

ABSTRACTS

of current literature on the platinum metals and their alloys

PROPERTIES

Chemistry of Acetylene on Platinum(111) and (100) Surfaces

E. L. MUETTERTIES, M. C. TSAI and S. R. KELEMEN, *Proc. Natl. Acad. Sci. U.S.A.*, 1981, **78**, (11), 6571-6575

An ultra high vacuum study of acetylene chemisorption on Pt(111) and Pt(100) and of the reaction of H₂ with the acetylene adsorbate has established distinguishing features of the C-H bond breaking and making processes as functions of pressure, temperature and surface crystallography. The rates for both processes are higher on the Pt(100) surface.

Coarsening Kinetics of Alloy Platinum-Palladium Particles on Oxide Substrates

R. W. CLARK, P. WYNBLATT and J. K. TIEN, *Acta Metall.*, 1982, **30**, (1), 139-146

The coarsening of small (5 nm initial radius) Pt-50at.%Pd particles supported on flat Al₂O₃ substrates was studied between 600 and 900°C under oxidising conditions. Particles or agglomerations of PdO were present in addition to the alloy particles after heat treatments at 600 and 700°C. Interparticle transport of PtO₂ oxide molecules appears to control the rate of coarsening at 800 and 900°C. At 600 and 700°C the inherent rates of interparticle transport of both alloy components are the same.

Permeability of Hydrogen Isotopes through Pd-25wt.%Ag Alloy Membrane at Comparatively High Pressure and Temperature

H. YOSHIDA, T. SHIMIZU, Y. MATSUDA and Y. NARUSE, Japan Atomic Energy Research Inst., Tokai, Ibaraki, JAERI-M-9677, Sept. 1981

Permeation data in Pd-25wt.%Ag alloy for H₂ and D₂ were determined at high pressures (120-1300kPa) and temperatures 653-853K to aid design for the purification system in a fusion reactor fuel circulation system. The permeabilities obeyed Sievert's law.

Thermoelectric Power of Palladium-Iron Alloys at Millikelvin Temperatures

D. I. BRADLEY, A. M. GUÉNAULT, V. KEITH, G. R. PICKETT and W. P. PRATT, *J. Low Temp. Phys.*, 1981, **45**, (3/4), 357-371

The thermoelectric power *S* of a pure Pd sample and four Pd-Fe alloys containing 77-400 ppm Fe was measured at temperatures down to 5mK. A sign change in *S* is observed at low temperatures in all the alloys consistent with the onset of spin-glass freezing, the cross over temperature varying as the square of Fe concentration. These alloys could be used as secondary thermometers down to at least 5mK.

Thermodynamics of Solutions of Hydrogen in Palladium-Manganese Alloys. II. Pd to PdMn

R. C. PHUTEA and O. J. KLEPPA, *J. Chem. Phys.*, 1982, **76**, (3), 1525-1534

The thermodynamic properties of dilute solutions of H₂ in Pd-50at.% Mn alloys were studied by a combined calorimetric equilibrium method at 555-909K. The results showed that for alloys up to 25at.% Mn the enthalpies of solution become increasingly negative with increasing Mn content. The changes are due to increased occupation by H atoms at higher temperatures of energetically less favourable sites.

On the Reduction in Magnetization by Cold Working on the Ferromagnetic Heusler Alloy Pd₂MnSn

T. SHINOHARA, K. SASAKI, H. YAMAUCHI, H. WATANABE, H. SEKIZAWA and T. OKADA, *J. Phys. Soc. Jpn.*, 1981, **50**, (9), 2904-2908

X-ray, magnetic and Mössbauer effect measurements were made on cold worked Pd₂MnSn. They show a remarkable reduction in magnetisation. Most of the reduced magnetisation is recovered when the strain is released by annealing the specimens at temperatures below 400°C where no appreciable recovery of the chemical order takes place.

Thermal Stability of Pd₂Si and PdSi in Thin Film and in Bulk Diffusion Couples

K. N. TU, *J. Appl. Phys.*, 1982, **53**, (1), 428-432

Thermal stability of films of Pd₂Si and PdSi formed on (111) Si wafer were studied by X-ray diffraction. Pd₂Si transformed to PdSi at 810±10°C and PdSi transformed back to Pd₂Si when annealed below that temperature. It is concluded that Pd₂Si rather than PdSi was the thermodynamically stable phase on Si at low temperature, contrary to the phase diagram.

