

ABSTRACTS

of current literature on the platinum metals and their alloys

PROPERTIES

Magnetic Properties and Co-operative Domain Structures in Early Stages of Ordering of Cobalt-Platinum Single Crystals under Compressive Loading

N. I. VLASOVA, G. S. KANDAUROVA, N. N. SHCHEGOLEVA, V. V. MAYKOV and A. E. ERMAKOV, *Fiz. Metal. Metallov.*, 1995, 80, (1), 27–40

Magnetic properties and the magnetic domain structure in various stages of atomic ordering were studied under compression in CoPt single crystals. A relationship between the magnetic properties and the domain structure of CoPt, which has monocrystalline characteristics, is established. A detailed description of the newly discovered magnetic domains in PtCo single crystals is given.

Specific-Heat Study of Nanocrystalline Palladium

Y. Y. CHEN, Y. D. YAO, S. S. HSIAO, S. U. JEN, B. T. LIN, H. M. LIN and C. Y. TUNG, *Phys. Rev. B*, 1995, 52, (13), 9364–9369

Studies of the low temperature specific heat for $T = 0.7$ – 20 K and magnetic susceptibility for $T = 1.6$ – 300 K of Pd nanocrystals with average particle size 84 \AA showed an enhancement at $T > 3.5$ K, which is related to both the softening and the size effect on the photons. The linear temperature coefficient of specific heat decreases to a lower value compared to that of bulk Pd. An estimated surface coefficient of the specific heat is $\sim 30\%$ that of the bulk.

Nanoscale Ag-Pd and Cu-Pd Alloys

H. N. VASAN and C. N. R. RAO, *J. Mater. Chem.*, 1995, 5, (10), 1755–1757

Nanoparticles of Ag-Pd and Cu-Pd alloys with diameters of 5 – 40 nm were prepared by heterogeneous reaction of dry MeOH or EtOH with intimate mixtures of $\text{AgNO}_3 + \text{PdO}_x$ and $\text{CuO}_x + \text{PdO}_x$, respectively. The nanoscale alloys have f.c.c. structure. All the alloy particles could be obtained in bulk quantities.

Synthesis and Hydrogen Permeation Properties of Ultrathin Palladium-Silver Alloy Membranes

V. JAYARAMAN and Y. S. LIN, *J. Membrane Sci.*, 1995, 104, (3), 251–262

Ultrathin (250 – 500 nm) Pd-Ag alloy films were efficiently deposited on porous ceramic supports by sputter deposition. At 250°C , the ceramic-metallic membrane showed a H: N_2 separation factor of 5.69 , which increases with permeation temperature. Under suitable preparation conditions, a pinhole-free $\gamma\text{-Al}_2\text{O}_3$ support ensures the gas-tightness and high selectivity of the coated Pd-Ag membrane.

Synergistic Alloying Behaviour of $\text{Pd}_{50}\text{Cu}_{50}$ Single Crystals upon Adsorption and Co-adsorption of CO and NO

Y. DEBAUGE, M. ABON, J. C. BERTOLINI, J. MASSARDIER and A. ROCHEFORT, *Appl. Surf. Sci.*, 1995, 90, (1), 15–27

The surface reactivity of $\text{Pd}_{50}\text{Cu}_{50}$ (111) and (110) single crystals was studied during adsorption and co-adsorption of CO and NO at low temperatures. CO and NO were more tightly bound to Cu and less tightly bound to Pd than to the pure metals. The calculated NO coverages on Pd-Cu were about four times lower than for CO due to the dissociation of a fraction of NO on the surfaces. Presaturation with NO leads to molecular adsorbed states and irreversible dissociated species not removed during exposure to CO.

Superconductivity and Magnetism in the $\text{La}_{2-x}\text{Nd}_x\text{Rh}_3\text{Si}_5$ System

N. G. PATIL, K. GHOSH and S. RAMAKRISHNAN, *Phys. Rev. B*, 1995, 52, (13), 9679–9690

The bulk superconductivity in $\text{La}_2\text{Rh}_3\text{Si}_5$ was established below 4.4 K together with bulk antiferromagnetism in $\text{Nd}_2\text{Rh}_3\text{Si}_5$, below 2.7 K, from resistivity, susceptibility and heat capacity studies. The superconducting transition temperature of $\text{La}_2\text{Rh}_3\text{Si}_5$ decreased with Nd substitution for La. The temperature dependence of the upper critical field of Nd-doped $\text{La}_2\text{Rh}_3\text{Si}_5$ alloys was also analysed.

Structure and Magnetic Properties of $\text{Sr}_{2-x}\text{A}_x\text{IrO}_4$ ($\text{A} = \text{Ca}$ and Ba)

T. SHIMURA, Y. INAGUMA, T. NAKAMURA, M. ITOH and Y. MORII, *Phys. Rev. B*, 1995, 52, (13), 9143–9146

Substitutions of Ca and Ba for Sr in Sr_2IrO_4 resulted in an increase in the Ir-O(2)-Ir bond angle in the IrO_2 plane. However, the IrO(2) distance was unchanged by Ba substitution, but was decreased by Ca substitution. Semiconductive behaviour of the resistivity was displayed by all compounds with increase in activation energy above 200 K.

Deposition and Characterization of Crystalline Conductive RuO_2 Thin Films

Q. X. JIA, S. G. SONG, S. R. FOLTYN and X. D. WU, *J. Mater. Res.*, 1995, 10, (10), 2401–2403

Highly conductive RuO_2 thin films were grown on (100) yttria-stabilised ZrO_2 (YSZ) substrates by pulsed laser deposition. Epitaxial growth of RuO_2 thin films with electrical properties similar to those of bulk single crystal RuO_2 was obtained. The crystalline RuO_2 thin films, deposited at 500 – 700°C , had a room temperature resistivity of $35 \pm 2 \mu\Omega\text{cm}$, and residual resistance ratio of ~ 5 . The RuO_2 films have much lower resistivity and a higher residual resistance ratio than polycrystalline ones.

