

ABSTRACTS

of current literature on the platinum metals and their alloys

PROPERTIES

Synthesis of Nanoscale Platinum Colloids by Microwave Dielectric Heating

W. YU, W. TU and H. LIU, *Langmuir*, 1999, 15, (1), 6–9
Polymer-stabilised Pt colloids (diameter 2 to 4 nm) with nearly uniform spherical shape were prepared by microwave dielectric heating of poly(*N*-vinyl-2-pyrrolidone)/H₂PtCl₆/NaOH/H₂O/ethylene glycol. Different sizes of Pt colloids can be obtained by changing the molar ratio of PVP/Pt. However, the particle dispersity remains the same, ~0.17, regardless of the molar ratios of PVP/Pt and NaOH/Pt.

Enhanced Perpendicular Magnetic Anisotropy in Chemically Long-Range Ordered (0001) Co_xPt_{1-x} Films

M. MARET, M. C. CADEVILLE, A. HERR, R. POINSOT, E. BEAUREPAIRE, S. LEFEBVRE and M. BESSIÈRE, *J. Magn. Mater.*, 1999, 191, (1–2), 61–71

Chemical long-range ordering along the growth direction has been observed in mostly h.c.p. Co₈₀Pt₂₀ films grown on a Ru(0001) buffer by molecular beam epitaxy (MBE). This ordering enhances perpendicular magnetic anisotropy in h.c.p. films. A Pt segregation effect at the advancing surface, caused by dominant surface diffusion, promotes this uniaxial long-range ordering during the MBE process.

Effects of Annealing on the Magnetic Properties and Structures of Sputtered Co-Pt Alloy Thin Films

T. YAMAMOTO, T. TEZUKA, M. NISHIMAKI and T. ISHIGURO, *Jpn. J. Appl. Phys.*, 1998, 37, (11), 5980–5983

The short-time annealing (< 6 h) of sputtered Co-Pt films with 0–50 at.% Pt was investigated. The coercivity of a Co₉₀Pt₁₀ film drastically increases by annealing at > 800 K, corresponding to an L1₀ ordered phase, formed by annealing at 940 K in < 1 h. The grain size greatly increases in the early stage of annealing. The grain size should be decreased in order to use the Co-Pt films as high density recording material.

Oxidation of Ordered Sn/Pt(111) Surface Alloys and Thermal Stability of the Oxides Formed

N. A. SALIBA, Y.-L. TSAI and B. E. KOEL, *J. Phys. Chem. B*, 1999, 103, (9), 1532–1541

Two Pt-Sn surface alloys were oxidised at 300 K by O₂ exposure in UHV. Despite the (2 × 2) and √3 Sn/Pt surface alloys being less reactive than Pt(111), oxidation was possible under UHV conditions using O₂. O adatoms are chemisorbed on Pt sites at large O coverage, giving PtO_x at highest coverage. The proximity of Pt resulting from Pt-Sn oxidation lowers the thermal decomposition temperature of SnO_x.

Nucleation and Growth Kinetics of Pd and CuPd Particles on NaCl(100)

F. GIMENEZ, C. CHAPON and C. R. HENRY, *New J. Chem.*, 1998, 22, (11), 1289–1294

The nucleation and growth kinetics of Pd and CuPd nanometric particles grown by condensation on UHV-cleaved NaCl(100) surfaces were studied. The nucleation of the CuPd particles is mainly controlled by the Pd adatoms. It is possible to obtain a homogeneous collection of bimetallic CuPd particles by condensing the two metals simultaneously. These uniform CuPd particles are suitable for use as supported model catalysts.

Structural Chemistry, Magnetism and Thermodynamic Properties of R₂Pd₂In

M. GIOVANNINI, H. MICHOR, E. BAUER, G. HILSCHER, P. ROGL and R. FERRO, *J. Alloys Compd.*, 1998, 280, (1–2), 26–38

Magnetisation, resistivity and specific heats of ternary intermetallics, R₂Pd₂In, synthesised with the nominal composition R₄₀Pd₄₀In₂₀ (R = rare earth elements including Y) were studied. Magnetic and thermodynamic measurements revealed antiferromagnetic order below 32 K for this series except for Y, La, Yb and Lu. A wide homogeneity range was found for Ce₂Pd_{2-x}In_{1+x} where ferro- or antiferromagnetic order or both occur with features typical of a Kondo lattice. Intermediate valence behaviour but no magnetic ordering were exhibited by Yb₂Pd₂In (≥ 0.3 K).