Resistivity and Temperature Coefficient of Resistivity of Ruthenium Oxide Layers. Influence of Morphology

G. LODI, C. DE ASMUNDIS, S. ARDIZZONE, E. SIVIERI and S. TRASATTI, *Surf. Technol.*, 1981, **14**, (4), 335-343

RuO₂ layers 1-2µm thick were prepared at 300, 400, 500 and 600°C on quartz supports by two different procedures which caused "cracked" and "compact" films. The films were characterised by chemical composition, crystalline structure and resistivity, ρ , and $\frac{d\rho}{dT}$. Differences in ρ and $\frac{d\rho}{dT}$ at constant chemical composition were attributed to film discontinuities at the grain boundaries. No metal-semiconductor transition was observed from 20-150°C and the electrical and electrocatalytic properties of the non-stoichiometric layers do not appear to be directly related.

Oxidation of Tertiary Polycyclic Amines by RuO₄

G. BETTONI, G. CARBONARA, C. FRANCHINI and V. TORTORELLA, *Tetrahedron*, 1981, **39**, (24), 4159-4164

The reactions of certain tertiary polycyclic amines with RuO₄ in heterogeneous and homogeneous systems have established an order of reactivity for various methylene groups adjacent to the N, with respect to this oxidising agent.

CHEMICAL COMPOUNDS

Synthesis of Bis(*cis*-dichloro(diamine) platinum(II)) Complexes with Variable Bridges and Study of Their Binding with Poly (dA-dT) by Melting Profiles

I.-B. PAK, P. A. SNYDER-ROBINSON and B.-K. TEO, *Inorg. Chem.*, 1981, **20**, (11), 4006-4009

The synthesis of a series of new bis(*cis*-dichloro(diamine)Pt(II)) complexes with a variable and flexible bridge is reported. Their reactions with synthetic DNA, poly(dA-dT) were investigated to find the effects of the bridging chain length on their binding to DNA. Their anti-tumour activity is related to their ability to interact with DNA.

Mixed Palladium-Platinum Complexes with Ph₂PCH₂PPh₂ (dppm)

P. G. PRINGLE and B. L. SHAW, *J. Chem. Soc., Chem. Commun.*, 1982, (1), 81-82

The first mixed Pd-Pt complexes with bis-(diphenylphosphino)methane (dppm), together with their "A-frame" adducts with CO, SO₂ and MeOCC≡CCOOMe are described. The complexes were characterised by elemental analysis (C, H, N and halogen), molecular weight determinations, i.r. spectroscopy and ³¹P ¹H, ¹H and ¹H ³¹P NMR spectroscopy.

Fluorosulfates of the Noble Metals. Part 4. Fluorosulfates of Iridium

K. C. LEE and F. AUBKE, *J. Fluorine Chem.*, 1982, **19**, (3-6), 501-516

The synthesis of the binary fluorosulphates Ir(SO₃F)₃ and Ir(SO₃F)₄ and of the ternary fluorosulphates (ClO₂)₂[Ir(SO₃F)₆], Cs₂[Ir(SO₃F)₆] and Ba[Ir(SO₃F)₆] is described. Structural characterisations are based on i.r. spectra and, in the case of the Ir(IV) compounds, on the temperature dependant magnetic susceptibility measurements.

Synthesis and Properties of Substituted Ruthenium Aqua Complexes

P. BERNHARD, H. LEHMANN and H. LUDI, *J. Chem. Soc., Chem. Commun.*, 1981, (23), 1216-1217

[Ru(H₂O)₆]²⁺ was prepared and then found to be a versatile reagent for the easy synthesis of a variety of complexes [Ru(H₂O)_nL_{6-n}]²⁺ (L = heterocyclic N-donor), whose spectroscopic and electrochemical properties are described.