CHEMICAL COMPOUNDS

The First Reported Structure of a Platinum(IV) Complex Containing Deprotonated Amide Ligands – A Model for Platinum(IV)-Peptide/Protein Interactions

C. J. CAMPBELL, A. CASTINEIRAS and K. B. NOLAN, *J. Chem. Soc., Chem. Commun.*, 1995, (19), 1939–1940
Unexpected product $\text{cis-Pt}(\text{LH}_2)\text{Cl}_2$ and also $\text{H}_2\text{L}[\text{PtCl}_4]$ were formed by reaction of 1,2-diaminoethane-*N,N,N',N'*-tetra(*N*-methylacetamide)*L* with $\text{K}_2[\text{PtCl}_4]$ in aqueous solution. This Pt(IV) complex, which contains deprotonated amide ligands, is novel and is used as a model for Pt(IV)-peptide/protein interactions. The formation of Pt(IV) complexes from the corresponding Pt(II) systems, even when two or more deprotonated amide groups are present, is new.

A Strongly Fluorescent Organoplatinum Complex

K.-T. AYE and R. J. PUDDPHATT, *Inorg. Chim. Acta*, 1995, 235, (1–2), 307–310

A novel organo Pt(IV) complex, $[\text{PtBrMe}_2(4\text{-CH}_2\text{-7-MeO-coumarin})(\text{phen})]$, where phen = 1,10-phenanthroline, was prepared and characterised. The coumarin substituent causes the complex to fluoresce strongly in fluid solution at room temperature. The emission appears to originate from the excited state which is centred on the coumarin substituent.

Structure of Polynuclear Hydroxo Complexes of Palladium(II) Formed by Alkaline Hydrolysis of Its Chloride Complexes

S. YU. TROITSKII, A. L. CHUVILIN, D. I. KOCHUBEI, B. N. NOVGORODOV, V. N. KOLOMIICHUK and V. A. LIKHOLOBOV, *Izv. Akad. Nauk Rossi, Ser. Khim.*, 1995, (10), 1901–1905

The structure of polynuclear hydroxo complexes of Pd^{II} (PHC) formed by alkaline hydrolysis of Pd^{II} chloro complexes was studied. The PHC particles were found to be filaments containing ~100 Pd atoms which were curled into a ball. The filaments consist of square-planar PdO_4 units linked via one or two O-bridges, the latter increases in number with PHC ageing. The interatomic distances around the Pd atoms, the size distribution of the PHC, and photomicrographs of the PHC particles adsorbed on graphite were obtained.

Selectivity in the Aliphatic Palladation of Ketone Hydrazones. An Example of Palladium-Promoted Intramolecular Addition of a *N,N*-Dimethylhydrazone to an Alkene

D. J. CÁRDENAS and A. M. ECHAVARREN, *Organometallics*, 1995, 14, (9), 4427–4430

A γ,δ -unsaturated dimethylhydrazone reacted with $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ to yield a palladacycle which resulted from the addition of the imino group to a (η^2 -alkene) Pd complex. The nucleophilicity of the hydrazone imino N diminishes the efficacy of the aliphatic palladation giving no benzylic or allylic C-H activation. This is the first example of intramolecular attack of the imino N of a hydrazone to an alkene promoted by Pd.

Iridium Complexes with α -Diimines: Catalytic Hydrogen Transfer from Isopropanol to Cyclohexanone

M. BIKRANI, L. FIDALGO and M. A. GARRALDA, *Polyhedron*, 1996, 15, (1), 83–89

Ir complex $[\text{Ir}(\text{COD})\text{Cl}]_2$ (COD = 1,5-cyclooctadiene) reacting with α -diimines (LL) derived from glyoxal (GLL) or biacetyl (BLL) gave different types of compounds depending on the ligand and on the stoichiometric ratios used; $[\text{Ir}_2(\text{COD})_2\text{Cl}_2(\text{GLL})]$ or $\text{IrCl}(\text{COD})(\text{LL})$ were formed when the ratio $[\text{Ir}(\text{COD})\text{Cl}]_2:\text{GLL}$ is 1:1 or 1:2, respectively. In the presence of bulky anions, cationic $[\text{Ir}(\text{COD})(\text{LL})]\text{A}$ species, which had high activity, were formed.

New Homoleptic Metal Carbonyl Cations: the Syntheses, Vibrational and ^{13}C MAS NMR Spectra of Hexacarbonyl-Ruthenium(II) and -Osmium(II) Undecafluorodiantimonate(V), $[\text{Ru}(\text{CO})_6][\text{Sb}_2\text{F}_{11}]_2$ and $[\text{Os}(\text{CO})_6][\text{Sb}_2\text{F}_{11}]_2$

C. WANG, B. BLEY, G. BALZER-JÖLLENBECK, A. R. LEWIS, S. C. SIU, H. WILLNER and F. AUBKE, *J. Chem. Soc., Chem. Commun.*, 1995, (20), 2071–2072

In a simple, one-step procedure, new homoleptic carbonyl cations $[\text{Ru}(\text{CO})_6]^{2+}$ and $[\text{Os}(\text{CO})_6]^{2+}$ were obtained as $[\text{Sb}_2\text{F}_{11}]^-$ salts by the reductive carbonylation of $\text{M}(\text{SO}_3\text{F})_2$ ($\text{M} = \text{Ru}, \text{Os}$), under very mild conditions of 1 atm CO and at 60–90°C. These $[\text{M}(\text{CO})_6][\text{Sb}_2\text{F}_{11}]_2$ salts are thermally stable.

ELECTROCHEMISTRY

Formation and Reduction of Hydrrous Oxide Films on Platinum in Aqueous Solution at 273 K

L. D. BURKE and D. T. BUCKLEY, *J. Appl. Electrochem.*, 1995, 25, (10), 913–922

Studies of Pt hydrrous oxide deposits, produced by potential cycling, with a lower limit of 0.2 V, in acid solution at 273 K, showed two reduction peaks which were attributed to the presence of the two oxide components, HO1 and HO2. Thick hydrrous oxide films were formed at 273 K, with ~0.25 V lower limit, giving a nearly pure HO2 deposit, but thinner deposits of either HO1 or mixtures of HO1 + HO2 were formed using a value of > 0.45 V for the lower cycling limit.

In Situ FTIR Spectroscopy Characterization of the NO Adlayers Formed at Platinum Single Crystal Electrodes in Contact with Acidic Solutions of Nitrite

A. RODES, R. GÓMEZ, J. M. ORTS, J. M. FELIU, J. M. PÉREZ and A. ALDAZ, *Langmuir*, 1995, 11, (9), 3549–3553

Adsorbed NO was formed on the Pt(100), Pt(111) and Pt(110) basal planes of Pt single crystal electrodes from acidic nitrite solutions. The effect of the electrode potential on the N-O stretching frequency was lower for NO adsorbed on the Pt(110) electrode than for Pt(111) and Pt(100). N_2O was detected as an intermediate during the reduction of nitrous acid at 0.6–0.4 V on Pt(100). At potentials of > 1.10 V, both adsorbed NO and nitrous acid in solution oxidised to nitrate.