The First Coordinatively Saturated, Quadruply Stranded Helicate and Its Encapsulation of a Hexafluorophosphate Anion

D. A. MCMORRAN and P. J. STEEL, *Angew. Chem. Int. Ed.*, 1998, 37, (23), 3295–3297

The self-assembly of four molecules of 1,4-bis(3-pyridyloxy)benzene and two Pd(II) ions allowed the encapsulation of a PF₆⁻ ion within a quadruply stranded helicate. It is reported as not only the first example of a co-ordinatively saturated quadruple helicate, but also the first example of the encapsulation of a complex anion by a helicate.

Superconductivity of MRhSi (M = Ti, Zr and Hf) Prepared at High Pressure

I. SHIROTANI, Y. KONNO, Y. OKADA, C. SEKINE, S. TODO and T. YAGI, *Solid State Commun.*, 1998, 108, (12), 967–970

Ternary Rh silicides TiRhSi (1), ZrRhSi (2) and HfRhSi (3) and alloys ZrRh_{1-x}Ru_xSi (x = 0.1, 0.3, 0.5) were prepared by reacting stoichiometric amounts of each metal and Si powders at ~4 GPa and > 1200°C in a wedge-type cubic-anvil high pressure apparatus. Superconducting transition temperatures in (1), (2) and (3) are 5.1, 10.3 and 2.3 K, respectively. These ternary Rh silicides are new superconductors.

Thermodynamic Characterization of Hydrogen Interaction with Iridium Polyhydride Complexes

R. A. ZIDAN and R. E. ROCHELEAU, *J. Mater. Res.*, 1999, 14, (1), 286–291

Studies of H₂ interaction with IrXH₂(PPr'₃)₂ (X = Cl, I) showed that H₂ reacts rapidly and reversibly with IrClH₂(PPr'₃)₂ forming IrClH₂(PPr'₃)₂H₂ at < 323 K. Equilibrium isotherms were used to obtain the relative partial molar enthalpy and entropy. The decrease in entropy with increasing H₂ concentration and the absence of plateaux in the equilibrium isotherms were consistent with a single phase solid solution having two chemical components. Due to stronger H₂ bonding at temperatures up to 350 K, H₂ could not be removed from the iodo complex.

Thermal Decomposition of [M₃(CO)₁₂] (M = Ru, Os) Physisorbed onto Porous Vycor Glass: a Route to a Glass/RuO₂ Nanocomposite

A. J. G. ZARBIN, M. D. VARGAS and O. L. ALVES, *J. Mater. Chem.*, 1999, 9, (2), 519–523

Glass/RuO₂ nanocomposites (average particle size 45 Å) were obtained by the impregnation and thermal decomposition of [M₃(CO)₁₂] (M = Ru, Os) carbonyl clusters inside the pores of porous Vycor glass. Thermal decomposition occurs via [HM₃(CO)₁₀(μ-O-Si≡)] and [M(CO)_n(OSi≡)₂] (n = 2, 3) intermediates which are formed at low temperatures.

Oxygen Vacancy Control in the Defect Bi₂Ru₂O_{7-y} Pyrochlore: a Way to Tune the Electronic Bandwidth

R. E. CARBONIO, J. A. ALONSO and J. L. MARTÍNEZ, *J. Phys. Condens. Matter*, 1999, 11, (2), 361–369

Bi₂Ru₂O_{7-y} pyrochlore (1) can be prepared with significant y oxygen vacancies by annealing Bi₂O₃ and RuO₂ at 1000°C, first in air and then under an inert atmosphere. At 4–290 K, (1) has a cubic structure and is metallic showing increased resistivity by one order of magnitude at 300 K, with respect to stoichiometric Bi₂Ru₂O₇. The control of the oxygen concentration in (1) is suggested as a clean way to tune the bandwidth of this material.

CHEMICAL COMPOUNDS

Synthesis, Electrochemistry, and Spectroscopy of Blue Platinum(II) Polyynes and Diynes

M. YOUNUS, A. KÖHLER, S. CRON, N. CHAWDHURY, M. R. A. AL-MANDHARY, M. S. KHAN, J. LEWIS, N. J. LONG, R. H. FRIEND and P. R. RAITHBY, *Angew. Chem. Int. Ed.*, 1998, 37, (21), 3036–3039

Soluble donor-acceptor polymers in which an *n*-butylphosphane-substituted Pt(II) acetylene group acts as donor, and a thieno[3,4-*b*]pyrazine as acceptor, were synthesised in order to obtain a system with a band gap < 2 eV. A blue rigid-rod polymer, prepared by the reaction of *trans*-[PtCl₂(P*n*Bu₃)₂] with 2,3-ethynyl-5,7-thieno[3,4-*b*]pyrazine, exhibited the smallest band gap observed so far (1.77 eV) for an organometallic polymer.