ELECTROCHEMISTRY

Behaviour of Hydrogen Peroxide on Platinum Anode

N. IA. KRAVCHENKO, V. G. FORMICHEV and G. A. CHERYSHEV, *Zh. Prikl. Khim. (Leningrad)*, 1981, **54**, (12), 2675-2680

Studies of anodic oxidation of H₂O₂ at potentials 1.0-1.7V were performed on a rotating Pt anode electrode in 0.5M H₂SO₄ at electrolyte temperature of 20 ± 0.1°C. The reaction formed PtO, O₂ and H₂O, with the rates of reaction depending on H₂O₂ concentration and energy of O-metal bond, but did not depend on the potential. H₂O₂ acted as an activator for the surface oxidation and a passivator for the multi-reduction.

Oxygen Evolution on Tantalum-Polypyrrole-Platinum Anodes

G. COOPER, R. NOUFI, A. J. FRANK and A. J. NOZIK, *Nature*, 1982, **295**, (5850), 578-580

Polypyrrole films were used as protective coating on Ta metal photoanodes to find if the films could protect the electrodes for self oxidation during O₂ evolution. The polypyrrole was stable in the presence of O₂ and was a poor electrocatalyst for O₂ evolution. Pt can be deposited on its surface to enhance O₂ evolution. Ta-polypyrrole-Pt electrode structures were found to be indistinguishable from naked Pt electrodes for O₂ evolution.

Electrocatalytic Oxidation of Methanol on Platinum Based Binary Electrodes

B. BEDEN, F. KADIRGAN, C. LAMY and J. M. LEGER, *J. Electroanal. Chem. Interfacial Electrochem.*, 1981, **127**, (1-3), 75-85

Four Pt-based binary catalysts (Pt + Sn, Pt + Pb, Pt + Re, Pt + Ru) used for the electrochemical oxidation of methanol were studied by linear and cyclic voltammetry. Except for the Pt + Ru system, which always gives increased electrocatalytic activity, the other ad-atom + Pt systems showed increased activity for some concentration ranges of the precursor salts, and for some ranges of electrode potential. In general the three ad-atoms behave as relatively strong catalytic poisons.

Selective Electro-Oxidation of Carbon Monoxide with Carbon-Supported Rh- and Ir-Porphyrins at Low Potentials in Acid Electrolyte

J. F. VAN BAAR, J. A. R. VAN VEEN and N. DE WIT, *Electrochim. Acta.*, 1982, **27**, (1), 57-59

Studies of C supported Group VIII metalloporphyrins as O₂ reduction electrocatalysts showed that catalysts based on Rh and Ir are very active in the electrochemical oxidation of CO, particularly when pretreated at high temperatures in an inert atmosphere. The Rh and Ir porphyrin-Norit BRX catalysts have the unique feature of selectively oxidising the CO component of carbon monoxide-hydrogen gas mixtures.

Mechanism of Saturated Hydrocarbon Oxidation in Aqueous Solutions of Ru(IV) Chloride Complexes. II. Oxidation of Alkanes by Strong Oxidants in the Presence of Ru(IV) Complexes

L. N. ARZAMASKOVA, A. V. ROMANENKO and I. I. ERMAKOV, *Kinet. Katal.*, 1981, **22**, (6), 1438-1445

Alkanes C₃-C₄ were easily oxidised in aqueous solutions of Ru(IV) chloride complexes under mild conditions (77.5°C) by strong oxidisers [IrCl₆]²⁻, SeO₄²⁻, Cl₂ and S₂O₈²⁻. The rate of oxidation of alkanes was determined by the value of the oxidative-reductive potential of the oxidiser. A reaction mechanism is presented.

PHOTOCONVERSION

The Photochemical Decomposition of Sulphuric Acid Catalysed by [HPt(PEt₃)₃]⁺

R. F. JONES and D. J. COLE-HAMILTON, *J. Chem. Soc., Chem. Commun.*, 1981, (24), 1245-1246

Far u.v. irradiation of Pt(PEt₃)₃ in dilute H₂SO₄ promoted cyclic photolysis, resulting in H₂ and probably also persulphate ions. This eliminates problems associated with back reactions in multi-component intermolecular electron transfer processes. There are no problems with concentration quenching and much higher catalyst concentrations can be used than for multicomponent catalysts. O₂ can be released from the persulphate ion in a subsequent step, giving a simple way of separating O₂ and H₂. Both H₂ and S₂O₈²⁻ production are favoured by low pH.