Electrochemical Deposition of Hydrogen on Platinum Single Crystals Studied by Infrared-Visible Sum-Frequency Generation

A. PEREMANS and A. TADJEDDINE, *J. Chem. Phys.*, 1995, **103**, (16), 7197–7203

Vibrational patterns of the hydride surface were monitored during under- and overpotential deposition of H₂ on polycrystalline Pt, Pt(100), Pt(110) and Pt(111) surfaces in H₂SO₄ by IR-visible sum-frequency generation (SFG). For Pt(100) and Pt(111), the observed double SFG resonance was most consistent with a bonding configuration in which H₂O dimers are each bonded to three H atoms adsorbed on the relaxed substrate. Significant H adsorption was detected on Pt(111) in H₂SO₄ electrolyte at underpotentials as high as 0.35 V/NHE.

Kinetics of Dissociative Adsorption of Formaldehyde on a Pt(111) Electrode in Sulphuric Acid Solutions Studied Using a Programmed Potential Step Technique and Time-Resolved Fourier Transform IR Spectroscopy

S.-G. SUN, G.-Q. LU and Z.-W. TIAN, *J. Electroanal. Chem.*, 1995, **393**, (1–2), 97–104

Quantitative studies of the kinetics of the dissociative adsorption of HCHO on a Pt(111) electrode showed the initial rate was around 10⁻¹¹ mol/cm²s, and proceeded as follows: HCHO adsorption onto the Pt(111) surface; interaction of adsorbed HCHO with the Pt(111) surface; breaking of chemical bonds and the formation of the final products. The products consisted of linear and bridge bonded CO. At -0.25 to 0.25 V, the rate of dissociative adsorption of HCHO on Pt(111) displayed a volcano curve with two maxima located at -0.06 and 0.15 V, respectively.

Preparation and Chemical Reduction of Pt(IV) Chloride-GICs: Supported Pt vs Pt Inclusion Graphite Compounds

J.-Y. TILQUIN, R. CÔTÉ, G. VEILLEUX, D. GUAY, J. P. DODELET and G. DENÈS, *Carbon*, 1995, **33**, (9), 1265–1278

Pt(IV) chloride-graphite intercalation compounds (M-GICs) were prepared from μm sized graphite powder and were subsequently chemically reduced. Pt(IV) chloride-GIC was obtained by isothermal vapour transport of PtCl₄ at 350–500°C under Cl₂ gas pressure in a very slow process. PtCl₄ or PtCl_{3.84} is also intercalated in graphite after the reaction of H₂PtCl₆ with graphite in SOCl₂ for 2 days under Ar.

Electro-Oxidation of D-Sorbitol on Platinum in Perchloric Medium: A Voltammetric Study

I. FONSECA, M. I. S. LOPES, J. L. SANTOS and L. PROENÇA, *Electrochim. Acta*, 1995, **40**, (17), 2701–2706

The electrocatalytic oxidation of D-sorbitol on a polycrystalline Pt electrode, in perchloric aqueous medium, was studied by cyclic voltammetry under different sweep rates, potential limits, stirrings, temperature, pH and D-sorbitol concentrations. A value of ~ 50 kJ/mol was obtained for the apparent activation enthalpy of the oxidation reaction at 0.1 V.

The Electrochemical Permeation of Hydrogen in Palladium: Boundary Conditions during a Galvanostatic Charging under Low Charging Current Densities

P. MANOLATOS, C. DURET-THUAL, J. LE COZE and M. JEROME, *Corros. Sci.*, 1995, **37**, (11), 1797–1807

The electrochemical permeation of H in Pd was studied and was easier than H permeation in steel. Total oxidation of the H diffusing through the Pd sample occurred, giving H efficiency of ~ 100%. The diffusion coefficient was evaluated as 7 × 10⁻⁷ cm²/s. Using electrochemical H permeation in Pd, the metal surface phenomena can be controlled and stationary conditions and good reproducibility can be obtained.

Oxygen Evolution and Reduction on Iridium Oxide Compounds

M. V. TEN KORTENAAR, J. F. VENTE, D. J. W. IJDO, S. MÜLLER and R. KÖTZ, *J. Power Sources*, 1995, **56**, (1), 51–60

Studies of the electrochemical properties of twelve Ir oxide compounds during the O-evolution reaction (OER) and the O-reduction reaction (ORR) showed that Pb₂(Pb_xIr_{2-x})O₇₋₉ and Nb₂IrO₇ compounds had the highest activity for both reactions. Steady-state current-potential curves were measured in 45% KOH. The catalytic activity of pyrochlores towards the ORR is more dependent on the presence of a Pb or Bi cation than is the catalytic activity towards OER.

Electrochemical Promotion of IrO₂ Catalyst for the Gas Phase Combustion of Ethylene

E. VARKARAKI, J. NICOLE, E. PLATTNER, C. COMINELLIS and C. G. VAYENAS, *J. Appl. Electrochem.*, 1995, **25**, (10), 978–981

An increase by up to a factor of 10 in the catalytic activity of IrO₂ catalyst films for the gas phase combustion of ethylene was achieved via anodic polarisation of the IrO₂ catalyst relative to a Au electrode, both deposited on Y₂O₃-stabilised ZrO₂ solid electrolyte. The steady state increase in the catalytic reaction rate was 200 times higher than the expected rate increase of ethylene combustion, calculated from Faraday's law. This is the first example of the effect of non-faradaic electrochemical modification of catalytic activity (NEMCA) using a metal oxide catalyst.

Mass Transport Study of Nafion® Coatings Saturated with [Os(bpy)₃]²⁺ by an Electrochemical Quartz Crystal Microbalance

M. SHIN, E.-Y. KIM, J. KWAK and I. C. JEON, *J. Electroanal. Chem.*, 1995, **394**, (1–2), 87–92

Studies of mass transport behaviour in [Os(bpy)₃]²⁺-saturated Nafion coatings on an electrode showed that the mass of the electrodes varies with the number of cycles, during cyclic voltammetry, after the start of the potential scan and approaches a steady state. The first cyclic voltammogram showed an anodic peak at ~ 0.85 V vs. Ag/AgCl, corresponding to ejection of [Os(bpy)₃]²⁺ complexes, while the frequency change-potential curve showed an increase in mass on the first positive scan. This is explained by the H₂O and the [Os(bpy)₃]²⁺ complexes moving in opposite directions.

