$, acac = CH$_3$COCH$_2$CH$_3$; $n$ = 1, 2, 3; X = F, Cl, Br, I) were prepared and purified. DTA and TGA studies showed the monosubstituted complexes to be the most volatile and disubstituted complexes to be less volatile. The volatility of γ-halogenated Ir(III) acetylacetonates is increased in comparison with the initial Ir(III) tris-acetylacetonate.

Structure and Magnetism in Pr$_2$RuO$_4$

The ordered fluoride, Pr$_2$RuO$_4$, (1) was synthesised for the first time and its crystal structure was assigned as Cmcm. Relatively well separated zig-zig chains of corner-sharing RuO$_4$ octahedra were present. Magnetic susceptibility data of (1) show a Curie-Weiss behaviour for $T > 225$ K with $C = 5.96(4)$ emu K mol$^{-1}$ and $\theta = +11(2)$ K. From the paramagnetic regime, an effective magnetic moment was assigned to Ru(5+) which is slightly reduced from the spin-only value, suggesting localised electrons at this site.

PHOTOCONVERSION
Multiple Ligand-Based Emissions from a Platinum(II) Tertiaryterpyridine Complex Attached to Pyrene
Attachment of an electron-rich aryl substituent at the 4’ position of 2,2':6',2"-terpyridine (trpy) in Pt(trpy)Cl₂ endows the low-lying excited state with intraligand charge-transfer character (ILCT), enhancing the emission intensity, extends the excited-state lifetime and inhibits exciplex quenching by Lewis bases. When pyrene is the substituent, the ILCT character of the absorption becomes dominant and the lifetime extends to 64 μs.

Photophysical and Photoelectrochemical Properties of the Bis(4,4’-arylpyridine)(4,4’-dimethylthio-2,2’-bipyridine) Ruthenium(II) Complex
[Ru(bipy)(Sbpy)]²⁺ (Sbpy = 4,4’-dimethylthio-2,2’-bipyridine) (1) exhibits strong charge-transfer bands at 450 nm and luminescence emission at 630 nm (T1/2 = 0.91 μs). The thioether groups of Sbpy were used as strong binding sites for pentacyanoferrate ions, allowing immobilisation of (1) into Ni Prussian-blue type films. These display photoaction response to visible light in the presence of dissolved O₂.

ELECTRODEPOSITION AND SURFACE COATINGS
Electrodeposition of Platinum from an Alkaline Electrolyte
Electrodeposition of Pt from an alkaline electrolyte at 65°C gave smooth Pt coatings with cauliflower surface morphology. Uniform, crack-free coatings of Pt were obtained when the thickness was < 5 μm. Based on XRD, the electrodeposited Pt films were polycrystalline with crystallite size from 6–15 nm.

Preparation and Characterization of Platinum Black Electrodes
Deposition time and cure temperature were found to influence the quality and morphology of electrochemically deposited Pt black layers on evaporated Pt electrodes. When the Pt black deposition time is < 60 seconds, large voids were clearly seen throughout the electrode due to possible passivating contaminants. Non-uniform outgrowth of Pt black was observed for deposition current densities > 100 mA cm⁻². The reproducibility of highly adherent platinised electrodes was achieved.

Chemical Fluid Deposition: A Hybrid Technique for Low-Temperature Metalization
High-purity films of Pt, Pd, Au and Rh have been deposited onto inorganic and polymer substrates by chemical reduction of organometallics in sc-CO₂ using the chemical fluid deposition technique. A 180 nm thick Rh film (1) was deposited onto Pd-seeded polyimide using [acac(Rh)(COD)] in sc-CO₂ and a forty-fold molar excess of H₂ at 60°C and 165 bar. (1) is polycrystalline and free of C contamination.

Surface Activation of Polyimide with Dielectric Barrier Discharge for Electroless Metal Deposition
A novel activation process (1) for the electroless plating of non-conductive materials using a dielectric barrier discharge (DBD) is reported. (1) is based on the plasma-induced chemical reduction at atmospheric pressure in air of Pd acetate layers resulting in the formation of Pd on non-active surfaces. Fast surface activation of polymers such as polyimide (2) occurs in only a few seconds using a simple DBD device. The DBD-induced Pd layers on (2) exhibit high activity with regard to initiation of electroless Cu plating.