Studies of Photoeffects on a Pt-Electrode under Laser Irradiation

A. V. GORODYSKII, G. IA. KOLBASOV, I. V. SEKIRIN and N. I. TARANENKO, *Ukr. Khim. Zh. (Russ. Ed.)*, 1981, **47**, (11), 1170-1174

Studies of photoeffects on a Pt electrode were performed during laser irradiation in H₂SO₄ and iodide ions. Laser irradiation of the Pt electrode by light of wavelength $\lambda \geq 0.337\mu\text{m}$ results in photodecomposition of surface oxides and changes in the electrocatalytic properties of Pt in relation to the formation of chemisorbed H₂ and O₂.

Efficiency of Some Platinum Catalysts in the Photochemical Water Reduction

M. MAESTRI and D. SANDRINI, *Nouv. J. Chim.*, 1981, **5**, (12), 637-641

A comparison of Pt catalyst efficiency and the effect of Pt concentration on the rate of H₂ evolution was studied in the EDTA/Ru(bpy)₂²⁺/MV²⁺/Pt photochemical cycle for H₂ production from H₂O. H₂ production increased with increasing Pt concentration and reached a plateau whose value was different for the various catalysts. Low H₂ production is due to low catalyst efficiency and low quenching efficiency leading to free MV⁺.

The Characterization and Behavior of Catalysts Prepared by Heterogeneous Photodeposition Techniques

W. W. DUNN and A. J. BARD, *Nouv. J. Chim.*, 1981, **5**, (12), 651-655

Pt and Pd were deposited on TiO₂ from an aqueous solution containing the metal salt and acetate, by a photodeposition process. The catalysts were characterised and their activities were compared for the solution phase hydrogenation of benzene with commercial Pt/Al₂O₃ and Pt black catalysts. Photo-oxidation of oxalic acid was also investigated.

Photocatalytic Hydrogen Production from Aliphatic Alcohols over a Bifunctional Platinum on Titanium Dioxide Catalyst

P. PICHAT, J.-M. HERRMANN, J. DISDIER, H. COURBON and M.-N. MOZZANEGA, *Nouv. J. Chim.*, 1981, **5**, (12), 627-636

Photocatalytic H₂ production from linear C₁-C₄ primary aliphatic alcohols and from propan-2-ol was studied at room temperature using a 4.85wt.%Pt/anatase catalyst in liquid or gas phase static photoreaction. Over u.v. illuminated TiO₂, H₂ formation was limited, and the surface was progressively reduced. Quantum yields were ~0.45 for CH₃OH, ~0.2 for C₂H₅OH and ~0.1 for other alcohols. H₂ production from liquid H₂O under the same conditions was at least 4 orders of magnitude less than from liquid methanol. The dehydrogenations correspond to a chemical storage of light energy.

The Photocatalytic Dehydrogenation of 2-Propanol by Using RhCl(PPh₃)₃

H. ARAKAWA and Y. SUGI, *Chem. Lett.*, 1981, (9), 1323-1326

RhCl(PPh₃)₃ catalyses the dehydrogenation of 2-propanol under photo-irradiation from a Hg lamp at room temperature. The catalytic activity of the reaction mixture is very high.

LABORATORY APPARATUS AND TECHNIQUE

Transition Metal-Gate MOS Gaseous Detectors

T. L. POTEAT and B. LALEVIC, *IEEE Trans. Electron Devices*, 1982, **ED-29**, (1), 123-129

MOS capacitors with gates of Pd, Pt and Ni are sensitive detectors of H₂, CH₄, C₄H₁₀ and CO. 1MHz and 10Hz C-V characteristics change by -1240 and -215mV when the Pd-gate MOS capacitor is exposed to H₂ at 760 and 2 × 10⁻⁸ torr, respectively. Pt-gate MOS capacitors show half the change of Pd-gate devices. Pd-gate devices absorb H₂ in 190-200ms at 760 torr H₂, but need 200 min to reach 63% of the total change at 2 × 10⁻⁸ torr H₂. Pt- and Ni-gate devices are slower than Pd. The detection is attributed to work function change.