PHOTOCONVERSION

Photocatalytic Hydrogenation by Using Platinized Titanium Dioxide for Carbon-Carbon Double Bonds of Linoleic Acid

A. A. WIDODO, K. MINE, T. KATO and Y. BUTSUGAN, *Denki Kagaku*, 1995, 63, (7), 678–679

The hydrogenation of linoleic acid using Pt/TiO₂ photocatalyst had oleic acid as an intermediate. Pt was photodeposited onto TiO₂ to increase the H₂ evolution rate. Hydrogenation on the Pt occurred smoothly in the presence of H₂ in the dark. A 100% yield in stearic acid formation from oleic acid was detected, after using Pt/TiO₂ in EtOH. The irradiation time was 20 h.

Effect of Platinum Loading on the Photocatalytic Activity of Cadmium(II) Sulfide Particles Suspended in Aqueous Amino Acid Solutions

B. OHTANI, J. KAWAGUCHI, M. KOZAWA, Y. NAKAOKA, Y. NOSAKA and S. NISHIMOTO, *J. Photochem. Photobiol. A: Chem.*, 1995, 90, (1), 75–80

Loading small amounts of Pt by colloidal deposition or PtO₂ by mechanical mixing, onto CdS particles inhibited the photocatalytic racemisation of L-lysine in aqueous suspension at ambient temperature under deaerated conditions, but promoted deamino-N-cyclisation of L-lysine into pipecolinic acid. Less than 0.3 wt.% of colloiddally deposited Pt is needed to separate the surface reaction sites, but a larger amount of mechanically deposited PtO₂ is needed.

Cadmium Sulfide with Iridium Sulfide and Platinum Sulfide Deposits as a Photocatalyst for the Decomposition of Aqueous Sulfide

I. B. RUFUS, B. VISWANATHAN, V. RAMAKRISHNAN and J. C. KURIAKOSE, *J. Photochem. Photobiol. A: Chem.*, 1995, 91, (1), 63–66

Studies of the effect of the in situ deposition of Pt and Ir on CdS during photocatalytic decomposition of aqueous sulphide showed the formation of a very effective bifunctional photocatalyst MS/CdS/M, where MS is Pt or Ir sulphide and M is Pt or Ir. The order of reactivity for the metallisation of CdS by the above method is: Rh > Pt > Pd > Ru = Ir > Co ≈ Ni = Fe. This method avoids oxidation of the metals by air.

Hydrogen Production from Water by Visible Light Using Zinc Porphyrin-Sensitized Platinized Titanium Dioxide

E. A. MALINKA, G. L. KAMALOV, S. V. VODZINSKII, V. I. MELNIK and Z. I. ZHILINA, *J. Photochem. Photobiol. A: Chem.*, 1995, 90, (2–3), 153–158

The rate of H₂ evolution from aqueous suspensions of Pt/TiO₂ with deposited Zn porphyrin in the presence of an electron donor, EDTA, triethanolamine, etc., during visible-light irradiation was optimised with respect to the concentrations of Pt, Zn porphyrin and electron donor. H₂ production increased sharply in alkaline solutions when triethanolamine molecules were deprotonated. Photostability is increased on the semiconductor.

Photo-Splitting of Water to Dihydrogen and Hydroxyl Radicals Catalysed by Rhodium-Deposited Perfluorinated Poly(*p*-phenylene)

T. KITAMURA, K. MARUO, Y. WADA, K. MURAKOSHI, T. AKANO and S. YANAGIDA, *J. Chem. Soc., Chem. Commun.*, 1995, (7), 2189–2190

Perfluorinated poly(*p*-phenylene) (1) with colloidal Rh metal deposited on it catalysed the photosplitting of H₂O under UV irradiation to H₂ and hydroxyl radicals which were scavenged by benzene to give phenol. Rh was an effective mediator for irreversible electron transfer from (1), and benzene as hydroxyl scavenger was also important in the heterogeneous photocatalytic H₂O-splitting reaction.

Photooxidation of Ru(bpy)(CN)₄²⁻ and Ru(DM bpy)(CN)₄²⁻

A. ŪLVEČKY and A. HORVÁTH, *Inorg. Chim. Acta*, 1995, 236, (1–2), 173–176

The photophysical and photochemical properties of Ru(bpy)(CN)₄²⁻ (1) and Ru(DM bpy)(CN)₄²⁻, where bpy = 2,2'-bipyridine and DM bpy = 4,4'-dimethyl-2,2'-bipyridine, are reported. The luminescence quantum yields of the lowest energy d-π* state are (8 ± 1) × 10⁻³ and (7 ± 1) × 10⁻³ for the bpy and DM bpy complexes, respectively, in aqueous solution at ambient temperature. Lifetimes are 125 and 115 ns, respectively, and luminescence lifetimes increase ~ 3-fold in D₂O. Photolysis of (1) was also studied in chloroform.

Laser Flash Photolysis and Matrix Isolation Studies of Ru[R₂PCH₂CH₂PR₂]₂H₂ (R = C₂H₅, C₆H₅, C₂F₅): Control of Oxidative Addition Rates by Phosphine Substituents

L. CRONIN, M. C. NICASIO, R. N. PERUTZ, R. G. PETERS, D. M. RODDICK and M. K. WHITTLESEY, *J. Am. Chem. Soc.*, 1995, 117, (40), 10047–10054

The primary photoproducts of the title Ru hydrides, Ru(drpe)₂H₂ (drpe = depe, dppe and dfep), respectively, are the 4-co-ordinate complexes Ru(drpe)₂, and their multiband UV-visible spectra are characteristic of a structure close to square planar for Ru(dmpe)₂, Ru(depe)₂ and Ru(dppe)₂. The reactivity of the complexes increased in the order: Ru(dfep)₂ < Ru(dppe)₂ < Ru(depe)₂ < Ru(dmpe)₂. The rate constant of each Ru(drpe)₂ complex increased with substrate, in the order C₂H₄ < CO < H₂, but the selectivity toward substrates was greater for Ru(depe)₂ and Ru(dppe)₂, than for Ru(dmpe)₂.