APPARATUS AND TECHNIQUE
Highly Sensitive MISFET Sensors with Porous Pt–SnO₂ Gate Electrode for CO Gas Sensing Applications
A new porous Pt–SnO₂-gate MISFET gas sensor (1) has been demonstrated for the detection of small amounts of CO. (1) combines the catalytic properties of Pt, and the spillover effect onto SnO₂, with surface-sensitive MISFET’s. Using (1), it was possible to detect 54 ppm of CO with a response time < 1 min at 27°C. The good response indicates that (1) can be used at a much lower temperature (27–100°C) than can conventional solid-state gas sensors.

Palladium-Modified Yttria-Stabilized Zirconia Membranes
Thin porous yttria-stabilised zirconia (YSZ) membranes (1) were modified with Pd by the reservoir method. Multiple Pd impregnations inside (1) resulted in a pore reduction and an increase in Pd concentration. He permeation experiments showed that the average permeability decreased from 3.13 × 10⁻³ to 7.34 × 10⁻⁴ mol/(m² s Pa) after four Pd impregnations. XRD indicated that the prepared (1) had pure YSZ and Pd phases. The Pd phase became continuous after four impregnations, which was confirmed by electrical conductivity measurements.
Iridium-Based Electrocatalytic Systems for the Determination of Insulin

A homogeneous electrochemical catalytic system for the determination of insulin is based on the oxidation of insulin by Cl complexes of Ir(IV) (1). The rate constants are equal to 25, 900 and 8400 s⁻¹ for the oxidation of insulin by IrCl₄, Ir(H₂O)Cl₂, and Ir(H₂O)₃Cl₄, respectively. Electroplating of aqurated (1) on glassy C electrode gave an IrO₂ surface film, which was used in a heterogeneous detection system for insulin.

Amperometric On-Line Sensor for Continuous Measurement of Hypoxanthine Based on Osmium-Polyvinylpyridine Gel Polymer and Xanthine Oxidase

An amperometric biosensor using Os-polyvinylpyridine gel polymer (Os-gel-horseradish peroxide (HRP)) and xanthine oxidase (XOD) bienezyme has been developed for use in a thin-layer radial flow cell for on-line measurement of hypoxanthine (1). In continuous-flow amperometric experiments, Os-gel-HRP/XOD/glasy coated electrodes show linear and sensitive responses towards (1) for concentrations of 0.5–80 μM with a detection limit of 0.2 μM.

HETEROGENEOUS CATALYSIS
Highly Selective and Stable Multimetallic Catalysts for Propane Dehydrogenation

Mono- (Pt), bi- (Pt-Sn, Pt-Pb, Pt-Ga) and trimetallic (Pt-Sn-Ga) catalysts based on Pt and supported on Al₂O₃, Al₂O₃ doped with K, and ZnAl₂O₄ were tested in propane dehydrogenation (both in continuous and in pulse reactors) under severe process conditions. Pt-Sn-Ga/ZnAl₂O₄ had a better and more stable performance (high yield to propene and low coke deposition) than the other bi- and trimetallic systems and a commercial catalyst.

Poly(N-isopropylacrylamide)-Grafted Silica as a Support of Platinum Colloids: Preparation Method, Characterization, and Catalytic Properties in Hydrogenation

Well-dispersed Pt colloids were synthesised in situ on the surface of poly(N-isopropylacrylamide)-grafted silica via the reduction of PtCl₄²⁻ by CH₃OH. The immobilised Pt colloids were active and stable heterogeneous catalysts (1) for hydrogenation of allyl alcohol in CH₃OH. (1) are recyclable after centrifugation.

Methyldienalin Hydrocracking over Palladium/Zeolite-X

Studies of hydrocracking of methyldienalin over Pd/rare earth exchange X-type zeolite showed that an increase in temperature from 325 to 350°C resulted in a shift from the preferred cracking products to aromatics, an enhanced amount of light hydrocarbon off-gases, and a higher coverage of C residues (and a lower coverage of reactant molecules). Pd is the agent for H₂ dissociation and repopulation of acid sites.

Catalytic Dehydrogenation of Hydrocarbons in Palladium Composite Membrane Reactors

Electroless Pd plating was confirmed to be a suitable method for coating ceramic supports. Composite Pd-steel membranes could be prepared by high velocity oxy-fuel spraying and a combined method of electroplating and electroless plating. Coated membranes were employed for H₂ separation in lab-scale membrane reactors during the dehydrogenation of ethylbenzene to styrene and propane to propylene. The removal of H₂ significantly increased the olefin yield, compared to the corresponding conventional packed-bed reactor results.