HETEROGENEOUS CATALYSIS

Interaction of Carbon Monoxide with Supported Platinum Catalyst

G. A. SAVELEVA, T. K. GALEEV, N. M. POPOVA, V. F. VOZDVIKHENSKII and V. M. MISHCHENKO, *Kinet. Katal.*, 1981, **22**, (5), 1253-1259

Thermal desorption and spectroscopic studies were performed on the CO interaction with 0.5-5wt.%Pt/ γ -Al₂O₃ catalysts. The CO adsorbed in three different forms corresponding to temperature intervals of desorption: 25-250°C (I), 250-700°C (II) and 550-850°C (III). During CO adsorption in the first two forms, the metal and substrate participate. The adsorption during the third form, however occurs on oxidised Pt centres forming stable carbonyl structures. Increasing temperature leads to CO adsorption in forms II and III.

Platinum-Tin Reforming Catalysts. 1. The Oxidation State of Tin and the Interaction between Platinum and Tin

R. BURCH, *J. Catal.*, 1981, **71**, (2), 348-359

Two series of bimetallic 0.3wt.% Pt-0.3-5wt.% Sn/Al₂O₃ catalysts were prepared by the impregnation of samples of industrial Pt/Al₂O₃ reforming catalysts with solutions of Sn(IV) chloride in acetone. Chemisorption shows that the amount of H₂ adsorbed by Pt is increased when Sn is present. This indicates that Sn increases the dispersion of the Pt. It is concluded that Sn is stabilised in the Sn(II) state by interaction with the support and consequently, that no proper Pt-Sn alloys are formed in these catalysts.

Hydrogenation of Nitrogen Oxide on Platinum-Carbon Catalysts in Acidic Medium

I. PASEKA, *Collect. Czech. Chem. Commun.*, 1982, **46**, (11), 2669-2675

Studies of the hydrogenation of NO in acidic solution over Pt/C catalysts showed it to be dependent on the experimental conditions either in the purely diffusion region, or in the diffusion and kinetically controlled region. The boundary between these two processes moves to the higher ratio of NO : H₂ partial pressure with increasing Pt content and decreasing agitation.

Oscillatory Behavior of Metallic Honeycomb Catalysts

V. HLAVACEK and J. RATHOUSKÝ, *Chem. Eng. Sci.*, 1982, **37**, (3), 375-380

Measurements of catalyst temperature and outlet conversion on a metal honeycomb system performed on a catalyst made of a thin layer of α -Al₂O₃ deposited on a metal honeycomb matrix impregnated by Pd showed that the CO oxidation may proceed chaotically in time over a range of inlet CO concentrations and temperatures. For higher inlet temperatures, chaotic oscillations become more "symmetrical" and finally disappear. The effect of surface memory was observed for 1% CO.

Amination of Phenols with Ammonia over Palladium Supported on Alumina

Y. ONO and H. ISHIDA, *J. Catal.*, 1981, **72**, (1), 121-128

The amination of phenol with NH₃ in the presence of H₂ over Pd/Al₂O₃ gives aniline at 250°C. The rate determining step is the hydrogenation of phenol into cyclohexanone. The catalytic behaviour of Pd is improved by making an alloy with Au or by co-supporting with La³⁺ or Al³⁺ ions.

Catalytic Properties of PdCl₂.CuCl₂/Zeolite Systems in the Oxidation of C₂-C₄ Olefins to Carbonyl Compounds

KH. M. MINACHEV, N. IA. USACHEV, A. P. RODIN and IA. I. ISAKOV, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1982, (1), 132-136

Studies of the catalytic behaviour of the PdCl₂.CuCl₂/zeolite system obtained by saturation were made during oxidation of C₂-C₄ olefins into carbonyl compounds. Activity, selectivity and stability of the synthetic faujasite systems exceed that of PdCl₂.CuCl₂.Al₂O₃ (SiO₂ amorphous aluminosilicate) and also that of ion exchanged PdCu/zeolites. Conditions for obtaining 98-99% selective conversion of C₂H₄ in acetaldehyde and C₃H₆ in acetone are given.

Transition Metal Templates for Selectivity in Organic Synthesis

B. M. TROST, *Pure Appl. Chem.*, 1981, **53**, (12), 2357-2370

Pd templates offer new ways of selectivity during organic syntheses. These are shown in four problems during allylic alkylation: chemoselectivity, regioselectivity, stereocontrol and enantioselectivity. For instance, Pd initiated cyclisations exhibit a remarkable degree of control of ring size not available in non-transition metals.