Photoelectrochemical Properties of RuS₂-Coated TiO₂ Electrodes

M. ASHOKKUMAR, A. KUDO and T. SAKATA, *Bull. Chem. Soc. Jpn.*, 1995, 68, (9), 2491–2496

RuS₂-coated TiO₂ electrodes displayed semiconductor sensitisation by RuS₂ fine particles on TiO₂ during photoelectrochemical studies. The electron-transfer efficiency from RuS₂ to TiO₂ was affected by the number of RuS₂ colloid coatings and the preparation temperature of the RuS₂ colloids. A band-gap value of around 2.8 eV was evaluated for the RuS₂ particles with high sensitisation efficiency.

ELECTRODEPOSITION AND SURFACE COATINGS

Some Experiences with a Platinum-Plated Titanium Anode for Chromium Electrodeposition

R. M. KRISHNAN, S. SRIVEERARAGHAVAN, S. JAYAKRISHNAN and S. R. NATARAJAN, *Met. Finish.*, 1995, 93, (9), 46–48

The behaviour of Pt-plated Ti anodes was studied in three different Cr electroplating solutions. A Ti sample was Pt plated in a dinitro platinous acid bath at a pH of 1.0–1.5, 70°C, current density of 5 mA/cm², using a Pt wire as an anode, to a thickness of 5 µm. The Pt/Ti electrode is most suitable for use in conventional Cr plating baths.

Novel Preparation of Pd/Vycor Composite Membranes

K. L. YEUNG, J. M. SEBASTIAN and A. VARMA, *Catal. Today*, 1995, 25, (3–4), 231–236

Pd film plated onto porous Vycor glass was prepared by electroless plating from typical hydrazine-based and formaldehyde modified baths. Two methods of improving the Pd film quality by modifying the plating solution and by osmosis were tested. The electroless Pd film obtained from the modified bath has a higher lustre and density, and smaller grain size. By combining electroless plating and osmosis, the microstructure of the Pd film can be manipulated to give both porous and dense films.

APPARATUS AND TECHNIQUE

Performance of Platinum-Based Spherical Mercury Microelectrodes in Cyclic Voltammetry and Stripping Analysis

M. A. BALDO, S. DANIELE, M. CORBETTA and G. A. MAZZOCCHIN, *Electroanalysis*, 1995, 7, (10), 980–985

The cyclic voltammetric (CV) and anodic stripping voltammetric performance of spherically shaped Hg microelectrodes, formed by electroreduction of Hg onto an inlaid Pt microdisk of radius r , and characterised by different Hg drop heights h , with $h:r$ ratios of 0.1–2, were tested in solutions containing Pb²⁺ and Cd²⁺ in NaCl and NaClO₄ + HClO₄, as supporting electrolytes. For CV the results depend on $h:r$. The thickness of the Hg deposit on the Pt microelectrodes affected the analysis of low Cd levels in H₂O.

Measurement of Pt Electrode Surface Area of Automotive ZrO₂ Oxygen Sensors

R. K. USMEN, E. M. LOGOTHETIS and M. SHELEF, *Sens. Actuators B*, 1995, 28, (2), 139–142

The application of a very sensitive CO methanation method is described for measuring Pt loading and dispersion on the outer sensing electrode of commercially heated exhaust-gas O₂ sensors. The Pt dispersion was determined using the methanation of adsorbed CO with H₂ by measuring the amount of CH₄ formed using a flame ionisation detector. In all sensors, the Pt dispersion was very low, with only 1–3 atoms in 10³ directly accessible to the gas phase.

Palladium-Doped Screen-Printed Electrodes for Monitoring Formaldehyde

J. WANG, M. PEDRERO and X. CAI, *Analyst*, 1995, 120, (7), 1969–1972

Disposable amperometric sensors for HCHO detection were fabricated by screen printing Pd-doped C strips. These sensors rely on the strong electrocatalytic action of the dispersed Pd particles in reducing the HCHO. The low detection limit of 2 × 10⁻⁶ mol/l was accompanied by a wide linear range and high selectivity. These single-use sensor strips allow on-site environmental and industrial HCHO monitoring.

H₂-Induced Surface and Interface Potentials on Pd-Activated SnO₂ Sensor Films

J. MIZSEI, *Sens. Actuators B*, 1995, 28, (2), 129–133

The surface and interface potentials of an SnO₂ gas-sensor film were studied by vibrating capacitor and other methods. Ultra thin, 2–5 nm, Pd films were sputtered as activators onto the SnO₂ layer. The work function of the Pd particles affects the charge-carrier concentration directly at the Pd-SnO₂ Schottky barriers, and indirectly by capacitive coupling between the Pd surface and Pd-free areas. The work-function change of the Pd surface layer controls the carrier concentration change, and thus the specific resistivity change in the whole layer.

Electrocatalytic Oxidation and Amperometric Detection of Aliphatic and Furanic Aldehydes at a Mixed-Valent Ruthenium Oxide-Ruthenium Cyanide Film on Glassy Carbon Electrodes

T. R. I. CATALDI, C. CAMPA and D. CENTONZE, *Anal. Chem.*, 1995, 67, (20), 3740–3745

A chemically modified glassy C electrode, with a mixed valent RuO-RuCN inorganic film was constructed and tested for the electrocatalytic oxidation of aliphatic and furanic aldehydes, such as 2-furaldehyde, etc., in acidic media. Such electrodes were used in cyclic voltammetry and flowing streams amperometric detection, and could catalyse the slow electrode reaction of the aldehydes. Low levels of RuCl₃ and K₂Ru(CN)₆ in the mobile phase improved the response stability.

HETEROGENEOUS CATALYSIS

The Hydrogenation of Naphthalene with Platinum/Alumina-Aluminum Phosphate Catalysts

T.-C. HUANG and B.-C. KANG, *Ind. Eng. Chem. Res.*, 1995, 34, (9), 2955–2963

A Pt/AAP_x catalyst, where AAP is Al₂O₃-Al phosphate and x is the Al:P atomic ratio, was used as a hydrogenation catalyst to reduce the aromatic content in diesel fuels. It showed better activity but lower *cis*-Decalin selectivity than Pt/γ-Al₂O₃, due to the higher acidity of the AAP_x support. The catalysts with 6 < x < 10 displayed the highest hydrogenation activity and the lowest *cis*-Decalin selectivity of all the Pt/AAP_x catalysts. For $x = 3$ a large pore size catalyst with good hydrogenation activity is obtained.