Behaviour of the One-Dimensional, Inorganic Polymer ¹/₂[MPS₄]⁻ Anions (M = Ni, Pd) in Organic Solutions

J. SAYETTAT, L. M. BULL, S. JOBIC, J.-C. P. GABRIEL, M. FOURMIGUÉ, P. BATAIL, R. BREC, R.-L. INGLEBERT and C. SOURISSEAU, *J. Mater. Chem.*, 1999, 9, (1), 143–153

The behaviour of the salts KMPS₄ (M = Ni, Pd) and some solid-solution phases, KNi₂Pd₂PS₄, when dissolved in DMF, was to form chains. For chains of ¹/₂[PdPS₄]⁻, the chain remains intact when heated up to 323 K, whereas the Ni derivative either fragments and/or rearranges into monomers, etc. This difference is accounted for in terms of M-S bond strengths.

PHOTOCONVERSION

Theoretical Study of CH₄ Photodissociation on Pd and Ni(111) Surfaces

Y. AKINAGA, T. TAKETSUGU and K. HIRAO, *J. Chem. Phys.*, 1998, 109, (24), 11010–11017

Photofragmentations of CH₄ adsorbed on Pd and Ni(111) surfaces were studied by density functional theory and *ab initio* molecular orbital calculations. These metal surfaces were represented approximately by finite metal clusters M_{*n*} (n = 1, 7, 10). The CH₄-3s Rydberg excited state was found to be stabilised by ~2.0 and 1.5 eV through physisorption on the Pd and Ni metal surfaces, respectively, by electron transfer.

Photochemistry of Os(dmpe)₂H₂: Matrix, Transient Solution, and NMR Studies of 16-Electron Os(dmpe)₂ (dmpe = Me₂PCH₂CH₂PMe₂)

M.-C. NICASIO, R. N. PERUTZ and A. TEKKAYA, *Organometallics*, 1998, 17, (25), 5557–5564

Os(dmpe)₂H₂, synthesised by the reaction of *trans*-Os(dmpe)₂Cl₂ with Na under H₂, was found to consist of *cis* and *trans* isomers (~60:1). UV irradiation of Os(dmpe)₂H₂ in Ar and CH₄ yielded Os(dmpe)₂ with a characteristic multiband UV-vis spectrum. In CO-doped matrices, Os(dmpe)₂(CO) was generated. Laser flash photolysis (266 nm excitation) of Os(dmpe)₂H₂ in cyclohexane gave the same species.

Dipyridophenazine Complexes of Os(II) as Red-Emitting DNA Probes: Synthesis, Characterization, and Photophysical Properties

R. E. HOLMLIN, J. A. YAO and J. K. BARTON, *Inorg. Chem.*, 1999, 38, (1), 174–189

By incorporating modifications in the ligand sphere of several dipyridophenazine(dppz) complexes of Os(II), the fundamental excited-state properties of these complexes could be characterised. With two ancillary ligands derived from bipyridine or phenanthroline, the Os(II) complexes exhibit emission maxima at ~740 nm and average excited-state lifetimes in the 10 ns range upon binding to DNA by preferential intercalation of the dppz ligand. The utility of dppz complexes of Os(II) as luminescent probes for DNA is illustrated.

The Scanning Microscope for Semiconductor Characterization (SMSC): Electrolyte Electroreflectance and Photovoltage Imaging Study of the Electrochemical Activation of RuS₂ Photoelectrodes for Oxygen Evolution

M. TURRIÓN, N. ALONSO-VANTE, H. TRIBUTSCH, A. MIR and P. SALVADOR, *J. Electroanal. Chem.*, 1998, **458**, (1-2), 99-105

The photoelectrochemical behaviour of the O₂ evolving n-RuS₂|H₂SO₄ interface was examined. Electrolyte electroreflectance and photovoltage digital images were obtained as a function of surface pretreatment and show that polishing gives a scarcely photoactive surface, while electrochemical etching gives a high photoactive surface. Direct evidence of the influence of doping on the electric field distribution of the liquid junction is obtained.

Substrates for Rapid Delivery of Electrons and Holes to Buried Active Sites in Proteins

J. J. WILKER, I. J. DMOCHOWSKI, J. H. DAWSON, J. R. WINKLER and H. B. GRAY, *Angew. Chem. Int. Ed.*, 1999, **38**, (1/2), 90-92

New reduced and oxidised states of cytochrome P450_{cam} were generated by electron transfer to and from the heme group of the buried active site. This was achieved by linking [Ru(bipy)₃]²⁺ through a hydrocarbon chain to a species with high affinity for the heme cavity, such as imidazole or adamantane.