Palladium Catalysts on Activated Carbon Supports
Influence of Reduction Temperature, Origin of the Support and Pretreatments of the Carbon Surface

Activated carbons produced from peat, coconut shell and by pyrolysis of hydrocarbons were treated with O₂, Cl₂, H₂ or NH₃ at elevated temperatures. Pd was deposited from anionic (H₂PdCl₆) neutral (Pd(OAc)₂ in acetonitrile) and cationic (Pd(NH₃)₄Cl₂NO₃) complexes. Temperature-programmed reduction, CO chemisorption and the olefin hydrogenation reaction were used to investigate the possible effects of preparation variables. The origin of the C support and the temperature of the catalyst reduction with H₂ had most influence on the properties of the catalysts.

Polymer-Supported Ruthenium Porphyrins: Versatile and Robust Epoxidation Catalysts with Unusual Selectivity

Carbonyl Ru(II) 5,10,15-tris(4-R-phenyl)-20-(4-hydroxyphenyl)porphyrins (R = Cl, Me) covalently bonded to Merrifield's peptide resin were prepared. These new heterogenised metalloporphyrin epoxidation catalysts (1) exhibit a high versatility and stability. (1) with R = Cl catalyse Cl₂pyNO epoxidation of alkenes such as aromatic and aliphatic terminal alkenes and α,β-unsaturated ketones. (1) are reusable.
Microwave-Assisted Rapid Incorporation of Ruthenium into Lacunary Keggin-Type Polyoxotungstates: One-Step Synthesis, $^{99}$Ru, $^{185}$W NMR Characterization and Catalytic Activity of [PW$_x$O$_y$Ru(DMSO)]$^{n+}$


The microwave-assisted rapid incorporation of a Ru atom into the polyoxometallate framework, and to the selective formation of the diamagnetic, air-stable [PW$_x$O$_y$Ru(DMSO)]$^{n+}$ (1). This exhibited remarkable catalytic activity in the presence of NaI$_2$O or KHSO$_3$ in the oxidation of cyclooctene and adamantane, respectively.

**HOMOGENEOUS CATALYSIS**

Palladium-Catalyzed Carbonylation of Aryl Halides – A Detailed Investigation of the Alkoxycarbonylation of 4-Bromoacetophenone


The homogeneous Pd-catalyzed alkoxycarbonylation of 4-bromoacetophenone with n-butanol to give the corresponding benzoic acid ester (1) was investigated. The highest catalyst efficiency was observed at 130°C and low CO pressures using neat n-butanol as the solvent, NEt$_3$ as the base and Pd(PPh$_3$)$_4$ as the catalyst precursor. Phosinobutane and K$_2$CO$_3$ in toluene resulted in the regioselective arylation of $p$-springene with trimethylhydroquinone under mild conditions. Further steps resulted in synthesis of vitamin E with an overall 50% yield. Other phenolic compounds and 2-substituted-1,3-diienes were also shown to undergo this transformation.

**Rhodium(I)-Catalyzed Addition of Phenols to Dienes. A New Convergent Synthesis of Vitamin E**


A catalytic amount of [RhCl(COD)$_2$], diphenylphosphinobutane and K$_3$CO$_3$ in toluene resulted in the regioselective arylation of $p$-springene with trimethylhydroquinone under mild conditions. Further steps resulted in synthesis of vitamin E with an overall 50% yield. Other phenolic compounds and 2-substituted-1,3-diienes were also shown to undergo this transformation.

**FUEL CELLS**

A Study of Methanol Electro-Oxidation Reactions in Carbon Membrane Electrodes and Structural Properties of Pt Alloy Electro-Catalysts by EXAFS


Transition metal alloy electrocatalysts (Pt-Fe/C, Pt-Co/C, Pt-Ni/C, Pt-Cu/C) were evaluated as potential alternatives to direct oxidation of DMFCs and compared with Pt group metal and alloy catalysts using CV and X-ray absorption spectroscopy. Pt-Co/C was found to be a better catalyst than the other transition metal alloys. Pt-C/Nafion showed the highest resistance $(10^6 \, \Omega \, cm^{-2})$ compared with Pt-Ru/C $(280 \, m\Omega \, cm^{-2})$. The unfavourable electrochemical performance of Pt-Ru can be correlated with the observed variations in geometric structural information obtained from EXAFS and XANES.