The Thioresistance of Platinum/Aluminum Borate Catalysts in Aromatic Hydrogenation

T.-C. HUANG and B.-C. KANG, *J. Mol. Catal.*, 1995, 103, (3), 163–174

Pt/AB_x and Pt/B_x-Al₂O₃ catalysts, where AB is Al borate, have higher hydrogenation activity and S tolerance than Pt/γ-Al₂O₃ (1) due to the higher acidity of the supports. The addition of B to (1) improved the catalyst hydrogenation activity and S tolerance of the catalyst due to the increasing acidity of the supports. The Pt metal distribution affects the S tolerance of (1). These studies were performed during naphthalene and benzothiophene dissolution in *n*-hexadecane to simulate the aromatics and S compounds in diesel fuels.

Study of Pt-Promoted Cobalt CO Hydrogenation Catalysts

D. SCHANKE, S. VADA, E. A. BLEKKAN, A. M. HILMEN, A. HOFF and A. HOLMEN, *J. Catal.*, 1995, 156, (1), 85–95

The effect of small amounts of Pt on supported Co catalysts was studied on samples prepared by co-impregnation of 9 wt.% Co and 0 or 0.4 wt.% Pt on Al₂O₃ or SiO₂. At 483 K, 1 bar pressure and H₂: CO = 7, CO hydrogenation rates for Pt-modified catalysts were 3–5 times higher than those on the unmodified ones. The Pt strongly affected the reducibility of the catalysts; this was most pronounced on the Al₂O₃-supported catalysts due to the reduction of highly dispersed surface Co oxides. The dispersion of metallic Co on Pt modified catalyst also increased.

Hydrocarbon Synthesis from CO and H₂ on (Fe + Pt)/SiO₂ Catalysts

V. I. KOVALCHUK and B. N. KUZNETSOV, *J. Mol. Catal. A: Chem.*, 1995, 102, (2), 103–110

Catalytic and adsorption properties of (Fe + Pt)/SiO₂ catalysts were studied on catalysts prepared by co-impregnation of SiO₂ with aqueous solutions of FeCl₃ and H₂PtCl₆. Fe-Pt particles of size 5–36 nm and b.c.c. or f.c.c. crystal lattice were formed during reduction of the catalysts by flowing H₂. Bimetallic catalysts had higher specific activity for the CO hydrogenation reaction than monometallic ones, and the increased activity of the Fe-Pt particles was shown by increased formation of C₄₊ olefins.

Promoter Effect of Pd in Hydrogenation of 1,3-Butadiene over Co-Pd Catalysts

A. SÁRKÁNY, Z. ZSOLDOS, G. STEFLER, J. W. HIGHTOWER and L. GUCZI, *J. Catal.*, 1995, 157, (1), 179–189

The effect of adding 0.1–1.0 wt.% Pd to 5 wt.% Co/Al₂O₃ was studied during the hydrogenation of pure 1,3-butadiene and butadiene in a mixture with 1-butene at room temperature. The presence of Pd increased the reducibility of the Co, and separate aluminate, Co, and Pd-Co bimetallic surface phases were identified. Increasing the Co : Pd ratio decreased the formation of *n*-butane at room temperature relative to the rate of butadiene conversion. The improved selectivity was achieved at the expense of increased olefin isomerisation and deactivation caused by the accumulation of carbonaceous residues on the surface.

Total Combustion of *m*-Xylene over Palladium Catalysts Supported by Stainless Steel Flakes

L. BORKÓ, Z. SCHAY and L. GUCZI, *Appl. Catal. A: Gen.*, 1995, 130, (2), 157–174

The ignition temperature of the combustion of *m*-xylene mixtures over metallic Pd/stainless steel flakes catalyst was lowered by ~ 330°C, compared to that of thermal oxidation, in order to study the total combustion of *m*-xylene. High and low activity states were observed during ignition at 200–250°C and ~ 400°C, respectively. Combustion in the high activity state was initiated by the catalyst, this was followed by a chain reaction which propagated into the gas phase. Active species which accumulated on the surface during the induction period before combustion, were thought to be responsible for this process.

Ruthenium Catalysts on Fullerene C₆₀ for Ammonia Synthesis

Y. IZUMI, S. HIKAZUDANI and K.-I. AIKA, *Shokubai*, 1995, 37, (6), 466–469

NH₃ synthesis was performed over Ru₃-C₆₀-Cs⁺/SiO₂ (1) catalysts prepared by the reaction of Ru₃(CO)₁₂ with C₆₀ followed by impregnation on Cs⁺/SiO₂. The rate of NH₃ synthesis was a maximum at the ratio Cs⁺ : Ru₃ = 1.5 for (1), containing 2.7 wt.% Ru and 9.8 wt.% C, and was higher by a factor of 7.0 than the maximum rate for C₆₀ free (1) (Cs⁺ : Ru₃ = 20). The promotion mechanism is discussed in terms of the structural effect of C₆₀ to bind the smaller Ru active species, particle size < 10 Å, and of the electronic effect of C₆₀ as the electron transport medium for (1).

HOMOGENEOUS CATALYSIS

A Novel PtCl₄-Catalyzed Cyclorearrangement of Allyl Propynyl Ethers to 3-Oxabicyclo [4.1.0]Heptenes

J. BLUM, H. BEER-KRAFT and Y. BADRIEH, *J. Org. Chem.*, 1995, 60, (17), 5567–5569

A one-pot synthesis of 3-oxabicyclo[4.1.0]hept-4-enes (1) by cyclorearrangement of allyl propynyl ethers (2) using a catalytic amount of PtCl₄ in O₂-free benzene during brief treatment at room temperature is reported. The transformation of (2) to (1) involves formation of Pt-allene intermediates. With [(CO)₂Rh(μ-Cl)]₂, the oxabicycloheptenes give cyclopropane-ring cleavage.

Asymmetric Hydroformylation of Styrene with PtCl₂(Atropoisomeric Diphosphine)/SnCl₂ Systems

A. SCRIVANTI, S. ZEGGIO, V. BEGHETTO and U. MATTEOLI, *J. Mol. Catal.*, 1995, 101, (3), 217–220

A Pt chiral complex [PtCl₂{(S)-(-)-MeOBIPHEP}] (1), where MeOBIPHEP is the atropoisomeric diphosphine 2,2'-bis(diphenylphosphino)-6,6'-dimethoxy-1,1'-biphenyl, was produced and its catalytic activity was examined. In the presence of SnCl₂, the Pt chiral complex was an efficient catalyst for the asymmetric hydroformylation of styrene. The effects of CO and H₂ partial pressures on the catalytic activity of the (1)/SnCl₂ system were also studied.