Analysis of Mechanism of Ethylene Hydrogenation by Hydrogen Permeating Palladium Membrane

H. NAGAMOTO and H. INOUE, *J. Chem. Eng. Jpn.*, 1981, **14**, (5), 377-382

A hydrogenation reactor with a Pd catalytic membrane permeated by H₂ was used for ethylene hydrogenation. There were two ethylene partial pressure regions, one where the overall reaction rate is ~ proportional to ethylene partial pressure, the other where the overall rate equals the permeation rate of H₂ into a vacuum at constant H₂ pressure.

Air Stability of Catalysts Derived from Osmium and Ruthenium Cluster Carbonyls

D. J. HUNT, D. JACKSON, R. B. MOYES, P. B. WELLS and R. WHYMAN, *J. Chem. Soc., Chem. Commun.*, 1982, (1), 85-86

Supported Os and Ru cluster carbonyl catalysts Os₆(CO)₁₈, Os₆(CO)₁₂ and Ru(CO)₁₂ impregnated on Al₂O₃, SiO₂ and TiO₂ were found to retain their activity after exposure to air.

Hydrogenation of Benzene to Cyclohexene on an Unsupported Ruthenium Catalyst. Effect of Poisons

C. U. I. ODENBRAND and S. T. LUNDIN, *J. Chem. Tech. Biotechnol.*, 1981, **31**, (11), 660-669

Studies of the effect of poisoning of Ru catalysts on the selective hydrogenation of benzene to cyclohexene showed the yield and the rate of hydrogenation to be greatly affected by the degree of poisoning. A reproducible catalyst was prepared by precipitating the catalyst precursor, as the hydroxide, in a glass vessel at 353K. An optimum H₂ pressure for maximum yield was obtained.

Ammonia Synthesis on Ruthenium Powder from 100 to 500°C and Hydrogenation of Preadsorbed Nitrogen down to -70°C

G. RAMBEAU and H. AMARIGLIO, *J. Catal.*, 1981, **72**, (1), 1-11

Kinetic analysis of NH₃ synthesis over Ru shows the reaction rate is inversely proportional to H₂ pressure and directly proportional to N₂ pressure, so the reaction is limited by N₂ adsorption and inhibited by H₂. NH₃ production has been observed down to -70°C. Hydrogenating the preadsorbed N₂ allows the N₂ coverage and rate of N₂ chemisorption on the bare surface to be measured. The latter indicates that the intrinsic catalytic activity of Ru is 500 to 2000 times higher than that of Fe between 400 and 250°C.

HOMOGENEOUS CATALYSIS

Dimerisation of a Diplatinum to a Tetraplatinum Complex during Catalysis of the Water Gas Shift Reaction: the X-Ray Crystal Structure of [Pt₄(μ₂-CO)₂(μ₂-Ph₂PCH₂PPh₂)₃][Ph₂PCH₂P(:O)Ph₂]

A. A. FREW, R. H. MILL, L. MANOJLOVIĆ-MUIR, K. W. MUIR and R. J. PUDDEPHATT, *J. Chem. Soc., Chem. Commun.*, 1982, (3), 198-200

The binuclear complex [Pt₂H₂(μ-H)(μ-dppm)₂][PF₆], dppm = Ph₂PCH₂PPh₂, is an active catalyst precursor for the water gas shift reaction, especially at low CO pressures. The catalytic solution contains cluster complexes such as tetranuclear [Pt₄(μ-CO)₂(μ-dppm)₃][Ph₂PCH₂P(:O)Ph₂].

Catalytic Activity of Some Palladium Complexes during Oligomerisation of Isoprene in Protone Solvents

R. BERGER, V. GAUBE and I. N. KUKUSHKIN, *Khim. Khim. Tekhnol.*, 1982, **24**, (10), 1291-1293

The systems based on sulphinate Pd complexes K[Pd(C₆H₅SO₂)₂(H₂O)Cl] and salicylaniline Pd complexes [Pd(OC₆H₄CH = NC₆H₅)₂] in the presence of phosphines and in alcohol media catalysed both the dimerisation and telomerisation of isoprene. The catalytic activity was equal to that of acetylacetonate based Pd systems.