ELECTRODEPOSITION AND SURFACE COATINGS

Preparation of a Palladium Alloy Composite Membrane Supported in a Porous Stainless Steel by Vacuum Electrodeposition

S.-E. NAM, S.-H. LEE and K.-H. LEE, *J. Membrane Sci.*, 1999, **153**, (2), 163-173

Pinhole-free and ultrathin (< 1 μm) 78% Pd-22% Ni composite alloy membranes were deposited on porous stainless steel (SUS) by vacuum electrodeposition. The SUS was sequentially pretreated with submicron Ni powder and CuCN solution to obtain a smooth surface and enhance the adhesive bond between the top layer and the substrate. The composite membranes had high H₂ permeances and selectivities.

APPARATUS AND TECHNIQUE

New Sol-Gel Oxygen Sensor Based on Luminescence Cyclometallated Platinum Complexes

Y.-G. MA, T.-C. CHEUNG, C.-M. CHE and J.-C. SHEN, *Thin Solid Films*, 1998, **333**, (1, 2), 224-227

Pt(MeOPhC₆H₄N₂)X, [MeOPhC₆H₄N₂ = C-anion of 3-phenyl-5-*p*-methoxyphenyl-2,2'-bipyridine, X = NH₂(CH₂)₃Si(OCH₂CH₃)₃], was immobilised in a sol-gel matrix by co-condensation with Si(OCH₂CH₃)₄. The resultant luminescent material shows a rapid and sensitive response to O₂: 58% luminescence is quenched in ~ 10 s when switching from N₂ to O₂.

In Situ Characterization of Ultra-Thin Palladium Deposits on α- and γ-Alumina

E. GILLET, M. H. EL YAKHLOUFI, J.-P. DISALVO and F. BEN ABDELOUAHAB, *Surf. Sci.*, 1999, **419**, (2-3), 216-225
Ultra-thin Pd films deposited at 300 and 600 K onto α- and γ-Al₂O₃ surfaces by SSIMS, were characterised. Early stages of growth were investigated by analysing the ion intensity ratios, Pd₂⁺:Pd⁺ and PdAlO⁺:AlO⁺, to discriminate between three deposition stages in the submonolayer Pd films. The ion yield was found to be closely related to the Pd-Al₂O₃ bonding, which determines the morphology and the electronic structure of the system. On α-Al₂O₃, Pd deposition gives weak Pd-Al bonding with nucleation of small 3D clusters. On γ-Al₂O₃, monolayers or flat islands grow, with the formation of Pd-Al and Pd-O bonds.

Determination of Sulfite in Sugar and Sulfur Dioxide in Air by Chemiluminescence Using the Ru(bipy)₃²⁺-KBrO₃ System

F. WU, Z. HE, H. MENG and Y. ZENG, *Analyst*, 1998, **123**, (11), 2109-2112

Sulfite has been determined by a chemiluminescence (CL) method using the Ru(bipy)₃²⁺-SO₃²⁻-KBrO₃ system (bipy = 2,2'-bipyridyl). The concentration of sulfite was found to be proportional to the CL intensity in the range 2.5 × 10⁻⁸ to 9.5 × 10⁻⁵ mol l⁻¹ sulfite solution. The detection limit is 3.8 × 10⁻⁹ mol l⁻¹ and the relative standard deviation for 5 × 10⁻⁵ mol l⁻¹ sulfite solution is 4.6%. The method was successfully applied to the determination of sulfite in sugar and SO₂ in air by using triethanolamine as the absorbent material.

Luminescence Quenching of Ru(II) Complexes in Polydimethylsiloxane Sensors for Oxygen

M. L. BOSSI, M. E. DARAIO and P. F. ARAMENDÍA, *J. Photochem. Photobiol. A: Chem.*, 1999, **120**, (1), 15-21

The luminescence quenching of tris(1,10-phenanthroline)Ru(II) and tris(4,7-diphenyl-1,10-phenanthroline)Ru(II) by O₂ in polydimethylsiloxane films was investigated by steady state and time-resolved methods. An algorithm for behaviour, with one oxygen-dependent parameter, was deduced. The correlation of this parameter with oxygen partial pressure is identical for both dyes, and shows saturation behaviour.

Application of Piezoelectric Ru(III)/Cryptand-Coated Quartz Crystal Gas Chromatographic Detector for Olefins

P. CHANG and J.-S. SHIH, *Anal. Chim. Acta*, 1999, **380**, (1), 55-62

A Ru(III)/cryptand-coated piezoelectric quartz crystal detector linked to a computer interface was prepared and used as a gas chromatographic detector for olefins. The oscillating frequency of the quartz crystal decreases on adsorption of organic molecules on the Ru(III)/cryptand coating. Alkynes show greater adsorption on the coating than alkenes and alkanes. The technique was subject to interference by H₂O.