New Synthetic Applications of Water-Soluble Acetate Pd/TPPTS Catalyst Generated *in Situ*. Evidence for a True Pd(0) Species Intermediate

C. AMATORE, E. BLART, J. P. GENÉT, A. JUTAND, S. LEMAIRE-AUDOIRE and M. SAVIGNAC, *J. Org. Chem.*, 1995, **60**, (21), 6829–6839

The H₂O-soluble catalyst, prepared *in situ* from Pd(OAc)₂ and P(C₆H₄-*m*-SO₃Na)₃, is an efficient catalyst for sp-sp and sp²-sp coupling reactions without Cu(I) promoter, in a homogeneous acetonitrile-H₂O system. Diynes are produced in moderate yields, and indolic and furanic products are formed from 2-iodophenols or 2-iodoanilines and terminal alkynes, respectively, in good yields. A Pd(0) complex is formed spontaneously in the reaction mixture.

Synthesis of Bis(α-Amino Acids) by Palladium-Catalyzed Allylic Double Substitution

A. MAZÓN, C. NÁJERA, J. EZQUERRA and C. PEDREGAL, *Tetrahedron Lett.*, 1995, **36**, (42), 7697–7700

The reaction of Li enolate, derived from glycine benzophenone imine ester, with allylic dihalides, in the presence of a catalytic amount of Pd(Ph₃P)₄ (5% mol) yielded the corresponding bis(imino-esters) (1). Subsequent hydrolysis of (1) gave the corresponding bis(α-amino acids). This methodology was used to synthesise α,α'-diaminosuberic acid.

Asymmetric Hydroformylation of Styrene Using Dithiolato Bridged Dirhodium Catalyst with BDPP as Chiral Ligand

A. M. MASDEU-BULTÓ, A. OREJÓN, S. CASTILÓN and C. CLAVER, *Tetrahedron: Asymmetry*, 1995, **6**, (8), 1885–1888

Asymmetric hydroformylation of styrene is performed using dinuclear thiolato bridged complexes [Rh₂(μ-dithiolate)(COD)]₂ with BDPP, where COD is cyclooctadiene and BDPP is (-)-(2*S*,4*S*)-2,4-bis(diphenyl phosphino) pentane, as the chiral auxiliary ligand. The optical yields depend upon the starting organometallic complex. When (+) and (-) dithiolate bridged complexes and (+) and (-) diphosphine were combined, one pair could enhance enantioselectivity. Styrene hydroformylation had a regioselectivity in 2-phenylpropanal of ≤ 94 % and ee of ≤ 43 %.

The Influence of the Aqueous Phase Composition on the Catalytic Properties of RhCl₃ Modified by Polycation in the Hydroformylation of Hexene-1

N. V. KOLESNICHENKO, M. V. SHARIKOVA, T. KH. MURZABEKOVA, N. A. MARKOVA and E. V. SLIVINSKII, *Izv. Akad. Nauk Rosii, Ser. Khim.*, 1995, (10), 1943–1945

Studies of H₂O-soluble catalytic systems based on RhCl₃ and polyelectrolytes, poly-*N,N*-diallyl-*N,N*-dimethylammonium chloride, etc., showed that the hydroformylation rate increased with increasing pH of the aqueous phase. Stable hydroformylation of hexene-1 at pH ≥ 5 was achieved by substitution of the alkyl group at the N atom for H. Increasing the charge of the anion of the salt used for varying the pH increased stability.

Hydroformylation with Water- and Methanol-Soluble Rhodium Carbonyl/Phenyl-Sulfonato-alkylphosphine Catalyst Systems. A New Concept for the Hydroformylation of Higher Molecular Olefins

S. KANAGASABAPATHY, Z. XIA, G. PAPADOGLIANAKIS and B. FELL, *J. Prakt. Chem.*, 1995, **337**, (6), 446–450

A Rh carbonyl/tertiary phosphine complex catalyst system, soluble both in MeOH and H₂O, was used for the homogeneous catalytic hydroformylation of olefins in methanolic solution. After the reaction, the product mixture was heterogenised by adding H₂O to form an aqueous phase containing the catalyst system. The hydroformylation of *n*-tetradecene-1 with the Rh carbonyl/phenylsulphonatoalkyl-phosphine catalyst system illustrated that this system could be used in the oxo reaction of high molecular olefins.

Cyclopropanation Catalysed by RuCl₂(PPh₃)₃ and OsCl₂(PPh₃)₃

A. DEMONCEAU, C. A. LEMOINE, A. F. NOELS, I. T. CHIZHEVSKY and P. V. SOROKIN, *Tetrahedron Lett.*, 1995, **36**, (46), 8419–8422

The cyclopropanation of ethyl diazoacetate with olefins to isoelectronic complexes was catalysed using RuCl₂(PPh₃)₃ (1) and OsCl₂(PPh₃)₃ (2) catalysts. Catalyst (2) was less active than (1) for the decomposition of the diazo reagent and the subsequent cyclopropanation. Using the above Ru and Os based catalysts, the cyclopropanation reactions remained limited to activated olefins, especially styrenes and isoprene.

Hydroxylation of Alkanes with Molecular Oxygen Catalyzed by a New Ruthenium-Substituted Polyoxometalate, [WZnRu₂^{III}(OH)(H₂O)(ZnW₉O₃₄)]¹¹⁻

R. NEUMANN, A. M. KHENKIN and M. DAHAN, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, (15), 1587–1588

The title diruthenium-substituted polyoxometalate was used as a catalyst for the hydroxylation of alkanes, such as adamantane, with O₂ at atmospheric pressure and under mild conditions. Hydroxylation occurred almost exclusively at the tertiary C positions. Highly selective aerobic hydroxylation of tertiary C centres in alkanes was achieved via O₂ activation. The regioselectivity showed that the Ru-substituted polyoxometalate activated O₂ in a non-radical way.

FUEL CELLS

Platinum Utilization in a Phosphoric Acid Fuel Cell

J. ARAGANE, H. URUSHIBATA and T. MURAHASHI, *Denki Kagaku*, 1995, **63**, (7), 642–647

Geometrical and electrochemical studies of Pt coverage in a gas diffusion electrode of a phosphoric acid fuel cell showed only ~ 50% utilisation of the Pt surface area compared with the nominal Pt surface area. The impregnation procedure was found to be of more importance than PTFE content and heat treatment temperature. The corrosion reaction of the C support is suppressed to improve the cell performance.