Palladium Catalysis in Natural Product Synthesis

J. TSUJI, *Pure Appl. Chem.*, 1981, **53**, (12), 2371-2378

A review of new syntheses for natural products, mostly steroids, based on Pd-catalysed reactions is presented. (23 Refs.)

Kinetic Investigations of the Synthesis of Acetic Anhydride by Homogeneous Catalysis

M. SCHROD and G. LUFT, *Ind. Eng. Chem., Prod. Res. Dev.*, 1981, **20**, (4), 649-653

A kinetic study of the carbonylation of methyl acetate to acetic anhydride over a catalyst system including RhCl₃ hydrate, methyl iodide, an organic base and Cr compounds was made at CO pressures of 5-75 bar and at 165-205°C. The reaction rate was independent of the CO pressure above 15 bar and did not depend on methyl acetate concentration. The reaction was first order for Rh, methyl iodide and the base, if its concentration was low. With rising base concentration the order of reaction decreased.

A Study of the Mechanism of Rhodium Phosphine-Catalysed Hydroformylation: Use of 1,1'-Bis(diarylphosphino)ferrocene Ligands

J. D. UNRUH and J. R. CHRISTENSON, *J. Mol. Catal.*, 1982, **14**, (1), 19-34

Rh phosphine-catalysed hydroformylation was studied using 1,1'-bis(diphenylphosphino)ferrocene and several derivatives containing substituents on the phenyl groups (*p*-Cl, *m*-F and *p*-CF₃). The most selective catalyst has three P atoms bound to each Rh atom and is postulated to be a diRh complex. It is confirmed that the linear : branched ratio increases as ligand basicity decreases.

Oxidation of Alcohols by Transition Metal Complexes—IV. The Rhodium Catalysed Synthesis of Esters from Aldehydes and Alcohols

R. GRIGG, T. R. B. MITCHELL and S. SUTTHIVAIYAKIT, *Tetrahedron*, 1981, **37**, (24), 4313-4319

Both RhH(CO)(PPh₃)₃ and a catalyst made in situ from RhCl₃·3H₂O, PPh₃ and Na₂CO₃ catalyse the reaction of aldehyde with simple primary alcohols to give esters, together with alcohols formed from aldehyde reduction. The proportion of ester can be increased by adding an efficient hydrogen acceptor.

Catalysis of the Water Gas Shift Reaction by Complexes of Rhodium and Iridium with 2,2'-Bipyridine and Similar Ligands

P. A. MARNOT, R. R. RUPPERT and J.-P. SAUVAGE, *Nouv. J. Chim.*, 1981, **5**, (11), 543-545

The water gas shift reaction is efficiently catalysed under mild temperature (< 100°C), pressure (1 atm) and pH in water by soluble complexes of Rh and Ir. Turnover frequencies > 50/hour have been obtained at 100°C, pH around neutrality under 1 atm CO.

Bimetallic Catalysts from Pseudotetrahedral Iridium-Tungsten Clusters. Syntheses and Crystal Structures of $(\eta^5\text{-C}_5\text{H}_5)\text{WIr}_3(\text{CO})_{11}$ and $(\eta^5\text{-C}_5\text{H}_5)_2\text{W}_2\text{Ir}_2(\text{CO})_{10}$

J. R. SHAPLEY, S. J. HARDWICK, D. S. FOOST, G. D. STUCKY, M. R. CHURCHILL, C. BUENO and J. P. HUTCHINSON, *J. Am. Chem. Soc.*, 1981, **103**, (24), 7383-7385

Convenient syntheses and molecular structures of two tetranuclear Ir-W clusters $\text{CpWIr}_3(\text{CO})_{11}$ (1) and $\text{Cp}_2\text{W}_2\text{Ir}_2(\text{CO})_{12}$ (2) ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5$) and their use as precursors to Al_2O_3 -supported bimetallic catalysts are reported during hydrogenolysis of n-butene. The $[\text{Ir}_4]$ catalyst had high selectivity for scission of the central C-C bond in butane, forming two molecules of ethane. The $[\text{WIr}_3]$ and $[\text{W}_2\text{Ir}_2]$ catalysts showed ethane selectivity of 70% or greater, but the $[\text{W}_2\text{Ir}_2]$ catalyst had < 50% ethane in the product stream.