HETEROGENEOUS CATALYSIS

Effect of Inert Sites on the Kinetic Oscillations in the Catalytic CO Oxidation on Pt(100)

F. CHÁVEZ, L. VICENTE, A. PERERA and M. MOREAU, *J. Chem. Phys.*, 1998, **109**, (19), 8617–8625

The effect of inert sites in the global oscillations in the oxidation of CO on Pt(100) for both random and clustered inert sites has been simulated by the cellular automaton technique. The structural phase transformation of the Pt substrate, the reaction kinetics of the adsorbed phase and diffusion of adsorbed species were accounted for by cellular automaton rules.

Characterization and Properties of Pt/ZrO₂-CeO₂ Catalyst for Purification of Automotive Exhaust

S. LI, S. LI, C. WU and L. SUN, *Chin. J. Catal.*, 1999, **20**, (1), 67–69

The effect of the additive, ZrO₂, in CeO₂ on the properties of the Pt/ZrO₂-CeO₂ three-way catalyst was investigated. The results show that the support ZrO₂-CeO₂ has higher oxygen storage capacity (OSC) than CeO₂ and that Pt/ZrO₂-CeO₂ catalyst has higher OSC than Pt/CeO₂. The Pt/ZrO₂-CeO₂ catalyst is reduced at < 200°C while Pt/CeO₂ is reduced at < 300°C. The second desorption of CO on Pt/ZrO₂-CeO₂ is at 570°C and that on Pt/CeO₂ is at 620°C. Thus Pt/ZrO₂-CeO₂ shows higher activity than Pt/CeO₂ for three-way catalytic reactions.

Behavior of Non-Promoted and Ceria-Promoted Pt/Rh and Pd/Rh Three-Way Catalysts under Steady State and Dynamic Operation of Hybrid Vehicles

S. TAGLIAFERRI, R. A. KÖPPEL and A. BAIKER, *Ind. Eng. Chem. Res.*, 1999, **38**, (1), 108–117

Honeycomb-type Pd and standard Pt catalysts for exhaust after treatment in hybrid drive systems were investigated on non-promoted and CeO₂-promoted Pd-Rh and Pt-Rh catalysts. The catalysts were tested by light-off experiments with steady and cycling feed stoichiometries, and pulsed-flow operation. Very different catalyst behaviours for NO_x, CO and HC conversions, depending on operation mode, were found.

Oxidation of Methane over Pd/Mixed Oxides for Catalytic Combustion

H. WIDJAJA, K. SEKIZAWA, K. EGUCHI and H. ARAI, *Catal. Today*, 1999, **47**, (1–4), 95–101

Pd catalysts supported on mixed oxides, Pd/Al₂O₃-MO_x (M = Co, Cr, Cu, Fe, Mn or Ni), were studied for the low temperature catalytic combustion of CH₄. Pd/Al₂O₃-36NiO showed excellent activity, despite its lower surface area, due to the small particle size of Pd. TPD showed that at low temperatures, the catalytic activity is dependent upon the adsorption state of O on Pd. Activity is enhanced by increasing amounts of adsorbed O₂. XRD showed that the PdO phase is thermally stabilised on Pd/Al₂O₃-36NiO. The stability of the PdO species at higher temperatures may directly correspond to the increased catalytic activity.

Adsorption Equilibrium and Catalytic Reaction of CFC-115 on Pd/Activated Carbon Powder

D. J. MOON, M. J. CHUNG, K. Y. PARK and S. I. HONG, *Carbon*, 1999, **37**, (1), 123–128

Adsorption equilibria of chloropentafluoroethane (CF₃CF₂Cl, CFC-115) on Pd/activated C powder and on activated C powder at 298.15–373.15 K were well represented by the BET equation. The isosteric heats of adsorption of the CFC-115 on both adsorbents were of approximately the same order of magnitude as the heats of condensation, and were mainly due to physical forces. CFC-115 can be converted to pentafluoroethane (CF₃CF₂H, HFC-125) with > 99% selectivity by hydrodechlorination over Pd/activated C. The Pd/activated C powder was an effective adsorbent with potential to recover CFC-115 and act as a catalyst to manufacture HFC-125 from CFC-115.