A Novel Cell Design for Simplifying SOFC System

T. HIBINO, K. USHIKI, T. SATO and Y. KUWAHARA, *Solid State Ionics*, 1995, **81**, (1, 2), 1-3

A new design for the solid oxide fuel cell is reported by attaching the Pd and Au electrodes to the same face of the $\text{BaCe}_{0.8}\text{Gd}_{0.2}\text{O}_{3-x}$ electrolyte. A mixture of CH_4 and O_2 ($\text{CH}_4 : \text{O}_2$ mole ratio = 2 : 1) is fed to the cell at 950°C and electric power is generated. The ohmic resistance of the cell was lowered by reducing the distance between the two electrodes, and the unit cells can be connected in series and parallel with one another on the same electrolyte.

ELECTRICAL AND ELECTRONIC ENGINEERING

Barrier-Height Non-Uniformities of PtSi/Si(111) Schottky Diodes

P. LAHNOR, K. SEITER, M. SCHULZ, W. DORSCH and R. SCHOLZ, *Appl. Phys. A*, 1995, **61**, (4), 369-375

The forward I-V characteristics of PtSi Schottky contacts on epitaxial *n*-type Si(111) were analysed at 100-300 K, and an excess current was found. This was caused by a few thousand patches of reduced Schottky barrier height. The patch radius is ~70-250 nm. The size of the patches correlates with the size of agglomerates that lead to bumps in the surface. The number of patches observed, which is a measure of the quality of the Schottky barrier, is reduced upon increasing the silicidation temperature, to $\leq 550^\circ\text{C}$.

Platinum Bottom Electrodes Formed by Electron-Beam Evaporation for High-Dielectric Thin Films

S. Y. CHA, H. C. LEE, W. J. LEE and K. G. KIM, *Jpn. J. Appl. Phys.*, 1995, **34**, (9B), 5220-5223

Pt bottom electrodes were formed on SiO_2/Si substrates at various deposition temperatures by electron-beam evaporation, followed by the growth of $(\text{Ba}_x\text{Sr}_{1-x})\text{TiO}_3$ (BST) films under the same conditions by r.f. magnetron sputtering. The crystallinity of BST thin films is strongly dependent on the crystallinity of the Pt films. The surface morphology of BST films appeared to be closely related to the change in the stress of Pt films during BST deposition; the stress affects the electrical properties.

Novel Technique to Form Pt-Silicided Shallow p^+n Junctions Using Low-Temperature Processes

K.-P. MA, C.-T. LIN and H.-C. CHENG, *Jpn. J. Appl. Phys.*, 1995, **34**, Part 2, (9A), L1100-L1102

Excellent Pt-silicided p^+n junctions were formed at low temperatures by implanting BF_2^+ ions into polycrystalline Si films on Si substrates. The samples implanted at $100 \text{ keV}/5 \times 10^{19}/\text{cm}^2$ showed a leakage of $7 \text{ nA}/\text{cm}^2$ and a junction depth of $\sim 0.05 \mu\text{m}$ after 500°C annealing. The current leakages further decreased to $\sim 2 \text{ nA}/\text{cm}^2$ when the annealing temperature reached 550°C . Implant energy was the most important factor for obtaining excellent junction characteristics.

Structural Design of CoCrPt(Ta,B)/Cr Magnetic Thin Film Media for Ultra High Density Longitudinal Magnetic Recording

P. GLIJER, K. SIN, J. M. SIVERTSEN and J. H. JUDY, *Scr. Metal. Mater.*, 1995, **33**, (10/11), 1575-1584

CoCrPt(Ta,B) thin films with Cr underlayers were studied as ultra-high density magnetic recording media for data storage at $10 \text{ Gbits}/\text{inch}^2$. Changes in structure and composition altering magnetic and noise properties were found. In-plane coercivities of 2700 Oe were obtained in CoCrPt films containing $< 20 \text{ at.}\%$ Pt; in CoCrPtTa with $< 12\%$ Pt and in CoCrPtB with $< 11\%$ Pt. Improvements to the noise characteristics, grain size and surface roughness are shown.

Thermally Stable, Low-Resistance PdGe-Based Ohmic Contacts to High-Low Doped *n*-GaAs

J. S. KWAK, H. N. KIM, H. K. BAIK, J.-L. LEE, H. KIM, H. M. PARK and S. K. NOH, *Appl. Phys. Lett.*, 1995, **67**, (17), 2465-2467

The development of low resistance, thermally stable PdGe-based ohmic contacts on high-low doped *n*-GaAs substrates is described. The lowest resistance obtained was two times lower than for prior reported PdGe ohmic contacts. The contacts were thermally stable even after isothermal annealing for 5 h at 400°C at atmospheric pressure.

RuO₂/TiN-Based Storage Electrodes for (Ba, Sr)TiO₃ Dynamic Random Access Memory Capacitors

K. TAKEMURA, S. YAMAMICHI, P.-Y. LESAICHERRE, K. TOKASHIKI, H. MIYAMORO, H. ONO, Y. MIYASAKA and M. YOSHIDA, *Jpn. J. Appl. Phys.*, 1995, **34**, (9B), 5224-5229

Sputtered (Ba, Sr)TiO₃ (BST) thin film capacitors were produced with thick RuO₂/TiN-based storage electrodes and poly-Si contact plugs. The electrode height was $> 450 \text{ nm}$ and the contact size was $0.8 \times 0.8 \mu\text{m}^2$. With increasing BST deposition temperature, the oxidised TiN thickness in the RuO₂/TiN electrode increases, raising electrode resistance. The resistance can be lowered by inserting a Ru layer at the RuO₂/TiN interface, by a TiN/TiSi₂/Si junction or by rapid thermal annealing of the TiN layer in N₂.

MEDICAL USES

Crystal Structure of Double-Stranded DNA Containing the Major Adduct of the Anticancer Drug Cisplatin

P. M. TAKAHARA, A. C. ROSENZWEIG, C. A. FREDERICK and S. J. LIPPARD, *Nature*, 1995, **377**, (6550), 649-652

Most cisplatin-DNA adducts are intrastrand d(GpG) and d(ApG) crosslinks and structural knowledge of cisplatin-DNA adducts was limited to short single-stranded deoxyoligonucleotides, such as *cis*-[Pt(NH₃)₂-{d(pGpG)}]. The X-ray structure at 2.6 \AA resolution of a double-stranded DNA dodecamer containing the adduct is described here. This should aid design of new Pt and other metal crosslinking antitumour drugs.