Carboxylic Acids from Syngas

J. F. KNIFTON, *Hydrocarbon Process.*, 1981, **60**, (12), 113-117

A new route for preparing short-chain aliphatic carboxylic acids using homogeneous Ru and Rh catalysts, where the products may be based optionally upon syngas feedstocks alone, is described. Lower molecular weight carboxylic acids are homologised by synthesis gas in the presence of a solubilised Ru or Rh species plus a suitable I-containing promoter. Catalysts such as RuO_2 , $\text{H}_4\text{Rh}_4(\text{CO})_{12}$, $\text{Ru}_3(\text{CO})_{12}$, $\text{Ru}(\text{acac})_3$, RuCl_3 , $\text{RuCl}_2(\text{PPh}_3)_3$, $\text{Rh}(\text{acac})_3$, Rh_2O_3 , RhCl_3 , $\text{Pd}(\text{OAc})_2\text{-8PPh}_3$ are used. Catalyst selection, operating conditions, the homologation reaction, process description, and costs are described.

Ru-Catalyzed Oxidation of Acetylene to α -Diketones with Iodosylbenzene

P. MÜLLER and J. GODOY, *Helv. Chim. Acta.*, 1981, **64**, (8), 2531-2533

Disubstituted acetylenes are oxidised with PhIO in the presence of $\text{RuCl}_2(\text{PPh}_3)_3$ to give α -diketones in 65-85% yield. Under the same conditions terminal acetylenes are cleaved to carboxylic acids.

NEW PATENTS

METALS AND ALLOYS

Dispersion Strengthened Precious Metal Alloys

OWENS-CORNING FIBERGLASS CORP.

British App. 2,075,552/3 A

Alloys with superior creep resistance are obtained by the mechanical introduction of the oxide material, such as Y for Pt or Pt alloys. The thermomechanical processing of the products is described.

ELECTRICAL AND ELECTRONIC ENGINEERING

Pd-Thin-SiO₂-Si Diode. I. Isothermal Variation of H₂-Induced Interfacial Trapping States. II. Theoretical Modelling and the H₂ Response

B. KERAMATI and J. N. ZEMEL, *J. Appl. Phys.*, 1982, **53**, (2), 1091-1099, 1100-1109

The current-voltage characteristic and the small-signal frequency dependent admittance response of a Pd-thin-SiO₂-Si diode were measured. A method was developed to calculate the d.c. response and the small signal admittance of a MIS diode under a given applied voltage. The generated interfacial trapping states were responsible for the induced electrical changes in the Pd-thin-SiO₂-Si diodes.

Anodic Evolution of Oxygen on Sputtered Iridium Oxide Films

S. HACKWOOD, L. M. SCHIAVONE, W. C. DAUTREMONT-SMITH and G. BENI, *J. Electrochem. Soc.*, 1981, **128**, (12), 2569-2573

The catalytic properties of sputtered Ir oxide films (SIROF'S) in acidic electrolytes were studied. Long term stability is demonstrated. Typical steady state currents are 75mA/cm² at 1.85V, which is 50% higher than previously reported. The high current density and absence of corrosion demonstrate the superior catalytic properties of SIROF's vs. Ir over the entire voltage range studied.

MEDICAL USES

Carcinostatic Effect of a Caffeine-8-Ether-Platinum Complex

H. KRÖGER and J. KLOSA, *Naturwissenschaften*, 1981, **68**, (12), 628

The caffeine-8-ether-Pt complex (Cofplatin) was synthesised and given to rats and mice with various sarcomas, when cessation in growth in the tumours was seen. Cofplatin is a stable non-aggressive substance and further research is being done.

Dispersion-Hardened Metal Alloys

KERNFORSCHUNGSZENTRUM KARLSRUHE G.m.b.H.

European Appl. 44,351

An alloy composition hardened by dispersed carbide particles is formed by decomposing a ternary or higher mixed carbide in a suitable matrix alloy. The carbides are derived from Group IVB, VB and VIB transition metals while the matrix is a solid alloy of Group IVB, VB and VIB metals with Re or one of the platinum group metals.