Catalytic Oxidation of Volatile Organic Compounds I. Oxidation of Xylene over a 0.2 wt% Pd/HFAU(17) Catalyst

M. GUINNET, P. DÉGÉ and P. MAGNOUX, *Appl. Catal.*, 1999, **20**, (1), 1–13

The transformation of *o*-xylene in low concentration (1700 ppmv) in air over 0.2 wt.% Pd/HFAU(17) zeolite catalyst, with Si:Al ratio of 17, was investigated in a flow reactor at 150–320°C. At short time-on-stream, whatever the temperature, no xylene appears at the reactor outlet. The xylene oxidation into CO₂ and H₂O is accompanied by the retention of various products of xylene transformation, “coke”, dependent on temperature, within the zeolite pores.

Alloying in Cu/Pd Nanoparticle Catalysts

A. M. MOLENBROEK, S. HAUKKA and B. S. CLAUSEN, *J. Phys. Chem. B*, 1998, **102**, (52), 10680–10689

The preparation of binary alloy nanoparticle catalysts on various supports was shown to be a new application for the atomic layer epitaxy technique. Cu/Pd bimetallic catalysts were prepared on SiO₂ and on γ -Al₂O₃. EXAFS measurements showed that alloying occurred in the Cu/Pd samples with a Cu-rich surface for the Al₂O₃-supported sample and random alloying for the SiO₂-supported sample. Particle sizes were in the range 20–60 Å.

Glucose Hydrogenation on Ruthenium Catalysts in a Trickle-Bed Reactor

P. GALLEZOT, N. NICOLAUS, G. FLÈCHE, P. FUERTES and A. PERRARD, *J. Catal.*, 1998, **180**, (1), 51–55

Ru catalysts, prepared in a highly dispersed state by cationic exchange or anionic adsorption on active charcoal pellets, were shown to be very active for glucose hydrogenation (initial specific activity = 1.1 mol h⁻¹ g⁻¹ Ru at 100°C). The activities of the catalysts were very stable over several weeks and no leaching of Ru occurred. The selectivity to sorbitol was > 99.2% at 100% conversion. The study showed the negative effect of high residence time, which favours epimerisation of sorbitol to mannitol, but can be minimised if the residence time is that of 100% conversion.

Highly Efficient Oxidation of Alcohols and Aromatic Compounds Catalysed by the Ru-Co-Al Hydrotalcite in the Presence of Molecular Oxygen

T. MATSUSHITA, K. EBITANI and K. KANEDA, *Chem. Commun.*, 1999, (3), 265–266

A Ru hydrotalcite (HT) with Co cations, Ru-Co-Al-CO₃ HT, was found to be an effective heterogeneous catalyst for the oxidation of various alcohols in the presence of O₂. The HT catalyst was easily separated from the reaction mixture and was reusable without an appreciable loss of activity and selectivity. This heterogeneous oxidation is environmentally friendly because of the use of O₂, the simple work-up procedure and the reusable HT catalyst.

Hydrogenation of the Carbonyl Group in α -Ketoesters and α -Ketoamides Catalyzed by Ruthenium Clay

R. ALDEA and H. ALPER, *J. Org. Chem.*, 1998, 63, (25), 9425–9426

Ru-phosphine-clay was prepared by a three-step process: reaction of a montmorillonite with (3-chloropropyl)trimethoxysilane, then treatment with KPPH₃, and finally reaction with RuCl₃·H₂O. The Ru clay is an excellent catalytic system for the reduction of the α -carbonyl group of α -ketoesters and α -ketoamides (50–89% yield). The catalyst is stable and retains high efficiency during consecutive catalytic cycles.

HOMOGENEOUS CATALYSIS

Tailoring Aqueous Solvents for Organic Reactions: Heck Coupling Reactions in High Temperature Water

L. U. GRON and A. S. TINSLEY, *Tetrahedron Lett.*, 1999, 40, (2), 227–230

High temperature water (HTW) (pressurised aqueous reactions at > 100°C) has been found to be an effective solvent for Heck coupling reactions of aromatic halides with cyclic alkenes in the presence of Pd(OAc)₂ catalyst. The dielectric constant of H₂O drops to ~6 at 373°C and 221 bar. No addition of co-solvents or specialised ligands was needed. Reactions in the presence of LiCl and quaternary ammonium salts indicated that the reaction takes place in the aqueous phase. The unusual properties of HTW provide a novel method for extending Heck coupling reactions into neat H₂O.

Selective Alkoxy-carbonylation of 2,3-Dichloropyridines

Y. BESSARD and J. P. RODUIT, *Tetrahedron*, 1999, 55, (2), 393–404

2,3-Dichloropyridines were shown to undergo mono- or dicarbonylation in the presence of CO, an alcohol, and a Pd catalyst to give selectively either alkyl 3-chloropicolinates or dialkyl pyridine-2,3-dicarboxylates in good yields, depending on the reaction conditions. These compounds are of interest as herbicide precursors or as intermediates for antifibrotics.

Heck Reaction Catalyzed by Phospha-Palladacycles in Non-Aqueous Ionic Liquids

W. A. HERRMAN and V. P. W. BÖHM, *J. Organomet. Chem.*, 1999, 572, (1), 141–145

Phospha-palladacycles are very efficient catalysts for the Heck reaction. The use of non-aqueous ionic liquids, such as tetra-*n*-butylammonium bromide or 1-methyl-3-propylimidazolium bromide, etc., with this catalyst system was found to be an effective alternative to traditional molecular solvents, such as acetonitrile or DMF. Easy product separation, possible catalyst recycling, and further increases in catalyst productivity were all shown. Preliminary results obtained with bromo- and chloro arenes are described.

The Palladium Catalysed Suzuki Coupling of 2- and 4-Chloropyridines

O. LOHSE, P. THEVENIN and E. WALDVOGEL, *Synlett*, 1999, (1), 45–48

Chloropyridines were shown to react smoothly with arylboronic acids in Pd-catalysed Suzuki couplings. Moderate to good yields of biaryls were obtained with 4-chloropyridines while 2-chloropyridines gave excellent yields. The reaction was easy to scale up and Pd(PPh₃)₄ could then advantageously be replaced in situ by Pd(0) generated from Pd(OAc)₂ and PPh₃, which showed even greater reactivity.

Fluoride-Catalyzed Reduction of Palladium(II) to Palladium(0)-Phosphine Complexes

P. A. MCLAUGHLIN and J. G. VERKADE, *Organometallics*, 1998, 17, (26), 5937–5940

Tetraco-ordinate Pd(0)-phosphine complexes are widely used in organic synthesis. In the presence of H₂O and excess PPh₃, fluoride ions catalyse the reduction of PdCl₂(PPh₃)₂ under mild conditions to form Pd(PPh₃)₄ in good yields. The inactivation of catalytic F⁻ by the formation of highly stable HF₂⁻, and of other polyhydrogen fluorides that can form in the reaction, was prevented by the addition of a strong non-ionic base, such as P(MeNCH₂CH₂)₃N.

Rhodium-Catalyzed Hydroformylation in Supercritical Carbon Dioxide

D. KOCH and W. LEITNER, *J. Am. Chem. Soc.*, 1998, 120, (51), 13398–13404

Supercritical CO₂ (scCO₂) was shown to be an environmentally benign medium for highly efficient Rh-catalysed hydroformylations. Olefinic substrates were hydroformylated, in scCO₂ at 40 to 65°C, to the corresponding aldehydes in near quantitative yields with unmodified, phosphine-modified, and phosphite-modified systems. With unmodified Rh catalysts, the hydroformylation rates were considerably higher in scCO₂ than in organic solvents or liquid CO₂. Modified catalytic systems with perfluoroalkyl-substituted triarylphosphine and triarylphosphite ligands lead to higher regioselectivities than those found in conventional solvents. Olefin isomerisation, which is a typical side reaction for phosphite-modified systems in conventional solvents, was suppressed in scCO₂.

Hydroformylation of Allyl Ethers. A Study of the Regioselectivity Using Rhodium Catalysts

N. RUIZ, A. POLO, S. CASTILLÓN and C. CLAVER, *J. Mol. Catal. A: Chem.*, 1999, **137**, (1-3), 93-100

The hydroformylation of various allyl benzyl ethers was studied using the precursor catalytic system $[\text{Rh}(\mu\text{-S}(\text{CH}_2)_2\text{NMe}_2)(\text{cod})_2 + \text{PR}_3]$, where R is Ph, or *O*-*o*-*t*-BuC₆H₄, to obtain γ -, β - and α -hydroxyaldehydes. High yields and low regioselectivities were obtained in the hydroformylation of allyl benzyl ether using both R radicals. 4-Benzyloxy-3-methyl-butanal and 4-benzyloxy-2-methyl-butanal were obtained in good to excellent yields, starting from benzyl-2-metallyl ether and benzyl-2-butenyl ether, respectively.

Ruthenium(II)-Catalyzed Asymmetric Transfer Hydrogenation of Ketones Using Chiral Oxazolonylferrocenylphosphines and One of Their Ru(II) Complex

Y. ARIKAWA, M. UEOKA, K. MATOBA, Y. NISHIBAYASHI, M. HIDAI and S. UEMURA, *J. Organomet. Chem.*, 1999, **572**, (2), 163-168

Chiral oxazolonylferrocenylphosphines were shown to be efficient ligands for the Ru(II)-catalysed asymmetric transfer hydrogenation of alkyl aryl ketones and alkyl methyl ketones to give the corresponding alcohols in moderate yields with moderate-to-good enantiomeric excesses. A new Ru(II) complex containing a chiral oxazolonylferrocenylphosphine was prepared and is active for this hydrogenation.

A Recyclable Ru-Based Metathesis Catalyst

J. S. KINGSBURY, J. P. A. HARRITY, P. J. BONITATEBUS and A. H. HOVEYDA, *J. Am. Chem. Soc.*, 1999, **121**, (4), 791-799

A Ru carbene complex that contains an internal metal-oxygen chelate was shown to be an active metathesis catalyst. The complex was readily obtained by the sequential treatment of Cl₂Ru(PPh₃)₂ with (2-isopropoxyphenyl)diazomethane and PCy₃ (Cy = cyclohexyl). This Ru catalyst is stable to air and moisture, and can be recycled in high yield. This complex is the first recyclable Ru-based system that catalyses an efficient homogeneous olefin metathesis reaction with no detectable loss of activity on reuse.

Syntheses of Ruthenium(II) Complexes Containing Polyphosphine Ligands and Their Applications in the Homogeneous Hydrogenation

K.-M. SUNG, S. HUH and M.-J. JUN, *Polyhedron*, 1998, **18**, (3-4), 469-479

Polyphosphine Ru(II) complexes, RuHCl(CO)(etp), RuHCl(CO)(tdpme) and RuHCl(PP₃) [where etp = PhP(CH₂CH₂PPH₂)₂; tdpme = CH₃C(CH₂PPH₂)₃; PP₃ = P(CH₂CH₂PPH₂)₃], were prepared from RuHCl(CO)(AsPh₃), and were used as catalyst precursors in the homogeneous hydrogenation of cyclohexene, cyclohexanone, propanal and 2-cyclohexen-1-one. These Ru(II) complexes show enhanced catalytic activities in comparison with monodentate or bidentate phosphine or arsine analogues.

FUEL CELLS

Morphology of Carbon Supported Pt-Ru Electrocatalyst and the CO Tolerance of Anodes for PEM Fuel Cells

S. D. LIN, T.-C. HSIAO, J.-R. CHANG and A. S. LIN, *J. Phys. Chem. B*, 1999, **103**, (1), 97-103

Commercial 20% Pt-10% Ru/C and synthesised 10% Pt-5% Ru/C (YZU) catalysts at a Pt:Ru atomic ratio of 1:1 were examined for CO tolerance for applications in polymer electrolyte membrane fuel cells. Both half-cell tests under 250 ppm of CO/H₂ and single-cell tests under 100 ppm of CO/H₂ showed that the YZU catalyst had a smaller increase in the overvoltage at a given current. X-ray absorption spectroscopy studies showed no Pt-Ru metal-metal interaction in the commercial catalyst, and only RuO₂ signals were observed. In contrast, the YZU catalyst contained a Pt-Ru bimetallic interaction. It was considered that the Pt-Ru alloy structure has better CO tolerance than the non-alloyed Pt-Ru structure.

GLASS TECHNOLOGY

Investigating the Concept of Direct Heated Platinum Systems

M. BÖTTGER, *Glass*, 1999, **78**, (1), 25-26

Direct-heated Pt systems (DHPS[®]) used in the glass industry worldwide are described. The heating of the Pt tubes comprising the feeder is very important. The DHPS[®] concept is based on distributing one or more current supply electrodes to the Pt-tube, around its circumference, and attached at precise, geometrically defined points on the tube contact ring. This achieves a temperature which does not vary by > 1°C over the entire tube cross-section.

ELECTRICAL AND ELECTRONIC ENGINEERING

Observation of a Square Flux-Line Lattice in the Unconventional Superconductor Sr₂RuO₄

T. M. RISEMAN, P. G. KEALEY, E. M. FORGAN, A. P. MACKENZIE, L. M. GALVIN, A. W. TYLER, S. L. LEE, C. AGER, D. MCK. PAUL, C. M. AEGERTER, R. CUBITT, Z. Q. MAO, T. AKIMA and Y. MAENO, *Nature*, 1998, **396**, (6708), 242-245

Small-angle neutron-scattering measurements of magnetic flux lines in the perovskite superconductor Sr₂RuO₄ are reported. The magnetic flux lines form a square lattice over a wide range of fields and temperatures, as previously predicted by a theory of *p*-wave superconductivity in Sr₂RuO₄. The theory also indicates that only a fraction of the electrons are strongly paired and that the orientation of the square flux lattice relative to the crystal lattice determines which parts of the 3-sheet Fermi surface of this perovskite material are responsible for superconductivity. The results suggest that superconductivity resides mainly on the 'γ' sheet.